

Ligand-Based Reduction of CO₂ and Release of CO on Iron(II)Zachary Thammavongsy,[†] Takele Seda,[‡] Lev N. Zakharov,[§] Werner Kaminsky,[‡] and John D. Gilbertson^{*,†}[†]Department of Chemistry and [‡]Department of Physics, Western Washington University, Bellingham, Washington 98225, United States[§]Department of Chemistry, University of Oregon, Eugene, Oregon 97403, United States[‡]Department of Chemistry, University of Washington, Seattle, Washington 98195, United States

Supporting Information

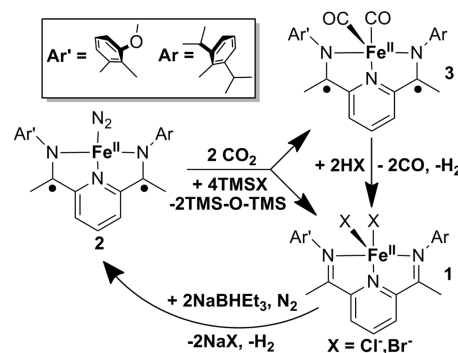
ABSTRACT: A synthetic cycle for the CO₂-to-CO conversion (with subsequent release of CO) based on iron(II), a redox-active pyridinediimine ligand (PDI), and an O-atom acceptor is reported. This conversion is a passive-type ligand-based reduction, where the electrons for the CO₂ conversion are supplied by the reduced PDI ligand and the ferrous state of the iron is conserved.

Carbon dioxide (CO₂) is a significant environmental contaminant, and sensible methods of CO₂ utilization are needed for its mitigation as a greenhouse gas.¹ The production of CO from CO₂ is an attractive route to utilization of CO₂ as a C₁ source. CO is produced industrially by steam reforming fossil fuels to produce syngas² and is a versatile chemical precursor and fuel.³ Nature utilizes CO₂ as a C₁ 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 CO₂ (or oxidation of CO) despite the large bond enthalpy of the C=O double bond in CO₂ (532 kJ/mol).⁶

Highly reducing metal complexes that facilitate the reductive cleavage of CO₂ 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 CO₂.^{8,9} The reductive cleavage of CO₂ 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 CO₂ 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 reagents¹⁰ to effectively scrub out the O atom. One particularly novel strategy was to utilize an active-type (AT; Scheme 1), ligand-based reduction of CO₂, whereby a terminal nitride ligand performs the CO₂ binding, avoiding the formation of the strong oxometal bonds.^{10d} We reasoned that it may be possible to

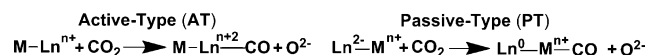
utilize a similar ligand-based reduction approach, albeit in a different manner. That is, instead of utilizing the ligand as the binding site¹¹ in an AT reduction, we envisaged that the ligand could act as the electron source in a passive-type (PT; Scheme 1) reduction,¹² allowing the use of late transition metals such as iron in the reductive cleavage of CO₂.

PT ligand-based reduction has been observed before in the catalytic cyclization of α,ω -dienes¹³ utilizing an iron(II) center and a bis(diisopropylaryl)pyridinediimine ligand (^{Pr}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 CO₂ 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 CO₂ reduction are stored

Scheme 2. PT Ligand-Based Reduction Cycle of CO₂

and subsequently released via the PDI scaffold, yielding a purely PT ligand-based reduction, and the ferrous state of iron is conserved throughout.

The PDI ligand scaffold¹⁴ 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-ⁱPrC₆H₃)N=CMe](2-MeO-6-MeC₆H₃)N=CMe)C₃H₃N] (^{MeO}PDI) was synthesized via the Schiff base condensation of [(2,6-ⁱPrC₆H₃)N=CMe](O=CMe)C₃H₃N] with 2-methoxy-6-methylaniline.¹⁶ Reaction of the ^{MeO}PDI with 1 equiv of FeBr₂ in THF resulted in a blue solution of

Scheme 1. AT and PT Ligand-Based Reductions of CO₂

$\text{Fe}^{\text{MeOPDI}}\text{Br}_2$ (**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

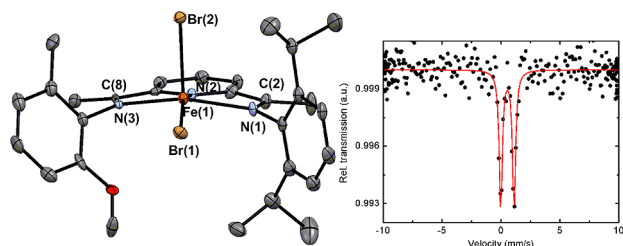
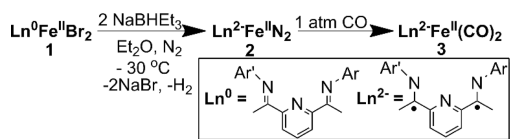


Figure 1. Solid-state structure (30% probability) of **1** (left). H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for one independent molecule in the unit cell: Fe(1)–Br(1) 2.4062(16), Fe(1)–Br(2) 2.5048(16), Fe(1)–N(1) 2.268(8), Fe(1)–N(2) 2.089(7), Fe(1)–N(3) 2.224(7), 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).

