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Electrocatalytic reduction of CO_2 to CO and HCO_2^- with Zn(II) complexes displaying cooperative ligand reduction⁺

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Air-stable zinc(11) pyridyl phosphine complexes, $[Zn(\kappa^2-2,6-\{Ph_2PNMe\}_2(NC_5H_3))Br_2]$ (1) and $[Zn(\kappa^2-2-\{Ph_2PNMe\}(NC_5H_3))Br_2]$ (2) are reported and 1 was capable of electrocatalytic reduction of CO₂ at -2.3 V vs. Fc^{+/0} to yield CO/HCO₂H in mixed water/ acetonitrile solutions. DFT computations support a proposed mechanism involving electron transfer reactions from a species with the anionic PN³P ligand ("L⁻/Zn(11)").

Any effort to balance the carbon cycle will rely on the reduction of CO_2 , the pervasive by-product from combustion with a well-established damaging impact on the environment. Conversion of CO_2 to yield chemical feedstocks, either electrochemically or photochemically, is a tantalizing goal and a broad assortment of homogeneous transition-metal complexes (*e.g.*, Mn-, Fe-, Co-, Ni-, Cu-, Ru-, and Re-based complexes), have been explored for electro- and photocatalytic reduction of CO_2 .¹⁻⁶ From a sustainability perspective, a critical feature of this process is the use of catalysts that rely on earth-abundant elements.

Among the 3d metals, perhaps not surprisingly, Zn is nearly absent from the metals that have been used for CO_2 reduction. The key obstacle to using Zn is that it is found almost exclusively in the 2+ oxidation state and this redox innocence blocks the ability to undergo the fundamental oxidative addition and reductive elimination steps typical of homogeneous catalyzed reactions.



However, Zn has documented roles in catalyzed reactions for capture and insertion of CO_2^{7-11} and ZnBr_2 has been shown to accelerate the reaction of PEt₃/CH₂I₂ with CO₂ to form CO.¹²

Among molecular Zn complexes, A-D stand out as unique catalysts for hydrogen generation and/or CO2 reduction. Tris (2-pyridylthio)methylzinc hydride, $[\kappa^3$ -Tptm]ZnH A, catalytically generated H₂ from triphenylsilane and performed catalytic hydrosilvlation of CO2.13 The square planar Zn(II) thiosemicarboazone complex B ("Zn(DMTH)") can convert CO2 to formate via a methoxide complex, Zn(HDMTH)(OCH₃), which can insert CO₂ yielding a methylcarbonate species. This carbonate can be subsequently reduced to HCO₂⁻ by chemical or electrochemically generated hydride sources.14 The electrochemical proton reduction to hydride is key to this transformation. In fact, complexes B and C can generate H₂ electrocatalytically from acetic acid through ligandcentered pathways.^{15,16} In acetonitrile, these complexes undergo ligand protonation by acetic acid to yield active catalysts, which displayed catalytic reduction currents at -2.3 V and -3.29 V vs. Fc^{+/0} for **B** and **C**, respectively. Aside from **B**, complex **D** represents the only other reported homogeneous Zn-centered catalyst for electrocatalytic CO2 reduction. Cyclic voltammetry of this pyridylphosphine ligated Zn complex showed an irreversible one-electron reduction at -2.03 V vs. Fc^{+/0} and current enhancement, indicating electrocatalysis, of this reduction was observed under a CO₂ atmosphere.¹⁷ When bulk electrolysis was carried out with D under a CO₂ atmosphere, CO formation was observed by mass spectrometry and IR spectroscopy. However, no quantification of this reduction

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product was reported. A partial mechanism employing the noncoordinated phosphorus center to activate the CO_2 by nucleophilic attack was proposed.

Our investigation of the prospective of Zn complexes for electrocatalytic CO2 reduction began with preparation of compounds 1 and 2. The direct reaction of ZnBr₂ with a stoichiometric quantities of the neutral pincer ligand, N, N'-bis(diphenylphosphino)-2,6-di(methylamino)pyridine $2,6-\{Ph_2PNMe\}_2(NC_5H_3)$ ("PN³P") yielded the new complex 1 as a colorless precipitate that was purified by crystallization from CH₂Cl₂. Complex 1 displayed ¹H, ¹³C and ³¹P NMR spectra consistent with a symmetrical coordination of the ligand to Zn. In particular, a single proton resonance for the N-Me groups as well as symmetrical signals for the pyridyl and the PPh₂ moieties were observed. Definitive structural confirmation came through single crystal X-ray analysis of this complex shown in Fig. 1 (Fig. S1 and Table S2, ESI⁺), which established $[Zn(\kappa^2-2,6-\{Ph_2PNMe\}_2(NC_5H_3))Br_2]$ (1) as a four coordinate Zn(II) dibromide species.

