

**Cu^I SNS Triazole and Imidazole Pincers as Electrocatalyst
Precursors for the Production of Solar Fuels**

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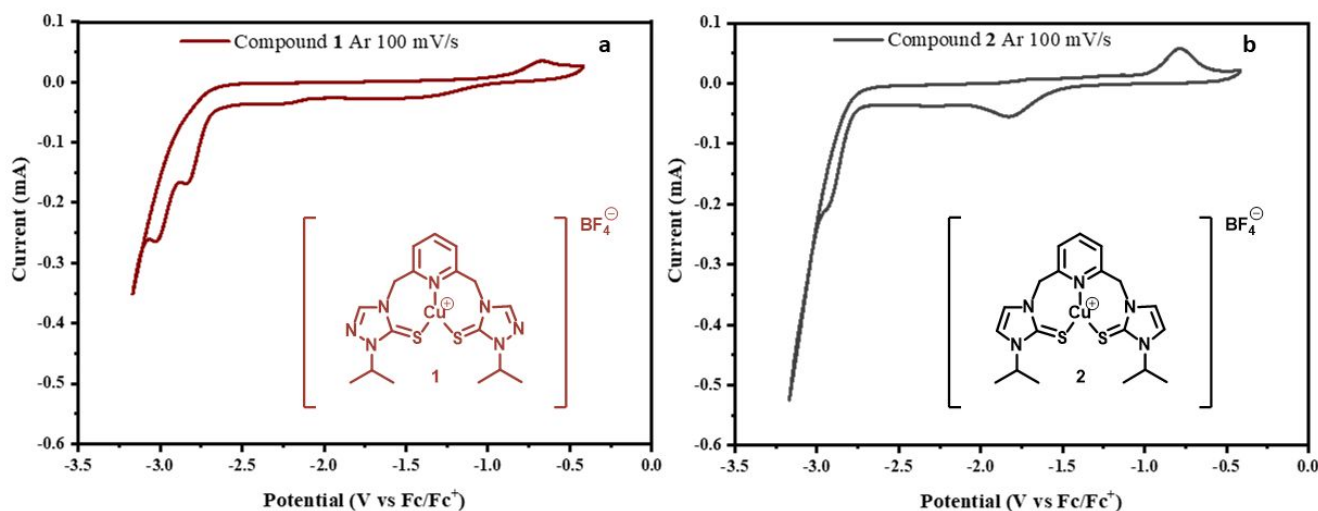
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This work reports the first example of mono-nuclear Cu pincers with SNS ligation acting as electrocatalyst precursors for the electrochemical conversion of carbon dioxide to CO and H₂ in protic organic media.

With the advent of societal interest towards 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 CO₂ to fuels and chemical precursors, has therefore been at the forefront of reaction development, with the specific target of efficient C-C-bond formation

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 CO₂ 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



reactions and the synthesis of complex carbon compounds.⁶⁻⁷ While CO₂ conversion⁸⁻⁹ remains a central effort in this arena, a synergistic

chemical reaction at the molecular level. In the arena of molecular electrocatalysis, multi-nuclear Cu coordination compounds have been reported to mediate C-C coupling reactions of CO₂ 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.

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Figure 1. *a* Cyclic Voltammogram of 5 mM Compound 1 in MeCN with 0.1 M TBA PF₆ as a supporting electrolyte at 100 mV/s 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 PF₆ as supporting electrolyte at 100 mV/s at a glassy carbon working electrode, referenced externally vs Fc/Fc⁺ under an argon atmosphere.

Against the backdrop of recent advances in molecular catalysis mediated by first-row metal pincers,²³ we identified Compounds **1** and **2** (Figure 1) as potential candidates for electrocatalysis for the conversion of CO₂.²⁴ To the best of our knowledge, these compounds are the first instance of electrocatalysts for CO₂ reduction based on mono-nuclear Cu^I pincer precursors.

Cyclic voltammetry in acetonitrile (MeCN) with 0.1 M

catalytic response for hydrogen production with the appearance of one single CV wave. (Figure S4) The voltammetry of Pincer **1** shows a distinct interaction with CO₂ and the current increases at -2 V in the presence of protons (Figure 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

