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Reduction of CO₂ to CO using Low-Coordinate Iron: Formation of a Four-Coordinate Iron Dicarbonyl Complex and a Bridging Carbonate Complex

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Abstract

A reduced diiron(I) complex reacts with CO₂ to give two iron-containing products. One product has a carbonate bridge, which isomerizes rapidly at -70 °C and may be derived from an oxodiiron intermediate. Formation of this product releases free CO, which leads to a four-coordinate iron dicarbonyl complex. This product is the first crystallographically characterized example of a four-coordinate iron dicarbonyl species, a moiety that may be present in the active site of Hmd (“iron-sulfur cluster free”) hydrogenase.

Carbon dioxide plays an important role in synthetic and biological chemistry as a one-carbon building block.¹ Despite the large bond enthalpy of the C=O double bond in CO₂ (532 kJ/mol),² nature is capable of using late first row transition metal ions to reduce CO₂ to CO in the enzymes acetyl-coenzyme A synthase/CO dehydrogenase³ and nitrogenase.⁴ This is also the reverse of the famous water-gas shift reaction.⁵ Interest in the reduction of CO₂ to CO has led to the investigation of numerous schemes for achieving the reduction of CO₂.¹ Transition metal promoted reduction of CO₂ to give CO and CO₃²⁻ has been observed in many systems and this type of transformation (eq 1) is known as reductive disproportionation.⁶



Recently, Peters reported the reductive cleavage of CO₂ by a low-coordinate iron(I) system.⁷ This reaction afforded as the major product a diiron(II) complex with a Fe(μ-CO)(μ-O)Fe core. Herein, we report the reaction of CO₂ with another iron(I) system, which gives a different outcome but may use a similar mechanism.

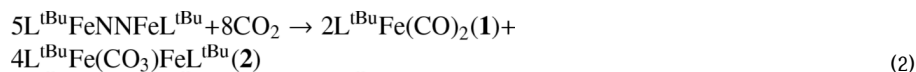
We have described the iron-dinitrogen complex L^{tBu}FeNNFeL^{tBu} (L^{tBu} = 2,2,6,6-tetramethyl-3,5-bis(2,6-diisopropylphenylimino)hept-4-yl).⁸ Spectroscopic and magnetic studies are consistent with assignment of its iron atoms as iron(II) and the dinitrogen ligand as N₂²⁻.⁹ However, in its reactivity, it generally behaves as a source of the iron(I) fragment L^{tBu}Fe.^{8b,10} For example, it reacts with neutral ligands C₆H₆ and PR₃ to give monomeric iron(I) complexes, and it reductively couples ketones and aldehydes to give diiron(II) pinacolate complexes.^{8b}

Treatment of L^{tBu}FeNNFeL^{tBu} with 2 equiv of dry carbon dioxide in pentane, benzene, or diethyl ether affords a mixture of the dicarbonyliron(I) compound L^{tBu}Fe(CO)₂ (**1**) and the

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bridging carbonatodiiron(II) compound $L^{tBu}Fe(\mu-OCO_2)FeL^{tBu}$ (**2**). The 1H NMR spectrum of the crude mixture from the reaction of $L^{tBu}FeNNFeL^{tBu}$ and carbon dioxide shows the formation of **2** as $70 \pm 5\%$ of the total iron (using an internal integration standard). The theoretical stoichiometry of this reaction is shown in equation 2, and the observed spectroscopic yield of **2** agrees fairly well with the 80% expected. Because **1** is not NMR active (see below), its presence was deduced by the observation of CO stretching vibrations at 1996 and 1917 cm^{-1} in the solid-state infrared spectrum of the crude product.



In this reaction 8 iron atoms are oxidized from iron(I) to iron(II), concomitant with the reduction of 8 molecules of carbon dioxide. This creates 4 carbonate anions that bind to iron(II), as well as 4 molecules of CO that are trapped by iron(I).

