



**Enhanced CO₂ Electroreduction Efficiency through
Secondary Coordination Effects on a Pincer Iridium Catalyst**

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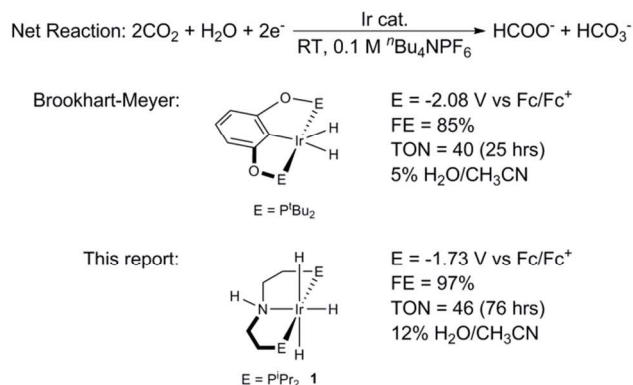
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An iridium(III) trihydride complex supported by a pincer ligand with a hydrogen bond donor in the secondary coordination sphere promotes the electrocatalytic reduction of CO₂ to formate in water/acetonitrile with excellent Faradaic efficiency and low overpotential. Preliminary mechanistic experiments indicate formate formation is facile while product release is a kinetically difficult step.

The electroreduction of CO₂ to fuels and commodity chemicals could represent a crucial component of a carbon economy that is based on renewable resources instead of fossil fuels.¹ While many molecular catalysts for CO₂ electroreduction have been reported, considerable improvements in catalyst efficiency are needed to spur more widespread application.² In most metal catalyzed electroreductions of CO₂ the primary sources of inefficiency are a combination of poor product selectivity and substantial overpotential. In particular, low selectivity has been a problem in the electrocatalytic reduction of CO₂ to formate/formic acid using homogeneous transition metal catalysts.³ Formic acid is a potentially valuable hydrogen storage material, which could also serve directly as a fuel or as a precursor to more valuable chemicals such as methanol.⁴ Recently, Brookhart and Meyer reported a significant advance toward the two-electron reduction of CO₂ to formate using the iridium(III) dihydride complex, (POCOP)IrH₂ (POCOP = C₆H₃-2,6-(OP^tBu)₂), which operates at a reduction potential of *ca.* -2.1 V (vs Fc/Fc⁺) in H₂O/MeCN solvent mixtures and limits the amount of H₂ and CO byproducts (Scheme 1).⁵ Variants of this remarkable catalyst have also been shown to function in aqueous solution and immobilized on carbon nanotubes.⁶ A considerable body of experimental and computational mechanistic work on (POCOP)IrH₂ suggests that water plays a significant role in the electroreduction, both as a proton source and as a stabilizing medium for the formate product.^{5,7} Given these results, our



Scheme 1. Comparison of iridium electrocatalysts for CO₂ hydrogenation to formate.

laboratories were motivated to assess the influence a hydrogen bond donating secondary amine ligand would have on the electroreduction of CO₂.

Prior studies within our laboratories and others have demonstrated that iron, ruthenium and iridium centers supported by the pincer ligand PN^HP (PN^HP = HN{CH₂CH₂(P^{Pr})₂})₂ facilitate reversible, thermochemical hydrogenations of CO₂ at the metal center.^{8,9} In particular, the iridium(III) trihydride complex, (PN^HP)IrH₃ (**1**), was identified as a highly active catalyst for the hydrogenation of CO₂ to HCOOK in 1M KOH solution.^{9a,b} Initially, the activity of **1** as an electrocatalyst for CO₂ conversion to formate was probed by cyclic voltammetry (CV) using 1 mM catalyst solutions under both N₂ and CO₂ atmospheres, with varying concentrations of water in MeCN (Figure 1). For experiments conducted under CO₂ in the presence of water, the onset potential for electrocatalytic current appeared at *ca.* -1.5 V. Similar CV experiments performed under N₂ lacked

