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## Fe(I)-mediated reductive cleavage and coupling of CO<sub>2</sub>: An Fe<sup>I</sup>(μ-O, μ-CO)Fe<sup>II</sup> core

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### Abstract

THF solutions of a new iron(I) source, “[PhBP<sup>CH<sub>2</sub>Cy<sub>3</sub></sup>]<sub>3</sub>Fe” ([PhBP<sup>CH<sub>2</sub>Cy<sub>3</sub></sup>] = [PhBP(CH<sub>2</sub>P(CH<sub>2</sub>Cy)<sub>2</sub>)<sub>3</sub>]<sup>−</sup>), effect the reductive cleavage of CO<sub>2</sub> via O-atom transfer at ambient temperature. The dominant reaction pathway is bimetallic and leads to the formation of a structurally unprecedented diiron Fe<sup>II</sup>(μ-O)(μ-CO)Fe<sup>II</sup> core. X-ray data are also available to suggest that bimetallic reductive CO<sub>2</sub> coupling to generate oxalate occurs as a minor reaction pathway. These initial observations forecast a diverse reaction landscape between CO<sub>2</sub> and iron (I) synthons.

Direct O-atom transfer from CO<sub>2</sub> 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<sub>2</sub>.<sup>1</sup> Later first row ions, while active for CO<sub>2</sub> binding, do not typically display similar cleavage transformations.<sup>2–3</sup> Nature, however, is presumed to exploit low-valent, later first row metal ions (e.g., Ni, Fe) to mediate CO<sub>2</sub> reduction/CO oxidation in the C cluster of CODH enzymes.<sup>4</sup>

We describe herein an unusual iron(I) system that reacts readily with CO<sub>2</sub> 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<sup>2</sup>: η<sup>2</sup>-oxalato)Fe. This iron system is therefore able to mediate both the reductive cleavage and coupling of CO<sub>2</sub>.<sup>5</sup>

Entry into the CO<sub>2</sub> chemistry of present interest was realized using a new tris(phosphino)borate ligand, [PhB(CH<sub>2</sub>P(CH<sub>2</sub>Cy)<sub>2</sub>)<sub>3</sub>]<sup>−</sup> (abbreviated as [PhBP<sup>CH<sub>2</sub>Cy<sub>3</sub></sup>]), featuring cyclohexylmethyl substituents at phosphorous. The yellow iron precursor [PhBP<sup>CH<sub>2</sub>Cy<sub>3</sub></sup>]<sub>3</sub>FeCl (**1**) was obtained in good yield from Ti[PhBP<sup>CH<sub>2</sub>Cy<sub>3</sub></sup>] and FeCl<sub>2</sub>. 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<sub>2</sub>, an intense lime-green solution is formed. This observation contrasts that of the Na/Hg reduction of its cousin [PhBP<sup>iPr<sub>3</sub></sup>]<sub>3</sub>FeCl under an N<sub>2</sub> atmosphere, which gives rise to the red-brown dinitrogen-bridged dimer {[PhBP<sup>iPr<sub>3</sub></sup>]<sub>3</sub>Fe}<sub>2</sub>(μ-N<sub>2</sub>).<sup>6</sup> We have no evidence for N<sub>2</sub> uptake upon Na/Hg reduction of the [PhBP<sup>CH<sub>2</sub>Cy<sub>3</sub></sup>]<sub>3</sub>FeCl system under an N<sub>2</sub> atmosphere. Combustion analysis data for the isolated reduction product confirms its empirical formula as “[PhBP<sup>CH<sub>2</sub>Cy<sub>3</sub></sup>]<sub>3</sub>Fe”, (**2**), and rules out the presence of nitrogen.

A sample of **2** in THF-*d*<sub>8</sub> exhibits complicated solution NMR spectra indicative of both paramagnetic and diamagnetic components that are likely undergoing rapid exchange. For example, its <sup>31</sup>P NMR spectrum features a single broad resonance that shifts from -29 ppm to

4 ppm when the temperature is varied from 60 to  $-60$  °C. A  $^1\text{H}$  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<sup>CH<sub>2</sub>Cy<sub>3</sub></sup>]<sub>3</sub>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  $2058\text{ cm}^{-1}$  (KBr pellet) and the formation of  $\text{CHCl}_3$  ( $\sim 40\%$ , detected by  $^1\text{H}$  and  $^{13}\text{C}$  NMR) upon the addition of one equivalent of  $\text{CCl}_4$  in THF-*d*<sub>8</sub>.<sup>7</sup>