Compound **1** can be synthesized independently by reacting $L^{tBu}FeNNFeL^{tBu}$ with 4 equiv of carbon monoxide in diethyl ether. Using excess CO results in a mixture of $L^{tBu}Fe(CO)_2$ and $L^{tBu}Fe(CO)_3$, as described in a recent publication.^{8b} In that work, we were frustrated by the cocrystallization of these dicarbonyl and tricarbonyl complexes, and an X-ray crystal structure showed a superposition of these two molecules. Here, use of the appropriate stoichiometry of starting materials gives the pure dicarbonyliron(I) complex, with CO stretching vibrations at 1994 and 1915 cm^{-1} in the solid-state IR spectrum.¹¹ Complex **1** has a low-spin d^7 ($S = 1/2$) electronic configuration, as shown by EPR spectroscopy in the solution and solid state.^{8b,11} The crystal structure of **1** is illustrated in Figure 1. The iron atom has a square planar geometry (sum of angles around iron 361.8(1) $^\circ$). The C-O bond lengths are 1.149(2) and 1.151(2) Å and the Fe-C-O units are slightly bent (172.8(1) $^\circ$ and 172.9(2) $^\circ$).

Compound **1** is interesting because it is the first example of a four-coordinate dicarbonyl complex of iron. This structural feature has been postulated to be present in the active site of the “Fe-S cluster free” hydrogenase Hmd, on the basis of infrared, Mössbauer, and X-ray absorption data.¹² Infrared spectra of the enzyme showed two bands of identical intensity, leading to an estimate of the C-Fe-C angle of 86–94 $^\circ$ based on the literature relationship $\tan \theta = I_{asym}/I_{symm}$.^{12a,13} However, **1** shows virtually identical intensities for the two CO stretching vibrations despite the C-Fe-C angle of 81.44(8) $^\circ$ in the X-ray crystal structure. On this basis, we suggest that a broader range of CO angles should be considered as possible in the enzyme.

The use of **1** for further comparison to the enzyme is limited because the iron atom in Hmd hydrogenase is diamagnetic, either low-spin iron(II) or low-spin iron(0), in contrast to the iron (I) oxidation state in **1**. So, although **1** is not an electronic match for the active site of Hmd, its structure is the best mimic yet known. The redox chemistry of **1** is clearly of interest, and will be reported in the future.

The other product of CO₂ reduction, $L^{tBu}Fe(\mu-OCO_2)FeL^{tBu}$ (**2**), could be isolated in pure form by performing the reaction of $L^{tBu}FeNNFeL^{tBu}$ and carbon dioxide in the presence of Pd/C to trap the carbon monoxide *in situ*. The crude product of this reaction shows no carbonyl stretching bands in the IR spectrum. The ability to divert the reaction shows that free CO is involved in the formation of complex **1**.

Complex **2** has been characterized by 1H NMR and infrared spectroscopies, X-ray diffraction, and elemental analysis. The IR spectrum of **2** shows two strong bands at 1493 and 1481 cm^{-1} that are characteristic of a bridging carbonate ligand.¹⁴ The solution magnetic moment of 6.0(3) BM/molecule in C₆D₆ suggests that the high-spin iron(II) centers in **2** have very weak

magnetic coupling. The solid-state structure of **2** has two different molecules in the unit cell (Figure 2). In one molecule (A) the bridging carbonate is coordinated in a $\mu\text{-}\eta^2\text{:}\eta^1$ mode and in the other (B) it is coordinated in a $\mu\text{-}\eta^2\text{:}\eta^2$ mode to the metal centers. The bond lengths and bond angles of these two molecules are compared in Table 1. Structural type A is unprecedented for a carbonate bridge on iron, but has been seen with other metals.¹⁵ Structural type B has precedent in a tris(pyrazolyl)boratoiron(II) complex, which was derived from a metal hydroxide and CO_2 .¹⁶

The ^1H NMR spectrum of **2** in C_6D_6 shows seven peaks, which is characteristic of the protons on β -diketiminato ligands in local C_{2v} symmetry. There is no decoalescence in the temperature range $+70$ to -70 °C. This implies at least two rapid dynamic processes. First, the bridging carbonate ligand must exchange between binding modes A and B rapidly, making the two metals equivalent on the NMR time scale. Second, the equivalence of the two faces of the β -diketiminato ligand indicates that there is rapid rotation of the iron atom around the Fe-O bond, probably in the iron ion with η^1 -carbonate binding.

