

Fe(I)-Mediated Reductive Cleavage and Coupling of CO₂: An Fe^{II}(μ -O, μ -CO)Fe^{II} Core

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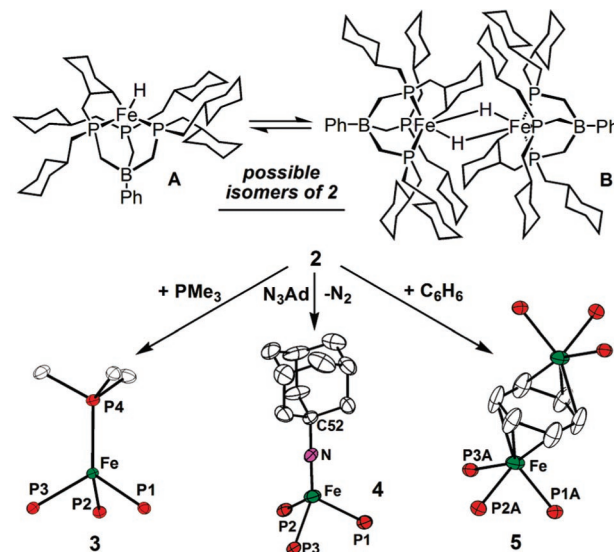
Direct O-atom transfer from CO₂ is a difficult transformation to realize given the molecule's thermodynamic and kinetic stability. Highly reducing early transition, lanthanide, and actinide metal complexes are known that facilitate reductive C–O cleavage of CO₂.¹ Later first row ions, while active for CO₂ 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 CO₂ reduction/CO oxidation in the C cluster of CODH enzymes.⁴

We describe herein an unusual iron(I) system that reacts readily with CO₂ 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 CO₂.⁵

Entry into the CO₂ chemistry of present interest was realized using a new tris(phosphino)borate ligand, [PhB(CH₂CH₂CH₂CH₂CH₂CH₂P(CH₂CH₂CH₂CH₂CH₂CH₂))₃][−] (abbreviated as [PhBPCH₂Cy₃]), featuring cyclohexylmethyl substituents at phosphorus. The yellow iron precursor [PhBPCH₂Cy₃]FeCl (**1**) was obtained in good yield from Ti[PhBPCH₂Cy₃] and FeCl₂. 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 N₂, an intense lime-green solution is formed. This observation contrasts that of the Na/Hg reduction of its cousin [PhBP^{Pr}₃]FeCl under a N₂ atmosphere, which gives rise to the red-brown dinitrogen-bridged dimer {[PhBP^{Pr}₃]Fe}₂(μ -N₂).⁶ We have no evidence for N₂ uptake upon Na/Hg reduction of the [PhBPCH₂Cy₃]-FeCl system under a N₂ atmosphere. Combustion analysis data for the isolated reduction product confirm its empirical formula as [PhBPCH₂Cy₃]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 ³¹P 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 [PhBPCH₂Cy₃]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)

Scheme 1

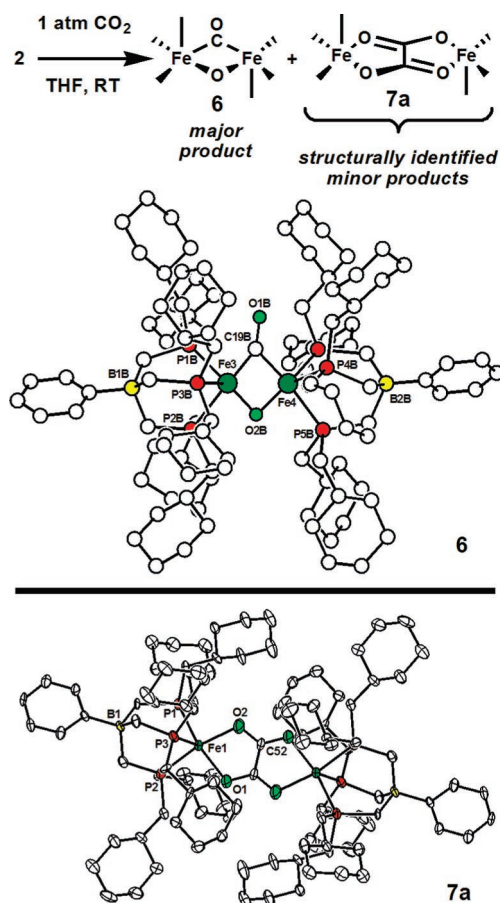


and the formation of CHCl₃ (~40%, detected by ¹H and ¹³C NMR) upon the addition of 1 equiv of CCl₄ in THF-*d*₈.⁷

Regardless of its exact structure/s in THF solution, **2** behaves chemically as a very clean [PhBPCH₂Cy₃]Fe(I) source. For instance, the addition of PMe₃ to a THF solution of **2** generates the d⁷ *S* = 3/2 complex [PhBPCH₂Cy₃]Fe(PMe₃) (**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 [PhBPCH₂Cy₃]Fe≡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 {[PhBPCH₂Cy₃]Fe}₂(μ - η^3 : η^3 -C₆H₆) (**5**). Given these observations, it seems likely that the iron center in **2** is reversibly solvated by THF to produce an *S* = 1/2 iron(I) species such as [PhBPCH₂Cy₃]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 CO₂ and found that an immediate though subtle color change occurs from lime-green to pine-green upon CO₂ exposure. Inspection of the reaction solution in situ by ¹H NMR spectroscopy indicates one major diamagnetic product (ca. 75% using 5 equiv of CO₂, five runs). This product can be crystallized in analytically pure form (65% isolated yield) and exhibits a single peak in the ³¹P NMR spectrum at 51.9 ppm and an intense ν (CO) IR stretch at 1730 cm^{−1} (KBr, C₆D₆; 1734 cm^{−1}, KBr pellet). This IR stretch represents a μ -CO ligand. Using ¹³C-labeled CO₂, a ¹³C NMR resonance for the μ -CO ligand at 289.8 ppm has been established. The ν (μ -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

Scheme 2



benzene/petroleum ether and have been examined by X-ray crystallography. As shown in Scheme 2, the major product is $\{[\text{PhBP}^{\text{CH}_2\text{Cy}_3}\text{Fe}]_2(\mu\text{-CO},\mu\text{-O})\}$ (**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/AgNO₃).

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 $\{[\text{PhBP}^{\text{CH}_2\text{Cy}_3}\text{Fe}]_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-oxalato})\}$ **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 $^{13}\text{C}\text{-CO}_2$. 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 ($\{[\text{PhBP}^{\text{CH}_2\text{Cy}_3}\text{Fe}(\text{CO})_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-oxalato})\}$; **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 $\text{Fe}(\mu\text{-O})(\mu\text{-CO})\text{Fe}$ 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 $[\text{PhB}(\text{CH}_2\text{P}(\text{CH}_2\text{Cy})_2)_3]\text{Ti}$, 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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