Inorganic Chemistry

Communication

Reduction of CO$_2$ to CO Using Low-Coordinate Iron: Formation of a Four-Coordinate Iron Dicarbonyl Complex and a Bridging Carbonate Complex

Azwana R. Sadique, William W. Brennessel, and Patrick L. Holland*

Department of Chemistry, University of Rochester, Rochester, New York 14627

A reduced diiron(I) complex reacts with CO$_2$ 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. The 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 CO$_2$ (532 kJ/mol),[2] nature is capable of using first-row late transition metal ions to reduce CO$_2$ to CO in the enzymes acetyl coenzyme A synthase/CO dehydrogenase[3] and nitrogenase.[4] This is also the reverse of the famous water–gas shift reaction.[5] Interest in the reduction of CO$_2$ to CO has led to the investigation of numerous schemes for achieving the reduction of CO$_2$.[1] Transition metal promoted reduction of CO$_2$ to give CO and CO$_3^{2-}$ has been observed in many systems, and this type of transformation (eq 1) is known as reductive disproportionation.[6]

$$2CO_2 + 2e^- \rightarrow CO + CO_3^{2-} \qquad (1)$$

Recently, Peters reported the reductive cleavage of CO$_2$ 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 CO$_2$ 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}, where L^{tBu} = 2,2,6,6-tetramethyl-3,5-bis-[(2,6-diisopropylphenyl)imino]hept-4-yl.[8] Spectroscopic and magnetic studies are consistent with the assignment of its iron atoms as Fe^{II} and the dinitrogen ligand as N$_2^{2-}$.[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 C$_6$H$_6$ and PR$_3$ to give monomeric iron(I) complexes, and it reductively couples ketones and aldehydes to give diiron(II) pinacolate complexes.[8b]

The treatment of L^{tBu}FeNNFeL^{tBu} with 2 equiv of dry CO$_2$ in pentane, benzene, or diethyl ether affords a mixture of the dicarbonyliron(I) compound L^{tBu}Fe(CO)$_2$ (**1**) and the bridging carbonatodiiron(II) compound L^{tBu}Fe(μ-OCO$_2$)-FeL^{tBu} (**2**). The ^{1}H NMR spectrum of the crude mixture from the reaction of L^{tBu}FeNNFeL^{tBu} and CO$_2$ shows the formation

* To whom correspondence should be addressed. E-mail: holland@chem.rochester.edu.

(1) Reviews: (a) Arakawa, H.; et al. *Chem. Rev.* **2001**, *101*, 953−996. (b) Louie, J. *Curr. Org. Chem.* **2005**, *9*, 605−623. (c) Omae, I. *Catal. Today* **2006**, *115*, 33−52. (d) Darensbourg, D. J. *Chem. Rev.* **2007**, *107*, 2388−2410. (e) Aresta, M.; Dibenedetto, A. *Dalton Trans.* **2007**, 2975−2992.

(2) Heats of formation taken from: *CRC Handbook*, 87th ed.; http://www.hbcpnetbase.com/.

(3) (a) Ragsdale, S. W.; Kumar, M. *Chem. Rev.* **1996**, *96*, 2515−2539. (b) Drennan, C. L.; Doukov, T. I.; Ragsdale, S. W. *J. Biol. Inorg. Chem.* **2004**, *9*, 511−515. (c) Hegg, E. L. *Acc. Chem. Res.* **2004**, *37*, 775−783.

(4) Rasche, M. E.; Seefeldt, L. C. *Biochemistry* **1997**, *36*, 8574−8585.

(5) (a) King, R. B.; King, A. D.; Yang, D. B. *ACS Symp. Ser.* **1981**, *152*, 123−132. (b) Ford, P. C. *Electrochem. Electrocatal. React. Carbon Dioxide* **1993**, 68−93. (c) Kochloefl, K. Water Gas Shift and COS Removal. In *Handbook of Heterogeneous Catalysis*; Ertl, G. et al., Eds.; Vol. 4; VCH: Weinheim, Germany, 1997; pp 1831−1843.