There are multiple possibilities for the mechanism through which **1** and **2** are formed. One is the reductive disproportionation of CO_2 , a series of one-electron reductions that is well-established in electrochemical and other reactions with reduced transition-metal complexes.¹ In other systems, reductive disproportionation is thought to proceed through the intermediacy of the radical $[\text{O}=\text{C}-\text{O}-\text{C}(=\text{O})-\text{O}]^-$, for which we have no evidence here. Another possibility is the reductive cleavage of CO_2 to give CO and CO_2^- . While this work was in progress, Peters reported an iron(I) complex that reacts with 0.5 equiv of CO_2 to give a diiron(II) complex with an $\text{Fe}(\mu\text{-CO})(\mu\text{-O})\text{Fe}$ core.⁷ This outcome corresponds to direct reductive cleavage of the C=O bond. Earlier low-valent iron complexes also give the overall reductive cleavage of CO_2 .¹⁷ In our system, we have reported the isolation of the oxodiiron(II) complex $[\text{L}^{\text{tBu}}\text{Fe}]_2\text{O}$, which would be the analogous oxo intermediate (Scheme 1).¹⁸ This hindered oxo complex binds a number of Lewis bases reversibly, so it is reasonable to assume that it could lose CO, at least transiently. Although we have no direct spectroscopic evidence that $[\text{L}^{\text{tBu}}\text{Fe}]_2\text{O}$ is formed during the course of the reaction of CO_2 and $\text{L}^{\text{tBu}}\text{FeNNFeL}^{\text{tBu}}$, treatment of isolated $[\text{L}^{\text{tBu}}\text{Fe}]_2\text{O}$ with CO_2 in C_6D_6 rapidly yields **2** as shown by ^1H NMR spectroscopy. Therefore, the oxo complex is kinetically competent to be an intermediate in the formation of **2**. As shown above, CO reacts rapidly with $\text{L}^{\text{tBu}}\text{FeNNFeL}^{\text{tBu}}$ to give **1** in independent experiments; further, formation of **1** can be suppressed by trapping CO with Pd/C. Therefore, Scheme 1 represents a reasonable mechanism for this interesting new CO_2 reduction reaction.

In conclusion, CO_2 can be reduced cleanly to CO and carbonate at a diiron(I) site. The CO (**1**) and CO_3^{2-} (**2**) containing products are notable because of a structural similarity between **1** and a newly discovered hydrogenase enzyme, and an interesting dynamic process in **2**. The formation of **2** may proceed through the intermediacy of an oxodiiron(II) complex.

Acknowledgements

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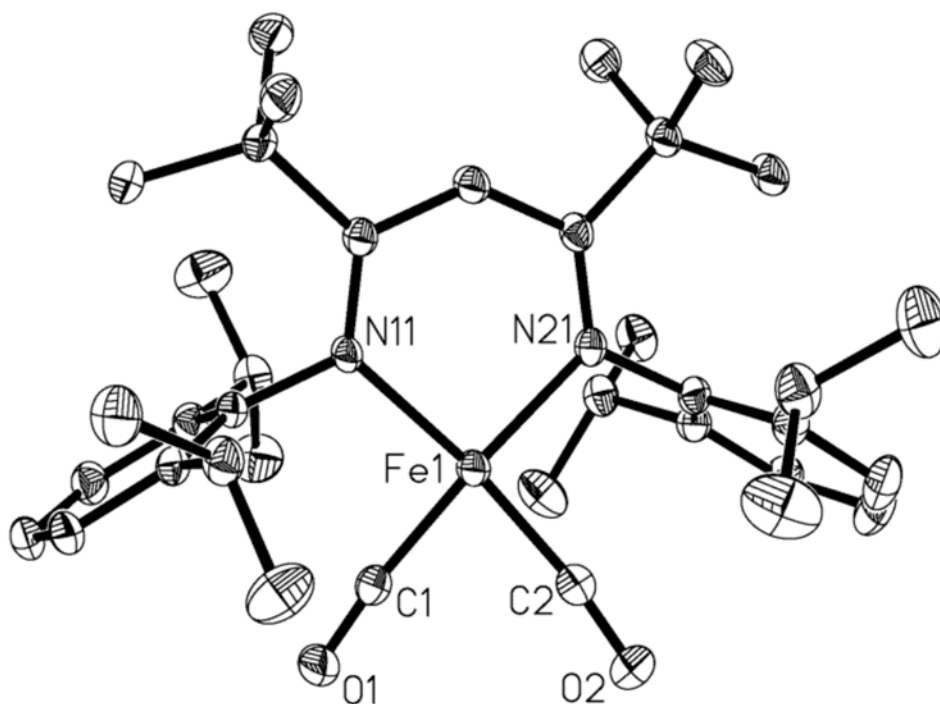