In 1 the potentially tridentate ligand binds to Zn only through the two phosphine groups that flank the central pyridyl group while the pyridyl-N(2) center remained beyond bonding distance to Zn at 2.680 Å. This group is directed toward the Zn(II) center, likely due steric restraints and electrostatic forces. For comparison the Zn-Npy distances in A are 2.076(3) Å and 2.078(2) Å¹⁸ while those for C are 2.061(4) Å, 2.067(4) Å.¹⁷ Complex 1 displayed two identical Zn-P distances (Zn-P(1) 2.424(3) Å, Zn-P(2) 2.42(3) Å) and only slightly different Zn-Br linkages (Zn-Br(1) 2.4016(13) Å, Zn-Br(2) 2.3868(15) Å). These bond distances are in-line with reported Zn bond distances.^{19,20} The N(1) and N(3) centers in the ligand were planar with Σ angles equaling 360°. Although the Zn-centered angles range from $101.92(8)^{\circ}$ to $115.50(5)^{\circ}$, the average for the six angles around the Zn center are 109.5° giving a coordination geometry that was appropriately categorized as pseudo-tetrahedral.

A similar room temperature reaction of a toluene suspension of $ZnBr_2$ with *N*-(diphenylphosphino)-2-methylaminopyridine produced [Zn(2-{Ph_2PNMe}(NC₅H₃))Br₂] (2) as a colorless precipitate. The ¹H and ¹³C NMR spectra gave resonances and intensities consistent with a single environment for the ligand. Evidence for coordination of the PPh₂ group was given by the ³¹P NMR resonance



at δ 27.7 ppm, an upfield shift from the free ligand at δ 51.0 ppm. The crystals were of sufficient quality to carry out a single crystal X-ray analysis and the results are represented in Fig. 1 (Fig. S2 and Table S3, ESI[†]). Complex 2 crystallized with two molecules of formula [Zn(2-{Ph₂PNMe}(NC₅H₃))Br₂] in the asymmetric unit and the two displayed very similar bonding parameters. One of these molecules is displayed in Fig. 1, which confirms that complex 2 possessed a four coordinate Zn(II) center bonded in a bidentate fashion by the diphenylaminopyridine ("PN") ligand and two bromide anions originating from the starting material. Overall, this yields distorted tetrahedral Zn(II) centers. The PN ligand forms an essentially planar five-membered chelate ring, consisting of the P-N-C-N ligand skeleton bonded to the Zn center with the ligand plane bisecting the Br-Zn-Br plane. The asymmetric unit gave Zn-N distances of 2.067(4) Å and 2.091(4) Å (average = 2.08 Å) and Zn-P distances of 2.4030(13) Å and 2.4045(13) Å (average = 2.40 Å) and these distances are comparable to reported bond distances. The Zn-Br distances are nearly identical and displayed average values of 2.34 Å, again comparable to reported values. While the six angles around each Zn center in 2 ranged from $80.53(11)^{\circ}$ to $124.86(4)^{\circ}$, the averages of all of these approach an ideal tetrahedral angle with values of 108.3° and 108.4°, respectively. The limitation of the bite angle in the PN ligand led to the smallest angle in the fivemembered ring being the P-Zn-N angle.

The structural features of complexes **1** and **2** bear some resemblance to the catalytic Zn complexes **A–D** that have demonstrated chemical and electrochemical catalysis for CO₂ reduction and H₂ formation. The potential for similar reactivity from **1** and **2** began by performing cyclic voltammetry (CV) measurements, at cathodic potentials, of a 1.0 mM acetonitrile solution of **1** [Zn(2,6-{Ph₂PNMe}₂(NC₅H₃))Br₂] under N₂ using a glassy carbon (GC) working electrode, a Pt counter electrode and a Ag pseudo-reference electrode, which was referenced to the ferrocene (Fc^{0/+}) redox couple. Fig. 2 revealed two irreversible reduction peaks at -2.42 and -2.69 V *vs.* Fc^{+/0}. Variation of the scan rate yielded linear *i vs.* (scan rate)^{1/2} which is an indication of a freely diffusing species (Fig. S5, ESI⁺).²²

A similar set of CV measurements were carried out on complex 2, $[Zn(2-{Ph_2PNMe}NC_5H_3)]Br_2]$ and are shown in Fig. 2 (Fig. S7 and S8, ESI†). Like complex 1, the CV for complex 2 showed two irreversible reductions at -2.33 V and -2.73 V *versus* Fc^{+/0}. The relationship of 1 and 2 can be seen in overlay of the CV's.