is five-coordinate with a distorted square-pyramidal geometry (average $\tau = 0.28$).¹⁷ The bond lengths and angles¹⁶ 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 ($\Delta E_{\text{Q}} = 1.13(2)$; $\delta = 0.644(9)$ mm/s).^{15,18d}

Similar to previous reports,¹⁹ the PDI ligand scaffold is capable of being reduced under N_2 to form the dinitrogen complex $\text{Fe}^{\text{MeOPDI}}\text{N}_2$. As shown in Scheme 3, a blue suspension of **1** in either diethyl ether or pentane reacts with 2 equiv of NaBHET_3 , forming $\text{Fe}^{\text{MeOPDI}}\text{N}_2$ (**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 $^{15}\text{N}_2$ (1975 cm^{-1} calcd).^{16,20} $^{15}\text{N}\{^1\text{H}\}$ NMR spectroscopy of a solution of **2** that was exposed to $^{15}\text{N}_2$ gas displays two resonances (Figure S9) at 113.5 and 104.7 ppm. These values fall within the range of previously reported²¹ reduced PDI dinitrogen complexes and can be attributed to $\text{N}\alpha$ and $\text{N}\beta$ of the terminally bound, end-on dinitrogen ligand.

Based on previous studies of similar compounds, the MeOPDI 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 $\text{Fe}^{\text{MeOPDI}}(\text{CO})_2$ (**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 ($\tau =$

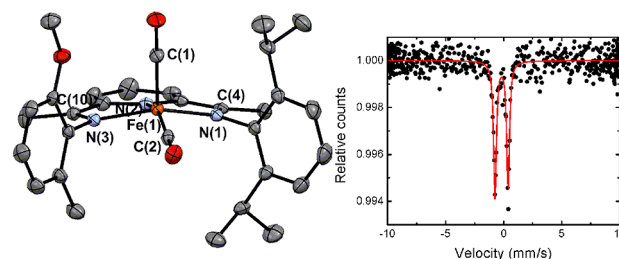


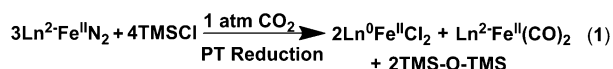
Figure 2. Solid-state structure (30% probability) of **3** (left). H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)–C(1) 1.774(2), Fe(1)–C(2) 1.784(2), Fe(1)–N(1) 1.9458(16), Fe(1)–N(2) 1.8526(17), Fe(1)–N(3) 1.9482(17), C(4)–N(1) 1.337(3), C(10)–N(3) 1.314(3);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

0.06). The $\text{C}_{\text{imine}}\text{--N}_{\text{imine}}$ 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 $\text{C}_{\text{imine}}\text{--C}_{\text{ipso}}$ 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 [$\Delta E_{\text{Q}} = 1.13(1)$; $\delta = -0.025(6)$ mm/s], suggest that complex **3** is best described as an iron(II) center with a doubly reduced MeOPDI ligand. **3** is diamagnetic in both the solid state and solution, yielding clean, diagnostic ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra.¹⁶ The FTIR spectrum of **3** displays two ν_{CO} at 1974 and 1914 cm^{-1} , respectively, identical with those of $\text{FePDI}(\text{CO})_2$ complexes best described as having diradical dianionic ligands with a $S = 0$ Fe(II) center.²²

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 $^{11}\text{B}\{^1\text{H}\}$ 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 $^{29}\text{Si}\{^1\text{H}\}$ NMR of the reaction mixture (Figure S22). $^{11}\text{B}\{^1\text{H}\}$ 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 $^{13}\text{CO}_2$ 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 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum reveals a resonance at 214.0 ppm attributed to the ^{13}C ligands (Figure S14).

Analysis of the paramagnetic blue precipitate reveal that it is $\text{Fe}^{\text{MeOPDI}}\text{Cl}_2$ (**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 ($\Delta E_{\text{Q}} = 0.88(2)$; $\delta = 0.677(9)$ mm/s) with a neutral MeOPDI ligand.

Equation 1 reveals that the electrons required to reduce CO_2 are supplied by the MeOPDI scaffold. (MeOPDI is reduced in 2



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 $\text{Me}^{\text{O}}\text{PDI}$ ligand.²³ These observations, and the recent report²⁴ that $\text{Fe}^{\text{Pr}}\text{PDI}(\text{CO})_2$ 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 $[\text{Fe}^{\text{MeO}}\text{PDI}(\text{CO})_2]^+$) and an irreversible oxidation event at 0.477 V (due to the oxidation to the neutral $\text{Me}^{\text{O}}\text{PDI}$, with concomitant irreversible release of CO). As shown in eq 2, reaction of 3 in diethyl ether at $-30\text{ }^\circ\text{C}$ with HCl results in the precipitation of 4 in $\sim 50\%$ yield. Analysis of the headspace reveals that the CO from 3 is liberated upon oxidation to the neutral $\text{Me}^{\text{O}}\text{PDI}$ 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



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 $\text{Me}^{\text{O}}\text{PDI}$ ligand and the ferrous state of the iron is conserved throughout. The neutral $\text{Fe}^{\text{MeO}}\text{PDI}\text{Cl}_2$ 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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