Scientific Laboratory, jointly supported by the U. S. Department of Energy and the NIH (RR-00962-02, Division of Research Resources). Dr. Chou-Hong Tann and Kazys Martinkus are warmly thanked for expert technical assistance. We are grateful to Dr. Donald Borders, Lederle Laboratories, Pearl River, NY, for generous gifts of streptothricin F and *Streptomyces* L-1689-23. Peter Demou of the Chemistry Department, Yale University, is thanked for obtaining the ^{13}C NMR spectra. The Bruker HX-270 NMR instrument facility at Yale used in this work was supported by the National Science Foundation, Grant CHE-7916210, from the Chemistry Division.

$(\mu\text{-H})Fe_4(CO)_{12}(\eta^2\text{-COH})$: Evidence for a Protonated η^2-CO Complex as an Intermediate in the Proton-Induced Reduction of CO

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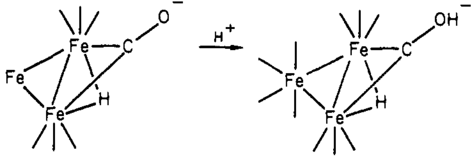
In their original NMR spectroscopic investigation of metal carbonyls in acid media, Wilkinson and co-workers demonstrated that protonation occurs on the metal.[1] Subsequent diffraction studies have confirmed this general concept and provided detailed structural information on the variety of bonding patterns between the proton and metal centers in polynuclear carbonyls.[2] In contrast to this earlier work it was recently shown that protonation of some metal carbonyl clusters also may occur at edge-bridging (eq 1)[3,4] or face-bridging carbonyl oxygens.[5]



(1)

The present research provides spectroscopic evidence for a new type of O-protonated carbonyl ligand, η^2-COH, resulting from the protonation of $[HFe_4(CO)_{13}]^-$. This new O-protonated compound appears to be a key intermediate in the recently discovered proton-induced reduction of CO in $[Fe_4(CO)_{13}]^{2-}$.[6]

In 1957, Hieber and Werner reported a compound with the empirical formula $H_2Fe_4(CO)_{13}$, which was described as soluble in ethers and benzene and stable for significant periods of time at room temperature.[7] Attempts to structurally characterize this compound in several laboratories have been uniformly unsuccessful,[8] so we have explored the possibility that, as with $HFe_3(CO)_{10}(COH)$, the anhydrous diprotonated form of the tetranuclear cluster may be stable only at low temperatures.

Anhydrous $(\mu\text{-H})Fe_4(CO)_{12}(\eta^2\text{-COH})$ (I) was prepared under an inert atmosphere by the addition of 30 μL of HSO_3CF_3 or HSO_3F to ca. 3 mL of a frozen (−196 °C) CD_2Cl_2 solution containing 0.13–0.18 mmol of $[PPN][HFe_4(CO)_{13}]$ (enriched to ca. 15% ^{13}CO) in an NMR tube. The tube was sealed under vacuum and warmed to −90 °C, and the ^{13}C and ^{1}H NMR spectra were determined. Additional ^{13}C NMR spectra were obtained on ^{13}CO enriched samples of $[HFe_4(CO)_{13}]^-$ (II) and $HFe_4(CO)_{12}(\eta^2\text{-COCH}_3)$ (III), both of which have been the subjects of X-ray structure determinations.[9,10]

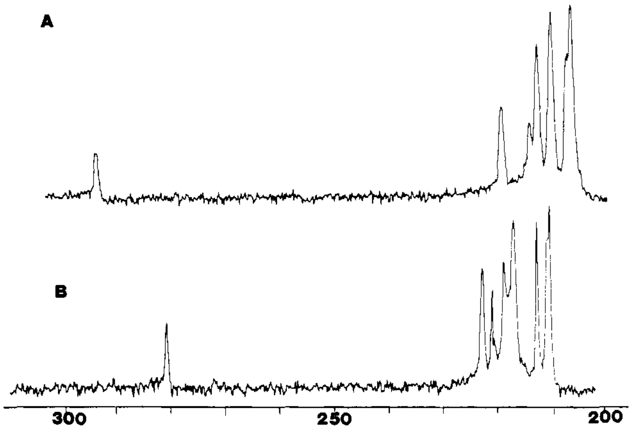


Figure 1. ^{13}C NMR spectra of (A) $(\mu\text{-H})Fe_4(CO)_{12}(\eta^2\text{-COH})$ (I) and (B) $[PPN][HFe_4(CO)_{13}]$ (II). These spectra were observed at 20 MHz on a Varian CFT-20 spectrometer at −90 °C in CD_2Cl_2.

