Reductive Disproportionation of Carbon Dioxide at an Iron(II) Center

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*Summary: The reaction of cis-Fe(dmpe)$_2$H$_2$ (**1**) with ^{13}C-labeled carbon dioxide (CO$_2$) was investigated, and trans-[Fe(dmpe)$_2$(CO)H]·[HCO$_3$] (**5**) was identified as a reaction byproduct. Both the carbonyl ligand and the bicarbonate anion are derived from CO$_2$, and this effectively constitutes a disproportionation of CO$_2$ to CO and CO$_3^{2-}$. trans-[Fe(dmpe)$_2$(CO)H].[HCO$_3$] (**5**) was characterized by crystallography and by NMR spectroscopy.*

The activation of carbon dioxide (CO$_2$) has been of much interest in recent times.[1–5] Carbon dioxide is an important environmental contaminant, and the development of practical methods for utilizing carbon dioxide is one method of managing this greenhouse gas.[4] One approach has been to use carbon dioxide as an inexpensive and abundant source of carbon in organic synthesis.[6–9] An alternative strategy is to reduce CO$_2$ to CO, and the disproportionation of CO$_2$ to give CO and CO$_3^{2-}$ promoted by a transition metal has now been observed in a number of systems.[10–14]

Previously, we have reported the reaction between Fe(dmpe)$_2$H$_2$ (**1**; dmpe = 1,2-bis(dimethylphosphino)ethane) and CO$_2$.[15] While the major products of this reaction were Fe(dmpe)$_2$(OCOH)H (**2**) and Fe(dmpe)$_2$(OCOH)$_2$ (**3**) (Scheme 1), an iron carbonate, Fe(dmpe)$_2$CO$_3$ (**6**), was always observed as a reaction byproduct. The reaction between Fe(dmpe)$_2$Me$_2$ (**4**) and CO$_2$ has also been reported to form the same carbonate byproduct, Fe(dmpe)$_2$CO$_3$ (**6**), alongside the expected acetate products derived from CO$_2$ insertion into the metal−carbon bonds.[16]

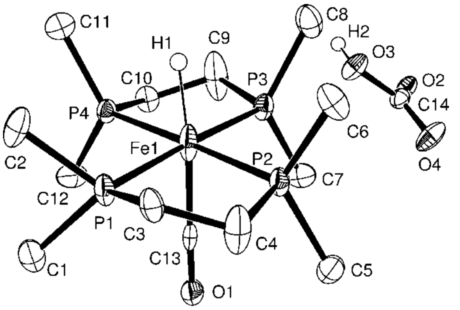
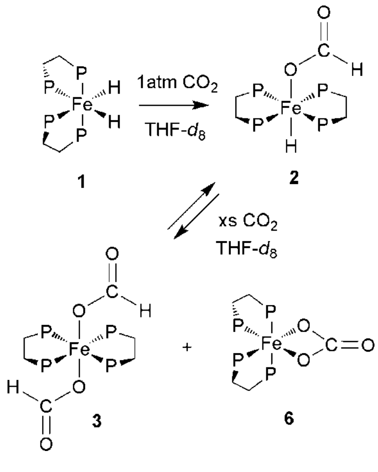


Figure 1. ORTEP diagram of [*trans*-Fe(dmpe)$_2$(CO)H][HCO$_3$] (**5**) (50% probability ellipsoids). Only the major component of the disordered atoms is shown, and selected hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe1−P1 = 2.2137(8), Fe1−P2 = 2.2190(7), Fe1−P3 = 2.2161(8), Fe1−P4 = 2.2158(7), Fe1−C13 = 1.952(8), Fe1−H1 = 1.5851(5), O1−C13 = 1.145(9); P1−Fe1−P1 = 86.05(3), P1−Fe1−P3 = 176.80(4), P1−Fe1−P4 = 93.87(3), P2−Fe1−P3 = 93.81(3), P2−Fe1−P4 = 178.29(4), P3−Fe1−P4 = 86.18(3), H1−Fe1−C13 = 173.96.

