for scholarship aid. J.C.B. thanks CIRIT of Barcelona for assistance.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, fractional atomic coordinates, and thermal parameters (13 pages). Ordering information is given on any current masthead page.

Interconversion of Tetrahedral and Π-CO Containing Butterfly Clusters: $[Fe_4(MPR_3)(CO)_{12}(\eta^2\text{-}CO)]^- \rightleftharpoons [Fe_4(MPR_3)(CO)_{13}]^-$ (M = Au, R = Et; M = Cu, R = Ph) and $Fe_4(AuPEt_3)(CO)_{12}(\eta^2\text{-}COMe)$

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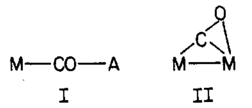
The interaction of both C and O of a carbon monoxide molecule is known to facilitate a wide range of CO chemistry, such as CO insertion and CO cleavage.[2] Systematic routes are available for the synthesis of Σ-CO complexes I; however, the designed synthesis of Π-CO complexes II containing three[3] or more[4-10] metal



I II

atoms has not been achieved. Previously, we attempted to induce Π-CO formation via the synthesis of highly crowded tetrahedral metal clusters, but the strain energy was relieved by a distortion of the clusters which did not yield a Π-CO.[11] In the present report we describe a systematic route to new Π-CO compounds, [K(18-crown-6)][$Fe_4(AuPEt_3)(CO)_{13}$] (III), $Fe_4(AuPEt_3)(CO)_{12}$(COMe) (IV), and their relation to some copper analogues.

Complex III was prepared according to eq 1.[12] Dissolution

$$K_2Fe_4(CO)_{13} + Et_3PAuCl \xrightarrow[\text{2. -MEOH}]{\text{1. MEOH}} \xrightarrow[\text{4. filter}]{\text{3. }Et_2O} \xrightarrow[\text{6. }CH_2Cl_2]{\text{5. }-Et_2O} \xrightarrow[\text{8. pentane}]{\text{7. 18-crown-6}} \underset{\text{III}}{[K(18\text{-crown-6})][Fe_4(AuPEt_3)(CO)_{13}]} \quad (1)$$

of the solid at −78 °C followed by ^{13}C NMR spectroscopy at this temperature yields a spectrum which has seven peaks in the terminal CO region (δ 224.0–212.4) as well as a downfield resonance at 284.6 ppm.[13] The intensity pattern and peak positions are similar to those for the butterfly form of $[HFe_4(CO)_{13}]^-$.[14] Warming the solution to room temperature and then recooling to −80 °C affords a ^{13}C NMR spectrum in which an additional resonance is at 222.4 ppm. The ^{31}P NMR spectrum of solutions which were prepared and run at −80 °C has two resonances at δ 62.5 and 57.7 (positive values are downfield of external H_3PO_4) in the intensity ratio 1:14. The downfield resonance gains intensity as the solution is warmed to room temperature and dominates the spectrum (10:1) when the solution is recooled to −80 °C. Thus, as in the case of $[HFe_4(CO)_{13}]^-$, there are two isomers of this cluster in solution: a Fe_4 butterfly with a Π-CO[4] and a Fe_4 tetrahedron containing only conventional C-bonded carbonyls.[14,15] Formation of a Π-CO in the crystalline state is also indicated by the appearance of a low-frequency CO stretch, 1412 cm^{-1}, in the IR spectrum of the solid. The vibrational frequency of the Π-CO in the $[PPN]^+$ and K^+ salts of $[HFe_4(CO)_{13}]^-$ occurs at 1415 and 1382 cm^{-1}, respectively.[16]

