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A nickel complex with a biscarbene pincer-type ligand shows high electrocatalytic reduction of CO$_2$ over H$_2$O

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We report a planar nickel complex coordinated with a pincer-type carbene-pyridine-carbene ligand which exhibits high selectivity for electrocatalytic CO$_2$ reduction in the presence of H$_2$O.

Catalytic conversion of CO$_2$ to fuels and value-added fine chemicals has the potential to offset some fossil fuel combustion.$^1$ To realize a large-scale deployment of CO$_2$ reduction, it is critical to develop low-cost catalysts that selectively reduce CO$_2$ over competing H$_2$ evolution reaction (HER). Heterogeneous transition-metal catalysts, such as Cu, Ag, Au, Sn, and Pd-based nanocomposites,$^{2,4}$ have emerged as promising CO$_2$ reduction catalysts, but the lack of molecular-level mechanistic understanding of catalytic active sites impedes further development. Discrete molecular/homogeneous catalysts offer the advantage of direct catalytic activity tuning through ligand design and direct catalyst performance testing through spectroscopic detection.

The two-electron/two-proton reduction of CO$_2$ to CO is an appealing process because CO can be directly utilized as a fuel or commodity chemical in mature industrial processes.$^7$ At pH 7 the thermodynamic potential of CO$_2$ reduction to CO is ~0.53 V vs standard hydrogen electrode (SHE)$^7$ while HER requires a less negative potential, ~0.413 V vs SHE. Therefore, it is imperative to develop CO$_2$ reduction catalysts with a particularly high selectivity over HER in the presence of H$_2$O or other proton sources that may divert reducing power and lower Faradaic efficiency. Many molecular CO$_2$ reduction catalysts utilize ligands of porphyrins,$^6$ phthalocyanines,$^7$ polypyridines,$^8$ and phosphines,$^9$ most of which require sophisticated synthetic routes and/or are moisture/air sensitive. Nearly two decades ago, Sauvage et al. reported nickel complexes bearing N$_7$-macrocycles (cyclam) that exhibited remarkable high selectivity for CO$_2$ reduction over HER.$^{10}$ Since Sauvage's seminal work, only a limited number of nickel catalysts have been reported showing comparable or better performance than the [Ni(cyclam)]$^{2+}$ system.$^{11}$

Following the design principle of [Ni(cyclam)]$^{2+}$, a number of planar tetradentate ligands have been employed in the development of nickel-based catalysts for CO$_2$ reduction.$^{15}$ In contrast, we reason that a tridentate pincer-type ligand would also support Ni$^{2+}$ in a pseudo square planar geometry if the fourth site can be occupied by a labile solvent molecule. Such a strategy not only allows the accessibility of the apical site of the nickel center towards CO$_2$, but also might lead to an exchange of the bound solvent molecule and CO$_2$ at one of the equatorial sites, enriching the interaction mode of CO$_2$ with the catalyst. Herein, we report the synthesis, experimental and computational characterization, and evaluation of a nickel complex coordinated with a pyridyl-biscarbene pincer-type ligand which shows high selectivity for electrocatalytic CO$_2$ reduction over HER.

The nickel [(CNC)NiBr]Br complex with a pincer-type biscarbene ligand (CNCBr$_2$, Fig. 1) was previously reported as a catalyst for Heck and Suzuki coupling reactions.$^{13}$ To avoid the influence of redox active Br$^-$ and Br$_2$, we treated CNCBr$_2$ with AgOTf (OTf = trifluoromethanesulfonate) to obtain CNC(OTf)$_2$. Subsequent metalation of CNC(OTf)$_2$ with nickel triflate in CH$_3$CN formed [(CNC)Ni(NCCH$_3$)$_2$](OTf)$_2$ (CNC-Ni, Fig. 1). Slow vapor diffusion
of diethyl ether into the concentrated CH$_2$CN solution of CNC-Ni produced light yellow crystalline needles. The structure of CNC-Ni was obtained by single crystal X-ray diffraction (Fig. 1). As expected, the diamagnetic Ni$^{II}$ CNC-Ni complex is in a pseudo square planar geometry. Similar to the crystal structure of [(CNC)NiBr]Br, the Ni-N5 and Ni1-N6 distances of CNC-Ni fall in the region of 1.83–1.85 Å, while Ni-C1 and Ni-C11 bonds are within 1.91–1.92 Å. The N5-Ni1-C11 angle (176.6°) slightly deviates from 180° angle expected for a square planar geometry. Geometric constraint of the pyridyl linker between the two imidazole rings results in a C1-Ni-C11 angle of 163.2°. Overall, the tridentate pincer-type ligand combined with a CH$_2$CN occupying the fourth planar coordination site provides a catalyst with the possibility to interact with CO$_2$ at either the apical site or the equatorial site if CH$_2$CN dissociates after catalyst reduction.

