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Ligand-Based Reduction of CO_2 and Release of CO on Iron(II)

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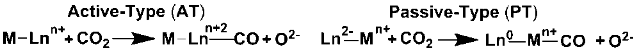
Supporting Information

ABSTRACT: A synthetic cycle for the CO_2-to-CO conversion (with subsequent release of CO) based on iron(II), a redox-active pydridinediimine ligand (PDI), and an O-atom acceptor is reported. This conversion is a passive-type ligand-based reduction, where the electrons for the CO_2 conversion are supplied by the reduced PDI ligand and the ferrous state of the iron is conserved.

Carbon dioxide (CO_2) is a significant environmental contaminant, and sensible methods of CO_2 utilization are needed for its mitigation as a greenhouse gas.[1] The production of CO from CO_2 is an attractive route to utilization of CO_2 as a C_1 source. CO is produced industrially by steam reforming fossil fuels to produce syngas[2] and is a versatile chemical precursor and fuel.[3] Nature utilizes CO_2 as a C_1 source on an immense scale for the synthesis of organic molecules.[4] One example is the Ni,Fe-CODHase enzymes,[5] which utilize late first-row transition metals to mediate the reduction of CO_2 (or oxidation of CO) despite the large bond enthalpy of the C=O double bond in CO_2 (532 kJ/mol).[6]

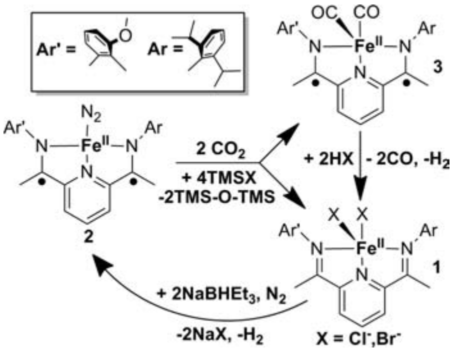
Highly reducing metal complexes that facilitate the reductive cleavage of CO_2 typically produce stoichiometric metal−oxygen or metal−carbon bonds that inhibit the possibility of catalytic turnover. These complexes often consist of early transition, or lanthanide and actinide metals,[7] and only a few iron complexes have been reported to reductively cleave CO_2.[8,9] The reductive cleavage of CO_2 on low-coordinate Fe(I) has been recently observed.[9a,b] However, to the best of our knowledge, only one example of the reductive cleavage of CO_2 to CO on Fe(II) has been reported,[9c] and no subsequent release of CO was observed. Strategies to bypass the formation of the catalyst−oxygen bonds include the use of O-atom acceptors such as diboron, borane, hydrosilane, or anhydride reagents[10] to effectively scrub out the O atom. One particularly novel strategy was to utilize an active-type (AT; Scheme 1), ligand-based reduction of CO_2, whereby a terminal nitride ligand performs the CO_2 binding, avoiding the formation of the strong oxometal bonds.[10d] We reasoned that it may be possible to utilize a similar ligand-based reduction approach, albeit in a different manner. That is, instead of utilizing the ligand as the binding site[11] in an AT reduction, we envisaged that the ligand could act as the electron source in a passive-type (PT; Scheme 1) reduction,[12] allowing the use of late transition metals such as iron in the reductive cleavage of CO_2.

Scheme 1. AT and PT Ligand-Based Reductions of CO_2



PT ligand-based reduction has been observed before in the catalytic cyclization of α,ω-dienes[13] utilizing an iron(II) center and a bis(diisopropylaryl)pyridinediimine ligand (^{iPr}PDI). The ferrous oxidation state is maintained during the cycle, and all redox activity is proposed to be ligand-based.[13b] In this paper, we report a cycle for the PT ligand-based reduction of CO_2 to CO utilizing a reduced iron(II) complex of the PDI scaffold and trimethylsilyl chloride (TMSCl) as an O-atom acceptor (Scheme 2). The electrons for the CO_2 reduction are stored and subsequently released via the PDI scaffold, yielding a purely PT ligand-based reduction, and the ferrous state of iron is conserved throughout.

