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## Molecular approaches to the electrochemical reduction of carbon dioxide\*\*

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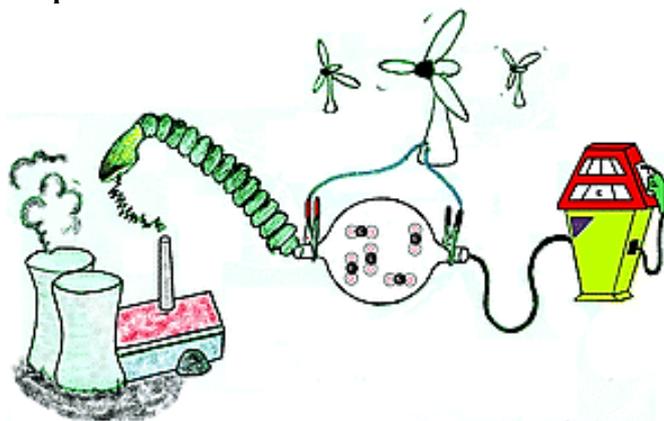
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(Illustration by Lesley Yellowlees)

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CO<sub>2</sub> fixation; homogeneous hydrogenation; palladium complex; methanol; activation; catalysts; dehydrogenase; conversion; hydrocarbons; insertion

## **Abstract**

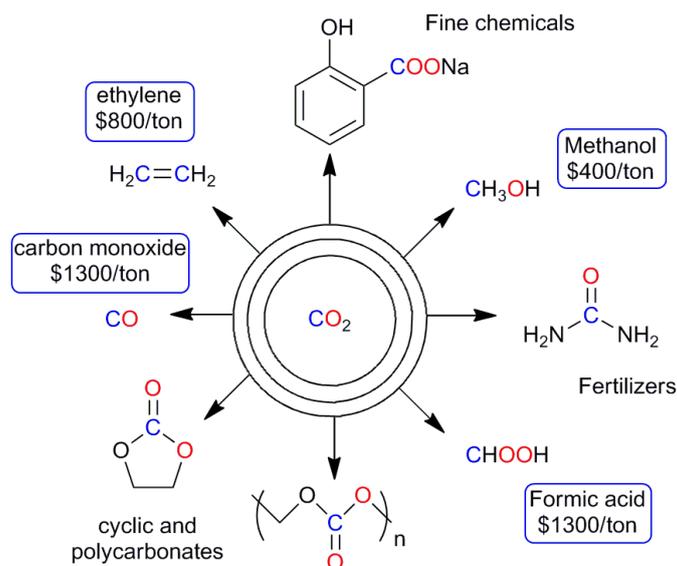
This article reviews recent progress in the exploitation of carbon dioxide as a chemical feedstock. In particular, the design and development of molecular complexes that can act as catalysts for the electrochemical reduction of CO<sub>2</sub> is highlighted, and compared to other biological, metal- and non-metal-based systems.

## **Introduction**

The global anthropogenic contribution of CO<sub>2</sub> to the atmosphere is estimated at 24 Gt per year and has increased significantly since the industrial revolution. At present rates of generation, atmospheric CO<sub>2</sub> is predicted to be at concentrations of 500 ppm in 2050 and exceeds that which can be balanced by the planet's natural carbon cycle in terrestrial, atmospheric, and biomass reservoirs.<sup>1</sup> It is predicted that this concentration of atmospheric CO<sub>2</sub> will result in a 0.7 to 1.5 °C global temperature rise, and that this will have significant environmental consequences. The publicity surrounding atmospheric CO<sub>2</sub> has influenced the Kyoto protocol and the UK carbon action plan which in turn has prompted researchers and energy generating companies to explore ways of reducing CO<sub>2</sub> emissions and to invest in carbon capture and storage (CCS). CCS is seen as a costly venture, using between 10-40 % of the energy output from a power station, and, as of yet, there is no set monetary price for the release of CO<sub>2</sub> into the environment.<sup>2,3</sup> However, making use of the potential chemical transformations of CO<sub>2</sub> to produce valuable chemical commodities may offer some recompense to the development of CCS technologies.<sup>4</sup> Indeed, CO<sub>2</sub> represents an important, non-toxic, abundant and cheap C<sub>1</sub> feedstock and should not be viewed as a waste material. It is therefore clear that the preparation of value-added compounds from CO<sub>2</sub> sequestered from the atmosphere has the advantages of generating new revenue streams as well as mitigating potential environmental impact.

## **Current industrial uses of CO<sub>2</sub>**

The global annual demand for carbon dioxide is estimated at 200 Mt, which is a fraction of the estimated annual production (24 Gt). Some of the major industrial processes such as enhanced oil recovery, preservative and beverage additive in the catering industry, fire suppression and as a coolant or solvent, only take advantage of the physical properties of CO<sub>2</sub>. Roughly 110 Mt of CO<sub>2</sub> are used annually in the production of chemicals, and some of the common transformations of CO<sub>2</sub> are outlined in Figure 1.<sup>5</sup> The main consumption of CO<sub>2</sub> is the production of urea for use in fertilisers, while salicylic acid and carbonates consume roughly 30 Mt of CO<sub>2</sub> per year.



**Figure 1.** Conversion of CO<sub>2</sub> into more valuable commodity chemicals.

### Target compounds

The most significant synthetic targets for CO<sub>2</sub> utilisation are methanol, dimethylether (DME), and formic acid as these chemicals could potentially be used as liquid fuels. The methanol economy has been highlighted as a scenario to exploit our existing hydrocarbon infrastructure in the face of diminishing fossil fuel reserves and rising atmospheric CO<sub>2</sub> concentrations.<sup>6</sup> DME is suggested as a potential fuel of the future in that it is non-toxic, environmentally-benign, and is already used as a fuel additive in some countries. Formic acid also has potential as a high-value fuel for use in formic acid fuel cell applications. An assessment of CO<sub>2</sub> utilisation by Det Norske Veritas for their ECFORM process suggests that formic acid would provide the highest monetary value from the energy required to form this product, in contrast to the more common targets of methanol and methane (Figure 1).<sup>7</sup> CO can also be viewed as a high value product from CO<sub>2</sub> reduction and could be exploited by chemists as a C<sub>1</sub> synthon. For example, an alluring target is the combined production of CO and H<sub>2</sub> (synthesis gas) from the reduction of both CO<sub>2</sub> and H<sub>2</sub>O, as this combination of gases can be exploited to make liquid fuels using existing Fischer-Tropsch technology. Indeed, this approach is being investigated by Air Fuel Synthesis (UK) who are developing integrated technology for fuel production that uses the energy from wind turbines to power combined water electrolysis, reverse water-gas shift, and Fischer-Tropsch catalysis.<sup>3</sup>