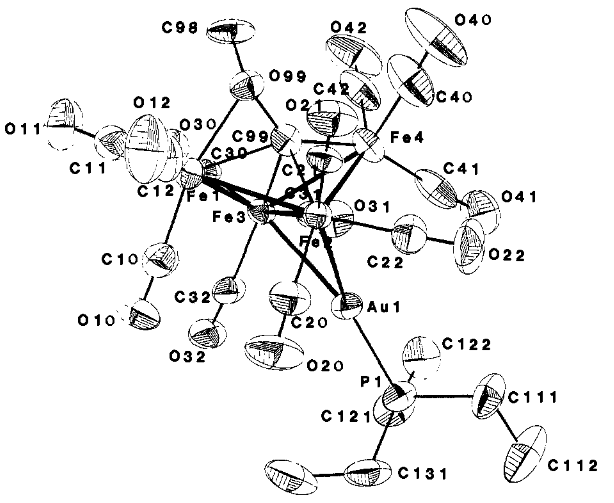


Figure 1. ORTEP diagram of $Fe_4(AuPEt_3)(CO)_{12}(COCH_3)$ showing thermal ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (°): C99–Fe1 = 2.14 (2), C99–Fe4 = 1.86 (2), C99–O99 = 1.37 (2), O99–Fe1 = 2.029 (9), Au1–Fe2 = 2.666 (2), Au1–Fe3 = 2.675 (3) [Fe–Fe bonding distances range 2.606 (3)–2.687 (4)]; C99–O99–C98 = 119 (2)°.

Preparation of $Fe_4(AuPEt_3)(CO)_{12}(COCH_3)$ (IV) is achieved by reaction 2. Both the IR and low-temperature ^{13}C NMR

$$K[Fe_4(CO)_{12}(COCH_3)] + PEt_3AuCl \xrightarrow[\text{2. -toluene}]{\text{1. toluene}} \xrightarrow[\text{4. filter, cool -20 °C}]{\text{3. pentane}} \underset{\text{IV}}{Fe_4(AuPEt_3)(CO)_{12}(COCH_3)} \quad (2)$$

spectra[17] (−78 °C) are similar to those for $HFe_4(CO)_{12}(COCH_3)$[18] (V), suggesting similar structures.[10] Figure 1 depicts the result of the single-crystal X-ray structure determination for compound IV.[19] As with its protonated analogue, IV provides an example of a CO ligand formally acting as an overall six-electron donor (4e$^-$ to the cluster framework and 2e$^-$ to the CH_3^+ group). Only one resonance in the ^{31}P NMR spectrum is observed, −80 to +20

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[12] The $[PPN]^+$ salt of III had been prepared but only the IR spectrum reported. Johnson, B. F. G.; Kaner, D. A.; Lewis, J.; Rosales, M. J. *J. Organomet. Chem.* **1982**, *238*, C73.

[13] IR (CH_2Cl_2) 2038 (m), 2004 (m, sh), 1972 (vs), 1920 (br, sh) cm^{-1}. ^{13}C NMR (22.49 MHz, $(CD_3)_2CO$, external Me_4Si), −80 °C δ 284.6 (Π-CO), 224.0, 223.1, 220.6, 217.8, 216.1, 213.5, 212.1 (*I* = 1:2:1:2:1:2:2:2); 18-crown-6, δ 70.5; PCH_2CH_3, δ 19.4 (d, J_{PC} = 29.3 Hz); PCH_2CH_3, δ 8.8. Anal. Calcd (Found) for $C_{31}H_{39}PFe_4O_{19}K$ Au: Fe, 18.53 (15.06); Au, 16.34 (17.09).

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[15] Initial observation of the absorption in the ^{31}P NMR due to the tetrahedral form at −78 °C might be precluded at lower temperatures.

[16] Horwitz, C.P.; Shriver, D. F., unpublished results.

[17] IR (CH_2Cl_2) 2072 (w), 2048 (sh), 2037 (vs), 2011 (vs), 1988 (br, m), 1920 (vw) cm^{-1}; ^{13}C NMR (22.49 MHz, $C_6D_5CD_3$, −80 °C) δ 304.5 ($COCH_3$), 219.7, 216.8, 214.8, 213.2, 213.0, 212.0, 208.5, 207.6 (*I* = 1:2:2:1:1:1:1:2:2); ^{31}P NMR (36.19 MHz, $(CD_3)_2CO$) δ 58.1. Anal. Calcd (Found) for $C_{20}H_{18}Fe_4AuO_{13}P$: Fe, 24.34 (24.38); Au, 21.46 (28.55).

[18] IR (hexane) 2085 (vw), 2046 (vs), 2020 (s), 1998 (s), 1990 (m), 1890 (s) cm^{-1}; ^{13}C NMR (90 MHz, CD_2Cl_2, −90 °C) δ 301 ($COCH_3$).