In order to more clearly analyze the reduction behavior of **1** and **2** a computational study of these complexes and their reduction products was undertaken. DFT optimization of $[Zn(2,6-{Ph_2PNMe}_2(NC_5H_3))Br_2]$ (**1**), starting from the crystallographic parameters, was performed with the B3LYP functional, def2TZVP basis set and using the IEFPCM model for solvation with acetonitrile. The resulting species was an excellent match with the experimental structural features (Fig. S8 and S9, ESI[†]). These computations yielded frontier orbitals for **1** that displayed little contribution from Zn, with the HOMO being a π molecular orbital of the ligand that was largely localized on the py and NMe groups with the fragment orbital allocation of 0.51 (py), 0.27 (NMe) (Fig. S10, ESI[†]). The LUMO was also ligand localized and mostly π in nature localized on





Fig. 2 Overlay of the CV's of complexes $[Zn(2,6-{Ph_2PNMe}_2(NC_5H_3))Br_2]$ (**1**, orange) and $[Zn(2-{Ph_2PNMe}(NC_5H_3))Br_2]$ (**2**, blue) in CH₃CN with tetrabutylammonium hexafluorophosphate (TBAHFP) supporting electrolyte using a glassy carbon (GC) working electrode, a Pt counter electrode. A potentials are referenced to the Fc^{+/0} couple.

the pendant Ph groups (56%) with some py contribution (22%)(Fig. S11, ESI⁺). The lowest energy, unoccupied, orbital with substantial Zn contribution was 0.2283 hartrees (6.21 eV) above the HOMO and was clearly σ antibonding with Zn s orbital (Fig. S12, ESI[†]). Beginning with the optimized structure of complex 1, an electron was added and a new DFT optimization was performed (B3LYP/def2TZVP/IEFPCM/CH₃CN). This led to an anionic complex $[Zn(2,6-\{Ph_2PNMe\}_2(NC_5H_3))Br_2]^-$ (1⁻) (Fig. S13, ESI[†]). The optimized anion gave a complex that maintained a tetrahedral environment on Zn with two phosphine and two bromo linkages. The anion vielded a Zn center that was less symmetrical than in the parent 1. One of the Zn-P bonds showed a slight decrease in Zn-P distance with an increase in bond order compared to the other Zn-P linkage. Both Zn-Br increased slightly in bond length. Consistent with these observations, the SOMO was localized on the "shorter" Zn-P side of 1⁻ (Fig. S14, ESI[†]). The orbital array of 1⁻ remains similar to 1 with the frontier orbitals dominate by ligand centered π -type orbitals. The SOMO is, as expected, localized on the phenyl substituents (67%). The SOMO-1 (formerly HOMO) retains similar orbital characteristics distributed predominantly on py (53%) and NMe (28%). According to these computations, there is no significant frontier electron character on the Zn center and that the added electrons reside in π orbitals on the Ph and py groups.

A similar process was carried out for the optimization of 2 $[Zn(2-{Ph_2PNMe}NC_5H_3))Br_2]$ and the corresponding anion 2⁻ (DFT/B3LYP/def2TZVP/IEFPCM/CH₃CN). The optimized structure for 2 was an excellent reflection of the experimental X-ray structure (Fig. S16 and S17, ESI†). For 2, the HOMO is a π orbital on py with contribution from the bridging amine NMe function (Fig. S18, ESI†) and the LUMO is of π character with the majority localized on the py portion of the ligand (Fig. S19, ESI†). For the single electron reduction product 2⁻ was successfully computationally modelled (Fig. S21 and Table S8, ESI†). Compound 2⁻ displayed a SOMO that was PN ligand centered (Fig. S22 and S23, ESI†). Again computational effort makes it clear that there is no significant frontier electron character on the Zn center and that the added electrons reside in π orbitals on the Ph and py groups.



Fig. 3 Cathodic CV measurements of complex [Zn(2,6-{Ph₂PNMe}₂ (NC₅H₃))Br₂] (1) in CH₃CN with a GC electrode under N₂ (blue), and under a CO₂ atmosphere with 2.5 M of added water (purple). All potentials are referenced to Fc⁺/Fc.

An investigation of the electrocatalytic ability of complex 1 toward CO_2 reduction, was carried out by performing a CV measurement of 1 under a CO_2 atmosphere with H_2O added as a proton source. As shown in Fig. 3, a characteristic increase in current was observed under these conditions, features consistent with electrocatalytic CO_2 reduction by 1. After electrolytic reaction, the electrode was removed, rinsed and immersed in fresh electrolyte/water solution containing no Zn complex and no catalytic response was observed.