### Some challenges for CO<sub>2</sub> reduction

Carbon dioxide is a non-polar, linear molecule representing carbon in its most oxidised state and is highly

thermodynamically stable. Reactions of CO<sub>2</sub> to form target compounds such as fuels require significant energy input to overcome the intrinsic thermodynamic cost that is primarily associated with the water oxidation half reaction. Furthermore, kinetic barriers necessitate the use of catalysts to limit overpotentials and promote product selectivity. It is clear that the energy requirements for CO<sub>2</sub> conversion should arise from sustainable, low-carbon sources to have an impact on atmospheric CO<sub>2</sub> concentrations. Intermittent electrical energy such as that supplied by wind turbines, solar, or tidal sources could be stored chemically as fuels derived from CO<sub>2</sub>.

The single-electron reduction of CO<sub>2</sub> to form the radical CO<sub>2</sub><sup>•-</sup> involves a significant energy penalty, as can be seen by the reduction potential of -1.9 V vs. NHE (Table 1), and is due to a rearrangement from a linear to bent structure. In contrast however, electrochemical reduction of CO<sub>2</sub> in the presence of proton sources can incur significantly less energy cost and lead to the formation of more desirable products such as methanol (Table 1). While the use of Proton-Coupled-Electron-Transfer (PCET) makes these transformations more electrochemically favourable, they also introduce added complexity with the requirement of the catalyst system to manage the multiple proton/electron inventory. This facet is particularly pertinent to reaction selectivity such that reduction of CO<sub>2</sub> leads to the desired product without the formation of hydrogen.

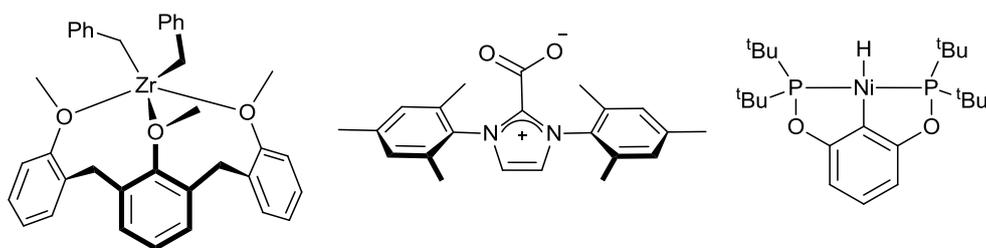
Selected reduction reactions of CO <sub>2</sub>	E°/V
CO <sub>2</sub> + e <sup>-</sup> → CO <sub>2</sub> <sup>•-</sup>	- 1.90
CO <sub>2</sub> + 2H <sup>+</sup> + 2e <sup>-</sup> → CO + H <sub>2</sub> O	- 0.53
CO <sub>2</sub> + 2H <sup>+</sup> + 2e <sup>-</sup> → HCO <sub>2</sub> H	- 0.61
CO <sub>2</sub> + 6H <sup>+</sup> + 6e <sup>-</sup> → CH <sub>3</sub> OH + H <sub>2</sub> O	- 0.38
CO <sub>2</sub> + 8H <sup>+</sup> + 8e <sup>-</sup> → CH <sub>4</sub> + 2H <sub>2</sub> O	- 0.24

**Table 1.** Electrochemical reduction of CO<sub>2</sub> in the presence of a proton source (aqueous solution, pH 7, vs. NHE)<sup>8</sup>.

### Molecular catalysts

This article will highlight chemical transformations of CO<sub>2</sub> and will focus on molecular compounds that can (potentially) act as catalysts for the electrochemical reduction of CO<sub>2</sub>. This general area has been the subject of several review articles.<sup>2, 8, 9</sup> There are many alternatives to electrochemical reduction methods, for example the use of high-energy reagents such as hydrogen to provide more favourable thermodynamic conditions.<sup>10</sup> Recently, hydrosilanes have been employed in the conversion of CO<sub>2</sub> into methane or methanol using zirconium phenoxide borane complexes or N-heterocyclic carbenes as catalysts (Figure 2).<sup>11</sup> Nickel diphosphine complexes have been shown to catalyse borane reduction of CO<sub>2</sub> to form boryl formates,<sup>12</sup> while

the use of tetramethylpiperidine-perfluoroborane Frustrated-Lewis-Pairs has facilitated the homogeneous hydrogenation of CO<sub>2</sub> to methanol.<sup>13</sup> An alternative route to the indirect conversion of CO<sub>2</sub> to methanol was recently reported, and used Ru pincer complexes as catalysts for the hydrogenation of carbonates, carbamates, and formates that are straightforwardly derived from CO<sub>2</sub>. These reactions are atom-economical and operate in the absence of solvent with good turnover numbers (10<sup>3</sup>-10<sup>4</sup>).<sup>14</sup> The photocatalytic reduction of CO<sub>2</sub> to CO is also well-studied using Co and Ni tetraaza-macrocyclic complexes as catalysts in concert with Ru(bipy)<sub>3</sub> photosensitisers and sacrificial amine donors.<sup>15</sup> More recently, the doping of metal-organic-frameworks with Re(bipy) complexes has been shown to promote photocatalytic CO<sub>2</sub> reduction to CO that is much enhanced compared to the complexes that are not incorporated into MOFs.<sup>16</sup> Significant advances in the copolymerisation of CO<sub>2</sub> with epoxides to form cyclic and/or polycarbonates have been made, and have been recently reviewed.<sup>17</sup> Furthermore, binuclear aluminium catalysts have been shown to be highly effective in cyclic carbonate formation and are being exploited by the spin-out company Dymeryx Ltd.<sup>3, 18</sup>