(6) (a) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1979**, *101*, 1767−1775. (b) Lee, G. R.; Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1987**, *109*, 2956−2962. (c) Alvarez, R.; Atwood, J. L.; Carmona, E.; Perez, P. J.; Poveda, M. L.; Rogers, R. D. *Inorg. Chem.* **1991**, *30*, 1493−1499.

(7) Lu, C. C.; Saouma, C. T.; Day, M. W.; Peters, J. C. *J. Am. Chem. Soc.* **2007**, *129*, 4−5. This paper reports an oxalate product as well, but in the work presented here, there is no sign of oxalate formation.

(8) (a) Smith, J. M.; Lachicotte, R. J.; Pittard, K. A.; Cundari, T. R.; Lukat-Rodgers, G.; Rodgers, K. R.; Holland, P. L. *J. Am. Chem. Soc.* **2001**, *123*, 9222−9223. (b) Smith, J. M.; Sadique, A. R.; Cundari, T. R.; Rodgers, K. R.; Lukat-Rodgers, G.; Lachicotte, R. J.; Flaschenriem, C. J.; Vela, J.; Holland, P. L. *J. Am. Chem. Soc.* **2006**, *128*, 756−769.

(9) Stoian, S. A.; Vela, J.; Smith, J. M.; Sadique, A. R.; Holland, P. L.; Münck, E.; Bominaar, E. L. *J. Am. Chem. Soc.* **2006**, *128*, 10181−10192.

(10) (a) Vela, J.; Stoian, S.; Flaschenriem, C. J.; Münck, E.; Holland, P. L. *J. Am. Chem. Soc.* **2004**, *126*, 4522−4523. (b) Yu, Y.; Smith, J. M.; Flaschenriem, C. J.; Holland, P. L. *Inorg. Chem.* **2006**, *45*, 5742−5751. (c) Sadique, A. R.; Gregory, E. A.; Brennessel, W. W.; Holland, P. L. *J. Am. Chem. Soc.* **2007**, *129*, 8112−8121.
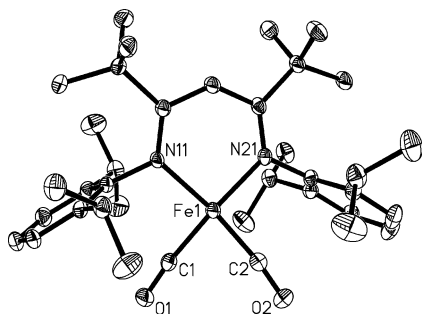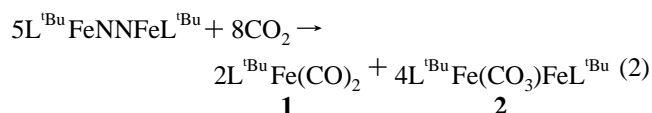
Figure 1. Crystal structure of **1**. Thermal ellipsoids are shown at 50% probability. H atoms have been omitted for clarity. Fe1−C1 = 1.784(2) Å, Fe1−C2 = 1.785(2) Å, Fe1−N11 = 1.967(1) Å, C1−O1 = 1.151(2) Å, C2−O2 = 1.149(2) Å, N11−Fe1−N21 = 93.43(5)°, C1−Fe1−C2 = 81.44(8)°, O1−C1−Fe1 = 172.8(1)°, O2−C1−Fe1 = 172.9(2)°.

of **2** as 70 ± 5% of the total iron (using an internal integration standard). The theoretical stoichiometry of this reaction is shown in eq 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 IR spectrum of the crude product.

$$5L^{tBu}FeNNFeL^{tBu} + 8CO_2 \rightarrow$$
$$2L^{tBu}Fe(CO)_2 + 4L^{tBu}Fe(CO_3)FeL^{tBu} \quad (2)$$
$$\mathbf{1} \qquad\qquad\qquad \mathbf{2}$$

In this reaction, eight Fe atoms are oxidized from Fe^I to Fe^{II}, concomitant with the reduction of eight molecules of CO$_2$. This creates four carbonate anions that bind to Fe^{II}, as well as four molecules of CO that are trapped by Fe^I.

