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Fe(I)-Mediated Reductive Cleavage and Coupling of CO_2: An $Fe^{II}(\mu\text{-O},\mu\text{-CO})Fe^{II}$ Core

Connie C. Lu, Caroline T. Saouma, Michael W. Day, and Jonas C. Peters*

Division of Chemistry and Chemical Engineering, Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125

Received July 31, 2006; E-mail: jpeters@caltech.edu

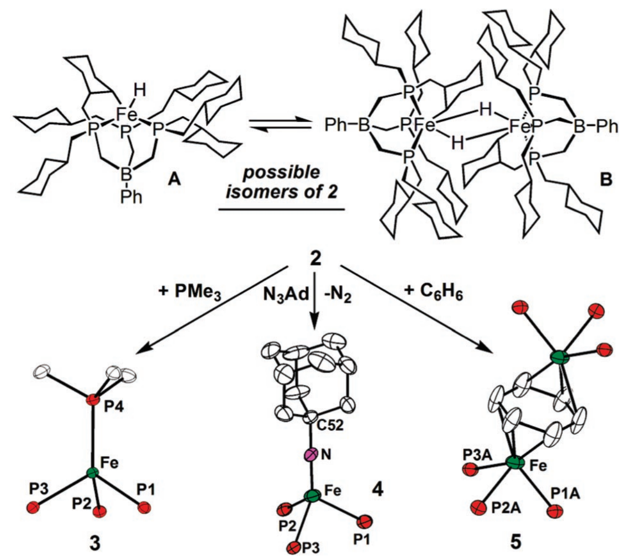
Direct O-atom transfer from CO_2 is a difficult transformation to realize given the molecule's thermodynamic and kinetic stability. Highly reducing early transition, lanthanide, and actinide metal complexes are known that facilitate reductive C−O cleavage of CO_2.[1] Later first row ions, while active for CO_2 binding, do not typically display similar cleavage transformations.[2,3] Nature, however, is presumed to exploit low-valent, later first row metal ions (e.g., Ni, Fe) to mediate CO_2 reduction/CO oxidation in the C cluster of CODH enzymes.[4]

We describe herein an unusual iron(I) system that reacts readily with CO_2 at ambient temperature to mediate its reductive cleavage. The dominant cleavage product is a structurally unprecedented bimetallic μ-carbonyl/μ-oxo core (i.e., Fe(μ-CO)(μ-O)Fe)). Structural evidence is also available for minor oxalate side products of the type Fe(μ-η^2:η^2-oxalato)Fe. This iron system is therefore able to mediate both the reductive cleavage and coupling of CO_2.[5]

Entry into the CO_2 chemistry of present interest was realized using a new tris(phosphino)borate ligand, $[PhB(CH_2P(CH_2Cy)_2)_3]^-$ (abbreviated as $[PhBP^{CH_2Cy}{}_3]$), featuring cyclohexylmethyl substituents at phosphorus. The yellow iron precursor $[PhBP^{CH_2Cy}{}_3]FeCl$ (**1**) was obtained in good yield from $Tl[PhBP^{CH_2Cy}{}_3]$ and $FeCl_2$. XRD, combustion analysis, and a solution magnetic moment determination establish that **1** is a monomeric, pseudotetrahedral $S = 2$ species. When compound **1** is chemically reduced by Na/Hg in THF under N_2, an intense lime-green solution is formed. This observation contrasts that of the Na/Hg reduction of its cousin $[PhBP^{iPr}{}_3]FeCl$ under a N_2 atmosphere, which gives rise to the red−brown dinitrogen-bridged dimer $\{[PhBP^{iPr}{}_3]Fe\}_2(\mu\text{-}N_2)$.[6] We have no evidence for N_2 uptake upon Na/Hg reduction of the $[PhBP^{CH_2Cy}{}_3]FeCl$ system under a N_2 atmosphere. Combustion analysis data for the isolated reduction product confirm its empirical formula as $[PhBP^{CH_2Cy}{}_3]Fe$ (**2**) and rules out the presence of nitrogen.

