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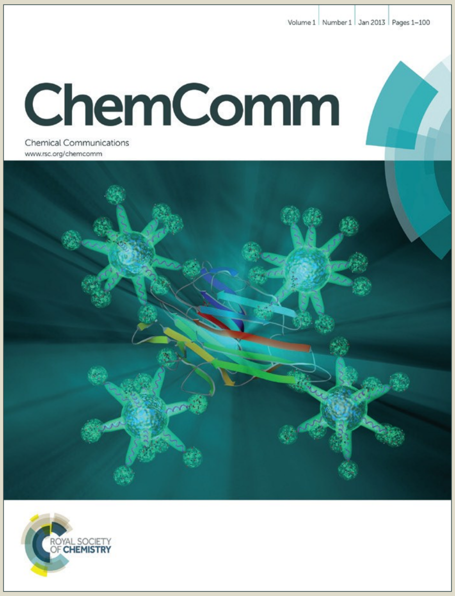

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Electrocatalytic Reduction of CO_2 using Mn Complexes with Unconventional Coordination Environments

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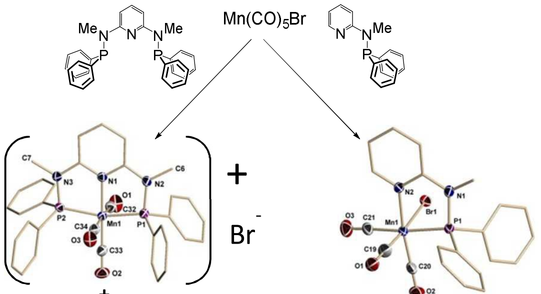
New complexes, Mn{κ^3-[2,6-{Ph_2PNMe}$_2$(NC_5H_3)]}$(CO)_3$$^+$$Br^-$ (1^+Br^-) and MnBr{κ^2-(Ph_2P)NMe(NC_5H_4)}$(CO)_3$ (2), are reported and present new ligand environments for CO_2 electrocatalytic reduction to CO. Compound 1^+ presents a unique metal geometry for CO production (96%) in the absence of added water while 2 required addition of water and generated both CO and H_2 products.

The catalytic reduction of CO_2 to yield C1 products presents a fundamental challenge in chemistry. Significant incentives for targeting this undertaking are the environmental concerns over release of CO_2 into the atmosphere combined with the potential to recycle this ubiquitous combustion byproduct into energy containing products. Since the appearance of ReX(α-diimine)$(CO)_3$ as a single component photocatalyst[1,2] and MnX(bipy)$(CO)_3$ (bipy = 2,2′-bipyridine) as a competent electrocatalyst for CO_2 reduction,[3] group 7 metal complexes have held a central position in this area.[4–10] While a variety of metal centers (e.g. Fe,[11] Co,[12–15] Ni,[16–19] Ru,[20–23] Pd,[24–27] Rh[28,29]) have been explored in this regard, there has been more limited variation of the ligand architecture. The majority of homogeneous catalysts for the electrochemical reduction of CO_2 are supported by nitrogen-based macrocycles, bipyridine or polyphosphine ligands. Specifically in the case of group 7 electrocatalysts, these species are almost exclusively limited to bidentate α-diimine ligands and *facial*-M$(CO)_3$ metal coordination geometries.[30–37]

One of our goals is to develop distinctive metal coordination geometries which we anticipate may lead to novel reactivity including reduction catalysis. To this end we now report on applying a planar coordinating tridentate PNP (neutral pincer) ligand in Mn^I chemistry and the potential of the resultant unprecedented metal coordination geometry in electroreduction of CO_2. The relative abundance of Mn, the anticipated hemilability of PNP ligands, and the documented selectivity of Mn complexes in electrocatalytic CO_2 reduction motivated our efforts. Furthermore, our success encouraged expanding this investigation to other PN ligated Mn complexes and thus demonstrate the variety of coordination geometries and ligation that are possible for active CO_2 reducing electrocatalysts.