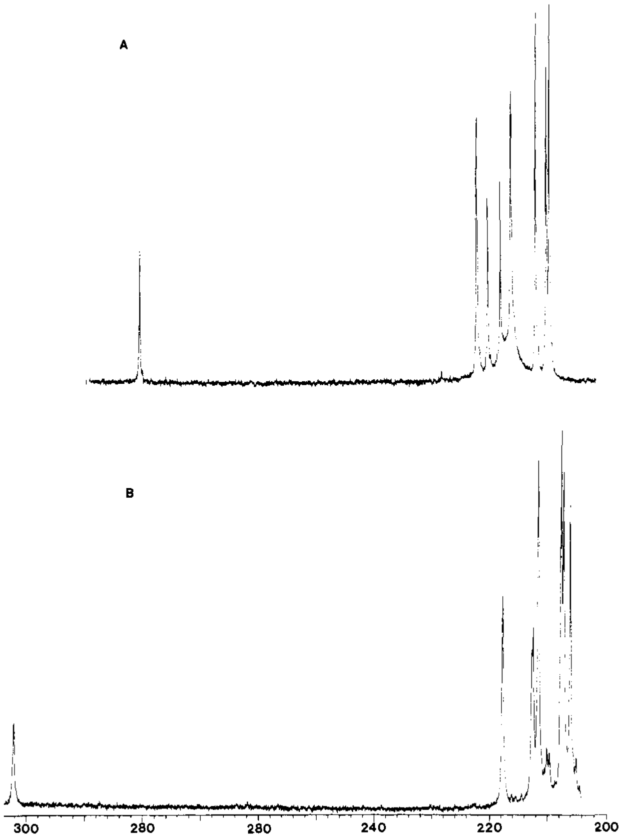


Figure 2. ^{13}C NMR spectra of (A) $[PPN][HFe_4(CO)_{13}]$ (II) and (B) $(\mu\text{-H})Fe_4(CO)_{12}(\eta^2\text{-COCH}_3)$ (III). Spectra were obtained at 90 MHz on a Nicolet NT-360 spectrometer at −90 °C in CD_2Cl_2.

The η^2-CO in II displays a characteristic low-field ^{13}C NMR feature (Figures 1 and 2) at 281 ppm relative to Me_4Si. Upon reaction with the methyl carbocation to produce III the resonance due to the η^2-CO shifts to even lower field, 301 ppm. Similarly, the protonation of II leads to a low-field shift of the resonance of the η^2-CO to 294 ppm, indicating that protonation has occurred

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[1] A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3653 (1962).

[2] "Transition Metal Hydrides", R. Bau, Ed., "Advances in Chemistry Series", American Chemical Society, Washington, DC, 1978, No. 167.

[3] H. A. Hodali, D. F. Shriver, and C. A. Ammlung, *J. Am. Chem. Soc.*, *100*, 5239 (1978).

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[6] K. Whitmire and D. F. Shriver, *J. Am. Chem. Soc.*, *102*, 1456 (1980).

[7] W. Hieber and R. Werner, *Chem. Ber.*, *90*, 286 (1957).

[8] B. T. Heaton and P. Chini, private communications.

[9] M. Manassero, M. Sansoni, and G. Longoni, *J. Chem. Soc., Chem. Commun.*, 919 (1976).

[10] K. Whitmire, D. F. Shriver, and E. M. Holt, *J. Chem. Soc., Chem. Commun.*, 780 (1980).

