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Cu^{I} SNS triazole and imidazole pincers as electrocatalyst precursors for the production of solar fuels†

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This work reports the first example of mono-nuclear Cu pincers with SNS ligation acting as electrocatalyst precursors for the electrochemical conversion of carbon dioxide to CO and H_2 in protic organic media.

With the advent of societal interest in renewable energy storage, the use of electricity in solar powered-chemical transformations has become a central research effort in modern chemical science.[1–5] Catalysis for electrochemical conversions of abundant carbon sources such as CO_2 to fuels and chemical precursors, has therefore been at the forefront of reaction development, with the specific target of efficient C–C-bond formation reactions and the synthesis of complex carbon compounds.[6,7] While CO_2 conversion[8,9] remains a central effort in this arena, a synergistic research vein in the field of water splitting aims to efficiently produce hydrogen fuel from protic media such as water.[10] As a consequence, electrocatalytic methods for cathodic production of hydrogen and anodic production of oxygen from water play key roles in the advancement of the field of solar fuel production.[11–16] This report focuses on the characterization of new catalysts for the reduction of carbon dioxide and protons.

In the field of heterogeneous electrocatalysis, copper is a privileged metal for CO_2 reduction,[17,18] showing excellent rates, but often poor product selectivity. Molecular catalysts therefore have the distinct advantage of structural tunability and can impart control of the chemical reaction at the molecular level. In the arena of molecular electrocatalysis, multinuclear Cu coordination compounds have been reported to enable C–C coupling reactions of CO_2 at cathodes,[19–21] with related metal sulfide clusters of Co and Ir also being active.[6] In recent work by Wang and co-workers, a Cu bis-phenanthroline complex was used as a heterogenized molecular catalyst on graphene with good reaction rates.[22] Given this precedent, we were therefore encouraged to consider the design of novel Cu mono-nuclear catalysts with S-containing coordination.

Against the backdrop of recent advances in molecular catalysis mediated by first-row metal pincers,[23] we identified compounds **1** and **2** (Fig. 1) as potential candidates for electrocatalysis for the conversion of CO_2.[24] To the best of our knowledge, these compounds are the first instance of electrocatalysts for CO_2 reduction based on mono-nuclear Cu^{I} pincer precursors.

Cyclic voltammetry in acetonitrile (MeCN) with 0.1 M tetrabutylammonium hexafluorophosphate (TBA PF_6) was performed to assess the reductive responses of two electrocatalyst candidates: Cu^{I} pincer compounds **1** and **2**. Fig. 1 shows the reductive scans of the two pincers of interest in this work at 100 mV s^{-1}. Pincer **1**, a triazole-based Cu^{I} complex exhibits two reductive features, one at −2.8 V *vs.* Fc/Fc^{+} and another one at −3 V with only one observable oxidation return at −0.7 V. This response suggests the reduction of the complex likely occurs with participation of the ligand, as has been observed in other pincer ligands with aromatic ligand fragments.[13,19] In comparison, the pyridine 2,6-bis-methyl (imidazole) Cu^{I} pincer **2** exhibits reduction responses at −1.8 V and −2.75 V *vs.* Fc/Fc^{+} but with a similar oxidation return at −0.77 V. Diffusional behaviour for both **1** and **2** was additionally confirmed through scan rate dependence experiments at 100, 200, 300, 400, 500 and 600 mV s^{-1} respectively. Linearity in plots of the observed peak currents *versus* (Sevçik plots) confirms that both complexes are freely diffusing in solution during the reductive scans (Fig. S3 and S7†). In addition, surface elemental analyses by Energy Dispersive Spectroscopy (EDS) of the electrolysis electrodes do not reveal detectable amounts of elemental copper (Fig. S9†).

With these diagnostics in hand, we proceeded to analyse the cyclic voltammograms of the two pincers in the presence