Reaction of soluble *N,N′*-bis(diphenylphosphino)-2,6-di(methylamino)pyridine[38–42] with MnBr$(CO)_5$ produced a complex displaying NMR spectra for a symmetrical ligand environment and a high resolution mass spectrum that was consistent with formation of a pincer complex Mn{κ^3-[2,6-{Ph_2PNMe}$_2$(NC_5H_3)]}$(CO)_3$$^+$$Br^-$ (**1^+Br^-**, MnPN$_3$P$(CO)_3$$^+$$Br^-$) that was formed via release of two equivalents of CO and autoionization of the starting material. Single crystal X-ray analysis provided definitive structural connectivity and the results are shown in Figure 1.



1^+Br^-   **2**

Figure 1. Reaction scheme and structural representations of **1^+Br^-** and **2**. For clarity, hydrogen atoms and the ligand carbon atoms are omitted for **1^+** and **2**. Full structural information can be found in the Supporting Information.

The MnPN$_3$P$(CO)_3$$^+$ cation component (**1^+**) displayed a planar-coordinated tridentate PNP ligand and three meridional CO ligands yielding a pseudo-octahedral coordination geometry. The bromide counterion was well-separated from this complex cation. The literature provides only two similar PNP complexes for Mn^I$(CO)_3$. The first, Mn{κ^3-[2,6-{Ph_2PNH}$_2$(NC_5H_3)]}$(CO)_3$$^+$ (**A**) is directly related to **1^+** by replacement of N-Me with N-H in the neutral ligand and this complex has been structurally

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characterized.[43] The second is a neutral complex, Mn{κ^3-[2-P(^{i}Pr)$_2$-4-MeC$_6$H$_3$]$_2$N}(CO)$_3$, and displays a metal environment similar to cation 1^+.[44] However, this complex is supported by an anionic PNP ligand rather than a neutral scaffold as in 1^+.

For $\mathbf{1^+}$**,** the symmetrical M-P distances (2.2305(7), 2.2435(7)Å) and the P(1)-Mn(1)-P(2) angle of 163.69(3)° compare favorably with the analogous parameters reported in **A** (2.247Å and 2.252Å, 163.57°). Similarly, the M-N$_{py}$ distance (2.053(2)Å) and Mn-CO distances (1.794(3), 1.846(3), and 1.852(3) Å) observed for $\mathbf{1^+}$ are comparable to **A** and to related bond distances in substituted-bipyridyl complexes of *fac*-MnX(bipyR$_2$)(CO)$_3$.[32,31] There are, of course, key differences between $\mathbf{1^+}$ and the documented CO$_2$ electrocatalysts, *fac*-MnX(bipyR$_2$)(CO)$_3$. These include the tridentate pincer ligation, the *mer*-Mn(CO)$_3$ geometry, the cationic charge and the lack of coordinated halo ligands.

The electrochemistry of $\mathbf{1^+Br^-}$ was examined in dry acetonitrile (1 mM $\mathbf{1^+Br^-}$, 100 mM (n-Bu)$_4$NPF$_6$) using a glassy carbon working electrode, Pt counter electrode and Ag wire pseudo-reference electrode. Cyclic voltammetry was carried out under nitrogen and referenced to the ferrocene/ferrocenium (Fc/Fc$^+$) couple.[45] The first reduction was observed at -2.01V (-1.63 vs SCE) and a return oxidation was observed at -1.94V (-1.56 vs SCE) indicating a reversible one electron couple (Figures S1-S3). On scanning to more negative potential, a second reduction to form $\mathbf{1^-}$ was observed at -2.31V (-1.93 vs SCE). An additional oxidation event was also observed at -1.26V. The full voltammetric curve is shown in Figure 2 and was reproducible for at least 1000 cycles. For comparison, the typical cyclic voltammograms of MnX(bipyR$_2$)(CO)$_3$ complexes show two one electron reduction waves whose positions depend on the substitution on the bipy.[3,32] The first reduction observed for $\mathbf{1^+}$ is similar in potential to that of the second reduction seen for the bipy compounds. The cathodic shift in this potential is likely due to increased electron donation experienced in $\mathbf{1^+}$ from a combination of tridentate ligation and changing the donor from N to less electronegative P.