Scheme 2. PT Ligand-Based Reduction Cycle of CO_2



The PDI ligand scaffold[14] was chosen for this work because of the ease of synthesis, potential for steric and electronic modification, and ability to serve as an electron reservoir.[15] The ligand $[(2,6\text{-}^iPrC_6H_3)N{=}CMe)(2\text{-}MeO\text{-}6\text{-}MeC_6H_3)N{=}CMe)C_5H_3N]$ (^{MeO}PDI) was synthesized via the Schiff base condensation of $[(2,6\text{-}^iPrC_6H_3N{=}CMe)(O{=}CMe)C_5H_3N]$ with 2-methoxy-6-methylaniline.[16] Reaction of the ^{MeO}PDI with 1 equiv of $FeBr_2$ in THF resulted in a blue solution of

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Fe($^{\mathrm{MeO}}$PDI)Br$_2$ (**1**). **1** was precipitated with diethyl ether and blue single crystals (which contained two independent molecules in the unit cell) were obtained by layering pentane into a solution of **1** in methylene chloride. An ORTEP view of one of the molecules of **1** is shown in Figure 1. The iron center is five-coordinate with a distorted square-pyramidal geometry (average $\tau = 0.28$).[17] The bond lengths and angles[16] are similar to other structurally characterized Fe(II)PDI complexes.[18] The measured μ_{eff} yielded values of 5.49 (solid) and 4.89 μ_B (solution) are consistent with a high-spin ($S = 2$) square-pyramidal Fe(II) center.[18a] The room temperature, zero-field Mössbauer parameters also confirm the assignment of a high-spin Fe(II) center ($\Delta E_Q = 1.13(2)$; $\delta = 0.644(9)$ mm/s).[15,18d]

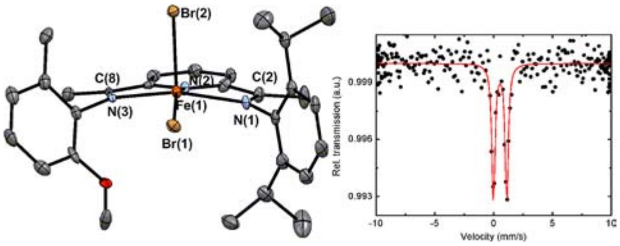
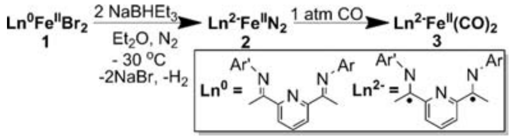


Figure 1. Solid-state structure (30% probability) of **1** (left). H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for one independent molecule in the unit cell: Fe(1)–Br(1) 2.4062(16), Fe(1)–Br(2) 2.5048(16), Fe(1)–N(1) 2.268(8), Fe(1)–N(2) 2.089(7), Fe(1)–N(3) 2.224(7), C(2)–N(1) 1.308(13), C(8)–N(3) 1.299(11); Br(1)–Fe(1)–Br(2) 108.38(6), N(2)–Fe(1)–Br(1) 158.3(2), N(1)–Fe(1)–N(3) 140.2(3). RT zero-field Mössbauer spectrum of **1** (right).

Similar to previous reports,[19] the PDI ligand scaffold is capable of being reduced under N$_2$ to form the dinitrogen complex Fe($^{\mathrm{MeO}}$PDI)N$_2$. As shown in Scheme 3, a blue suspension of **1** in either diethyl ether or pentane reacts with 2 equiv of NaBHEt$_3$, forming Fe($^{\mathrm{MeO}}$PDI)N$_2$ (**2**).

Scheme 3. Reduction of 1 under N$_2$ and Reaction with CO



Multiple attempts to isolate **2** in crystalline form were unsuccessful, so the complex was characterized in solution. As shown in Figure S7, the liquid FTIR spectrum of **2** in pentane displays a N$_2$ stretch at 2045 cm^{-1}, which shifts to 1959 cm^{-1} upon isotopic substitution with ^{15}N$_2$ (1975 cm^{-1} calcd).[16,20] ^{15}N{^{1}H} NMR spectroscopy of a solution of **2** that was exposed to ^{15}N$_2$ gas displays two resonances (Figure S9) at 113.5 and 104.7 ppm. These values fall within the range of previously reported[21] reduced PDI dinitrogen complexes and can be attributed to Nα and Nβ of the terminally bound, end-on dinitrogen ligand.