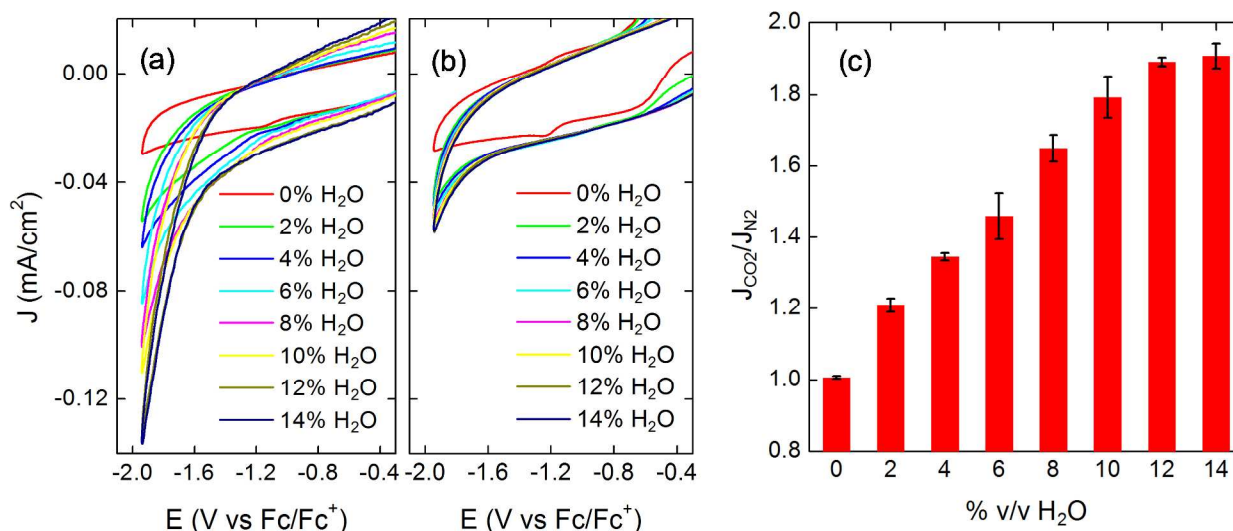
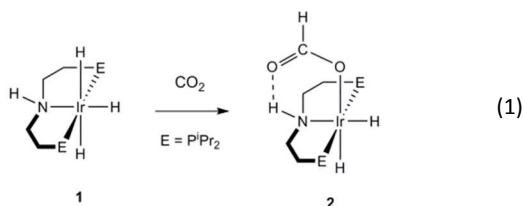


Fig. 1 CVs of 1 mM **1** in CH₃CN, 0.1 M tBu₄NPF₆ electrolyte, 10 mV/s scan rate with 0-14% added H₂O under (a) CO₂ and (b) N₂. (c) Ratio of peak current with and without CO₂ (J_{CO₂}/J_{N₂}) vs % H₂O measured at -1.73 V vs Fc/Fc⁺. Error bars based on three independent measurements.

catalytic current at this potential. Instead, current associated with the electroreduction of water was observed at *ca.* -1.9 V (see ESI Figure S6). There was a strong correlation between water concentration and the reductive current in CO₂ reduction. When normalized to the corresponding non-Faradaic peak current observed under N₂, a steady increase in reductive current was observed with increasing percentage of water to a maximum at 12% H₂O/MeCN.

The selectivity of CO₂ electroreduction using **1** was subsequently examined through a bulk electrolysis at -1.73 V in 12% H₂O/MeCN over 24 hrs (7.1 mm² glassy carbon electrode). Quantitation of the reduction products by ¹H NMR spectroscopy and GC analysis revealed formate was produced at >99% Faradaic efficiency, with no detectable H₂ or CO byproduct. Taken together with a reduced overpotential of ~350 mV, the selectivity of electroreduction by **1** represents a substantial gain in efficiency in comparison to (POCOP)IrH₂. The primary drawback of CO₂ electroreduction catalyzed by **1** is the modest 0.45 mA/cm² current density observed during electrolysis (see ESI Figure S4). The low current densities are consistent with relatively slow kinetics to produce formate. This trend was evident in comparative experiments with (POCOP)IrH₂ (Figure 1). Under optimized conditions for each catalyst, **1** afforded enhanced selectivity (97%) at lower potential with similar TON, but required a 3-fold increase in time to pass an equivalent charge (19.6 mm² electrode). The reduced rate of catalysis is also evident from comparison of the *k*_{cat} = 0.56(1) s⁻¹ (12% H₂O in MeCN at 25 °C) obtained from CV experiments using **1**, which is markedly lower than the *k*_{cat} = 20(2) s⁻¹ (5% H₂O in MeCN at 25 °C) reported for (POCOP)IrH₂ under their respective optimum conditions.⁵

A series of NMR spectroscopy and CV experiments were performed to gain insight into the pathway for CO₂ electroreduction using **1**, the origin of its modest kinetics, and the possible role of the ancillary ligand. Prior studies of **1** have shown exposure to 1 atm of CO₂ results in rapid insertion to afford the iridium(III) formate complex, (PN^HP)IrH₂(HCO₂) (**2**) (eq 1).