To definitively establish the catalytic behavior of complex 1, controlled potential coulometry (CPC) experiments were performed and the reactor headspace was examined by GC and solution NMR analysis was employed to probe the formation of condensed phase products such as formic acid (Fig. S25, ESI⁺). CPC measurements were carried out at -2.3 V and -2.7 V vs. $Fc^{+/0}$ under a CO₂ atmosphere with either 200 µL or 500 µL of added water. The results of these investigations, presented in Table 1 (Table S9, ESI[†]), documented the formation of CO and H_2 as the only observed gas phase products and HCO_2^- in solution. Both formate and CO formation confirm the unique electrocatalytic abilities of 1 as the only reported Zn-based catalyst with quantified CO formation.¹⁷ Furthermore, in contrast to **B**, which reduced CO₂ through a methylcarbonate intermediate, 1 generated formate directly from CO2 and H₂O.¹⁴

These measurements gave competitive and significant (10–100 μ mol) H₂ gas formation (Table S9, ESI[†]). Furthermore,

Table 1 Controlled potential coulometry of 1 mM (15 micromoles) solution of $[Zn(2,6-{Ph_2PNMe}_2(NC_5H_3))Br_2]$ (1) in acetonitrile under CO_2 atmosphere

Potential (V) vs. Fc ^{+/0}	Time (h)	Added water $(\mu L)/[H_2O](M)$	CO (µmol)/ select. ^b	HCO ₂ H (µmol)	FE^a (%)	
-2.3 -2.3 -2.3 -2.7 2.7	5 5 11 5	200/0.7 500/1.9 500/1.9 200/0.7	14.2/1 49/0.78 80.9/0.79 24.7/1 142 1/0 76	0 13.5 21.8 0 44.8	70 69 64 74	

^a Corrected for background H₂ formation shown in Table S9 (ESI).
 ^b Select. = μmol CO/(CO + HCO₂H) μmol.





HCO₂H appeared at 1.9 M H₂O, concomitant with CO selectivity dropping to \approx 78%. Similar observations were made when a more negative reduction potential was employed. Analogous measurements carried out in the absence of complex 1 yielded no CO₂ reduction products and only at -2.7 V was a background generation of 2–3 µmol H₂ observed. Finally, CPC measurements made under an N₂ atmosphere produced no detected H₂ at -2.3 V and only 3–6 µmol of H₂ were observed at -2.7 V. These CPC experiments documented the ability of the Zn(II) complex 1 to electrocatalytically reduce both CO₂, to give CO and formic acid, and water to yield H₂.

For comparison, a parallel set of measurements were carried out with $[Zn(2-{Ph_2PNMe}(NC_5H_3))Br_2]$ (2), which displayed enhanced cathodic current in the presence of H_2O with no additional enhancements when the atmosphere was changed to CO_2 (Fig. S26, ESI†). Initial CPC measurements of 2 at -2.6 V in acetonitrile with added water (0.7 M) and under a CO_2 atmosphere gave 22 µmol H_2 and no indications of CO_2 reduction products.

A proposed mechanism for the electrocatalytic reduction of CO_2 by complex 1 is presented in Fig. 4. The first step in this proposal is based on a ligand-centered reduction and on the proximity of the free pyridyl base and a Lewis acidic Zn center.12,17 The increased basicity of the reduced ligand together with the additional coordination by the zinc ion facilitate the binding of CO2 and formation of pyridyl-N coordinated CO₂ intermediate.^{21,22} The bound and activated CO₂ then proceeds along two alternate pathways to yield either CO or HCOO^{-.23} In one case, protonation leads to a metallacarboxylic acid (A), which is commonly invoked intermediate in reduction of CO₂ to yield CO. Subsequent protonation coupled with reduction leads to water elimination, release of CO and closes that leg of the cycle. A path leading to formate complex (B) was envisioned to be directly linked to electrochemical generation of hydrogen, a process with literature precedent.¹⁴ Alternatively, formation of a transient Zn-H species and insertion of CO₂ could result in complex **B**.¹³ Substitution of formate with bromide completes this portion of the cycle. In the case of

complex 2, the lack of a free basic site (*i.e.* pyridyl) on the ligand does not allow for the bifunctional activation of CO_2 consistent with the lack of reduction products from this species.

Electrocatalytic reduction of CO_2 to yield CO and $HCO_2^$ presents a key process in the utilization of CO_2 as a C1 source for further synthesis of as a fuel. Significantly, this report presents a unique multifunctional Zn complex that can effectively catalyze both of these transformations in the presence of water. This is unique among a rare set of Zn complexes that can perform CO_2 reduction. The observed reactivity is attributed to a synergy between a reduced, basic ligand and the acidity of the Zn(π) center. Our further efforts are focused on examining the competitive water reduction to yield H₂, investigating parameters to improve on product selectivity and on exploring the role of pendant basic sites in bifunctional electroreduction.

Conflicts of interest

There are no conflicts to declare.

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