Based on previous studies of similar compounds, the $^{\mathrm{MeO}}$PDI ligand in **2** (Scheme 3) is proposed to be in the diradical dianionic form.[22] The assignment is supported by the structural and spectral data of the CO-functionalized complex Fe($^{\mathrm{MeO}}$PDI)(CO)$_2$ (**3**), synthesized by exposing a solution of **2** to 1 atm CO. An ORTEP view of **3** is shown in Figure 2. The iron center is five-coordinate, square-pyramidal geometry (τ = 0.06). The C$_{\mathrm{imine}}$–N$_{\mathrm{imine}}$ bonds are elongated from a value of 1.299(9) and 1.204(7) Å (average of both independent molecules) in **1** to 1.337(3) and 1.314(3) Å. The C$_{\mathrm{imine}}$–C$_{\mathrm{ipso}}$ bonds are contracted from 1.467(9) and 1.489(9) Å in **1** to 1.412(3) and 1.427(3) Å. These data, taken in conjunction with the room temperature, zero-field Mössbauer parameters [($\Delta E_Q = 1.13(1)$; $\delta = -0.025(6)$ mm/s)], suggest that complex **3** is best described as an iron(II) center with a doubly reduced $^{\mathrm{MeO}}$PDI ligand. **3** is diamagnetic in both the solid state and solution, yielding clean, diagnostic ^{1}H and ^{13}C{^{1}H} NMR spectra.[16] The FTIR spectrum of **3** displays two ν_{CO} at 1974 and 1914 cm^{-1}, respectively, identical with those of FePDI(CO)$_2$ complexes best described as having diradical dianionic ligands with a $S = 0$ Fe(II) center.[22]

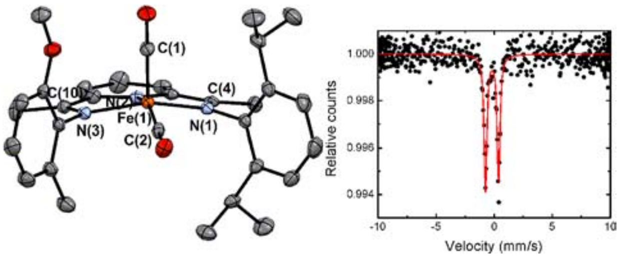


Figure 2. Solid-state structure (30% probability) of **3** (left). H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)–C(1) 1.774(2), Fe(1)–C(2) 1.784(2), Fe(1)–N(1) 1.9458(16), Fe(1)–N(2) 1.8526(17), Fe(1)–N(3) 1.9482(17), C(4)–N(1) 1.337(3), C(10)–N(3) 1.314(3); C(1)–Fe(1)–C(2) 96.00(10), N(2)–Fe(1)–C(2) 156.29(9), N(1)–Fe(1)–N(3) 152.48(7). RT zero-field Mössbauer spectrum of **3** (right).

To further explore the hypothesis that a PT ligand-based reduction of CO$_2$ is possible with Fe(II), **2** was generated and reacted with CO$_2$ (eq 1). **2** was formed in situ in diethyl ether from NaBHEt$_3$. Once all of the hydride was consumed (indicated by ^{11}B{^{1}H} NMR),[16] the solution was filtered and 1.33 equiv of TMSCl and TMS (internal standard) were added to the solution. The solution was charged with 1 atm CO$_2$, immediately turning brown and then back to green, with subsequent formation of a blue precipitate over 6 h. Analysis of the green solution reveals that it contains **3** along with TMS-O-TMS in a molar ratio of 1:2, as indicated by ^{29}Si{^{1}H} NMR of the reaction mixture (Figure S22). ^{11}B{^{1}H} NMR of the reaction mixture (with TMSCl) before and after addition of CO$_2$ show that virtually all boron exists as BEt$_3$.[16] Reactions with ^{13}CO$_2$ prove that the CO in **3** originates from CO$_2$ (Figure S15). The ν_{CO} bands in the FTIR spectrum at 1974 and 1914 cm^{-1} due to **3** are shifted to 1923 and 1867 cm^{-1}, respectively (1935 and 1876 cm^{-1} calcd). The ^{13}C{^{1}H} NMR spectrum reveals a resonance at 214.0 ppm attributed to the ^{13}CO ligands (Figure S14).