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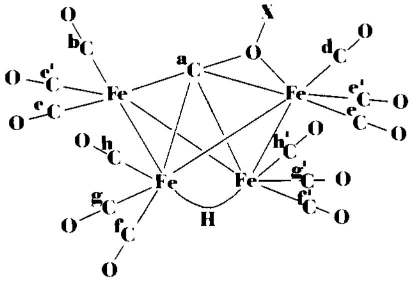
on oxygen.[11] Further evidence for the existence of the η^2-COH species is provided by the observation of ^1H NMR resonances of δ 13.2 and −26.5 which are assigned to an oxygen-bound proton and a bridging metal hydride, respectively.

The ^{13}C NMR spectrum in the terminal CO region is more complicated, but comparison of the spectra of I–III shows consistent trends. The ^{13}CO resonances of II display an intensity pattern of 1:2:1:1:2:2:2:2, consistent with the symmetry found in the crystal structure. That of III is similar, 1:2:2:2:2:2:2 (Figure 2). In the case of III, two of the unique CO's, b and d, have accidental, near degeneracy. This is supported by the slight splitting in the peak at 212.5 ppm. Compound I shows a pattern of 1:2:1:2:3:4. The resonance of area three is assigned to one of the unique CO's (b or d) which has achieved accidental degeneracy with two other carbonyls. It also is possible that upon protonation a fluctional process causes rapid interchange of these three carbonyls; however, the first hypothesis is more consistent with observations for II and III. The feature of area 4 is assigned to two resonances of area 2, indicated by the asymmetry. These are also unresolved for II on the 20-MHz instrument.[12]



I, X = H
II, X = e^-
III, X = CH_3

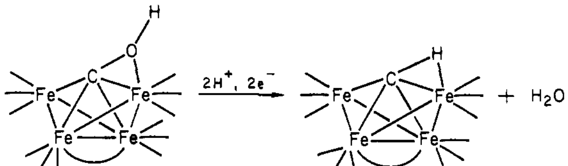
As found for $(\mu\text{-H})Fe_3(CO)_{10}(\mu\text{-COH})$, $(\mu\text{-H})Fe_4(CO)_{12}(\eta^2\text{-COH})$ is highly unstable at room temperature in CH_2Cl_2 solution. Reexamination of the product reported earlier as $H_2Fe_4(CO)_{13}$[7] leads us to question the original formulation. When $[Fe_4(CO)_{13}]^{2-}$ was treated with a large excess of aqueous 6 M HCl according to the method of Hieber and Werner[7] and then dried over Na_2SO_4 overnight, the resulting infrared spectrum showed bands characteristic of $[HFe_4(CO)_{13}]^-$ and H_2O or $H_3O^+{\cdot}nH_2O$ (intense broad bands around 3450 and 1630 cm^{-1}). In a different attempted preparation of $H_2Fe_4(CO)_{13}$, addition of a small excess of concentrated hydrochloric acid to an ether slurry of $[PPN]_2[Fe_4(CO)_{13}]$ produced a precipitate of 2 equiv of [PPN]Cl. The carbonyl stretching region of the spectrum was again identical with that of $[HFe_4(CO)_{13}]^-$. Therefore this product is formulated as $[H_3O{\cdot}nH_2O][HFe_4(CO)_{13}]$, which is analogous to the previously isolated $[H_3O{\cdot}nH_2O][HFe_3(CO)_{11}]$.[3] When dried under vacuum a brown solid results which display a complex ^{13}C NMR spectrum, indicating the presence of a mixture of iron carbonyls (IR:ν_{CO} (hexane) 2045 vs, 2020 s, 1998 m, 1985 sh, 1980 sh, 1894 w, 1865 w cm^{-1}). An identical IR spectrum is obtained for "$H_2Fe_4(CO)_{13}$" when the synthesis is attempted at room temperature under anhydrous conditions. Thus we conclude that the original "$H_2Fe_4(CO)_{13}$" was a complex mixture.