**Figure 2.** Compounds used as catalysts in CO<sub>2</sub> reduction by silanes and boranes.

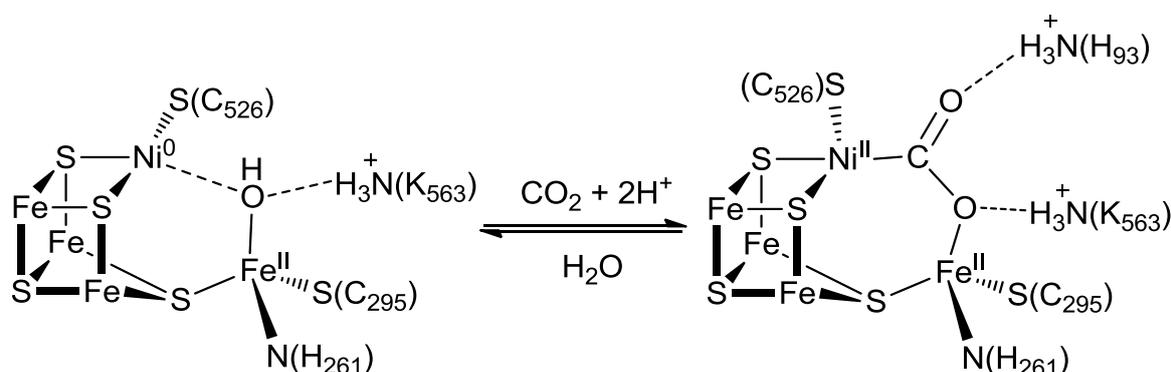
## Biological inspiration

Idealized catalysts for small molecule transformations are often found as metalloenzymes in biological systems, and this is the case for CO<sub>2</sub> chemistry. For example, enzymatic conversion of CO<sub>2</sub> to methanol has been shown to be feasible and enhanced by encapsulating three different dehydrogenases, formate dehydrogenase, formaldehyde dehydrogenase, and alcohol dehydrogenase, in sol-gel matrices.<sup>19</sup> The use of reduced nicotinamide adenine dinucleotide as the terminal electron donor allowed the enzymatic reactions to run in reverse, so forming the desired products. It was suggested that confinement of the multienzyme system in the nanopores of the sol-gel alters the reaction thermodynamics and final equilibrium of the reaction.

Tungsten-containing formate dehydrogenases (FDH1) from anaerobic *Syntrophobacter fumaroxidans* have been adsorbed on pyrolytic edge-plane-graphite and act as electrocatalysts for the conversion of CO<sub>2</sub> into formate HCO<sub>2</sub><sup>-</sup>.<sup>20</sup> As electrocatalysis by FDH1 is thermodynamically reversible, only small overpotentials are required to drive the CO<sub>2</sub> reduction, with formate being the sole product. While this large and oxygen-sensitive protein is not a realistic target for technological exploitation, it is possible that structure-function

relationships derived from studying this system may lead to the development of more robust catalysts.

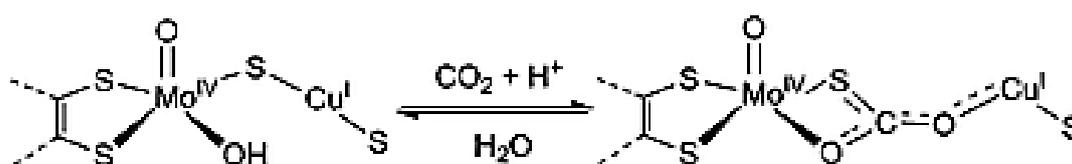
Carbon monoxide dehydrogenases (CODH) catalyze the room temperature interconversion of CO<sub>2</sub> and CO. The active site of anaerobic CODH from *Carboxydotherrmus hydrogenoformans* has been characterised by X-ray crystallography in the presence of CO<sub>2</sub> and contains a NiFe<sub>4</sub>S<sub>4</sub> cluster (Scheme 1) of similar overall topology to the Mn, Ca oxo cluster seen in Photosystem II.<sup>21</sup>



**Scheme 1.** Carbon dioxide activation at the Ni, Fe-cluster of anaerobic carbon monoxide dehydrogenase.

In its reduced form, a hydroxide partially-bridges the heterobimetallic Ni, Fe site, and is supplemented by hydrogen-bonding interactions to the protein. In the presence of protons, CO<sub>2</sub> was found to bridge the Ni and Fe centres and was reduced to formate. The Ni centre acts as a Lewis base and binds to the carbon, while the Fe centre is Lewis acidic and coordinates to one oxygen atom of the CO<sub>2</sub> molecule. Again, hydrogen-bonding interactions stabilise this structure, and C-O bond cleavage results in the elimination of CO. When adsorbed on pyrolytic edge-plane graphite under anaerobic conditions, CODH II from *Carboxydotherrmus hydrogenoformans* displays efficient and reversible electrocatalytic activity for both CO oxidation and CO<sub>2</sub> reduction.<sup>22</sup> As with formate production by FDH1, no enzyme-inherent overpotential is present.

Aerobic CO dehydrogenases from *Oligotropha carboxidovorans* have also been characterised structurally and contain a binuclear molybdopterin-Cu active site which has similar structural facets to the Ni, Fe-cluster described above (Scheme 2).<sup>23</sup>