Carrying out this same measurement with a solution saturated with and under an atmosphere of CO$_2$ produced an 8x enhancement of the reduction current indicating electrocatalytic CO$_2$ reduction as shown in Figure 2. Control measurements were carried out under the same conditions both in the absence of $\mathbf{1^+Br^-}$ and with only free ligand. In these cases, there was no observed current change in the presence or absence of CO$_2$. Compound $\mathbf{1^+Br^-}$, therefore, represents a unique metal complex environment for electrocatalytic CO$_2$ reduction. The catalytic current enhancement observed for $\mathbf{1^+}$ occurs at a similar voltage (-2.0V *vs.* Fc$^+$/Fc) that has been reported for catalytic reduction with *fac*-MnX(bipyR$_2$)(CO)$_3$[3,32,31] and for manganese complexes where one half of the bipy ligand has been replaced with an N-heterocyclic carbene to give a pyridyl/NHC coordinated species, *fac*-MnBr(N⌒C)(CO)$_3$.[33,37]

Perhaps the most intriguing aspect of the electrocatalytic behavior of $\mathbf{1^+Br^-}$ is the fact that the reaction occurred in dry solvent. Other than the recent report employing the local protons provided by hydroxyl substitutents on the ligand,[46] the majority of reported Mn-based electrocatalysts function with 5% added water or with added weak Brønsted acid.[3,32,31,33]

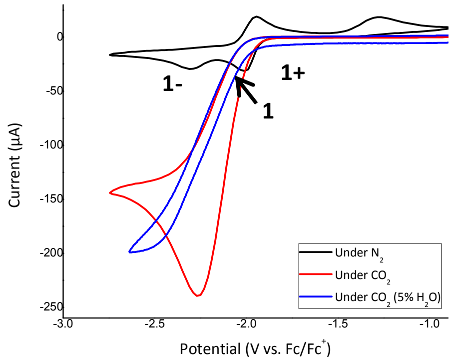

Figure 2.Cyclic voltammograms of 1.0mM [Mn(PN$_3$P)(CO)$_3$]Br ($\mathbf{1^+Br^-}$) under N$_2$ (black), CO$_2$ (red) and CO$_2$/5% H$_2$O (blue) in CH$_3$CN with 0.1M (n-Bu)$_4$NPF$_6$ supporting electrolyte at 100 mV/s. Experimental details are provided in Supporting Information.

Bulk electrolysis was carried out with $\mathbf{1^+Br^-}$ under CO$_2$ in order to measure the evolved products, the current efficiency for this reaction, and to gain some insight into catalyst stability. The catalytic reduction of CO$_2$ with $\mathbf{1^+Br^-}$ in dry acetonitrile gave exclusively CO as the gaseous product as presented in Figure 3. In order to confirm the source of CO and to help identify additional by-products of the reduction, a similar electrolysis experiment was carried out with ^{13}CO$_2$. After 120 min of bulk electrolysis, the reaction head space was admitted into a previously evacuated gas cell and examined by FTIR which demonstrated the formation of ^{13}CO (Figure S7). In addition, at the completion of this experiment, the solvent was collected, evaporated to dryness and the resulting residue, when examined by ^{13}C NMR in DMSO, yielded a signal at δ 166.7 ppm attributed to labelled carbonate, ^{13}CO$_3^{2-}$.[47] Although the reaction to produce CO/CO$_3^{2-}$ has been discussed in the literature, these are not the products from conventional Mn electrocatalysts.[35,48] Importantly, this signal was not observed in analogous experiments under natural abundance CO$_2$.

The direct correlation between the production of CO and the transfer of electrons corresponded to an average coulombic efficiency of 96% over the first 125 minutes of electrolysis. The rate of CO production remained relatively constant at about 6 micromoles CO/hr for an additional 200 minutes.

