Surprisingly big linker-dependence of activity and selectivity in CO₂ reduction by an iridium(i) pincer complex†

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Here, we report the quantitative electroreduction of CO₂ to CO by a PNP-pincer iridium(i) complex bearing amino linkers in DMF/water. The electrocatalytic properties greatly depend on the choice of linker within the ligand. The complex 3-N is far superior to the analogues with methylene and oxygen linkers, showing higher activity and better selectivity for CO₂ over proton reduction.

The electroreduction of CO₂ to CO provides a pathway for conversion of electrical energy from renewable sources into liquid fuels and useful organic chemicals.†−25 Despite notable progress in the development of several efficient CO₂ reduction catalysts (metals, metal oxides, organometallic complexes, and main-group compounds),†−5,7−15 it remains challenging to improve the rate and selectivity of multielectron reduction reactions at low overpotentials.

Iridium complexes have been widely studied as efficient catalysts for the production of formate, oxalate, and carbon monoxide (CO).‡ Previously reported, while the NH linkers are replaced by CH₂ groups (3-C) as well as oxygen (3-O) linkers (Chart 1), the activity and selectivity of Ir(I) complexes towards CO₂ reduction has drastically lower catalytic activity, we therefore analysed the origin of this unexpected variation in product selectivity at the density functional theory (DFT) level.

The preparation and characterization of complex 3-C was previously reported, while 3-N and 3-O were synthesized by cyclometallation of the corresponding pincer ligands with [IrCl(COE)2]2 and [Ir(COE)2(acetone)2]PF₆ (COE = cyclooctene), respectively, followed by ligand exchange with CO (Scheme S1, ESI†). The successful substitution of COE by CO was confirmed by the disappearance of the aliphatic protons of the COE ligand in the ¹H NMR spectrum and the appearance of IR bands at 1962 cm⁻¹ for 3-N and 3-O (Fig. S1, ESI†).

The electrochemical properties of the complexes were investigated using cyclic voltammetry (CV) in aqueous DMF (5 M H₂O)
with glassy carbon as the working electrode and 0.1 M [\text{Bu}_{4}N][PF_6] as the supporting electrolyte. Under argon, the CV of 3-N shows the first irreversible reduction peak at −1.91 V, and the second at −2.39 V (Fig. 1A and Fig. S3, ESI†). All potentials are listed versus Ag/AgCl (see ESI†). DFT calculations predicted successive one-electron reductions at −1.93 V and −2.39 V vs. Ag/AgCl, in excellent agreement with our measurements (Fig. S4, ESI†). The plots of peak current versus square root of the scan rate are linear, as expected for a diffusion-controlled process (inset in Fig. S5, ESI†).

Catalytic CO₂ electroreduction of 3-N was identified by comparing CV measurements in DMF under Ar with those under CO₂ both with and without 5 M water as the proton source. Fig. 1 shows the normalized current \(i_{\text{cat}}/i_p\), where \(i_p\) is the peak current for the first reduction for each species under argon, and \(i_{\text{cat}}\) is the measured catalytic current. In CO₂-saturated dry DMF, a cathodic current increase is observed at \(i_{\text{cat}}/i_p = 4.3\), along with a 100 mV cathodic shift of the peak potential to −2.01 V (Fig. 1A, blue). The cathodic shift in the reduction potential indicates substrate binding to 3-N. Further CV measurements in the presence of CO₂ and water (5 M) afforded a significant catalytic current \(i_{\text{cat}}/i_p = 8.7\), corresponding to CO₂ reduction (Fig. 1A, red). The overpotential was estimated to be 0.86 V, using the half-wave potential (−1.89 V vs. Ag/AgCl) and the thermodynamic potential for CO₂ to CO conversion in DMF/H₂O mixture from the literature (see ESI†). The catalytic activity is retained and that no metal demetallation are insignificant during CPE. Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS) and X-ray Photoelectron Spectroscopy (XPS) were performed on the carbon fibre paper after CPE (Fig. S15–S17, ESI†). The absence of an iridium signal in either the EDS or XPS spectra suggests no significant iridium demetallation at the carbon electrode. The carbon electrode of 3-N was gently washed with DMF after CPE and used again as the working electrode in a fresh electrolyte solution (DMF with 5 M water) without 3-N.
CO₂ reduction product was detected, further confirming that the active species for CO₂ reduction is homogeneous 3-N, rather than its heterogenized form, or deposited iridium metal.