**Scheme 2.** Carbon dioxide activation at the Mo,Cu-active site of aerobic carbon monoxide dehydrogenase.

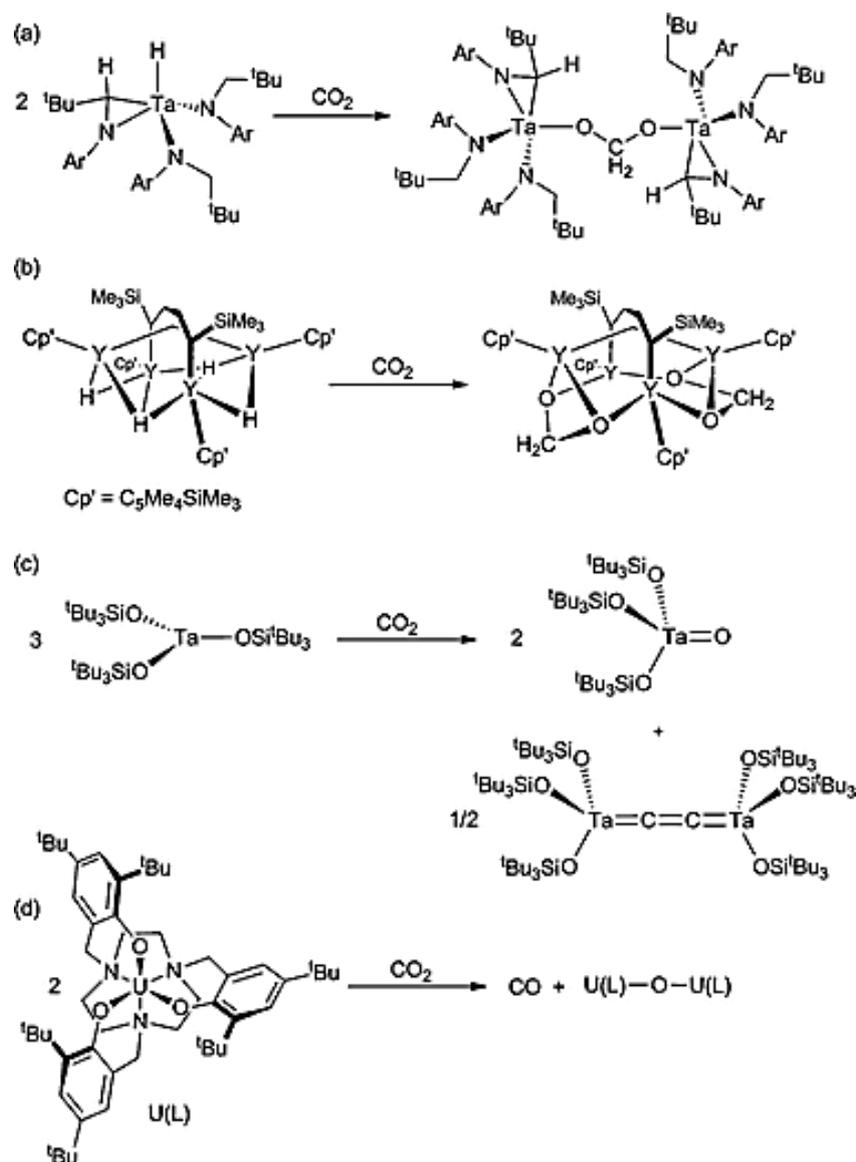
Crystallographic analysis of the reduced and oxidised (not shown) states of this enzyme provided insight into the CO oxidations process, and hence its microscopic reverse, CO<sub>2</sub> reduction. In the latter case, elimination of H<sub>2</sub>O on protonation allows the CO<sub>2</sub> to interact with the Mo and Cu centres, and also the non-innocent sulfido ligand, which binds to the electropositive carbon atom to form a multiply-bridged formate. Cleavage of a C-O bond results in the formation of CO and generation of the oxidised form, a Mo(VI) hydroxide.

### **Electrochemical CO<sub>2</sub> reduction by transition metals and their alloys**

Transition metal electrodes and their alloys have a long history in CO<sub>2</sub> reduction chemistry and have been the subject of some recent review articles.<sup>24, 25</sup> The choice of metal has the greatest influence in the distribution of CO<sub>2</sub>-reduction products. For example, metals such as Hg, Cd, Pd, and Sn favour two-electron reduction to formate while Pt, Ni, Al, and Ti generate CO as a minor product and catalyse H<sub>2</sub> production. Cu electrodes are unique in this area as they can give rise to multi-electron reduction products such as hydrocarbons. Methane is produced from CO<sub>2</sub> reduction with Cu electrodes in bicarbonate solutions with high current efficiency albeit at very large overpotentials (1.5 V). Recent analysis of Cu-catalysed reduction using density functional calculations suggests that the rate-limiting step is the protonation of adsorbed CO, derived from the reduction of CO<sub>2</sub>, to form adsorbed CHO.<sup>26</sup> Improvements in CHO-stabilisation at the surface should lead to a significant reduction in overpotential. As such, attention has been focussed on the use of metal-complex modified electrodes in an attempt to overcome these kinetic hurdles as they can adopt the dual roles of mediating electron transfer and stabilising the reduced fragments.

### **Electropositive metal complexes**

Transition metal hydrides have long been used as catalysts for CO<sub>2</sub> hydrogenation due to the propensity of CO<sub>2</sub> to insert into the M-H bond.<sup>27</sup> More recently, a tantalaziridine-hydride has been shown to react with CO<sub>2</sub> to form binuclear methylene diolate complexes (Scheme 3a).<sup>28</sup> These complexes were characterised by X-ray crystallography and show that the new methylene diolate ligand (H<sub>2</sub>CO<sub>2</sub><sup>2-</sup>), derived formally from the two-electron reduction of CO<sub>2</sub> by two terminal Ta hydrides, bridges the two Ta centres through Ta-O bonds.



**Scheme 3.** Reactions of electropositive metal complexes with  $\text{CO}_2$ .

In a similar manner, tetranuclear yttrium hydride clusters were shown to react with  $\text{CO}_2$  to produce the methylene diolate, two-electron reduced product, which, in this latter case was found to bridge three Y centres through the two oxygen atoms in the solid state (Scheme 3b).<sup>29</sup> Further reaction with  $\text{CO}_2$  produced new Y carbonate clusters, and this work as a whole could shed light on mechanistic aspects of heterogeneous  $\text{CO}_2$  hydrogenation processes.

The high oxophilicity of the early transition metals inevitably directs their reactivity with  $\text{CO}_2$ , and generally results in O-atom abstraction reactions. Indeed, Ta(III) and Nb(III) siloxides were found to undergo redox reactions with  $\text{CO}_2$  to form CO and Ta(V) and Nb(V)=O oxo complexes as a result of O-atom abstraction

(Scheme 3c).<sup>30</sup> In contrast to the above tantalaziridines, siloxide-ligated Ta(V) hydrides do not undergo straightforward CO<sub>2</sub> insertion reactions, but instead undergo H<sub>2</sub>-elimination and O-atom abstraction reactions. In some cases, Ta and Nb dicarbide formation was observed as a result of O-atom abstraction from CO. These reactions suggest that these early-metal systems would be best employed in a combined water-gas shift/Fischer-Tropsch process to effect overall CO<sub>2</sub> reduction to useful products.