![Fig. 2](image1)

Fig. 2 (a) UV-visible absorbance of free ligand (black) and CNC-Ni (red) in acetonitrile under air. (b) Comparison of the UV-visible absorbance spectra of CNC-Ni in acetonitrile under air (black), N$_2$ (red), and CO$_2$ (blue).

![Fig. 3](image2)

Fig. 3 M06 molecular orbitals corresponding to TD-DFT excitations for CNC-Ni.

UV-visible absorbance spectra of CNC-Ni and the free ligand CNC(OTf)$_2$ in CH$_2$CN are compared in Fig. 2(a). The absorbance of CNC(OTf)$_2$ only features a strong peak at 281 nm (4,681 M$^{-1}$ cm$^{-1}$) in the UV region, potentially due to a π-to-π* transition. To model this and other absorbances, we carried out (U)M06/LANL2TZ(f)(6-311+G(2d,p))/M06/LANL2DZ(6-31G(d,p)) TD-DFT calculations in Gaussian 09 (see SI for details). With the implicit SMD solvent model for CH$_2$CN the major excitation calculated above 250 nm is at 276 nm. Indeed, this excitation is principally a π-to-π* (HOMO to LUMO) transition.

The pale yellow solution of CNC-Ni shows a prominent peak at 290 nm (6,899 M$^{-1}$ cm$^{-1}$) with two shoulder peaks at 268 nm (5,782 M$^{-1}$ cm$^{-1}$) and 318 nm (3,967 M$^{-1}$ cm$^{-1}$). In addition, there exists another broad feature with a maximum at 377 nm (1,501 M$^{-1}$ cm$^{-1}$). The major calculated excitation at 284 nm corresponds to ligand-to-metal charge transfer (LMCT) from HOMO-2 to LUMO (Fig. 3). There is a TD-DFT excitation at 307 nm that corresponds to a weak HOMO-1 to LUMO transition. The TD-DFT calculations also show a very weak transition at 361 nm, which can be attributed to a HOMO-LUMO excitation that results in LMCT.

In order to test whether CO$_2$ is able to bind CNC-Ni, UV-visible absorbance was also measured under different atmospheres. As shown in Fig. 2b, the perfect overlap of the absorbance spectra of CNC-Ni under air, N$_2$, and CO$_2$ excludes the possibility of CO$_2$ binding to CNC-Ni prior to electrochemical reduction. Our DFT calculations also suggest that both CO$_2$ and CO$_2$/H$_2$O apical coordination to CNC-Ni are not stable. Additionally, the coordination energy of CH$_2$CN to CNC-Ni is ~25 kcal/mol and therefore at ambient temperature CO$_2$ is also unlikely to interchange with CH$_2$CN.

We next assessed the capability of CNC-Ni as an electrocatalyst for CO$_2$ reduction in CH$_2$CN. Fig. 4 displays the cyclic voltammogram of CNC-Ni under N$_2$. Two irreversible reduction peaks were observed at −1.19 and −1.38 V vs. Fe$^{3+}$/Fe (Fe$^{3+}$ = ferrocenium/ferrocene redox couple; unless otherwise noted, all the potentials reported are versus Fe$^{3+}$/Fe$^{2+}$). Scanning towards further negative potential reveals a third irreversible peak at −1.77 V. The blank glassy carbon is redox silent in this potential region. Plotting the peak currents at these potentials versus the square root of scan rates leads to a linear relationship for each redox process (Fig. S1 in the SI), confirming the molecular nature of CNC-Ni dissolved in the bulk electrolyte and no absorbed species on the electrode surface was contributing to the measured electrochemical signal. The free ligand CNC(OTf)$_2$ only exhibits one irreversible peak at −1.79 V prior to −2 V under the same condition (Fig. S2a). Because of the similarity between the third reduction peak (−1.77 V) of CNC-Ni and the reduction peak (−1.79 V) of CNC(OTf)$_2$, the former is attributed to a ligand-based redox process.

The calculated Ni$^{II}$ absolute reduction free energy of CNC-Ni is −87.6 kcal/mol. Relative to the experimental Fe$^{3+}$/Fe$^{2+}$ couple value of −114.8 kcal/mol (−4.98 V) in CH$_2$CN, this results in a calculated Ni$^{II}$ value of −1.19 V that is identical to experiment (see SI for prediction of alternative density functionals). A plot of the α-spin density...
M Bu$_4$PF$_6$ as the supporting electrolyte (scan rate: 100 mV/s).

