the convenient and powerful procedure of laser desorption.

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Formate Ion as a Monodentate Ligand. Synthesis, Structure, and Decarboxylation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2O_2CH$

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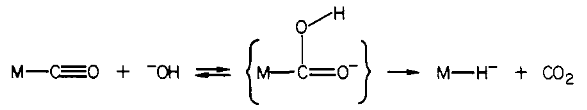
There has been considerable current interest in the homogeneous catalysis of the water–gas shift reaction (eq 1) by transition-metal

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (1)$$

carbonyl complexes.[1] Several of the catalytically active systems involve mono- or multinuclear metal carbonyls in alkaline solutions. A common mechanistic feature in all such processes consists of the nucleophilic addition of hydroxide ion at the carbon center of the metal-bound carbon monoxide ligand with subsequent formation of a metal hydride species and CO_2 (eq 2). It is of



$$M{-}C{\equiv}O + {}^-OH \rightleftharpoons \left\{M{-}\overset{\overset{\displaystyle O{-}H}{|}}{C}{=}O^-\right\} \rightarrow M{-}H^- + CO_2 \qquad (2)$$

importance to appraise the role of metal formate species in these reactions because of the ubiquitous nature of the formate ion in these alkaline solutions ($CO + {}^-OH \rightleftharpoons HCO_2^-$) and the known ability of metal formates to undergo decarboxylation to metal hydrides and CO_2 (eq 3).[2] Hence there are potentially two

(3)

intermediates,[3] a metallocarboxylic acid and a metalloformate, capable of affording H_2 and CO_2 during base catalysis of the water–gas shift reaction. We have recently begun rather extensive reactivity studies on metal carbonyl species possessing the M–COOH and M–O_2CH functionalities and herein report some preliminary observations with $(\eta^5\text{-}C_5H_5)Fe(CO)_2O_2CH$. This is a judicious species to investigate, since the metallocarboxylic acid analogue, $(\eta^5\text{-}C_5H_5)Fe(CO)_2COOH$, has briefly been described by Crice, Kao, and Pettit.[4]

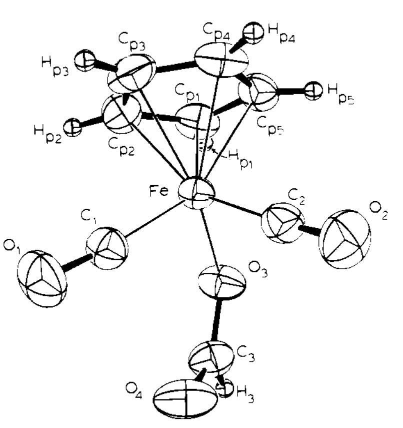


Figure 1. A perspective drawing of $(\eta^5\text{-}C_5H_5)Fe(CO)_2O_2CH$. Some bond lengths are as follows: Fe–O(3), 1.957 (2); Fe–C(1), 1.781 (3); Fe–C(2), 1.784 (3); O(1)–C(1), 1.135 (3); O(2)–C(2), 1.133 (4); O(3)–C(3), 1.277 (3); O(4)–C(3), 1.208 (4); C(3)–H(3), 1.03 (3); Fe–Cp(av), 2.096 (3) Å. The distal Fe–O(4) distance is 3.172 (2) Å. All hydrogen atoms were located and refined.