Isotope labeling experiments demonstrated that when III undergoes proton-induced reduction the carbon monoxide being reduced is derived from the η^2-$COCH_3$ moiety.[10] By analogy it was proposed that I is an intermediate when $[Fe_4(CO)_{13}]^{2-}$ is exposed to strong acid,[13] but firm evidence for the existence of a four-iron butterfly with an η^2-COH was lacking. The present characterization of I adds credence to the original proposal. The conversion of I to another reaction intermediate, $HFe_4(CO)_{12}(\eta^2\text{-CH})$ (eq 2), requires 2 equiv of protons and electrons. The latter appears to be supplied by sacrificial oxidation of an iron species, because addition of $[Fe_2(CO)_8]^{2-}$, which does not produce CH_4 upon reaction with HSO_3CF_3, increases the yield of CH_4 (Table I).

Table I. Proton-Induced Reduction Reactions with and without Added Reducing Agents[a]

iron complex	amount of complex used, mol	CH_4	CO	H_2
$[PPN]_2[Fe_4(CO)_{13}]$	1.14×10^{-4}	0.56	2.2	0.20
$[PPN]_2[Fe_2(CO)_8]$	8.14×10^{-5}	trace	2.2[b]	0.57[b]
$[PPN]_2[Fe_4(CO)_{13}]$ $[PPN]_2[Fe_2(CO)_8]$	1.97×10^{-4} 7.65×10^{-5}	0.76	2.2	0.37
$[PPN]_2[Fe_4(CO)_{13}]$ $[PPN]_2[Fe_2(CO)_8]$	1.09×10^{-4} 6.29×10^{-5}	1.0	3.0	0.37

[a] Yields, after three days reaction, are given in mol/mol of Fe_4 cluster. [b] Yield based on moles of $Fe_2(CO)_8{}^{2-}$.



(2)

In summary, the present results provide an example of a new type of protonated carbon monoxide ligand and indicate that the protonation of a carbon monoxide ligand activates CO toward C–O bond scission and reduction.

Acknowledgment. This research was supported by the National Science Foundation through Grant CHE-7918010. High-field ^{13}C NMR measurements were made at the University of Illinois NSF Regional Instrumentation Facility, (Grant CHE 97-16100). We appreciate informative correspondence and conversations with Brian Heaton and the late Paolo Chini during our initial attempts to characterize the elusive $H_2Fe_4(CO)_{13}$.

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[11] The shift to lower field in the ^{13}C NMR signal of a bridging carbonyl upon complex formation of the CO oxygen with an electrophile is well documented. See J. R. Wilkinson and L. J. Todd, *J. Organomet. Chem.*, *118*, 199 (1976); H. A. Hodali and D. F. Shriver, *Inorg. Chem.*, **18**, 1236 (1979).

[12] Because of the instability of $(\mu\text{-H})Fe_4(CO)_{12}(\eta^2\text{-COH})$, its ^{13}C NMR spectrum was obtained at Northwestern University where only a 20-MHz instrument was available. The 90-MHz spectra were obtained at the NSF Regional NMR Facility at the University of Illinois, Urbana, IL.

[13] E. M. Holt, K. Whitmire, and D. F. Shriver, *J. Organomet. Chem.*, *213*, 125 (1981).

Photocatalytic Oxidations of Lactams and *N*-Acylamines

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Although there is considerable interest in the use of semiconductors in photovoltaic cells and in the synthesis of high-energy compounds as potential fuels,[1] their use as photocatalysts in organic synthesis has received much less consideration.[2] As part of our program to explore the utility of semiconductors in synthetic organic photochemistry, we wish to report that the 5- and 6-membered lactams and *N*-acylamines undergo photocatalytic oxidation to the corresponding imides upon irradiation in the presence of oxygenated aqueous suspensions of TiO_2.

Irradiation of 10 mL of 0.2 M aqueous solutions of amides **1–6** in the presence of 100 mg of suspended unreduced anatase TiO_2

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[1] See, for example: Heller, A.; Miller, B.; Lewerenz, H. J.; Bachmann, K. J. *J. Am. Chem. Soc.* **1980**, *102*, 6555. Wrighton, M. S. *Acc. Chem. Res.* **1979**, *12*, 303. Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 5985 and references therein.

[2] Kanno, T.; Oguchi, T.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* **1980**, 467.