A sample of **2** in THF-d_8 exhibits complicated solution NMR spectra indicative of both paramagnetic and diamagnetic components that are likely undergoing rapid exchange. For example, its ^{31}P NMR spectrum features a single broad resonance that shifts from −29 to 4 ppm when the temperature is varied from 60 to −60 °C. A ^1H NMR spectrum of the sample contains broad, temperature-dependent resonances ranging from −7 to 72 ppm and sharp resonances in the diamagnetic region of the spectral window. Also, an axial EPR signal indicative of an $S = {}^1/_2$ iron center is observed in a THF glass of **2** at 4 K. Scheme 1 shows two possible isomeric structures that would be consistent with these spectral data and the empirical formula $[PhBP^{CH_2Cy}{}_3]Fe$. They include an Fe(III) alkyl hydride wherein one of the cyclohexyl C−H bonds of the ligand is cyclometalated (**A**, $S = {}^1/_2$) and an antiferromagnetically coupled dimer of such a structure with the hydride ligands in bridging positions (**B**, $S = 0$). Direct evidence for the presence of a metal hydride includes an IR stretch at 2058 cm^{-1} (KBr pellet) and the formation of $CHCl_3$ (∼40%, detected by ^1H and ^{13}C NMR) upon the addition of 1 equiv of CCl_4 in THF-d_8.[7]

Scheme 1



Regardless of its exact structure/s in THF solution, **2** behaves chemically as a very clean $[PhBP^{CH_2Cy}{}_3]Fe(I)$ source. For instance, the addition of PMe_3 to a THF solution of **2** generates the d^7 $S = {}^3/_2$ complex $[PhBP^{CH_2Cy}{}_3]Fe(PMe_3)$ (**3**). Also, the addition of 1 equiv of 1-adamantyl azide to **2** triggers oxidative nitrene transfer to provide the $S = {}^1/_2$ Fe(III) imide $[PhBP^{CH_2Cy}{}_3]Fe{\equiv}NAd$ (**4**).[8] Both **3** and **4** are formed almost quantitatively and have been structurally characterized (Scheme 1). Additionally, reconstitution of a THF solution of **2** into benzene provides, almost quantitatively, the dinuclear benzene complex $\{[PhBP^{CH_2Cy}{}_3]Fe\}_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-}C_6H_6)$ **5**. Given these observations, it seem likely that the iron center in **2** is reversibly solvated by THF to produce an $S = {}^1/_2$ iron(I) species such as $[PhBP^{CH_2Cy}{}_3]Fe(THF)_2$ in THF. Such a species could in fact account for the $S = {}^1/_2$ signature of **2** in THF at 4 K, rather than the cyclometalated hydride A shown in Scheme 1.

We next explored the reactivity of THF solutions of **2** with CO_2 and found that an immediate though subtle color change occurs from lime-green to pine-green upon CO_2 exposure. Inspection of the reaction solution in situ by ^1H NMR spectroscopy indicates one major diamagnetic product (ca. 75% using 5 equiv of CO_2, five runs). This product can be crystallized in analytically pure form (65% isolated yield) and exhibits a single peak in the ^{31}P NMR spectrum at 51.9 ppm and an intense ν(CO) IR stretch at 1730 cm^{-1} (KBr, C_6D_6; 1734 cm^{-1}, KBr pellet). This IR stretch represents a μ-CO ligand. Using ^{13}C-labeled CO_2, a ^{13}C NMR resonance for the μ-CO ligand at 289.8 ppm has been established. The $\nu(\mu\text{-CO})$ vibrations shift to 1692 cm^{-1} (calcd 1691 cm^{-1}) upon isotopic substitution. Blue−green plate-like crystals of **6** can be grown from