Regardless of its exact structure/s in THF solution, **2** behaves chemically as a very clean “[PhBP<sup>CH<sub>2</sub>Cy<sub>3</sub></sup>]<sub>3</sub>Fe(I)” source. For instance, the addition of  $\text{PMe}_3$  to a THF solution of **2** generates the  $d^7$   $S = 3/2$  complex [PhBP<sup>CH<sub>2</sub>Cy<sub>3</sub></sup>]<sub>3</sub>Fe(PMe<sub>3</sub>) (**3**). Also, the addition of one equivalent of 1-adamantyl azide to **2** triggers oxidative nitrene transfer to provide the  $S = 1/2$  Fe(III) imide [PhBP<sup>CH<sub>2</sub>Cy<sub>3</sub></sup>]<sub>3</sub>Fe≡NAd (**4**).<sup>8</sup> Both **3** and **4** are formed ca. quantitatively and have been structurally characterized (Scheme I). Additionally, reconstitution of a THF solution of **2** into benzene provides, ca. quantitatively, the dinuclear benzene complex {[PhBP<sup>CH<sub>2</sub>Cy<sub>3</sub></sup>]<sub>3</sub>Fe}<sub>2</sub>( $\mu$ - $\eta^3$ : $\eta^3$ -C<sub>6</sub>H<sub>6</sub>) **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 [PhBP<sup>CH<sub>2</sub>Cy<sub>3</sub></sup>]<sub>3</sub>Fe(THF)<sub>2</sub> 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 I.

We next explored the reactivity of THF solutions of **2** with  $\text{CO}_2$  and found that an immediate though subtle color change occurs from lime-green to pine-green upon  $\text{CO}_2$  exposure. Inspection of the reaction solution *in situ* by  $^1\text{H}$  NMR spectroscopy indicates one major diamagnetic product (ca. 75% using 5 equiv of  $\text{CO}_2$ , 5 runs). This product can be crystallized in analytically pure form (65% isolated yield) and exhibits a single peak in the  $^{31}\text{P}$  NMR spectrum at 51.9 ppm and an intense  $\nu(\text{CO})$  IR stretch at  $1730\text{ cm}^{-1}$  (KBr, C<sub>6</sub>D<sub>6</sub>;  $1734\text{ cm}^{-1}$ , KBr pellet). This IR stretch represents a  $\mu$ -CO ligand. Using  $^{13}\text{C}$ -labeled  $\text{CO}_2$ , a  $^{13}\text{C}$ -NMR resonance for the  $\mu$ -CO ligand at 289.8 ppm has been established. The  $\nu(\mu\text{-CO})$  vibrations shift to  $1692\text{ cm}^{-1}$  (calcd:  $1691\text{ cm}^{-1}$ ) upon isotopic substitution. Blue-green plate-like crystals of **6** can be grown from benzene/petroleum ether and have been examined by X-ray crystallography. As shown in Scheme II, the major product is {[PhBP<sup>CH<sub>2</sub>Cy<sub>3</sub></sup>]<sub>3</sub>Fe}<sub>2</sub>( $\mu$ -CO, $\mu$ -O), (**6**), indicating a net 2-electron reductive cleavage of  $\text{CO}_2$  to CO and  $\text{O}^{2-}$ . 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.<sup>9</sup> An isotropic structure of **6** is therefore depicted in Scheme II. Its most striking structural feature pertains to its diiron  $\mu$ -carbonyl/ $\mu$ -oxo core. To our knowledge a bimetallic  $\mu$ -oxo/ $\mu$ -CO structure type had yet to be reported.<sup>10</sup> Complex **6** features a very short Fe-Fe distance (2.35 Å). CV data in THF show a reversible 1-electron couple at  $-0.2\text{ V}$  (vs Ag/AgNO<sub>3</sub>).

Varying the conditions of the  $\text{CO}_2$  reaction with **2** invariably leads to the same major product **6**. This is true whether 0.5 equiv of  $\text{CO}_2$  is employed or a  $\text{CO}_2$  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  $\text{CO}_2$ , 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 II). The IR spectrum of **7a** shows a broad and intense vibration centered at  $1647\text{ cm}^{-1}$  (KBr pellet) that shifts to  $1598\text{ cm}^{-1}$  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 the crystals, the presence of a  $\mu\text{-oxalato}$  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 SI. Studies are now underway to try to control the selectivity of the  $\text{CO}_2$  reaction profile so as to favor the  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2$  coupling process that is also kinetically competent to generate oxalate. These initial observations establish that Fe(I) participates in rich  $\text{CO}_2$  reaction chemistry motivate continued studies in this context.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