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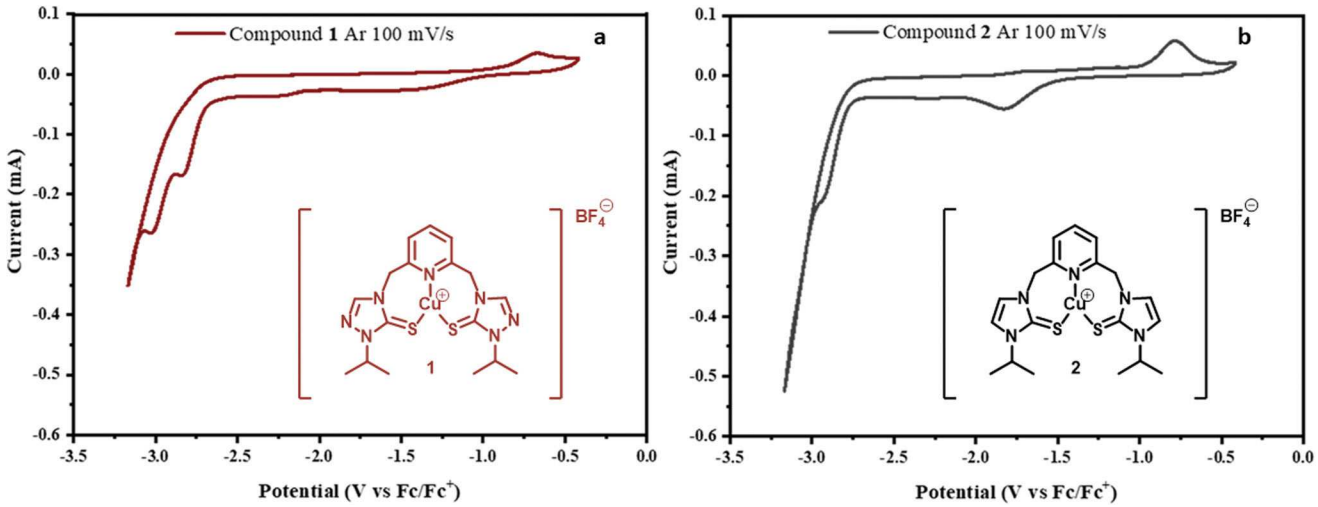

Fig. 1 (a) Cyclic voltammogram of 5 mM compound **1** in MeCN with 0.1 M TBA PF_6 as a supporting electrolyte at 100 mV s^{-1} at a glassy carbon working electrode, referenced externally *vs.* Fc/Fc^+ under an argon atmosphere. (b) Cyclic voltammogram of 5 mM compound **2** in MeCN with 0.1 M TBA PF_6 as supporting electrolyte at 100 mV s^{-1} at a glassy carbon working electrode, referenced externally *vs.* Fc/Fc^+ under an argon atmosphere.

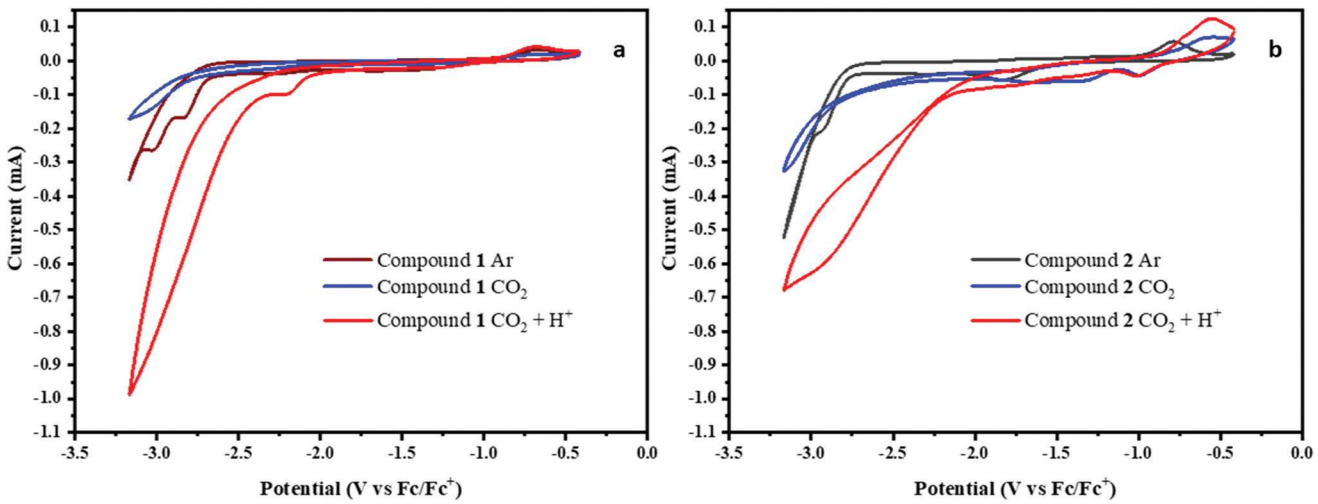

Fig. 2 Left (a) Cyclic voltammogram of 5 mM compound **1** in MeCN with 0.1 M TBA PF_6 as a supporting electrolyte at 100 mV s^{-1} at a glassy carbon working electrode, referenced externally *vs.* Fc/Fc^+ under argon atmosphere (black), CO_2 atmosphere (blue), and CO_2 atmosphere with 100 μL 2,2,2-trifluoroethanol (TFE) as a proton source (purple) Right (b). Cyclic voltammogram of 5 mM compound **2** in MeCN with 0.1 M TBA PF_6 as a supporting electrolyte at 100 mV s^{-1} at a glassy carbon working electrode, referenced externally *vs.* Fc/Fc^+ under argon atmosphere (black), CO_2 atmosphere (blue), and CO_2 atmosphere with 100 μL TFE as a proton source (red).

