

Synthesis, Structure and Reactions of a Carbon Dioxide Complex of Iron(0) containing 1,2-Bis(diethylphosphino)ethane Ligands

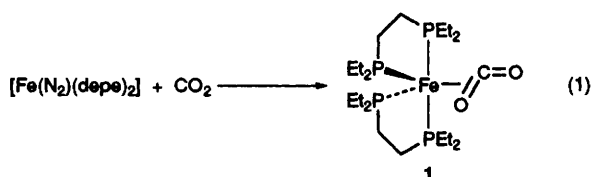
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Reaction of $[\text{Fe}(\text{N}_2)(\text{depe})_2]$ with carbon dioxide gives trigonal bipyramidal $[\text{Fe}(\eta^2\text{-CO}_2)(\text{depe})_2]$, where the coordinated CO_2 lies on equatorial plane by an η^2 -fashion and converts into dimethyl ether and $[\text{FeX}(\text{CO})(\text{depe})_2]\text{X}$ ($\text{X} = \text{I}, \text{OTf}$) on interaction with methyl halide or triflate.

Chemical transformation of carbon dioxide into various organic compounds by means of transition metals has attracted attention in recent years.¹ It is very important to evaluate the relationship between the coordination mode and reactivity of CO_2 on transition metals. To date, however, only a limited number of transition metal CO_2 complexes has been structurally determined: the $\eta^2\text{-CO}$ coordination mode has been found in Nb,² Mo,³ and Ni⁴ complexes, $\sigma\text{-C}$ coordination mode in Ru⁵ and Rh,⁶ and others in Co,⁷ and Ir.⁸ On the other hand, chemical reactivities of well defined coordinated CO_2 complexes are also relatively less explored.^{9,10} Though the iron(0) complex having trimethylphosphine ligands is also capable of binding carbon dioxide¹¹ and the coordination mode is spectroscopically postulated as an intermediate between $\sigma\text{-C}$ and $\eta^2\text{-CO}$, no structural study of a CO_2 complex of iron has been reported so far. We previously reported the formation of a dinitrogen complex of iron(0) $[\text{Fe}(\text{N}_2)(\text{depe})_2]$ having 1,2-bis(diethylphosphino)ethane ligands.¹² We now report the isolation of a new carbon dioxide complex of iron(0) $[\text{Fe}(\text{CO}_2)(\text{depe})_2]$.

A slight excess of carbon dioxide gas was introduced into a THF solution of $[\text{Fe}(\text{N}_2)(\text{depe})_2]$ under vacuum to give a red homogeneous solution at room temp. in 1 h. After removal of all volatiles, the residual solid was recrystallized from diethyl ether affording red prisms of $[\text{Fe}(\text{CO}_2)(\text{depe})_2]$ **1** in 70% yield,† eqn. (1).



The molecular structure of **1** was unequivocally determined by X-ray structure analysis.‡ An ORTEP drawing is shown in Fig. 1. **1** has essentially trigonal bipyramidal structure, where the CO_2 ligand lies on the equatorial plane in an η^2 -fashion. Thus, the mean bond angles of $\text{P}_{\text{ax}}\text{-Fe-P}_{\text{eq}}$, $\text{P}_{\text{ax}}\text{-Fe-C}(21)$, and $\text{P}_{\text{ax}}\text{-Fe-O}(1)$ are 91.5, 87.7, and 88.0°, $\text{P}(2)\text{-Fe-P}(4)$ angle is 175.4°, and $\text{P}(1)\text{-Fe-P}(3)$ angle is 110.6°, being consistent with the typical characteristics of a trigonal bipyramidal structure. The CO_2 ligand is coordinated essentially in an $\eta^2\text{-CO}$ fashion, where one of the oxygen atom is placed away from the Fe metal centre. $\text{Fe-C}(21)$ bond distance (1.86 Å) is significantly shorter than $\text{Fe-O}(1)$ (2.08 Å) when the covalent bond diameter of the atoms is taken into account. This is in good agreement with the spectroscopic presumption that the bonding of iron(0) with CO_2 is between a $\sigma\text{-CO}_2$ and a side-on arrangement.¹³ $\text{Fe-P}(1)$ bond distance (2.27 Å) is longer than $\text{Fe-P}(3)$ (2.19 Å), reflecting the geometry of CO_2 ligand; the former lies *trans* to the carbon atom and the latter *trans* to the oxygen.