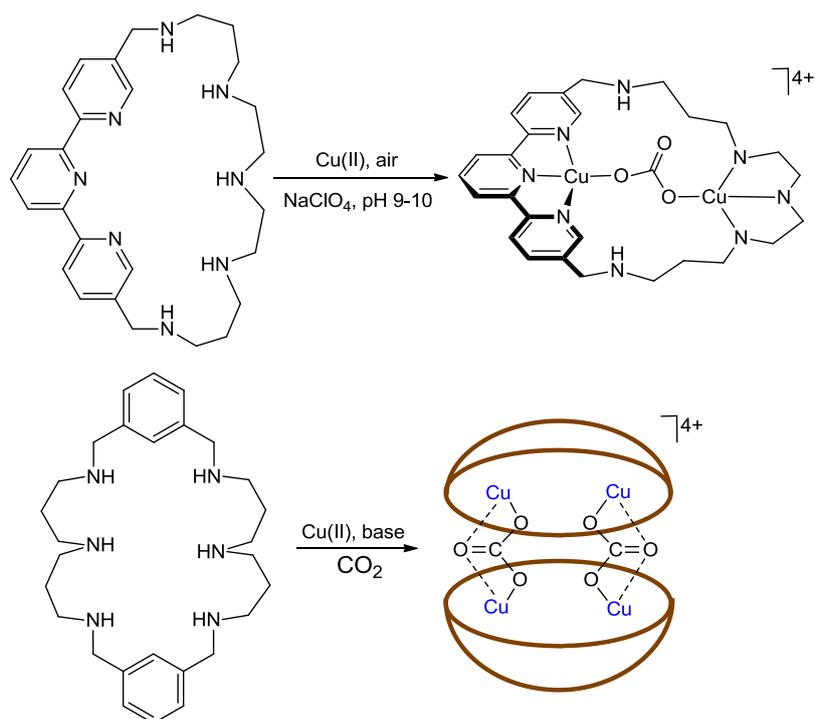
Low-valent, U(III) complexes also show a propensity for O-atom abstraction from CO<sub>2</sub>. Triazacyclononane-aryloxide complexes of U have been shown to stabilise an unusual linear end-on binding mode of CO<sub>2</sub>,<sup>31</sup> and react further to form oxo-bridged binuclear complexes and CO (Scheme 3d).<sup>32</sup> The eliminated CO was seen to react with further equivalents of U(III) complex to form an unusual f-element bridging carbonyl complex. More recently, simple tris(aryloxide) complexes of U(III) have been shown to undergo combined O-atom abstraction and insertion reactions with CO<sub>2</sub> to generate aryloxide-derived, binuclear carbonate complexes.<sup>33</sup>

It is clear from the above examples that the CO<sub>2</sub> chemistry of the electropositive early-transition metals is dominated by their oxophilicity, resulting in the formation of strong M-O bonds that are unlikely to be easily cleaved in catalytic cycles. Furthermore, no work has been carried out to drive any of these reactions electrochemically. As such, the majority of recent CO<sub>2</sub> reduction chemistry has focussed on the use of complexes of the later transition metals as catalysts.

## Copper complexes

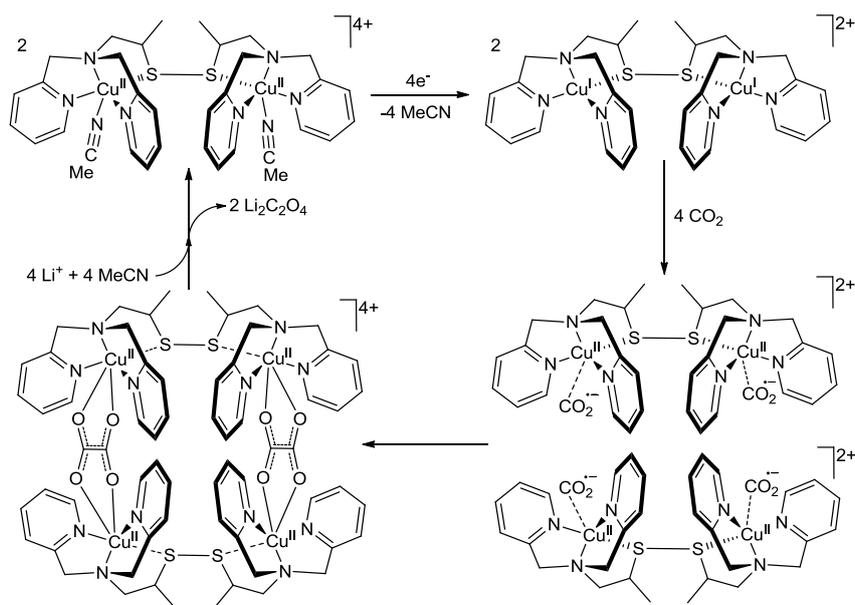
An important step in designing a process for the reduction of CO<sub>2</sub> is to be able to sequester, or fix, CO<sub>2</sub> from the atmosphere. Copper complexes are well known to carry out this feat under basic conditions to form carbonate complexes. Recently, copper complexes of polydentate macrocyclic terpyridine-amine ligands were found to react with CO<sub>2</sub> from the air at pH > 7. While mononuclear Cu complexes form carbamates, the presence of a second Cu centre blocks the amine site and results in the formation of binuclear copper carbonates (Scheme 4, top),<sup>34</sup> these structures are stabilised by intramolecular H-bonding interactions. Electrochemical analysis of the binuclear complexes under air or CO<sub>2</sub> revealed a sharp response between -1.0 and -1.25 V vs. Ag/AgCl due to the formation of CO<sub>2</sub><sup>-</sup> which spontaneously disproportionates into CO and CO<sub>3</sub><sup>2-</sup>.<sup>35</sup> Furthermore, carboxylation of indigo was observed when this electrochemistry was carried out using an indigo-modified fluorinated indium-tin oxide electrode.

The reversible fixation of CO<sub>2</sub> by a series of macrocyclic binuclear copper hydroxide complexes has been reported. Under a high pH regime, reversible formation of copper carbonates was seen, forming tetranuclear, bowl-shaped structures (Scheme 4, bottom).<sup>36</sup> Kinetic studies indicated that either direct addition of CO<sub>2</sub> to the hydroxyl ligand occurs or OH<sup>-</sup> ligand substitution by HCO<sub>3</sub><sup>-</sup>, generated by CO<sub>2</sub> hydration, operates, the latter process being extremely rapid.