Scheme 1



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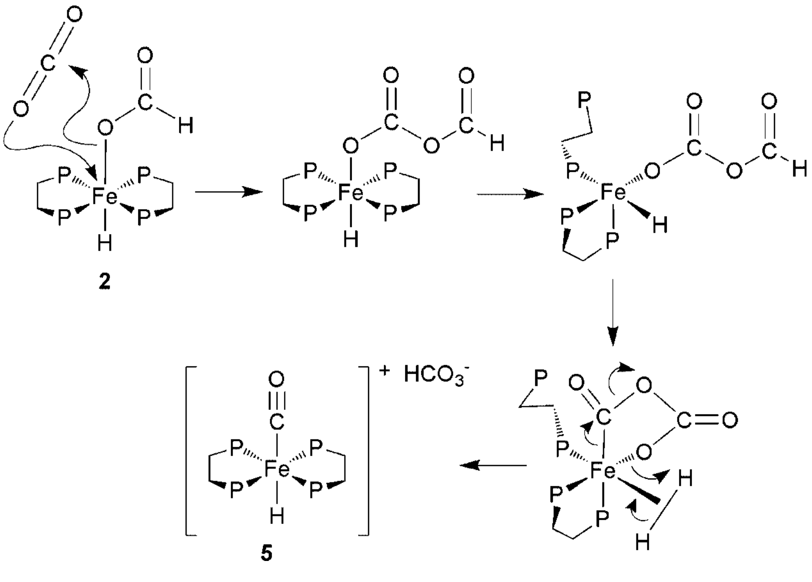
Scheme 2



We have been attempting to understand how metal carbonate complexes are formed from reactions with CO_2. In this paper, the reaction of complex **1** with 3−4 atm of $^{13}CO_2$ has been reinvestigated and the first disproportionation of CO_2 by an Fe(II) center is reported.

Addition of $^{13}CO_2$ to **1** immediately forms the previously reported formate products **2** and **3**. However, when the reaction mixture is heated for several days at 343 K, the iron carbonate $Fe(dmpe)_2CO_3$ (**6**) is formed together with pale yellow crystals of $[Fe(dmpe)_2(CO)H][HCO_3]$ (**5**) that precipitated from the THF-d_8 solution. X-ray crystallographic analysis and NMR spectroscopy confirmed the structure of the product to be *trans*-$[Fe(dmpe)_2(CO)H][HCO_3]$ (**5**) (Figure 1).[17] This experiment clearly demonstrates that both the carbon monoxide ligand and the bicarbonate anion are derived from the CO_2 starting material in the reaction mixture and that this reaction effectively disproportionates CO_2 to carbon monoxide and carbonate.[18]

The $^{31}P\{^1H\}$ NMR spectrum of *trans*-$[Fe(dmpe)_2(CO)H][HCO_3]$ (**5**) displays a ^{13}C-coupled doublet at 66.6 ppm with a $^{31}P-^{13}C$ coupling of 15.0 Hz, corresponding to a metal complex with four chemically equivalent phosphorus atoms coupling to a single carbon atom. In the ^1H NMR spectrum, there is a distinctive doublet of pentets at −11.89 ppm with a $^{31}P-^1H$ coupling of 49.9 Hz and $^{13}C-^1H$ coupling of 9.8 Hz, indicative of an iron-bound hydride coupling to four equivalent phosphorus atoms and one labeled ^{13}C atom. There is also a broad ^{13}C-coupled doublet in the ^1H NMR spectrum at 8.51 ppm representing the proton on the hydrogencarbonate anion with a $^{13}C-^1H$ coupling of 191.3 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, there is a pentet at 211.5 ppm with a $^{13}C-^{31}P$ coupling of 15.0 Hz corresponding to the metal-bound carbonyl ligand.

$[Fe(dmpe)_2(CO)H][HCO_3]$ (**5**) is one of the very few iron bidentate phosphine carbonyl hydride complexes to be characterized crystallographically. $Fe(dppe)(CO)_2(SiMe_3)H$ and $Fe(dppe)(CO)(Si(OEt_3))H_3$ (dppe = 1,2-bis(diphenylphosphino)ethane ligand) have been reported previously.[19,20] Complex **5** has a slightly distorted octahedral geometry with significant disorder in the dmpe ligands and about the Fe−CO and Fe−H bonds. The Fe−CO bond length of 1.952(8) Å is 0.27 Å longer than the comparable Fe−C bond of 1.69(1) Å in the structure of $[Fe(PP_3)(CO)H][BPh_4]$[21] (PP_3 = tris[2-(diphenylphosphino)ethyl]phosphine) and 0.2 Å longer than the Fe−C bond of 1.75(1) Å in $[Fe(P(OEt)_3)_4(CO)H][BPh_4]$.[22] The Fe−P bond lengths are in the usual range for complexes of this type, and the Fe−H bond is also in the usual range at 1.5851(5) Å in comparison to other iron hydride complexes such as $Fe(dmpe)_2(H)(NH_2)$[23] (1.63(5) Å) and $Fe(dmpe)_2(BH_4)H$ (1.69 Å).[24] A number of phosphine carbonyl hydride complexes have been prepared in the past,[25,26] but until now, few have been characterized by X-ray crystallography and none by ^{13}C NMR spectroscopy.