In the IR spectrum of **1**, characteristic $\nu_{\text{C=O}}$ bands are observed at 1630 and 1096 cm^{-1} . The ^{31}P NMR spectrum of **1** shows an ABMX pattern, supporting the trigonal bipyramidal structure.

Reaction of **1** with methyl iodide in toluene at room temp.

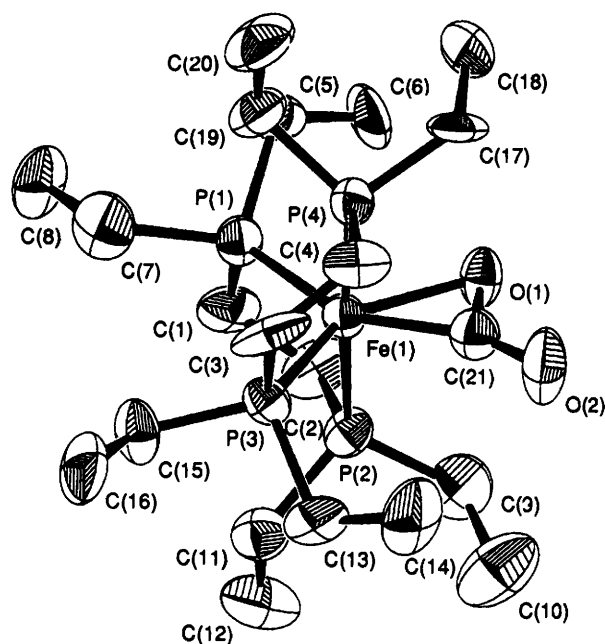
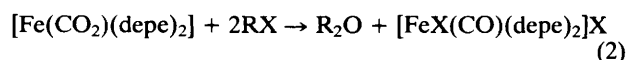


Fig. 1 An ORTEP drawing of $[\text{Fe}(\text{CO}_2)(\text{depe})_2]$, **1** with numbering scheme. Selected bond lengths (Å): $\text{Fe-P}(1)$ 2.271(6), $\text{Fe-P}(2)$ 2.247(6), $\text{Fe-P}(3)$ 2.192(6), $\text{Fe-P}(4)$ 2.225(6), $\text{Fe-O}(1)$ 2.08(1), $\text{Fe-C}(21)$ 1.86(3), $\text{O}(1)\text{-C}(21)$ 1.28(2), $\text{O}(2)\text{-C}(21)$ 1.25(3). Bond angles (°): $\text{P}(1)\text{-Fe-P}(2)$ 84.3(2), $\text{P}(1)\text{-Fe-P}(3)$ 110.6(2), $\text{P}(1)\text{-Fe-P}(4)$ 98.9(2), $\text{P}(2)\text{-Fe-P}(3)$ 97.0(2), $\text{P}(2)\text{-Fe-P}(4)$ 175.4(3), $\text{P}(2)\text{-Fe-O}(1)$ 86.1(4), $\text{P}(2)\text{-Fe-C}(21)$ 90.9(7), $\text{P}(3)\text{-Fe-P}(4)$ 84.9(2), $\text{P}(4)\text{-Fe-O}(1)$ 89.8(4), $\text{P}(4)\text{-Fe-C}(21)$ 84.5(7), $\text{O}(1)\text{-Fe-C}(21)$ 37.4(6), $\text{O}(1)\text{-C}(21)\text{-O}(2)$ 124(2).