This reaction seemed a plausible first step in the electroreduction of CO₂. Comparative CV experiments carried out using **1** and **2** under N₂ and CO₂ support this hypothesis. Both complexes exhibited nearly identical CVs (Figure 2) consistent with **1** and **2** each serving as kinetically competent reaction intermediates along the catalytic cycle (Scheme 2). The extrusion of formate product and subsequent proton/electron transfer to iridium would regenerate **1** and complete the cycle. A similar reaction sequence has been proposed for (POCOP)IrH₂, with a cationic acetonitrile adduct of iridium implicated as the initial product of formate loss. By analogy, formate loss from **2** would be expected to afford [(PN^HP)IrH₂(MeCN)]⁺ (**3**).

Initial attempts to detect complex **3** via ligand substitution in either dry *d*₃-MeCN or 1:1 H₂O/*d*₃-MeCN mixture yielded no evidence for **3** or its H₂O bound equivalent by NMR spectroscopy. Instead, **3** was generated *in situ* via protonation of **1** with H[B(Ar^F)₄]⁻(Et₂O)₂ (B(Ar^F) = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate in *d*₃-MeCN (eq 2).

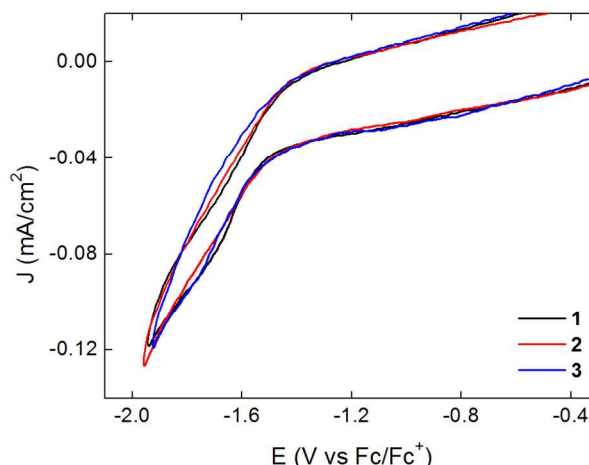
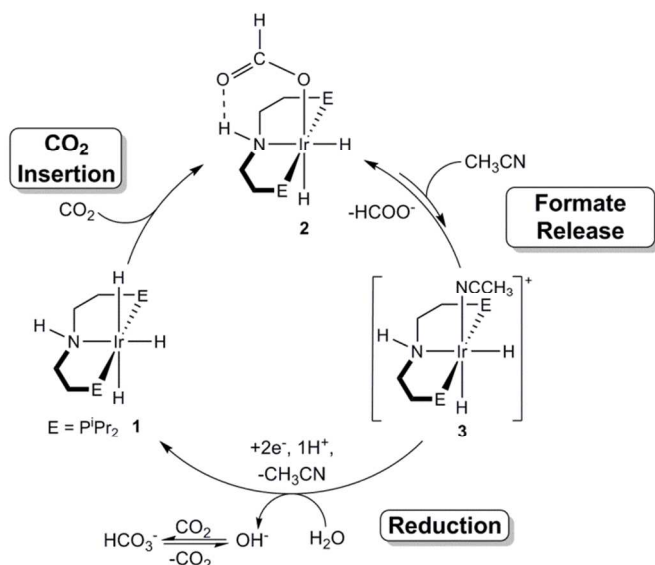
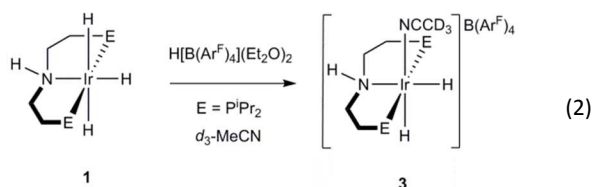


Fig. 2 CVs of 1 mM **1**, **2**, and *in situ* generated **3** under 1 atm CO₂. Experimental conditions: glassy carbon electrode (7.1 mm²), 12% H₂O/CH₃CN solvent, 0.1 M tBu₄NPF₆ electrolyte, 10 mV/s scan rate.