The addition of 5% H$_2$O to this system revealed that water was, in fact, an inhibitor for the catalysis with $\mathbf{1^+}$. Figure 2 shows that in order to achieve an equivalent current, a significantly more negative potential is required than with dry solvent and bulk electrolysis (Figure 3) revealed that reduction not only converted CO$_2$ to CO but also resulted in production of H$_2$.[23,49] Over the course of this bulk electrolysis (100 min), evolved H$_2$ was, on average, 41% of the gas produced meaning that a significant percentage of the reducing Coulomb equivalents go toward H$_2$ production. Again, these results contrast with reported Mn catalytic systems which operate without hydrogen production.[37] Clearly, $\mathbf{1^+}$ is not only a unique

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structure for this electrocatalysis but also appears to follow a different pathway for CO_2 electroreduction than more conventional catalysts.

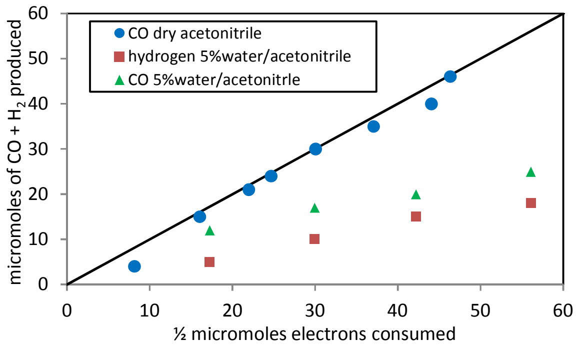

Figure 3.Controlled potential electrocatalytic production of CO from CO_2 by 1.0mM $[Mn(PN3P)(CO)_3]Br$ (1^+Br^-) over 325 min in dry acetonitrile at −2.30 V (blue). For measurements in 5% H_2O/acetonitrile at -2.30V the products are CO (green) and H_2 (red). All potentials are vs. Fc^+/Fc. A black line indicating 100% efficiency is shown to guide the eye.

Our observation of the first P-ligated Mn^I catalyst for CO_2 reduction coupled with the reported competency for mixed ligand pyridyl/NHC coordinated species, *fac*-$MnBr(N{\frown}C)(CO)_3$[33,37] prompted the consideration of a bidentate PN ligand scaffold in the design of new catalyst for this reaction. As shown in Fig. 1, $Mn(CO)_5Br$ was allowed to react with *N*-(diphenylphosphino)-2-methylaminopyridine to yield a new complex, **2**, with spectroscopic data and HR-MS data indicating the anticipated formulation $MnBr\{\kappa^2\text{-}(Ph_2P)NMe(NC_5H_4)\}(CO)_3$. Single crystal X-ray analysis of **2** confirmed the structural details of the *fac*-tricarbonyl species which was supported by a bidentate PN ligand. The sixth coordination site of the pseudo-octahedral geometry was completed by a bromo ligand. Coordination of 2-(dipheny1phosphinoamino)pyridine and 2-(diphenylphosphinoamino)-6-methylpyridine to the $MnBr(CO)_3$ fragment has been reported but no NMR or structural data was provided for these species.[50] In the structure of **2**, the Mn-N_{py} and Mn-P distances (2.075(2) and 2.2753(9) Å respectively) and the N_{py}-Mn-P angle (80.73(8)°) were similar to the analogous parameters observed in $\mathbf{1}^+$. Furthermore, the bond parameters of **2** are comparable to related bond distances in substituted-bipyridyl complexes of $MnX(bipyR_2)(CO)_3$.[32,31]