[19] Crystal data for $Fe_4(AuPEt_3)(CO)_{12}(COCH_3)$: a = 14.764 (3) Å, b = 9.574 (1) Å, c = 11.094 (2) Å, α = 87.26 (1)°, β = 82.33 (2)°, γ = 112.13 (1)°, Z = 2, d_{calcd} = 2.129 g cm^{-3}, space group $P\bar{1}$, R_W = 0.067.

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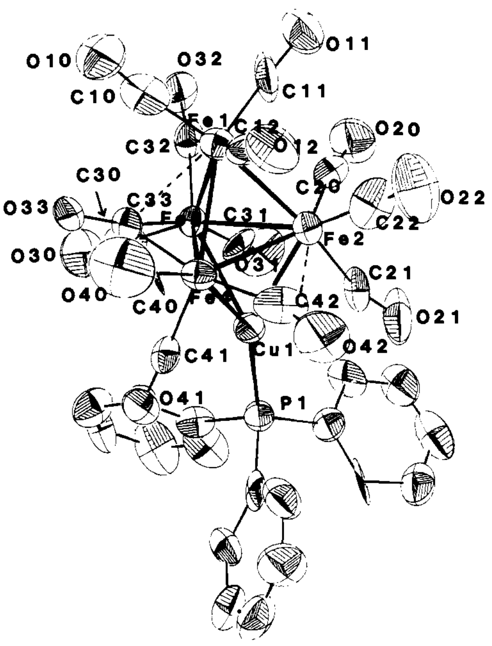

Figure 2. ORTEP diagram of $[\mathrm{Fe_4(CuPPh_3)(CO)_{13}}]^-$ anion thermal ellipsoids at the 50% probability level. Selected bond distances (Å): Fe–Fe distances range 2.576 (6)–2.644 (5), Cu1–Fe2 = 2.561 (5), Cu1–Fe3 = 2.525 (6), Cu1–Fe4 = 2.580 (6), C33–Fe3 = 2.09 (2), C33–Fe4 = 1.88 (3), C33–Fe1 = 2.44 (2).

°C, suggesting only one isomer in solution.[17]

The R_3PAu^+ cation is often used as a proton mimic in cluster chemistry,[20] and the isolobal LCu^+ cation has received some use.[21] We therefore prepared the complex $[\mathrm{PPN}][\mathrm{Fe_4(CuPPh_3)(CO)_{13}}]$ (VI) according to eq 3. The solution IR spectra of this complex

$$[\mathrm{PPN}]_2[\mathrm{Fe_4(CO)_{13}}] + [\mathrm{Cu(CH_3CN)_4}]\mathrm{PF_6} \xrightarrow[\text{2. Et}_2\text{O}]{\text{1. CH}_2\text{Cl}_2} \xrightarrow[\text{4. -solvents}]{\text{3. filter}} \xrightarrow[\text{6. PPh}_3]{\text{5. MeOH}} \underset{\mathrm{VI}}{[\mathrm{PPN}][\mathrm{Fe_4(CuPPh_3)(CO)_{13}}]} \quad (3)$$

and III are nearly identical, with VI having an additional weak absorption at 1723 $\mathrm{cm^{-1}}$.[22] The spectrum of VI in the solid state does not have an absorption in the Π-CO region (1420–1380 $\mathrm{cm^{-1}}$) but rather is similar to that in solution. The −80 °C ^{13}C NMR spectrum of the solid dissolved at −78 °C displays only a single resonance at δ 220.4. Warming this solution to room temperature and then recooling to −80 °C generates a ^{13}C NMR spectrum with a weak downfield resonance at 286.7 ppm, four new resonances in the terminal CO region, and the main resonance at 220.4 ppm.[23] From these data, it appears that the solid-state structure possesses a tetrahedral core of iron atoms which in solution opens into a butterfly with a Π-CO as a second, minor isomer. As shown in Figure 2 the solid-state structure of complex VI does have a tetrahedral iron core.[24] From this result, we conclude that for both $[\mathrm{HFe_4(CO)_{13}}]^-$ and $[\mathrm{Fe_4(AuPEt_3)(CO)_{13}}]^-$ the resonances in the ^{13}C NMR spectrum at δ 216.7 and 222.4, respectively, arise from similar face-capped tetrahedra. The crystallization of two forms of analogous molecules, III and VI, and NMR spectra on solutions demonstrate that the energy difference between the butterfly and tetrahedral isomers is small, just as it is in $[\mathrm{HFe_4(CO)_{13}}]^-$.[14] Our results, along with theoretical calculations which reveal basicity centerd at the Fe–Fe hinge bond of similar butterfly molecules[25] indicate that other simple acceptors should induce the tetrahedron to butterfly transformation.