Compound **1** can be synthesized independently by reacting L^{tBu}FeNNFeL^{tBu} with 4 equiv of CO 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 ($S = \frac{1}{2}$) electronic configuration, as shown by electron paramagnetic resonance (EPR) spectroscopy in the solution and solid state.[8b,11] The crystal structure of **1** is illustrated in Figure 1. The Fe atom has a square-planar geometry [sum of the angles around Fe = 361.8(1)°]. 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)° and 172.9(2)°].

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 IR, Mössbauer, and X-ray absorption data.[12] IR spectra of the enzyme showed two bands of identical intensity, leading to an estimate of the C−Fe−C angle of 86−94° based on the literature relationship tan $\theta = I_{asymm}/I_{symm}$.[12a,13] However, **1** shows virtually identical intensities for the two CO stretching vibrations despite the C−Fe−C angle of 81.44(8)° 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 Fe atom in Hmd hydrogenase is diamagnetic, either low-spin Fe^{II} or low-spin Fe^0, in contrast to the Fe^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 CO$_2$ reduction, L^{tBu}Fe(μ-OCO$_2$)FeL^{tBu} (**2**), could be isolated in pure form by performing the reaction of L^{tBu}FeNNFeL^{tBu} and CO$_2$ in the presence of Pd/C to trap the CO. 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 ^{1}H NMR and IR 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) μ_B/molecule in C$_6$D$_6$ suggests that the high-spin Fe^{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 μ-η^2:η^1 mode, and in the other (B), it is coordinated in a μ-η^2:η^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 ^{1}H NMR spectrum of **2** in C$_6$D$_6$ shows seven peaks, which is characteristic of the protons on β-diketiminate ligands in local C_{2v} symmetry. There is no decoalescence in the temperature range of +70 to −70 °C. This implies that there are at least two rapid dynamic processes. First, the

(11) In ref 8b, we reported bands at 2036, 2000, 1967, 1953, and 1922 cm^{-1} in a pentane solution of L^{tBu}Fe(CO)$_n$ (n = 2 and 3) and at 2042, 1971, and 1960 in a pentane solution of L^{Me}Fe(CO)$_3$. This implies that the 2000 and 1922 cm^{-1} solution bands are from L^{tBu}Fe(CO)$_2$, consistent with the solid-state bands at 1994 and 1915 cm^{-1} in solid **1** as isolated here. The IR spectrum of a solution of **1** in pentane shows that, in solution, **1** undergoes partial disproportionation to form some L^{tBu}Fe(CO)$_3$. This disproportionation in solution is also evident in X-band EPR spectra at 77 K. See the Supporting Information for more detail.

(12) (a) Lyon, E. J.; Shima, S.; Boecher, R.; Thauer, R. K.; Grevels, F.-W.; Bill, E.; Roseboom, W.; Albracht, S. P. J. *J. Am. Chem. Soc.* **2004**, *126*, 14239−14248. (b) Shima, S.; Lyon, E. J.; Thauer, R. K.; Mienert, B.; Bill, E. *J. Am. Chem. Soc.* **2005**, *127*, 10430−10435.

(13) Beck, W.; Melnikoff, A.; Stahl, R. *Angew. Chem., Int. Ed.* **1965**, *4*, 692−693.

(14) Palmer, D. A.; Van Eldik, R. *Chem. Rev.* **1983**, *83*, 651−731.

(15) For example, see: Chatt, J.; Kubota, M.; Leigh, G. J.; March, F. C.; Mason, R.; Yarrow, D. J. *J. Chem. Soc., Chem. Commun.* **1974**, 1033−1034.