Scheme 2. Proposed pathway for electrocatalytic reduction of CO₂.



Complex **3** was characterized by NMR spectroscopy and tentatively assigned as the *cis*-iridium dihydride isomer based on NOE correlations between the two Ir-H resonances at -20.13 and -22.26 ppm and the absence of strong ²J_{H-H} *trans* coupling (for comparison the *trans* ²J_{H-H} coupling between hydride ligands in **1** is 5.7 Hz).¹⁰ CV of *in situ* generated **3** under catalytic conditions displayed a catalytic wave comparable to those observed for **1** and **2**, suggesting the iridium(III) dihydride cation is also a viable reaction intermediate.

Having identified several probable intermediates in the catalytic electroreduction cycle, our attention turned to factors that may influence the reaction kinetics. One qualitative observation of note is a dramatically lower current for electrocatalytic reduction waves in CVs obtained at high scan rates (100 mV/s) compared to lower scan rates (10 mV/s). This observation suggests the kinetics of catalytic electroreduction are strongly influenced by a thermochemical step. The inability to observe equilibria between **2** and **3** in H₂O/*d*₃-MeCN implicates formate extrusion as a kinetically slow step. This hypothesis is also supported by the dependence of catalytic current of **1** on the amount of H₂O present (Figure 1) since water could stabilize the free formate ion. Such an influence cannot be completely separated from water's role as a proton source in the reduction step, yet release of the CO₂ reduction product from **2** could be hindered by hydrogen bonding between the bound formate and ancillary ligand N-H moiety. In an effort to improve formate extrusion, 10 equiv. (per iridium) of the Lewis acid NaPF₆ were added to a solution of **1** and CV experiments performed in a manner identical to those in Fig 2.[†] The presence of the Lewis acid produced a notable enhancement in the electrocatalytic current, nearly doubling the current density at a potential of -1.6 V between otherwise identical reactions (see ESI Figure S7). NaPF₆ has proven an effective stabilizer of formate species in related reactions, such as formic acid dehydrogenation, and likely serves a similar role in facilitating formate release.^{87a} Unfortunately, quantitation of the

Lewis acid enhancement during electrolysis was obviated by the build-up of a solid-electrolyte interface (SEI) from decomposition of NaPF₆ on the electrode,¹¹ which began depleting the catalytic current within 30 min. Still, the initial current enhancement induced by Lewis acid, along with the mild overpotentials and excellent selectivity observed in the electrocatalyzed production of formate by **1**, motivate ongoing studies in our laboratories to use this platform to develop highly efficient catalyst systems for CO₂ electroreduction.

In conclusion, an iridium(III) trihydride complex bearing a bifunctional PNP ligand has proven to be an exceptionally mild and selective electrocatalyst for CO₂ reduction to formate, with >99% Faradaic efficiency and an onset potential at -1.5 V vs. Fc/Fc⁺. Preliminary mechanistic studies indicate the reaction proceeds via a sequence involving insertion of CO₂ into an Ir-H bond, equilibrium release of formate ion, and electroreduction/proton transfer to regenerate the iridium(III) trihydride species. The kinetic performance of (PNHP)IrH₃ appears limited by the thermochemical extrusion of the formate product, which can be enhanced by the addition of formate stabilizing agents such as water and Lewis acidic salts.