The synthesis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2O_2CH$ was achieved by stirring $(\eta^5\text{-}C_5H_5)Fe(CO)_2(THF)^{+}$[5] with an aqueous solution of NaO_2CH for 2.5 h at room temperature under nitrogen. Upon removal of water the residue was extracted with methylene chloride, filtered through Celite, and concentrated under vacuum. Addition of hexane with cooling afforded red crystals of the desired product.[6] The ν(CO) spectrum in heptane exhibited two bands of comparable intensity at 2055 and 2016 cm^{-1}. The infrared spectrum in the $\nu(CO_2)$ region is indicative of monodentate metal formate species, consisting of a strong antisymmetric $\nu(CO_2)$ vibration at 1620 cm^{-1} and a somewhat weaker symmetrical $\nu(CO_2)$ at 1293 cm^{-1}.[7] The detailed geometry of the complex has been established by X-ray crystallography.[8] The structural results are shown in Figure 1. The complex has approximate C_s symmetry with the mirror plane containing the atoms of the formate moiety and the C_{p_1} carbon atom of the cyclopentadienyl ligand and bisecting the OC–Fe–CO angle. The monodentate formate ligand is oriented in the solid state so as to place its uncoordinated oxygen atom [O(4)] in the proximity of the metal center which concomitantly maximizes the Fe–H(3) nonbonding distance. This observation may be of importance when considering intimate mechanistic aspects of the decarboxylation process (vide infra). Similar orientations for the acetate and trifluoroacetate groups are seen in low-valent metal carbonyl derivatives possessing these moieties.[9]

When $(\eta^5\text{-}C_5H_5)Fe(CO)_2O_2CH$ is placed in a ^{13}CO-saturated heptane solution, a facile intermolecular CO exchange process is noted (eq 4). Infrared spectral traces in the ν(CO) region

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2O_2CH + n\,{}^{13}CO \rightleftharpoons (\eta^5\text{-}C_5H_5)Fe(CO)_{2-n}({}^{13}CO)_nO_2CH + nCO \qquad (4)$$

observed during the course of this ligand exchange reaction are depicted in Figure 2. As seen in Figure 2, upon replacement of the ^{13}CO atmosphere with ^{12}CO, bands due to the all-^{12}CO $(\eta^5\text{-}C_5H_5)Fe(CO)_2O_2CH$ reappear with an attendant decrease in bands assignable to the ^{13}CO-enriched species. Hence, metal–

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[2] See, e.g., the review by: Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79.

[3] Additionally, bidentate formate species are known to undergo this decarboxylation process. See, e.g., the review by: Kolomnikov, I. S.; Grigoryan, M. Kh. *Russ. Chem. Rev.* **1978**, *47*, 334.

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[6] An alternative preparation of the complex has been previously reported by: Dombek, B. D.; Angelici, R. J. *Inorg. Chim. Acta* **1973**, *7*, 345.

[7] In unidentate complexes the separation between the two $\nu(CO_2)$ vibrations is larger than that in the free ion [where $\Delta\nu(CO_2)$ = 200 cm^{-1}], whereas the opposite trend is seen in bidentate complexes. See, e.g.: Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley-Interscience: New York, 1977.

[8] Single crystals of $(\eta^5\text{-}C_5H_5)Fe(CO)_2O_2CH$ were grown from CH_2Cl_2/hexane. They belong to the space group $P2_1/n$ with a = 6.799 (2), b = 12.325 (4), c = 10.440 (3) Å; β = 106.84 (2)°; Z = 4. R = 2.9% for 1782 reflections with $I > 3\sigma(I)$. Crystallographic analysis was carried out by Dr. Cynthia S. Day at Crystalytics Co., Lincoln, NE.

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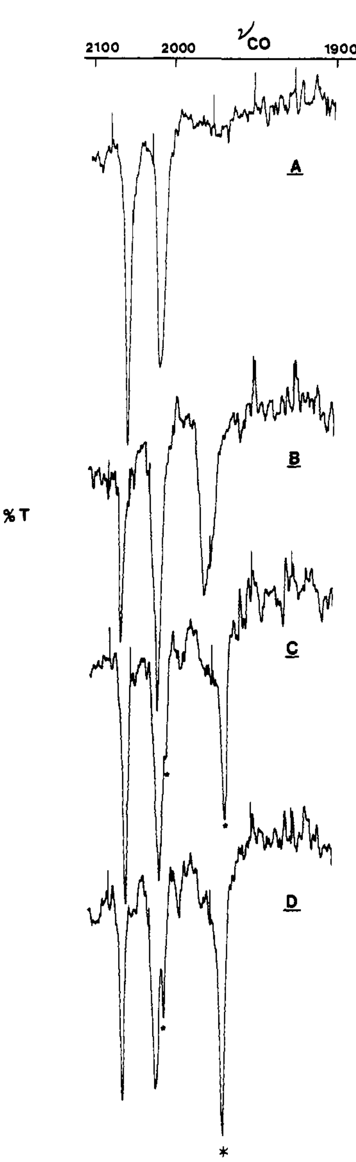