At this stage, the mechanism of formation is speculative. Complex **5** is probably formed via insertion of a second molecule of CO_2 into the metal−oxygen bond of the formate

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(17) Crystal data for **5**: $C_{18}H_{42}FeO_5P_4$, $M_r = 518.25$, space group $P2_1/c$, $a = 9.2623(7)$ Å, $b = 17.5775(11)$ Å, $c = 16.5780(13)$ Å, $\beta = 103.317(2)°$, $V = 2626.5(3)$ Å^3, $D_c = 1.311$ Mg/m^3, $Z = 4$, μ(Mo Kα) = 0.845 mm^{-1}, crystal size 0.45 × 0.38 × 0.36 mm, minimum and maximum transmission factors 0.6682 and 0.7515, 23 795 reflections collected, 4547 reflections observed. The final residuals R and R_w were 0.0417 and 0.1123 for the observed data.

(18) Procedure for the preparation of **5**; CO_2 (1 atm) was added to a NMR tube containing a degassed solution of *cis*-$Fe(dmpe)_2H_2$ (**1**; 0.023 g, 0.05 mmol) in THF-d_8 at room temperature. The NMR tube was warmed to room temperature, and after 30 min the NMR spectrum displayed resonances attributable to **2** and **3**. The NMR tube was heated for several days at 333 K before large yellow crystals of $[Fe(dmpe)_2(CO)H][HCO_3]$ (**5**) precipitated in approximately 20% yield. $^{31}P\{^1H\}$ NMR (THF-d_8, 121.5 MHz, 298 K): δ 66.6 ppm (d, J_{PC} = 15.0 Hz). ^1H NMR (THF-d_8, 300 MHz, 298 K): δ−11.89 (dp, 1H, FeH, J_{PH} = 50.1 Hz, J_{CH} = 9.8 Hz), 1.57 (s, 12H, PCH_3), 1.61 (s,12H, PCH_3), 1.95 (m, 8H, PCH_2), 8.51 ppm (d, 1H, HCOO, J_{CH} = 191.3 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz, 298 K): δ 18.5 ($FePCH_3$), 21.4 ($FePCH_3$), 31.7 ($FePCH_2$), 165.9 (HCOO), 211.5 ppm (FeCO, J_{CP} = 15 Hz).

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complex **2**. Decarbonylation of the terminal formate would give the hydrido carbonyl complex with the liberation of bicarbonate, as observed (Scheme 2). An iridium analogue of the C_2O_4 intermediate has been characterized previously by X-ray crystallography,[27] and CO_2 insertion into metal−alkoxide bonds has been observed previously in a number of different reaction sequences.[28–31]

In a related system, Karsch et al.[32] have also observed reduction of CO_2 to CO by an iron complex during the reaction of CO_2 with $Fe(PMe_3)_4$. Along with the expected side-on-bound CO_2 adduct $Fe(PMe_3)_4CO_2$, the carbonyl carbonate product $Fe(PMe_3)_3(CO)(CO_3)$ was also observed in addition to $Fe(PMe_3)_3(CO)_2$, Me_3PO, and $Fe(PMe_3)_4CO$. In this paper it was thought that the reduction of CO_2 is induced by the loss of a PMe_3 ligand.

In conclusion, we have isolated an iron carbonyl complex with a bicarbonate counterion, $[Fe(dmpe)_2(CO)H][HCO_3]$ (**5**), resulting from the iron(II)-mediated reductive disproportionation of CO_2. Metal carbonates have been consistent products observed in the reaction of CO_2 with iron complexes, and this set of experiments now provides a rationalization for the formation of carbonate in the reaction mixture and hence to the formation of stable metal carbonates as reaction byproducts. This also suggests that there may well be effective methods for catalytically oxidizing carbon dioxide with appropriate oxidants to form stable carbonates.

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Supporting Information Available: A CIF file giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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