Figure 1. Crystal structure of **1**. Thermal ellipsoids shown at 50% probability. Hydrogen atoms have been omitted for clarity. Fe1-C1 1.784(2) Å, Fe1-C2 1.785(2) Å Fe1-N11 1.967(1) Å, C1-O1 1.151(2) Å, C2-O2 1.149(2) Å, N11-Fe1-N21 93.43(5)°, C1-Fe1-C2 81.44(8)°, O1-C1-Fe1 172.8(1)°, O2-C1-Fe1 172.9(2)°.

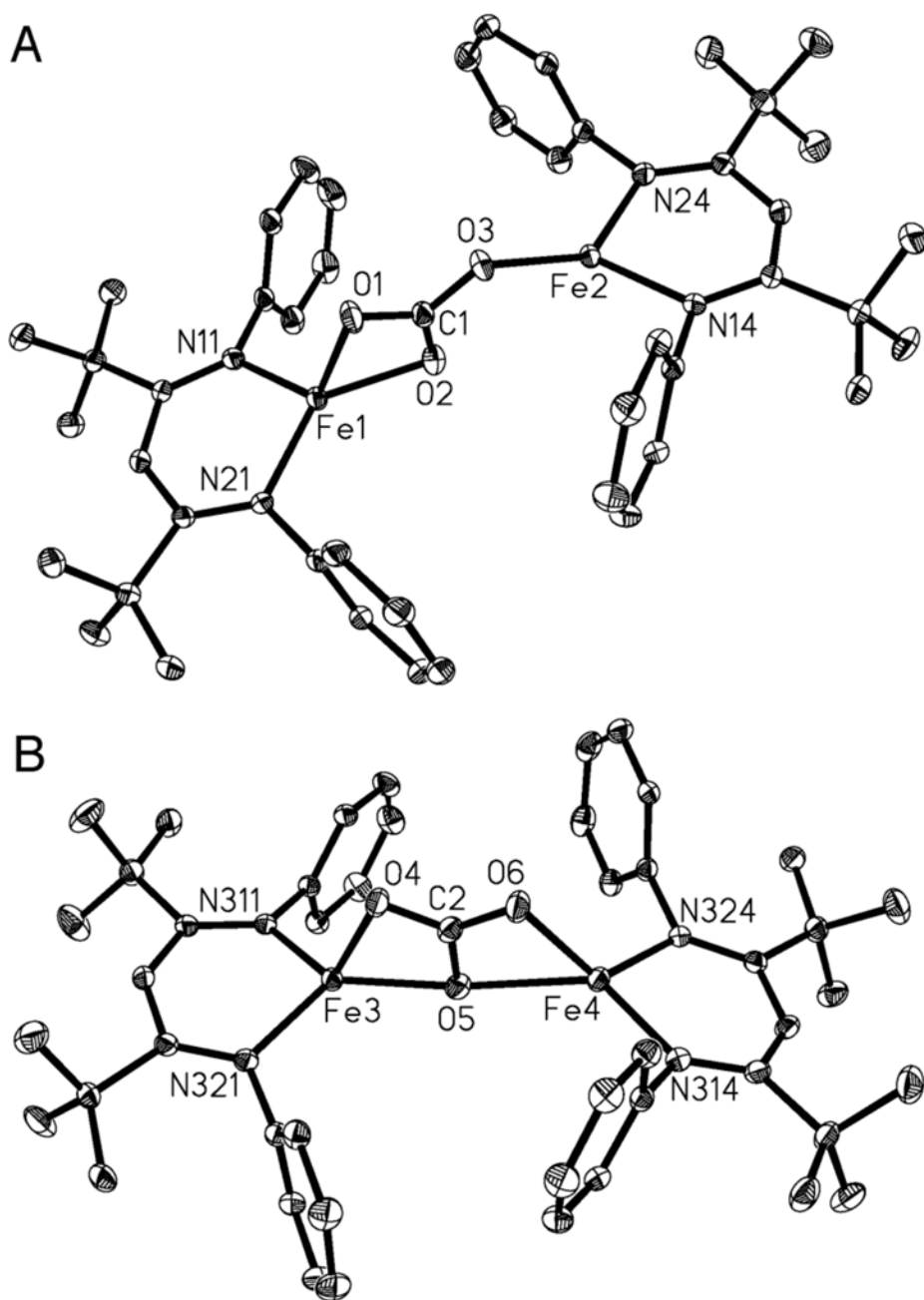
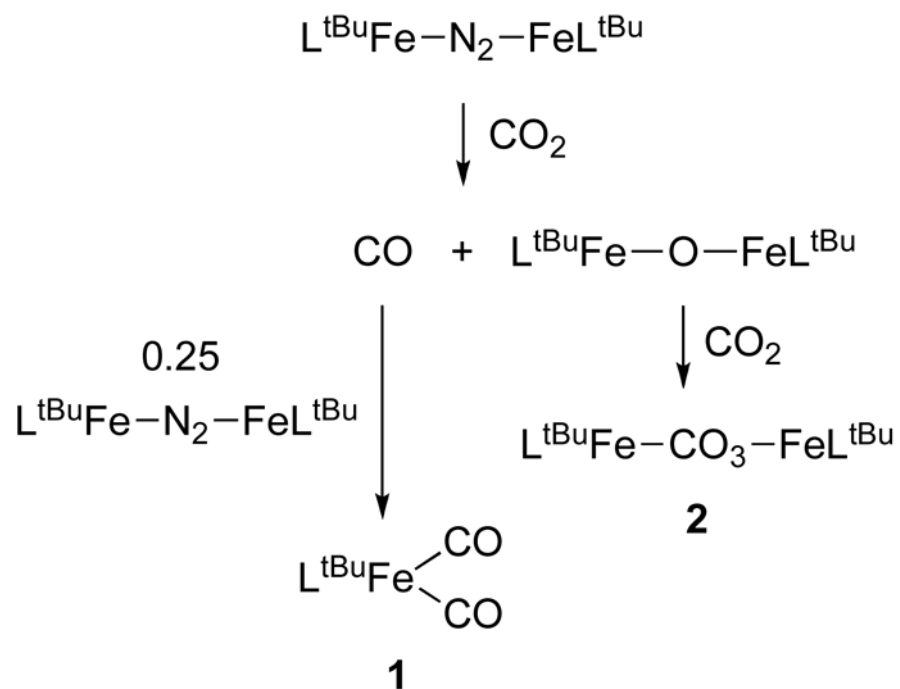


Figure 2. Crystal structure of **2**, showing molecules A and B with different bridging modes. Thermal ellipsoids shown at 50% probability. Hydrogen atoms and isopropyl groups have been omitted for clarity. See Table 1 for metrical parameters.



Scheme 1.
Proposed mechanism for formation of **1** and **2**.

Table 1

Bond lengths (Å) and bond angles (°) of Fe(μ -CO₃)Fe cores in the two independent molecules found in the X-ray crystal structure of **2**.

	A	B
Fe1-O1	2.079(1)	2.079(1)
Fe1-O2	2.034(1)	2.107(1)
Fe2-O3	1.881(1)	1.982(1)
Fe2-O2	3.156(1)	2.358(1)
C1-O1	1.270(2)	1.256(2)
C1-O2	1.291(2)	1.323(2)
C1-O3	1.293(2)	1.275(2)
O1-Fe1-O2	64.52(4)	63.53(4)
O2-Fe2-O3	--	60.45(4)
O1-C1-O2	118.1(1)	117.4(1)
O1-C1-O3	120.9(1)	126.2(1)
O2-C1-O3	121.0(1)	116.4(1)