Analysis of the paramagnetic blue precipitate reveal that it is Fe($^{\mathrm{MeO}}$PDI)Cl$_2$ (**4**), the dichloride of the starting material. An ORTEP view of **4** is shown in Figure S33. The iron center is five-coordinate with square-pyramidal geometry ($\tau = 0.12$). The bond lengths and angles are similar to **1**.[16] The measured μ_{eff} of 5.58 (solid) and 4.94 μ_B (solution) are consistent with a high-spin ($S = 2$) Fe(II) center. The room temperature, zero-field Mössbauer parameters (Figure S18) also confirm a high-spin Fe(II) center ($\Delta E_Q = 0.88(2)$; $\delta = 0.677(9)$ mm/s) with a neutral $^{\mathrm{MeO}}$PDI ligand.

Equation 1 reveals that the electrons required to reduce CO$_2$ are supplied by the $^{\mathrm{MeO}}$PDI scaffold. ($^{\mathrm{MeO}}$PDI is reduced in **2**

$$3\mathrm{Ln}^{2-}\mathrm{Fe}^{\mathrm{II}}\mathrm{N}_2 + 4\mathrm{TMSCl} \xrightarrow[\text{PT Reduction}]{\text{1 atm CO}_2} 2\mathrm{Ln}^{0}\mathrm{Fe}^{\mathrm{II}}\mathrm{Cl}_2 + \mathrm{Ln}^{2-}\mathrm{Fe}^{\mathrm{II}}(\mathrm{CO})_2 + 2\mathrm{TMS\text{-}O\text{-}TMS} \quad (1)$$

and neutral in **4**.) The PT mechanism is also supported by the fact that all isolable products contain Fe(II), as indicated by the structural and spectroscopic data. Equation 1 also reveals that the two molecules of CO produced reside in **3** (no CO is found in the headspace) as CO is unable to bind to Fe(II) in the neutral form the $^{\mathrm{MeO}}$PDI ligand.[23] These observations, and the recent report[24] that Fe($^{\mathrm{iPr}}$PDI)(CO)$_2$ can be chemically oxidized, prompted us to explore the release of CO from **3** by chemical oxidation. The cyclic voltammogram (Figure S30) of **3** reveals a quasi-reversible oxidation event at −0.524 V (due to the formation of [Fe($^{\mathrm{MeO}}$PDI)(CO)$_2$]$^+$) and an irreversible oxidation event at 0.477 V (due to the oxidation to the neutral $^{\mathrm{MeO}}$PDI, with concomitant irreversible release of CO). As shown in eq 2, reaction of **3** in diethyl ether at −30 °C with HCl results in the precipitation of **4** in ~50% yield. Analysis of the headspace reveals that the CO from **3** is liberated upon oxidation to the neutral $^{\mathrm{MeO}}$PDI ligand, and H_2 is generated from the reduction of protons,[16] completing the PT ligand-based reduction of CO_2-to-CO cycle on Fe(II).[25]

$$\mathrm{Ln}^{2-}\mathrm{Fe}^{\mathrm{II}}(\mathrm{CO})_2 + 2\mathrm{HCl} \longrightarrow \mathrm{Ln}^{0}\mathrm{Fe}^{\mathrm{II}}\mathrm{Cl}_2 + 2\mathrm{CO} + \mathrm{H}_2 \quad (2)$$

In conclusion, we have developed a synthetic cycle for the CO_2-to-CO conversion based on Fe(II), the redox-active PDI ligand scaffold, and an O-atom acceptor. This conversion is a PT ligand-based reduction, where the electrons for the CO_2 conversion are supplied by the reduced $^{\mathrm{MeO}}$PDI ligand and the ferrous state of the iron is conserved throughout. The neutral Fe($^{\mathrm{MeO}}$PDI)Cl$_2$ is able to be regenerated, releasing CO. Reactions in our lab are currently underway to further investigate the mechanism, other O-atom acceptors, and alternative oxidants in eq 2 to increase the yield.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, spectroscopic data, more detailed ORTEP structures, and X-ray crystallographic data in table and CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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