Fig. 5 Cyclic voltammograms of CNC-Ni under (a) N$_2$ and (b) CO$_2$ with increasing addition of H$_2$O from 0 to 1.1 mM. (c) The comparison of I$/p$ versus the concentration of H$_2$O ([H$_2$O]) in CH$_3$CN for CNC-Ni under N$_2$ (black) and CO$_2$ (red). I$_c$ is the cathodic current at $-1.77$ V (N$_2$) or $-1.85$ V (CO$_2$); while I$_p$ is the cathodic current of the first reduction peak in each cyclic voltammogram. Background current from the blank glassy carbon electrode was subtracted in calculating I$/p$.

polarization for [(CNC)Ni(NCCH$_3$)$_3$]$^+$ suggests that the excess spin density upon reduction of CNC-Ni occurs at the Ni metal center, but is also partially delocalized onto the CNC ligand framework.

In CO$_2$-saturated CH$_3$CN, the first two reduction peaks of CNC-Ni remained at the same potentials (Fig. 4), implying the parent nickel complex did not interact with CO$_2$ substantially which is consistent with the UV-vis absorbance results. However, a current enhancement was observed prior to the third reduction peak, showing an onset at $-1.55$ V. Such a dramatic current increase is indicative of electrocatalytic CO$_2$ reduction. It should be noted that the catalytic onset is less negative compared to that of Chang’s nickel catalyst for CO$_2$ reduction (beyond $-1.6$ V) under a similar condition. Furthermore, the intrinsic turnover frequency of CNC-Ni calculated from its cyclic voltammogram in Fig. 4 is $90$ s$^{-1}$ (see ESI for details) higher than those ($4-6$ h$^{-1}$) of the reported nickel catalysts coordinated with tetradeutate pyridyl-carbene ligands. The CNC(OTf)$_2$ free ligand exhibited negligible current enhancement under the same condition (Fig. S2a), demonstrating the observed CO$_2$ reduction was due to the intact CNC-Ni.

Upon addition of water, further enhancement of catalytic current of CNC-Ni was observed under CO$_2$ (Fig 5b). In contrast, as plotted in Fig. 5a and c, under N$_2$ CNC-Ni showed a negligible cathodic current enhancement upon addition of water, suggesting CNC-Ni was not effective in water reduction to produce H$_2$. Further increasing water concentration beyond 0.8 mM did not lead to increased catalytic current under either N$_2$ or CO$_2$. We also evaluated the influence of D$_2$O addition as shown in Fig. S3, which did not exhibit any substantial difference from those upon addition of H$_2$O under CO$_2$. Although H$_2$O facilitated CO$_2$ reduction, the lack of a hydrogen isotope effect excludes proton transfer as a rate-limiting step. It should be noted that the addition of H$_2$O did not affect the reduction feature of the free ligand CNC(OTf)$_2$, demonstrating it was not effective in activating either CO$_2$ or H$_2$O.

Long-term controlled potential electrolysis of CNC-Ni at $-1.773$ V for two hours in CO$_2$-saturated CH$_3$CN with 0.4 mM H$_2$O was conducted (Fig. S4). Only CO was produced as the major product and no detectable H$_2$ was obtained via gas chromatography (Fig. S5), further confirming the high selectivity of CNC-Ni for electrocatalytic reduction of CO$_2$ over H$_2$O. Overall, these results demonstrated that CNC-Ni acts as a highly selective electrocatalyst for CO$_2$ reduction over HER in the presence of a proton source and its catalytic rate is not limited by proton transfer.

Based on these experimental and computational results, a possible mechanism of CO$_2$ reduction catalysed by CNC-Ni proceeds via two consecutive one-electron reductions from Ni$^{II}$ to Ni$^0$, where CH$_3$CN may dissociate and allow coordination of CO$_2$. Subsequent proton facilitated steps result in the formation of CO. The exact catalytic intermediates and mechanistic steps are under further investigation.

In summary, we have presented a nickel complex supported by a pincer-type carbene-pyridyl-carbene ligand exhibiting high selectivity for the electrocatalytic reduction of CO$_2$ over H$_2$O. The facile synthesis of the platform will allow us to modify the electronic substituents of the ligand, investigate the catalytic selectivity for reducing CO$_2$ employing other first-row transition metals, and couple to chromophores for photocatalytic CO$_2$ reduction, which are our current pursuits.

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