(16) Kitajima, N.; Hikichi, S.; Tanaka, M.; Moro-oka, Y. *J. Am. Chem. Soc.* **1993**, *115*, 5496−5508.
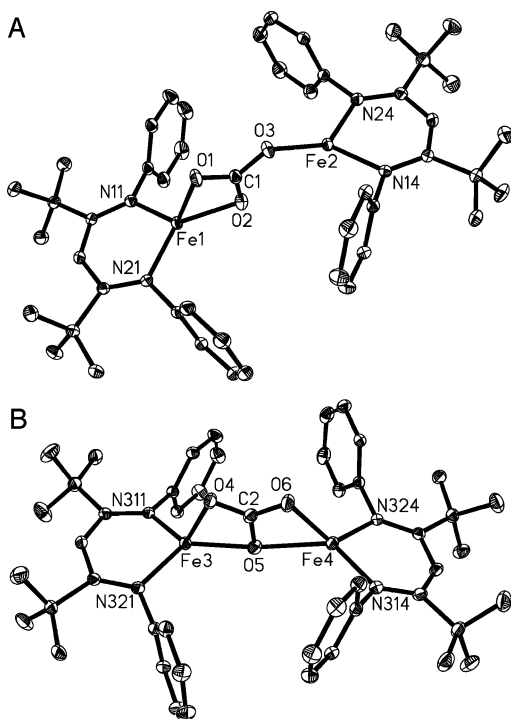
Figure 2. Crystal structure of **2**, showing molecules A and B with different bridging modes. Thermal ellipsoids are shown at 50% probability. H atoms and isopropyl groups have been omitted for clarity. See Table 1 for metrical parameters.

Table 1. Bond Lengths (Å) and Bond Angles (deg) of Fe(μ-CO$_3$)Fe Cores in the Two Independent Molecules Found in the X-ray Crystal Structure of **2**

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

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-diketiminate ligand indicates that there is rapid rotation of the Fe atom around the Fe−O bond, probably in the Fe 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 [O=C−O−C(=O)−O]$^-$, for which we have no evidence here. Another possibility is the

Scheme 1. Proposed Mechanism for the Formation of **1** and **2**
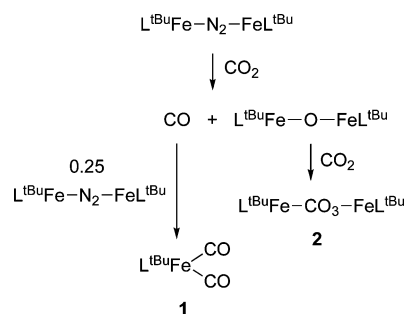
reductive cleavage of CO$_2$ to give CO and O^{2-}. While this work was in progress, Peters reported an iron(I) complex that reacts with 0.5 equiv of CO$_2$ to give a diiron(II) complex with an Fe(μ-CO)(μ-O)Fe core.[7] This outcome corresponds to direct reductive cleavage of the C=O bond. Earlier low-valent 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 [L^{tBu}Fe]$_2$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 [L^{tBu}Fe]$_2$O is formed during the course of the reaction of CO$_2$ and L^{tBu}FeNNFeL^{tBu}, the treatment of isolated [L^{tBu}Fe]$_2$O with CO$_2$ in C$_6$D$_6$ rapidly yields **2**, as shown by ^{1}H 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 L^{tBu}FeNNFeL^{tBu} to give **1** in independent experiments; further, the 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 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.

Supporting Information Available: Synthetic, spectroscopic, and crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org.

IC701914M

(17) Karsch, H. H. *Chem. Ber.* **1977**, *110*, 2213−2221.
(18) Eckert, N. A.; Stoian, S.; Smith, J. M.; Bominaar, E. L.; Münck, E.; Holland, P. L. *J. Am. Chem. Soc.* **2005**, *127*, 9344−9345.