The cyclic votammetry of **2** was examined in dry acetonitrile under an N_2 atmosphere and the cathodic scan gave a broad reduction current arising from two poorly resolved irreversible reductions at -2.43V and -2.69V versus Fc/Fc^+ (-2.05 and -2.31 V vs SCE respectively, see Figure S8). On the return anodic scan, a small oxidation was observed at -1.56V. An additional 400 mV potential is require to reduce **2** as compared to $\mathbf{1^+Br^-}$ or to reported $MnX(bipyR_2)(CO)_3$ complexes. Repeating this experiment under a CO_2 atmosphere showed no enhancement of current during the reduction of **2**. However, addition of 5% H_2O to these solutions led to an increase in cathodic current of >1.7x (Figure S8). These observations are in line with the observations for *fac*-$MnX(bipyR_2)(CO)_3$[3,32,31] and with the mixed pyridyl/NHC ligated complex.[33,37] The similarity of conditions between these reported Mn complexes and **2** is appropriate given that these complexes fall into the same broad class of bidentate coordinated, *fac*-$MnBrL_2(CO)_3$ species. This general similarity further accentuates the uniqueness of $\mathbf{1^+Br^-}$.

As with $\mathbf{1^+Br^-}$, bulk electrolysis was carried out with **2** under CO_2 in $5\%H_2O/CH_3CN$ in order analyze the products, examine the coulombic efficiency and stability for CO_2 reduction with this species. The data shown in Figure 4 (200 minutes of reaction time) documents an evolution in the identity of the reduction products in this system. During the first 50 minutes the transferred electrons selectively generate CO. After this point, H_2 production begins and increases during the experiment with concomitant decrease in CO production. The direct correlation between the production of CO and H_2 corresponded to an excellent coulombic efficiency (>96%). These electrochemical observations suggest that complex **2** follows a similar CO_2 reduction mechanism as with the published Mn complexes. Furthermore, a DFT optimization carried on **2** reduced by two electrons yielded five-coordinate $Mn\{\kappa^2\text{-}(PN)\}(CO)_3^-$ and free bromide anion (Figure S13). This is analogous to the first step in the currently accepted catalytic pathway of $MnBr(bipyR_2)(CO)_3$, and supports a proposal that **2** follows a similar reduction route to reported α-diimine Mn complexes.

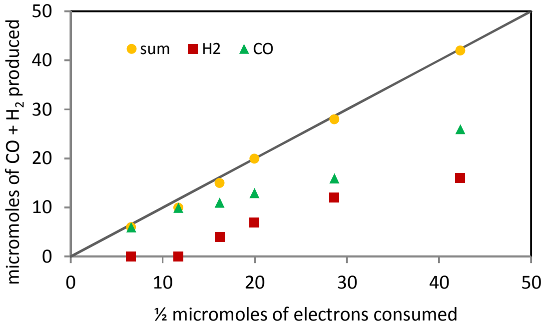

Figure 4. Controlled potential electrocatalytic reduction using 1.0mM 2 in $5\%H_2O/CH_3CN$ at -2.50V vs. Fc/Fc+. The products are CO (green) and H_2 (red). A black line indicating 100% efficiency is shown to guide the eye.

The drive to uncover new catalysts for electrocatalytic reduction of CO_2 is a significant and active endeavor and our efforts to bring novel metal coordination environments to bear on this issue led to synthesis of the pincer complex $Mn\{\kappa^3\text{-}[2,6\text{-}\{Ph_2PNMe\}_2(NC_5H_3)]\}(CO)_3{}^+Br^-$ ($\mathbf{1^+Br^-}$). In contrast to reported Mn electrocatalysts, this species does not possess a coordinated halide, has a *mer*-tricarbonyl geometry and a PN_3P neutral pincer ligand. Like other Mn^I catalysts, $\mathbf{1}^+$ is selective, yielding only CO under electrocatalytic conditions. However, in contrast to the majority of reported Mn catalysts, $\mathbf{1}^+$ has excellent efficiency in the absence of added water. Credence for the ability of PN ligation to support active electrocatalytic reduction was further provided by the activity observed for $MnBr\{\kappa^2\text{-}(Ph_2P)NMe(NC_5H_4)\}(CO)_3$ (**2**). While this compound

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possesses some features similar to known Mn catalysts, it differs significantly in possessing a PN supporting ligand. Effective electrocatalytic reduction of CO_2 with this species required a mixed 5% H_2O/CH_3CN solvent system. Our continuing efforts are directed in expanding on the ligand frameworks that support active CO_2 reduction catalysts, revealing additional details for the mechanism of action for these species.

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