## Acknowledgments

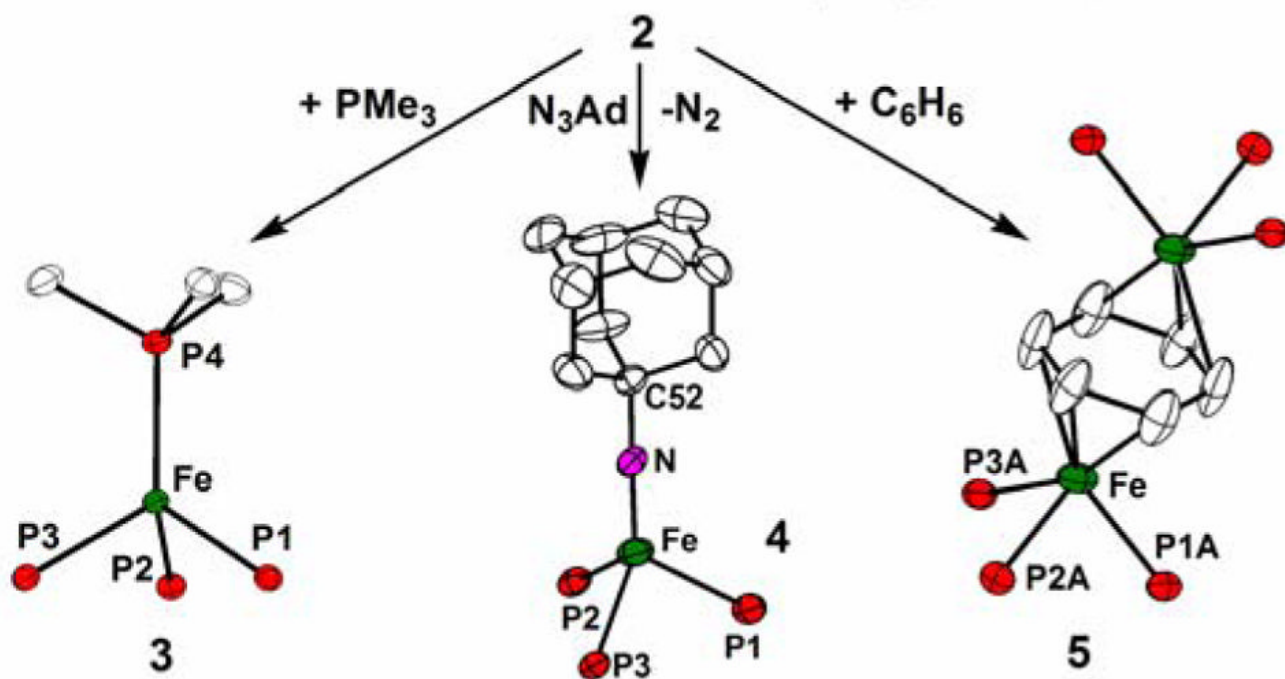
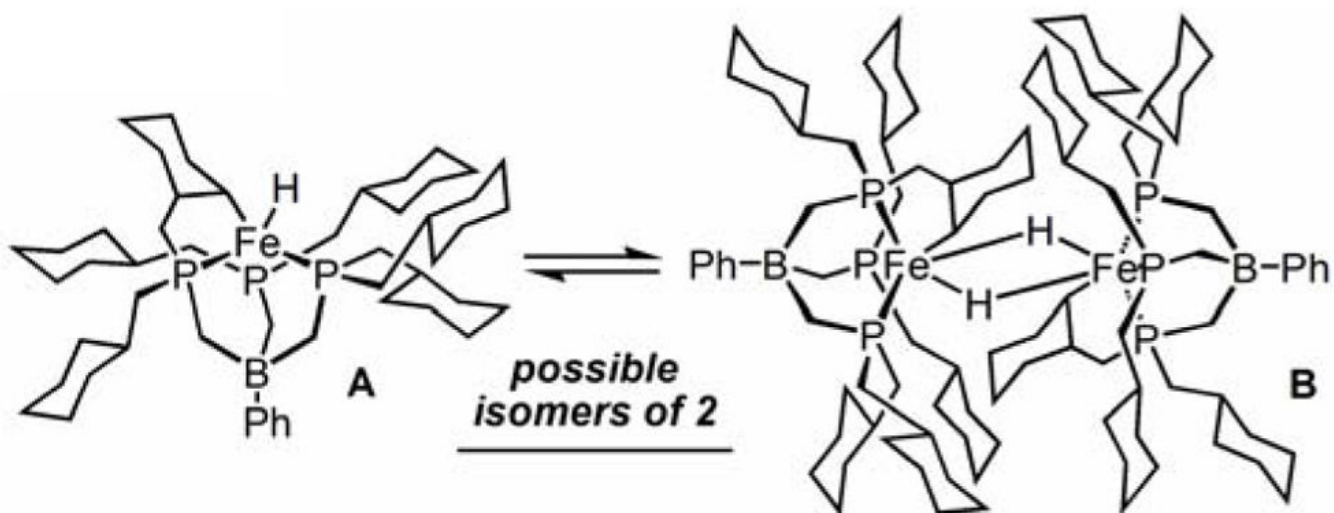
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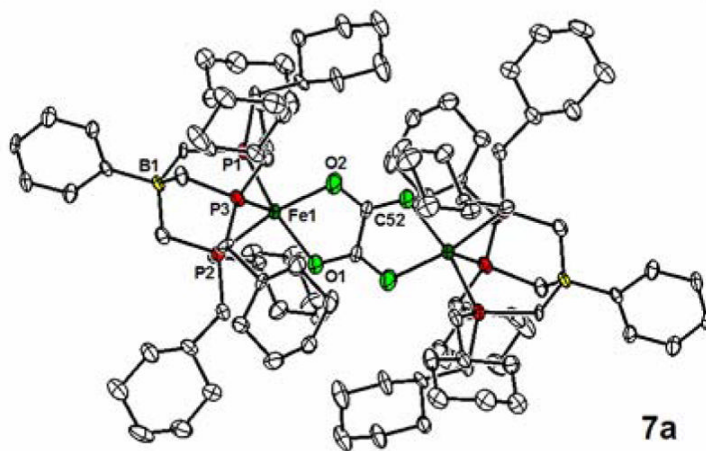
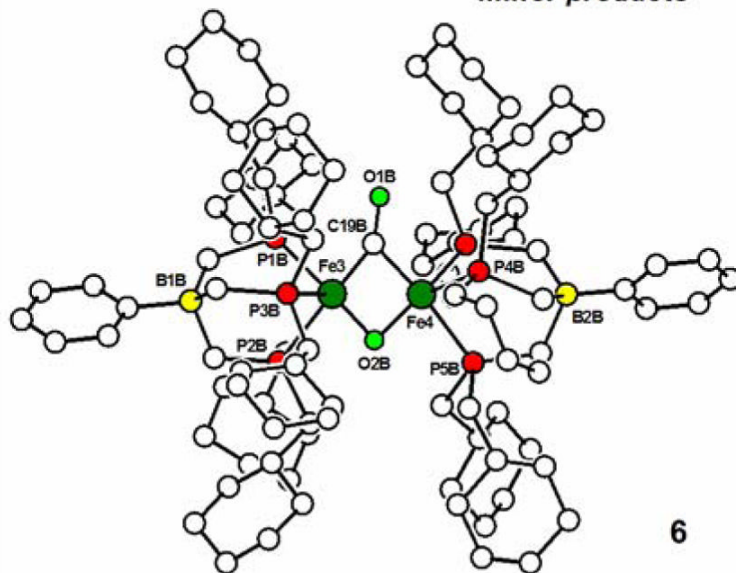
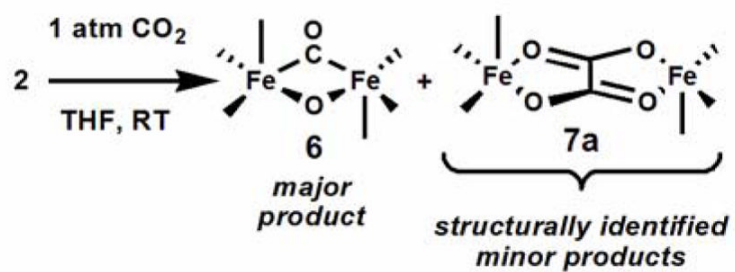
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Supporting Information). In the monoclinic crystals, 6 was very disordered in addition the disordered solvent molecules. The tetragonal crystal form yielded no atomic information.

10. There are a few examples of dimetal  $\mu$ -sulfide/ $\mu$ -CO core structures. See, for example: (a) Kubiak CP, Woodcock C, Eisenberg R. *Inorg Chem* 1980;19:2733. (b) Balch AL, Catalano VJ, Olmstead MM. *Inorg Chem* 1990;29:1638.



Scheme I.



Scheme II.