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Notes and references

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- 1 A. A. Appel, J. E. Bercaw, A. B. Bocarsly, H. Dobbek, D. L. Dubois, M. Dupuis, J. G. Ferry, E. Fujita, R. Hille, P. J. A. Kenis, C. A. Kerfeld, R. H. Morris, C. H. F. Peden, A. R. Portis, S. W. Ragsdale, T. B. Rauchfuss, J. N. H. Reek, L. C. Seefeldt, R. K. Thauer and G. L. Waldrop, *Chem. Rev.* 2013, **113**, 6621.
- 2 (a) X. Lu, D. Y. C. Leung, H. Wang, M. K. H. Leung and J. Xuan, *ChemElectroChem*. 2014, **1**, 836; (b) R. J. Lim, M. Xie, M. A. Sk, J.-M. Lee, A. Fisher, X. Wang and K. H. Lim, *Cat. Today*, 2014, **233**, 169; (c) C. Costentin, M. Robert and J.-M. Savéant, *Chem. Soc. Rev.*, 2013, **42**, 2423; (d) C. Finn, S. Schnittger, L. J. Yellowlees and J. B. Love, *Chem. Commun.* 2012, **48**, 1392; (e) E. E. Benson, C. P. Kubiak, A. J. Sathrum, and J. M. Smieja, *Chem. Soc. Rev.* 2009, **38**, 89.
- 3 (a) S. Slater and J. H. J. Wagenknecht, *J. Am. Chem. Soc.* 1984, **106**, 5367; (b) H. Ishida, H. Tanaka, K. Tanaka, and T. J. Tanaka, *J. Chem. Soc., Chem. Commun.* 1987, 131; (c) C. M. Bolinger, N. Story, B. P. Sullivan and T. J. Meyer, *Inorg. Chem.* 1988, **27**, 4582. (d) C. Arana, S. Yan, M. Keshavarzk, K. T. Potts and H. D. Abruna, *Inorg. Chem.* 1992, **31**, 3680; (e) C. Caix, S. Chardon-Noblat, and A. J. Deronzier, *Electroanal. Chem.* 1997, **434**, 163; (f) M. D. Rail, and L. A. Berben, *J. Am. Chem. Soc.* 2011, **133**, 18577.
- 4 (a) M. Grasemann and G. Laurenczy, *Energy Environ. Sci.* 2012, **5**, 8171; (b) C. Ziebart, and M. Beller, In *Transformation and*

Utilization of Carbon Dioxide.; B. M. Bhanage, M Arai, Eds.; Springer: Berlin, 2014.

- 5 P. Keng, C. Cheng, Z. Chen, C. K. Schauer, T. J. Meyer and M. Brookhart, *J. Am. Chem. Soc.* 2012, **134**, 5500.
- 6 (a) P. Kang, Z. Chen, M. Brookhart and T. J. Meyer, *Top. Catal.* 2014, 10.1007/s11244-014-0344-y; (b) P. Kang, S. Zhang, T. J. Meyer and M. Brookhart, *Angew. Chem., Int. Ed.* 2014, **53**, 8709; (c) P. Keng, T. J. Meyer and M. Brookhart, *Chem. Sci.* 2013, **4**, 3497.
- 7 L. Cao, C. Sun, N. Sun, L. Meng and D. Chen, *Dalton Trans.* 2013, **42**, 5755.
- 8 (a) E. A. Bielinski, P. O. Lagaditis, Y. Zhang, B. Q. Mercado, C. Wurtele, W. H. Bernskoetter, N. Hazari, and S. Schneider, *J. Am. Chem. Soc.* 2014, **136**, 10234; (b) A. Monney, E. Barsch, P. Sponholz, H. Junge, R. Ludwig and M. Beller, *Chem. Commun.* 2014, **50**, 707; (c) E. Alberico, P. Sponholz, C. Cordes, M. Nielsen, H.-J. Drexler, W. Baumann, H. Junge and M. Beller, *Angew. Chem., Int. Ed.* 2013, **52**, 14162.
- 9 (a) W. H. Bernskoetter and N. Hazari, *Eur. J. Inorg. Chem.* 2013, 4032; (b) T. J. Schmeier, G. E. Dobreiner, R. H. Crabtree and N. Hazari, *J. Am. Chem. Soc.* 2011, **133**, 9274.
- 10 Z. E. Clarke, P. T. Maragh, T. P. Dasgupta, D. G. Gusev, A. J. Lough and K. Abdur-Rashid, *Organometallics*, 2006, **25**, 4113.
- 11 (a) A. Bhide, J. Hofmann, A. K. Dürr, J. Janek and P. Adelhelm, *Phys. Chem. Chem. Phys.* 2014, **16**, 1987. (b) L. Terborg, S. Nowak, S. Passerini, M. Winter, U. Karst, P. R. Haddad and P. N. Nesterenko, *Anal. Chim. Acta.* 2012, **714**, 121.