**Scheme 4.** Macrocyclic copper complexes that can sequester CO<sub>2</sub> under basic conditions to form carbonates.

Sequestration of CO<sub>2</sub> followed by its electrocatalytic reduction to oxalate was observed recently using a binuclear copper complex of a pre-organised, binucleating tetrapodal disulfide ligand (Scheme 5).<sup>37</sup>

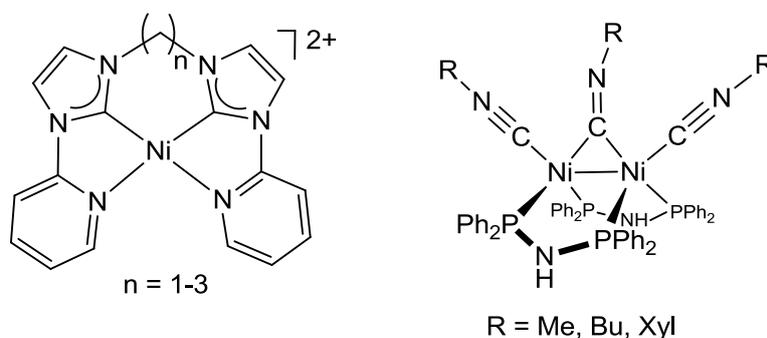


**Scheme 5.** Fixation and reduction of CO<sub>2</sub> to oxalate.

Reduction of the binuclear Cu(II) complex and exposure to CO<sub>2</sub> led to a new tetranuclear Cu(II) bis(oxalate) complex in which the oxalate ligands were found to bridge two adjacent Cu centres by X-ray crystallography. Surprisingly, the Cu(I) system is oxidised by CO<sub>2</sub> rather than O<sub>2</sub>, which suggests that this complex offers a low-energy pathway to the formation of the CO<sub>2</sub><sup>•-</sup> radical anion, which can then dimerise to form the thermodynamically-favoured oxalate complex. Significantly, the binuclear oxalate complex was found to react with LiClO<sub>4</sub> to regenerate the starting material and produce insoluble Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. Catalytic turnover was subsequently achieved by reducing Cu(II) to Cu(I) at a potential of -0.03 V, a potential that is nearly 2 V less negative than that required for the outer-sphere reduction of CO<sub>2</sub> to CO<sub>2</sub><sup>•-</sup> but closer to that for oxalate of -0.39 V.<sup>38</sup> While the turnover frequency is extremely low, generating only 12 equivalents of oxalate (6 turnovers) in 7 hours, the reaction appears inhibited by precipitation of the Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub> on the electrode surface which hampers efficient electron transfer. Also, the Li salt required to complete the catalytic cycle is too expensive for this chemistry to be incorporated into carbon capture and utilisation (CCU) technology, although cheaper alternatives are being considered.

### Nickel and palladium complexes

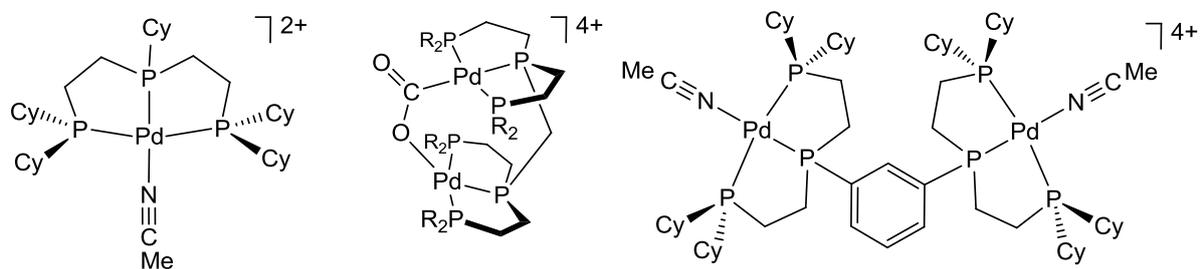
Nickel complexes of N<sub>4</sub> macrocycles, in particular [Ni(cyclam)]<sup>2+</sup> have a high selectivity for activating CO<sub>2</sub> over H<sub>2</sub>O under reducing electrocatalytic conditions.<sup>8</sup> Based on these precedents, attempts have been made to tune the electronic environment of the Ni centre with the synthesis of a homologous series of Ni complexes of N-heterocyclic carbene-pyridine chelating ligands (Figure 3, left).<sup>39</sup> These nickel complexes were found to favour the selective electrocatalytic reduction of CO<sub>2</sub> to CO with no formation of H<sub>2</sub>, albeit with moderate turnover frequencies of 4-6 h<sup>-1</sup>. Significantly, elongation of the linking alkyl chain between the two NHCs from 1 to 3 carbons resulted in a positive shift of the Ni<sup>III/I</sup> couple from -1.69 to -1.46 V, resulting in a less cathodic CO<sub>2</sub> reduction potential. Stoichiometric reactions on the complexes with n = 1 or 2 with one equivalent of C<sub>8</sub> K led to reduction and dimerisation to form binuclear Ni(I) complexes that displayed different electrochemical responses to the mononuclear species.



**Figure 3.** Ni complexes that act as catalysts for the electrochemical reduction of CO<sub>2</sub>.

Diphosphine ligands such as bis(diphenylphosphino)methane (dppm) and bis(diphenylphosphino)amine (dppa) display a propensity to bridge two or more metals and generate bi- and polynuclear clusters. Air-sensitive, binuclear Ni(0) complexes of dppa (Figure 3, right) have recently been prepared and their activity in the electrocatalytic reduction of CO<sub>2</sub> evaluated.<sup>40</sup> For R = Bu, an irreversible 1-electron reduction at -0.99 vs. Fc<sup>+</sup>/Fc was observed in the CV which underwent substantial current enhancement on exposure to CO<sub>2</sub>. The use of spectroelectrochemistry and isotopic labelling showed that the singly-reduced Ni complex reacts with CO<sub>2</sub> to yield the disproportionation products CO and CO<sub>3</sub><sup>2-</sup>. In the presence of residual water (acidic donors), reduction of CO<sub>2</sub> to formate was seen as a competing process.

Palladium(II) complexes of sterically-demanding, chelating triphosphines also display activity in CO<sub>2</sub> reduction chemistry. In mononuclear systems (Figure 4, left), rate constants between 5 and 300 M<sup>-1</sup>s<sup>-1</sup> were seen in the selective reduction of CO<sub>2</sub> to CO.<sup>41</sup> Evaluation of the mechanism of this reaction revealed that the rate-determining step at high acid concentrations was binding of CO<sub>2</sub> to the Pd(I) intermediate, whereas at lower acid concentrations it was the cleavage of the C-O bond; this latter route was found to be dependent on solvent loss from the active centre. Significantly, the use of bulky phosphorus substituents such as cyclohexyl resulted in faster reaction rates due to the inhibition of both solvent binding and of the formation of catalytically-inert binuclear palladium complexes.