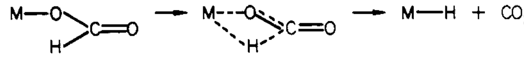
Figure 2. Infrared spectral traces in ν(CO) region of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{O}_2\text{CH}$ in heptane: (A) initial spectrum; (B) after 2 h at 50 °C in ^{13}CO atmosphere; (C) after evacuation of ^{13}CO and admission of ^{12}CO with further heating at 50 °C for 1.2 h; (D) further reaction in ^{12}CO atmosphere for 1 h at 50 °C. Peaks marked by asterisks are due to $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2$.

carbon monoxide bond lability in low-valent metal carbonyl derivatives containing oxygen donor ligands is emerging as a general phenomenon.[9-12] At longer reaction periods ν(CO) bands are observed which correspond to formation of the $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2$ species. Simultaneous analysis of the gaseous reaction components by gas chromatography revealed the production of H_2 and CO_2 as well. This decarboxylation process probably proceeds via the $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{H}$ intermediate which is unstable under the reaction conditions (eq 5). While reaction

$$(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{O}_2\text{CH} \xrightarrow{\Delta} (\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{H} + \text{CO}_2 \rightarrow {}^1/_2[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2 + {}^1/_2\text{H}_2 \quad (5)$$

5 proceeds to completion over several hours at 50 °C, Pettit and co-workers have reported that the metallocarboxylic acid analogue, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{COOH}$, spontaneously decomposes in solution to $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2$ plus H_2 and CO_2 at ambient temperature.[4] Therefore, of the two intermediates capable of affording H_2 and CO_2, the metallocarboxylic acid pathway is energetically more favorable.

These experiments unambiguously demonstrate that CO ligand exchange in the $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{O}_2\text{CH}$ derivative occurs at a faster rate than decarboxylation. The commonly envisaged mechanism for rupture of the C–H bond in the formate ligand involves the β elimination of a hydrogen atom to the metal center (eq 6).[13,14] Indeed this description would appear to be enhanced

 (6)

by the availability of a vacant coordination site on the metal.[15] An added requirement in the $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{O}_2\text{CH}$ species, assuming the solid-state structure is retained in solution, is a 180° rotation about the O(3)–C(3) bond in order to achieve the proper rotatomer for β-hydrogen transfer. This effect may not be important in this instance, since rotation about the O(3)–C(3) single bond is expected to be rapid in solution. Although we have not as yet observed the reduction of CO_2 in this system, i.e., the reverse of eq 6, preliminary results on analogous processes in group 6b metal anionic derivatives are in hand (eq 7), where the insertion

$$\text{M-O}_2\text{CH}^- \rightleftharpoons \text{M-H}^- + \text{CO}_2 \quad (7)$$

of CO_2 into the M–H$^-$ bond is found to be quite rapid.[16]

We are continuing to explore these two reaction processes, namely, dehydrogenation of formate ion in the presence of metals and its retrogradative counterpart, CO_2 insertion into the M–H bond. These reactions are not only of consequence in the homogeneous catalysis of the water–gas shift reaction by metal carbonyls but also in the oxidation of carbon monoxide to carbon dioxide by bacteria.[17]

Acknowledgment. The financial support of this research by the National Science Foundation (Grants CHE 78-01758 and CHE 80-09233) is greatly appreciated.

Supplementary Material Available: A listing of positional and thermal parameters derived from full-matrix least-squares refinements (2 pages). Ordering information is given on any current masthead page.

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Luminescence and Redox Photochemistry of the Molybdenum(II) Cluster $Mo_6Cl_{14}{}^{2-}$ [1]

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The search for schemes for photochemical energy storage has generated intense interest in the electron-transfer properties of excited states of transition-metal complexes.[2] In the first study of oxidative quenching of a metal complex excited state, tris-

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