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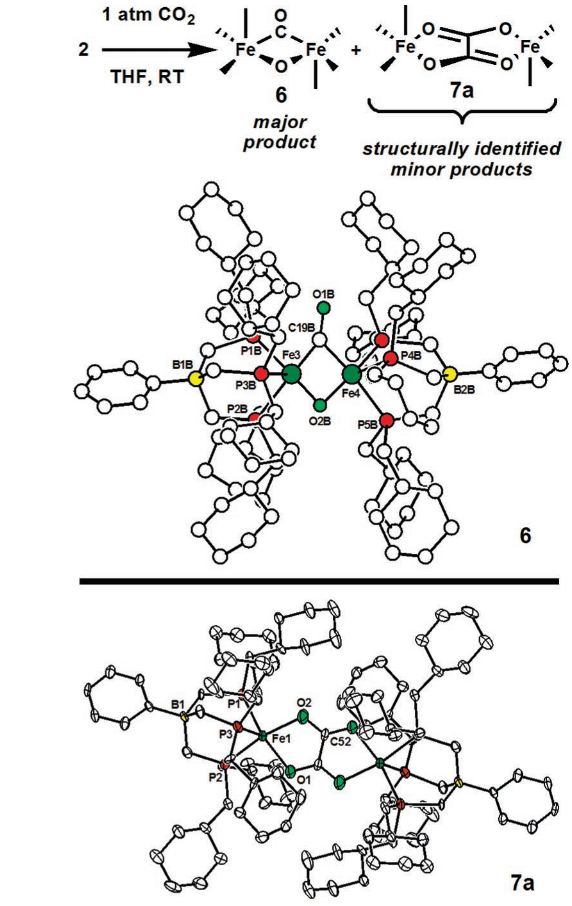
Scheme 2



benzene/petroleum ether and have been examined by X-ray crystallography. As shown in Scheme 2, the major product is $\{[PhBP^{CH_2Cy}{}_3]Fe\}_2(\mu\text{-}CO,\mu\text{-}O)$ (**6**), indicating a net two-electron reductive cleavage of CO_2 to CO and O^{2-}. The connectivity of **6** is very well-established, but of the various sets of crystals that have been examined by XRD, each has suffered from problematic disorder, in part due to the floppy methylcyclohexyl substituents.[9] An isotropic structure of **6** is therefore depicted in Scheme 2. Its most striking structural feature pertains to its diiron μ-carbonyl/μ-oxo core. To our knowledge, a bimetallic μ-oxo/μ-CO structure type had yet to be reported.[10] Complex **6** features a very short Fe−Fe distance (2.35 Å). CV data in THF show a reversible one-electron couple at −0.2 V (vs Ag/$AgNO_3$).

Varying the conditions of the CO_2 reaction with **2** invariably leads to the same major product **6**. This is true whether 0.5 equiv of CO_2 is employed or a CO_2 pressure of 10 atm. Moreover, **6** is the major product whether the reaction is carried out at −41 °C (complete in ca. 12 h) or at 22 °C (complete in ca. 15 min). The iron(I) phosphine adduct **3** also produces **6** as its major product upon exposure to CO_2, albeit much more slowly.

During the course of these studies, we have consistently observed a substantial secondary paramagnetic product by NMR spectroscopy (ca. 15−25% depending on exact conditions). By fractional crystallization of crude product mixtures, we have been able to pick out red−brown crystals for XRD analysis of the primary side product to establish its identity as $\{[PhBP^{CH_2Cy}{}_3]Fe\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}$oxalato) **7a** (see Scheme 2). The IR spectrum of **7a** shows a broad and intense vibration centered at 1647 cm^{-1} (KBr pellet) that shifts to 1598 cm^{-1} upon isotopic labeling with $^{13}C{-}CO_2$. In one case, pale pink crystals also formed that were subjected to XRD analysis. For these crystals, the presence of a μ-oxalato ligand was also established, but in this case, terminal CO ligands were also present ($\{[PhBP^{CH_2Cy}{}_3]Fe(CO)\}_2(\mu\text{-}\eta^2\text{:}\eta^2$-oxalato); **7b**). The structure of **7b** is provided in the Supporting Information. Studies are now underway to try to control the selectivity of the CO_2 reaction profile so as to favor the CO_2 coupling product/s for further studies.

In summary, THF solutions of **2** provide an effective Fe(I) source for substrate binding and group transfer reactions. Such solutions effect the reductive cleavage of CO_2 via O-atom transfer to provide a structurally unique Fe(μ-O)(μ-CO)Fe core. XRD studies reveal a reductive CO_2 coupling process that is also kinetically competent to generate oxalate. These initial observations establish that Fe(I) participates in rich CO_2 reaction chemistry and motivate continued studies in this context.

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Supporting Information Available: Detailed experimental procedures and characterization data for $[PhB(CH_2P(CH_2Cy)_2)_3]Tl$, ligand precursors, and compounds **1**−**6**. Crystallographic details for **1**, **3**−**6**, **7a**, and **7b** are provided in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. This material is available free of charge via the Internet at http://pubs.acs.org.

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