gave $[\text{Fe}(\text{CO})(\text{depe})_2]^+\text{I}^-$ **2**† and liberated dimethyl ether (97%/Fe) in addition to a trace amount of methanol. Addition of a trace amount of water suppressed the formation of the ether (2%/Fe) but increased the yield of methanol instead (76%/Fe), suggesting the formation of a methoxyiron intermediate in the reaction. Thus, a similar reaction of **1** with methyl triflate also gave a quantitative amount of dimethyl ether (99%/Fe) and an analogous carbonyl iron complex **3**. These reactions may be interpreted by the electrophilic attack of the methyl group toward the oxygen atom of the CO_2 ligand, followed by coupling between the methoxy group with excess methyl triflate. These results are in contrast to the fact that $[\text{Mo}(\text{CO}_2)(\text{C}_5\text{H}_5)_2]$, in which CO_2 is coordinated by a typical $\eta^2\text{-CO}$ mode, shows no reactivity with methyl iodide.⁹ The facts suggest that the nucleophilicity of the CO_2 ligand is higher on the iron complex than on the Mo analogue. This may, at least in part, arise from the slight contribution of the $\sigma\text{-C}$ coordination mode of the CO_2 ligand in **1**, eqn. (2).



1

R = Me, X = I **2**
X = OTf **3**

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Footnotes

† *Physical and spectroscopic data for 1, 2 and 3.* **1:** Yield 70%; mp 94–96 °C(decomp.); M_w (cryoscopic method) 501 (calc. for $C_{21}H_{48}FeO_2P_4$ 512); Molar conductivity in THF, $\Lambda = 0.009 \text{ S cm}^2 \text{ mol}^{-1}$; $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , PPh_3), δ 68.13 (dt, J 17, 29 Hz), 83.44 (ddd, 29, 42, 127 Hz), 85.40 (ddd, 17, 49, 127 Hz), 92.44 (ddd, 29, 42, 49 Hz); ^1H NMR (200 MHz, C_6D_6 , $SiMe_4$): δ 0.5–1.5 (m); IR (KBr, ν/cm^{-1}): 1630, 1096 ($\nu_{C=O}$). **2:** Yield 97%; mp 242–244 °C(decomp.); Molar conductivity in THF, $\Lambda = 31.5 \text{ S cm}^2 \text{ mol}^{-1}$; ^1H NMR (200 MHz, C_6D_6 , $SiMe_4$): δ 1–3 (m); IR (KBr, ν/cm^{-1}): 1937 (ν_{CO}). **3:** Yield 89%; mp 148–151 °C(decomp.); Molar conductivity in THF, $\Lambda = 15.7 \text{ S cm}^2 \text{ mol}^{-1}$; ^1H NMR (200 MHz, C_6D_6 , $SiMe_4$): δ 1–3 (m); IR (KBr, ν/cm^{-1}): 1931 (ν_{CO}). Satisfactory elemental analyses were obtained for **1**, **2** and **3**.

‡ *Crystal data for 1:* $C_{21}H_{48}FeO_2P_4$, $M_w = 512.35$, monoclinic, space group Cc ; $a = 12.681(1)$, $b = 15.948(2)$, $c = 13.354(3)$ Å; $\beta = 90.75(1)^\circ$; $V = 2700.5(6)$ Å³; $Z = 4$; $D_c = 1.260 \text{ g cm}^{-3}$; $Mo-K\alpha$ ($\lambda = 0.71069$ Å); $\mu = 8.09 \text{ cm}^{-1}$, $3 < 2\theta < 50^\circ$. Intensity data collected at room temp. on a Rigaku AFC-5R four-circle diffractometer; structure solved and refined using TEXSAN program system, no absorption correction was applied. 2035 Unique reflections of which 1104 [$I > 3\sigma(I)$] are observed. The structure was solved by the heavy-atom method and refined by a full-matrix least-squares procedure. All the non-hydrogen atoms were refined anisotropically. A test for an enantiomorph was made by inverting the coordinates of all atoms and refining again; however, this did not improve the R factors. Hydrogens were included in the calculation, but they were not refined. Final R (R_w) = 0.058 (0.038). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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