**Figure 4.** Mono- and binuclear Pd complexes of chelating phosphines.

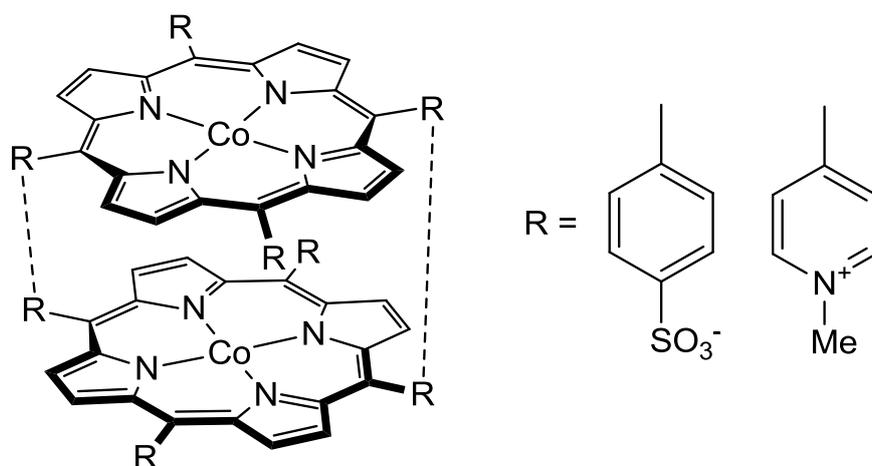
Binuclear palladium complexes in which the two Pd(P<sub>3</sub>) compartments are separated by a methylene spacer (Figure 4, middle) show very high catalytic rates for CO<sub>2</sub> reduction (> 10<sup>4</sup> M<sup>-1</sup>s<sup>-1</sup>) that are similar to those of Ni, Fe CO dehydrogenase enzymes; unfortunately, turnover numbers are low (*ca.* 10).<sup>42</sup> These palladium complexes show some structural similarities to the active site of the enzyme, in particular requiring two site binding to CO<sub>2</sub>, with one metal interacting with C, the other with O. In order to overcome the problems with low turnover, the Pd(P<sub>3</sub>) compartments were separated by a *m*-substituted aryl spacer from which binuclear Pd complexes were synthesised that acted as catalysts for CO<sub>2</sub> electroreduction to CO in acidic dimethylformamide solutions.<sup>43</sup> Unfortunately, in this case, the rates of reduction were similar to monometallic analogues (2-300 M<sup>-1</sup>s<sup>-1</sup>), which suggests that no cooperative effects operate. However, turnover

numbers were significantly higher (80% activity after 200 turnovers), and was attributed to an inability of these complexes to form inert Pd dimers.

### Cobalt complexes

Tetra-aza macrocyclic and porphyrinic complexes, especially those of cobalt, have been shown to be active catalysts in the reduction and photoreduction of CO<sub>2</sub> to CO, albeit at relatively high overpotentials (−1.3 to −1.6 vs. SHE) with low turnover frequencies.<sup>24</sup> Density functional theory calculations have been applied to analyse the mechanism of CO<sub>2</sub> reduction to CO in water catalysed by cobalt porphyrins, and it has been determined that CO<sub>2</sub> binds to the singly-reduced species [Co(I)P]<sup>−</sup> (where P = porphyrin).<sup>44</sup> The presence of water was seen to be important, as hydrogen-bonding interactions were found to stabilise the key intermediates [Co(I)P-CO<sub>2</sub>]<sup>2−</sup> and [Co(II)P-CO<sub>2</sub>H]<sup>−</sup>, resulting in an exothermic C-O bond cleavage step.

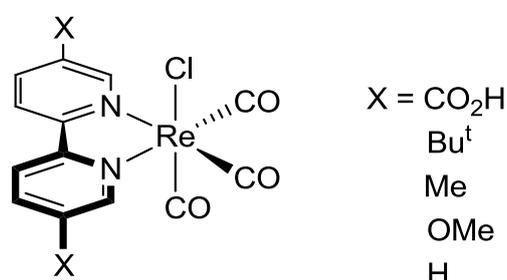
Considering the proclivity of binuclear cobalt cofacial diporphyrins for electroreduction chemistry, in particular that related to oxygen redox chemistry,<sup>45</sup> it is surprising that these systems are little used in relation to CO<sub>2</sub> reduction chemistry. Self-assembled cofacial diporphyrins have been generated in solution through Coulombic interactions between mixtures of cation- and anion-appended Co porphyrins (Figure 5).<sup>46</sup> According to cyclic voltammetry, a species active for CO<sub>2</sub> reduction was generated at −1.8 V vs. Ag<sup>+</sup>/Ag and was considered to be a Co(I) porphyrin complex. Using rotating disk voltammetry, the binuclear complex exhibited a 2-fold enhancement in activity compared to the mononuclear analogue, which was ascribed to anionic porphyrin acting as an electron mediator and not to the assembly of a specific cofacial porphyrin arrangement.



**Figure 5.** Self-assembled Co cofacial diporphyrins.

## Rhenium Complexes

Rhenium complexes of modified bipyridine ligands have been evaluated systematically as catalysts for CO<sub>2</sub> electroreduction to CO (Figure 6).<sup>47</sup> Variation of the 4, 4'-substituents according to increasing pyridyl pK<sub>a</sub> (X = CO<sub>2</sub>H < H < Me < Bu<sup>t</sup> < OCH<sub>3</sub>) resulted in increasingly negative reduction potentials (-1.72 to -1.86 V). The rhenium complex with X = Bu<sup>t</sup> was identified as the best catalyst, with the reduction wave at -1.83 V displaying large catalytic enhancement under a CO<sub>2</sub> atmosphere. A second order rate constant of 1000 M<sup>-1</sup>s<sup>-1</sup> was measured and the Faradaic efficiency for the gaseous product was determined as 99%. In terms of rate constant this Re catalyst is a marked improvement over previously-studied bipyridine complexes (e.g. X = H) and is similar to the best binuclear Pd catalyst described above.