of CO_2 and added proton source: 2,2,2-trifluoroethanol (TFE) (Fig. 2). Incremental addition of protons to compound **1** in the absence of CO_2 indicates a catalytic response for hydrogen production with the appearance of one single CV wave (Fig. S4†). The voltammetry of pincer **1** shows a distinct interaction with CO_2 and the current increases at −2 V in the presence of protons (Fig. 2a) with a corresponding return oxidation at −0.6 V. The appearance of the catalytic wave suggests two redox events are involved in turnover. Compound **2** under argon does not respond to protons at low concentrations by cyclic voltammetry (Fig. S8†). We believe this is the case due to relative timescale of the rates of catalytic responses in relation to the electrochemical reduction steps. The voltammetry of pincer **2** also shows an interaction with CO_2 at −2 V *vs.* Fc/Fc^+ and a catalytic response upon the addition of protons (Fig. 2b). Both compounds show similar catalytic onset potentials, with compound **1** showing a distinct prewave prior to turnover. While redox electrocatalysis has been often associated with a redox wave in the starting metal complex, this is not always the case, responses often being associated with the redox-response of an electrochemically-generated intermediate or an alternate physical process[13] (Fig. 2b).

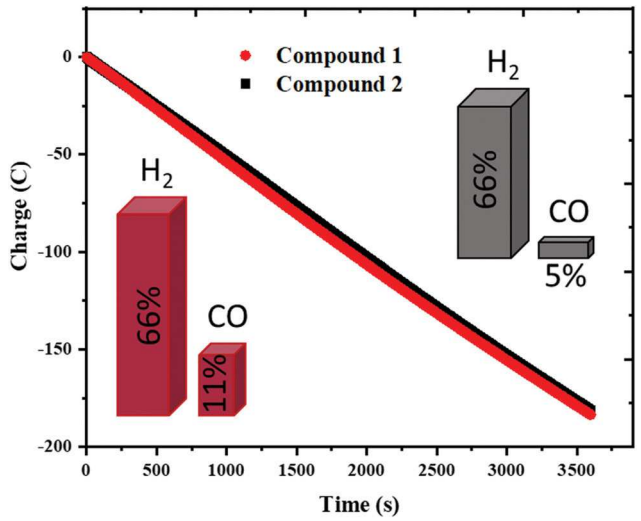

Fig. 3 Plots of charge passed (C) *vs.* time (s) for 1 h electrolyses at −2.6 V *vs.* Fc/Fc^+ of compounds **1** and **2** with the respective observed faradaic efficiencies for the formation of H_2 and CO.

Given the positive result of the CV diagnostics of pincers **1** and **2** from Fig. 2, we proceeded to identify product distributions and faradaic efficiencies for the observed currents using bulk electrolysis. Bulk electrolysis experiments were run in a two-chamber H-cell separated by a glass frit with carbon cloth working electrodes and a Ag single-junction reference, referenced externally *vs.* Fc/Fc^+. Electrolyses at −2.6 V *vs.* Fc/Fc^+ passed 183 C and 178 C for pincers **1** and **2**, respectively. Headspace analyses of the reactions were performed using gas chromatography with a thermal conductivity detector (GC-TCD). (Detailed experimental procedures and analyses are provided in the ESI.†)

While the charge passed through the cell is similar for the two compounds under study, the observed product distributions indicate that triazole pincer **1** is more active for the conversion of CO_2 over protons than pincer **2** with observed ratios of H_2 : CO of 6 : 1 for **1** and 12.6 : 1 for **2**, respectively. faradaic efficiencies for H_2 formation during the electrolysis experiments are similar, with ~66% of the current being committed to the reduction of protons in both cases (additional details available in Table S5†). In contrast, faradaic efficiencies for the formation of CO vary between the two pincers: pincer **1** exhibits a faradaic efficiency of 11.02 ± 0.40%, while pincer **2** has an efficiency of 5.23 ± 0.65%. These efficiencies correlate with the production of CO with 4 observed turnovers per hour for compound **1**, while compound **2** turns over only 0.6 times over the same duration for CO production (Fig. 3).

Conclusions

In conclusion, we now report the first instance of mononuclear catalyst precursors for the electrochemical conversion of CO_2 to CO and H_2 based on Cu^I. While the observed activities remain modest, this work sets the stage for further development of pincer electrocatalysis based on first row, inexpensive Cu coordination complexes. Additional mechanistic studies will focus on elucidating speciation and identification of electrocatalytically-active species.

Conflicts of interest

There are no conflicts to declare.

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