Acknowledgment. This research was funded by NSF Grant CHE-8204401. C.P.H. was the recipient of an E. I. du Pont de Nemours and Co. fellowship.

Supplementary Material Available: Complete listings of positional parameters, bond angles and distances, anisotropic thermal parameters, and observed and calculated structure factors for $\mathrm{Fe_4(AuPEt_3)(CO)_{12}(COCH_3)}$ and $[\mathrm{PPN}][\mathrm{Fe_4(CuPPh_3)(CO)_{13}}]$ (128 pages). Ordering information is given on any current masthead page.

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(22) IR ($\mathrm{CH_2Cl_2}$) 2040 (m), 2000 (m, sh), 1974 (vs), 1912 (m, sh), 1723 (vw) $\mathrm{cm^{-1}}$. ^{31}P NMR (36.19 MHz, $\mathrm{CD_2Cl_2}$) $\mathrm{Ph_3P}$, δ 3.03; $[\mathrm{(Ph_3P)_2N}]^+$, δ 21.9. Anal. Calcd (Found) for $\mathrm{C_{67}H_{45}O_{13}P_3NFe_4Cu}$: Fe, 15.40 (11.33); Cu, 4.38 (4.12).

(23) ^{13}C NMR (22.49 MHz, $\mathrm{CD_2Cl_2}$) δ 286.7, 221.5, 220.4, 217.4, 212.9, 209.7 (after warming to room temperature and recooling).

(24) Crystal data for $[\mathrm{PPN}][\mathrm{Fe_4(CuPPh_3)(CO)_{13}}]$: a = 16.352 (5) Å, b = 15.169 (6) Å, c = 13.811 (4) Å, α = 99.06 (2)°, β = 78.17 (2)°, γ = 76.88 (3)°, Z = 2, d_{calcd} = 1.511 g $\mathrm{cm^{-3}}$, space group $P\bar{1}$, R_W = 0.078.

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Book Reviews[*]

Annual Reports of the Progress of Chemistry. Volume 79. 1982. Section C. Physical Chemistry. Senior Reporter: M. C. R. Symons (University of Leicester). The Royal Society of Chemistry: London. 1983. xiv + 297 pp. $95.00.

This volume provides review chapters on seven areas. Of these, four are follow-on reviews by the same authors of chapters that appeared in Volume 76 of the same series. These include the sections on Thermochemistry by M. N. Jones and H. A. Skinner, a compilation of data with some interpretation, such as questioning the suitability of using benzoic acid sublimation as a standard when the product may not be solely the monomer; Macromolecular Chemistry by E. A. Boucher, a brief survey of polymer chemistry supplementing Volume 2 of the Specialist Periodical Reports of the same name; Catalysis by D. A. Dowden, who, after indicating that "there has been no major advance despite the outpouring of published material" since his last review, produces an extensive review, though with lower coverage of the surface science currently in vogue among chemical physicists in this country; and Spectroscopic Studies of Liquids and Solutions at High Pressures by D. J. Gardiner, a short chapter focusing on Raman, IR, UV–vis, and NMR spectroscopic applications. The other three chapters in Volume 79 consist of a chapter entitled Kinetics of Reactions in Solution. Part II. Fast Reactions, covering proton transfer, electron transfer, radical, metal-complex formation, association, and micellar reactions, by J. E. Crooks, which is the complement to a previous chapter from Volume 76, and two new topics termed "middle of the road reviews" by the Senior Reporter.

The first of these new topics is Spectroscopic Studies of Intermolecular Forces in Dense Phases by J. Yarwood which focuses on optical spectra through shifts, broadening, and line widths of IR and Raman spectra. The ability to separate relaxation processes into homogeneous and inhomogeneous components is examined, as is the relation between macroscopic and microscopic correlation times, which includes discussions of recent theoretical developments and of the errors induced because collision-induced intensities have been incorporated. Yarwood discusses attempts to correlate experimental work with intermolecular forces by using interaction induced spectra and includes a section on studies of

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[*] Unsigned book reviews are by the Book Review Editor.