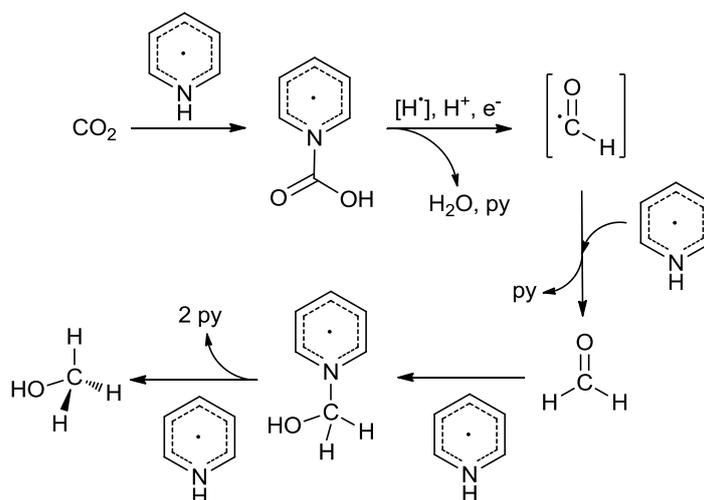


**Figure 6.** Bipyridyl complexes of Re for CO<sub>2</sub> reduction.

## No metals – nitrogen bases as one-electron shuttles

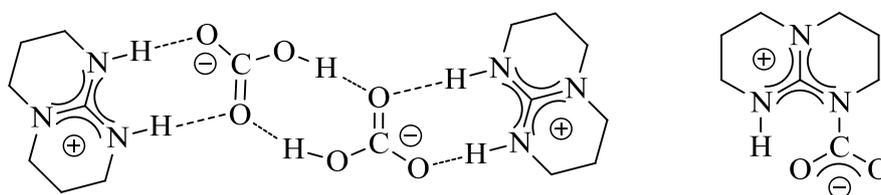
The electrochemical reduction of CO<sub>2</sub> catalysed by the metal complexes described above have almost exclusively produced two-electron reduction products such as CO, formate, and oxalate. The formation of further-reduced products such as methanol and methane could be considered more desirable yet are generally only produced through hydrogenation or silylation procedures. It is clear that there is difficulty in catalysing these multiple PCET processes and while this problem is frequently discussed in the redox chemistry of O<sub>2</sub> it is rarely tackled in CO<sub>2</sub> chemistry. However, some significant advances have been made using the pyridinium cation, which, at certain metal electrodes, catalyses the selective reduction of CO<sub>2</sub> to methanol.<sup>48</sup> Using this system, Faradaic efficiencies for the production of methanol were ~30%, observed at overpotentials of only ~0.2 V. Cyclic voltammetry analysis showed that pyridinium is a solution-dissolved species that must diffuse to the electrode. More recently, this chemistry was exported to a p-GaP photochemical system which yielded nearly 100% Faradaic efficiency for methanol at potentials 0.3 V below the thermodynamic potential for the reaction.<sup>49</sup> The mechanism for this catalytic reaction was investigated and was seen to proceed through six sequential single-electron transfers, ultimately, and selectively, forming methanol (Scheme 6).<sup>50</sup> No direct interaction between the pyridinium cation and CO<sub>2</sub> was seen, and CO<sub>2</sub> binding was only observed on single

electron reduction to the pyridinium radical. Several intermediates, including formic acid and formaldehyde were identified, and are stabilised through coordinative interactions. While it was clear that there are surface-sensitive aspects to this chemistry, the mechanism is dominated by solution processes, and operates in the absence of any metal-containing species.



**Scheme 6.** Aqueous CO<sub>2</sub> reduction to methanol catalysed by the pyridinium radical.

In a similar manner, polymers rich in nitrogen-bases such as benzimidazole and pyridine were assessed in the electrocatalytic reduction of CO<sub>2</sub> and were found to react irreversibly, undergoing electrochemically-driven carboxylation.<sup>51</sup> In contrast, polymers based on bipyridines exhibited catalytic reduction currents at -1.5 V under CO<sub>2</sub>, although the product(s) of this reaction were not identified. It was thought that these polymers would exhibit electrochemistry similar to that seen for the pyridinium cation described above.



**Figure 7.** Guanidinium bicarbonate and carboxylate salts derived from CO<sub>2</sub>.

Nitrogen bases are well known to sequester CO<sub>2</sub>, and form the basis of much of the technology currently being assessed for CCS.<sup>2</sup> Recently however, hindered amidines and guanidines, which are useful catalysts for

the formation of organic carbonates and urethanes, were found to react directly with CO<sub>2</sub> (Figure 7).<sup>52</sup> In the presence of ambient moisture, the guanidine base 1,5,7-triazabicyclo[4.4.0]dec-5-ene was found to form a bicarbonate adduct that was crystallographically-characterised as a dimer formed through H-bonding interactions (Figure 7, left). More significantly however, was the reaction in the absence of moisture, which resulted in the formation of the first nitrogen base-CO<sub>2</sub> adduct (Figure 7, right). This compound is stable at room temperature in the solid state and in solution, and was described as having a zwitterionic electronic structure by X-ray analysis and DFT calculations. While no electrochemical studies have been carried out, the similarity of these systems to those containing N-heterocyclic carbene and pyridine bases is clear and so they would be expected to act as organocatalysts for CO<sub>2</sub> transformation.

## Conclusions

Over recent years, CO<sub>2</sub> has become increasingly recognised as a valuable resource, and its large scale conversion into useful chemicals such as fuels has the potential for reducing fossil fuel consumption and mitigating atmospheric CO<sub>2</sub> pollution. However, even if thermodynamic considerations are ignored, it is clear that the present state-of-the-art catalysts for CO<sub>2</sub> reduction are not yet compatible with these grand aims. While enzymes are capable of the multiple electron reduction of CO<sub>2</sub> to valuable products such as methanol at very low overpotentials, they are rarely robust enough to be used in industrial processes. Metal and metal alloy electrodes can be considered robust, but usually generate CO as the major reduction product at large overpotentials. Cu electrodes are unique in that hydrocarbons are produced, although with some lack of selectivity and at the expense of large overpotentials.

Molecular catalysts should be able to bridge the biological and industrial and provide unique insight into mechanisms. New catalyst designs have been reported, some of which resemble the active sites of CO<sub>2</sub>-reducing enzymes. However, these complexes suffer from a tendency to promote only two-electron reduction to CO, formate, and oxalate, and do not have sufficiently high rates and chemical robustness for use in large-scale operations. Metal complexes have been promoted as a necessity for controlling multiple PCET reactions, yet the simple pyridinium cation has been shown to catalyse the selective reduction of CO<sub>2</sub> to methanol at very modest overpotentials.

While exciting new approaches to carbon capture and utilisation have been realised, it is clear that new invention is required in this area. This may involve the evaluation of compounds known to exhibit catalytic activity in related processes such as oxygen reduction.<sup>53</sup> Alternatively, the development of complexes that incorporate ditopic CO<sub>2</sub> binding sites and/or the potential for control of secondary interactions could be fruitful.<sup>54</sup> Whatever new approaches are envisaged, this area of research requires a combination of scientific expertises, ranging from synthesis and electrochemistry to theory and chemical engineering.

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