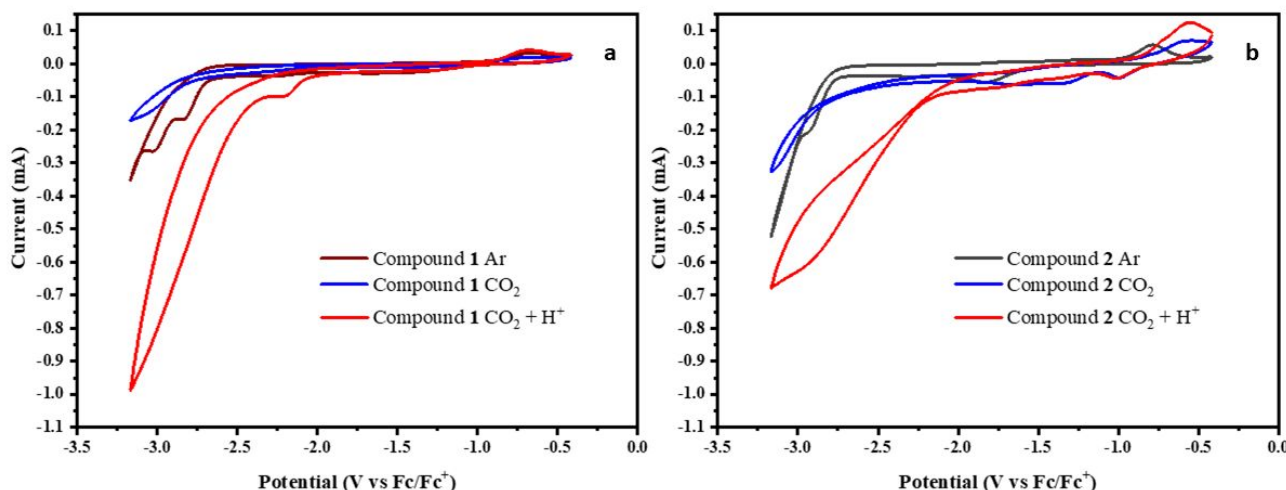


Figure 2. Left a Cyclic Voltammogram of 5 mM Compound **1** in MeCN with 0.1 M TBA PF₆ as a supporting electrolyte at 100 mV/s at a glassy carbon working electrode, referenced externally vs Fc/Fc⁺ under argon atmosphere (black), CO₂ atmosphere (blue), and CO₂ atmosphere with 100 μL 2,2,2-Trifluoroethanol (TFE) as a proton source (purple) Right b. Cyclic Voltammogram of 5 mM Compound **2** in MeCN with 0.1 M TBA PF₆ as a supporting electrolyte at 100 mV/s at a glassy carbon working electrode, referenced externally vs Fc/Fc⁺ under argon atmosphere (black), CO₂ atmosphere (blue), and CO₂ atmosphere with 100 μL TFE as a proton source (red).

tetrabutylammonium hexafluorophosphate (TBAPF₆) was performed to assess the reductive responses of two electrocatalyst candidates: Cu^I pincer compounds **1** and **2**. Figure 1 shows the reductive scans of the two pincers of interest in this work at 100 mV/s. 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 respectively.

Linearity in plots of the observed peak currents versus $\sqrt{\text{scan rate}}$ (Sevcik plots) confirms that both complexes are freely diffusing in solution during the reductive scans (Figures 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 (Figure S9).

With these diagnostics in hand, we proceeded to analyse the cyclic voltammograms of the two pincers in the presence of CO₂ and added proton source: 2,2,2-trifluoroethanol (TFE). (Figure 2) Incremental addition of protons to compound **1** in the absence of CO₂ indicates a

voltammetry. (Figure 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 CO₂ at -2 V vs Fc/Fc⁺ and a catalytic response upon the addition of protons (Figure 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, with responses being associated with the redox-response of an electrochemically-generated intermediate or an alternate physical process.¹³ (Figure 2b)

Given the positive the CV diagnostics of pincers **1** and **2** from Figure 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 CO₂ over protons than pincer **2** with observed ratios of H₂:CO of 6:1 for **1** and 12.6:1 for **2**, respectively. Faradaic efficiencies for H₂ formation

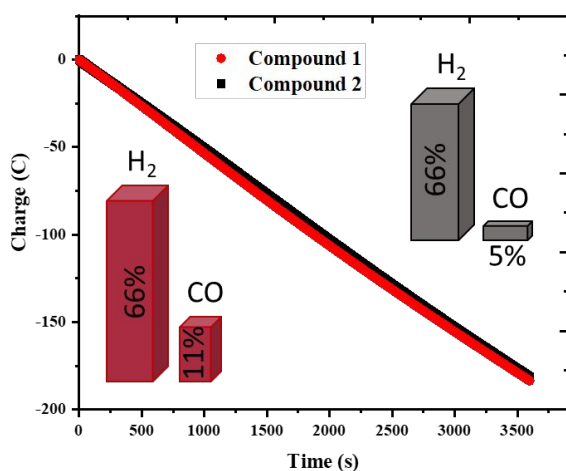


Figure 3. Plots of charge passed (Coulombs) vs time (s) for 1h electrolyses at -2.6 V vs Fc/Fc⁺ of Compounds **1** and **2** with the respective observed Faradaic efficiencies for the formation of H₂ and CO.

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.

Conclusions

In conclusion, we now report the first instance of mononuclear catalyst precursors for the electrochemical conversion of CO₂ to CO and H₂ 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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