The electronic properties of the three complexes, before and after reduction, were analysed by DFT calculations that provided insights into the origin of the unexpected changes in catalytic activity and selectivity induced by the change of linker. The calculations reproduced the experimental trends in carbonyl stretching frequencies (Table S2, ESI†) and the reduction potentials for the three complexes (Table S3, ESI†). The calculated one-electron reduction potentials, \( \overline{E_{1}} = -1.93 \) V for 3-N, \( \overline{E_{1}} = -1.81 \) V for 3-C, and \( \overline{E_{1}} = -1.67 \) V for 3-O, are in good agreement with the experimental potentials. As expected, the trend in reduction potentials correlates with the relative LUMO energies of the three complexes, with higher energy LUMOs corresponding to more negative reduction potentials (Fig. 3). A relationship between LUMO energies and electron affinity follows from Koopmans’ theorem,\(^{36}\) and a linear correlation between DFT LUMO energies and reduction potentials has previously been demonstrated.\(^{37}\) For all three complexes, the HOMOs are centred on the Ir, while the LUMOs are delocalized over the ligand and metal centre (Fig. S21, ESI†). The LUMO of 3-N has more Ir character, suggesting that the reduction is predominantly centred on the metal.

DFT calculations shed light on the effect of reduction. The comparison of spin densities in the reduced complexes (Fig. 4) reveals that the unpaired electron in 3-N is most localized on the Ir centre. This may be the key factor that makes 3-N more reactive than the other complexes in the series for CO₂ reduction. The SOMOs of the reduced complexes (Fig. S22, ESI†) and corresponding spin population analysis (Fig. S23 and Table S4, ESI†) further support the idea that the Ir centre of 3-N is more affected upon reduction than those of 3-C, or 3-O. In all cases, the linker atoms themselves have negligible spin population, suggesting that the linker substitution alters the reactivity by tuning the electronic properties of the ligand. Additionally, electron density...
difference plots (Fig. S24, ESI†) show that 3-N has the largest increase in electron density at the metal centre after reduction. Before reduction, 3-C has the most electron density on the Ir consistent with the experimental and calculated CO stretching frequencies (Table S2, ESI†) and CM5 partial charges (Table S5, ESI†). After reduction, 3-N has the more electron density on the Ir, and corresponding lower CO stretching frequency and more negative partial charge on the Ir atom than for the other members of the series. Taken together, these calculations suggest that the linker atoms modulate the electron density at the catalytic centre by tuning the electronic properties of the ligand.

In summary, we find that the electrocatalytic properties of a series of three pincer-iridium(i) complexes are strongly modulated by the nature of the ligand. Complex 3-N with amino linkers in the pincer ligand exhibited prolonged stability and nearly quantitative efficiency for CO2-to-CO conversion, with no significant proton reduction observed with a half-wave overpotential about 0.86 V. The complex remained molecular throughout the course of electrolysis. Replacing the amino unit with a methylene group resulted in complex 3-C, with poor selectivity, while replacing the amino group by an oxygen unit leads to 3-O which has no significant catalytic activity. DFT calculations suggest that 3-N is most active possibly because of the highest electron density on the iridium centre after reduction, leading to a more active catalytic centre for CO2 reduction. Increased electron density at the metal centre has previously been shown to result in higher activities and increased faradaic efficiency for CO production.39,40 In-depth mechanistic studies are in progress. These results suggest that variation of the linkers in pincer ligands can strongly affect the catalytic performance by modulating the spin density on the CO2 binding site and could thus be exploited for ligand screening in computational catalyst design.41

We thank the staff at the Yale West Campus Analytical Core and the Yale Chemical and Biophysical Instrumentation Centre for their help with the instrumentation. This work was supported by the U.S. Department of Energy, Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science (Grant DEFG02-07ER15909) and partly by the U.S. National Science Foundation (grant CHE-1651717). Additional support was provided by a generous donation from the TomKat Charitable Trust. V. S. B. acknowledges computational time from NERSC and Yale HPC.

Conflicts of interest

There are no conflicts to declare.

Notes and references