Liberman,[49] and the form factor for hydrogen from Stewart, Davidson, and Simpson.[50] In the final cycles of refinement all non-hydrogen atoms were assumed to vibrate anisotropically.

The formyl hydrogen atom parameters were refined in the final cycles of refinement of the formyl complex 1. The final values of the discrepancy indices were $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.047$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2} = 0.057$ for 1. The estimated standard deviation of an observation of unit weight was 1.61, with a final data/variable ratio of 13.3. The final difference electron density map was featureless. The final values of the discrepancy indices for 4 were $R_1 = 0.062$, $R_2 = 0.082$, and the estimated standard deviation of an observation of unit weight = 2.31. The final data/variable ratio was 12.7. There were no significant features on the final difference electron density map.

Acknowledgment. Support from the Department of Energy, Division of Basic Energy Science, is gratefully acknowledged.

Registry No. 1, 60606-70-4; 2, 70459-98-2; 3, 92641-73-1; 4, 92641-75-3; 5, 92641-77-5; 8, 36432-47-0; 9, 18475-06-4; 10, 92641-78-6; $N(CH_2CH_3)_4^+[cis\text{-}(CO)_9ReH]^-$, 92669-26-6; PCl_3, 7719-12-2; $Fe(CO)_5$, 13463-40-6; $Re_2(CO)_{10}$, 14285-68-8; (3,5-dimethylphenyl)phenol, 108-68-9.

Supplementary Material Available: Tables of final atomic coordinates, listings of the observed and calculated structure factors (×10), the coordinates and thermal parameters for the fixed hydrogen atoms, and the anisotropic thermal parameters for both compounds (51 pages). Ordering information is given on any current masthead page.

(49) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891–1898.
(50) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

Crystal and Molecular Structure of the $[\{(C_6H_5)_3P\}_2N]^+$ Salt of $[Fe_4(CO)_{13}]^{2-}$. A Structural Isomer of the Anion along a Valence Tautomeric Coordinate[1]

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The complex $[Et_4N]_2[Fe_4(CO)_{13}]$, 1, is synthesized in 74% yield by thermolysis of $[Et_4N][HFe_3(CO)_{11}]$ for 48 h in tetrahydrofuran solution. The [PPN] salt, $[PPN]^+ = [\{(C_6H_5)_3P\}_2N]^+$, is isolated by precipitation with [PPN][Cl]. Due to differences in the carbonyl absorptions between these materials and salts containing other cations isolated in the past, a structure determination was undertaken on a single crystal of the title compound at 115 K. Data were collected on a Syntex P$\bar{1}$ automated diffractometer using graphite-monochromatized Mo Kα radiation. The salt crystallizes in space group $R\bar{3}$ with $a = b = c = 18.039$ (7) Å, $\alpha = \beta = \gamma = 81.51$ (3)°, $V = 5694$ (4) Å^3, $Z = 3$, ρ_{obsd}(298 K) = 1.48 (1) g cm^{-3}, and ρ_{calcd}(115 K) = 1.46 g cm^{-3}. Phenyl group atoms of the cation were refined as rigid bodies. All nongroup atoms were located by using standard direct methods, Fourier, and least-squares techniques. The final discrepancy indices are $R_F = 5.94\%$ and $R_{wF} = 5.29\%$ for 2369 independent reflections having $I > 3\sigma(I)$ in the range $0° < 2\theta < 50°$. Two tetrahedra of iron atoms each face capped by one carbonyl group are symmetry related and ordered; the third tetrahedron of iron atoms similarly capped is disordered, lying on the crystallographic center of symmetry. The iron interactions are all bonding, ranging from 2.545 (2) to 2.610 (2) Å. The principal features of the molecular structure are the (symmetry related) M–C–O angles of 172.1 (9)° in the basal plane of the iron tetrahedron and the long nonbonded Fe–C(O) contacts in the range 2.62–2.82 (1) Å. These parameters denote a significant departure from the semibridging observed in the structure of the $[Fe(py)_6]^{2+}$ (py = pyridine) salt of the title anion determined earlier. The occurrence of a new conformer in the solid must be due to a rather shallow and perhaps flat barrier in the coordinate involving fluxional processes of the basal carbonyl groups in the cluster anion. Appropriately, at −90 °C the ^{13}C NMR of 1 shows rapid equilibration of all but one (presumably the face capping) carbonyl groups.

Introduction

Recent studies with salts of the $[HFe_3(CO)_{11}]^-$ anion[2] in refluxing tetrahydrofuran revealed its conversion within 48 h, in approximately 75% yield, to a species with a relatively simple absorption pattern in the infrared; for the $[Et_4N]^+$ salt, in acetonitrile solution (cm^{-1}): 2020 (w), 1949 (vsbr), 1896 (sh), 1772 (vvw), 1635 (vw). Further heating beyond this period leads (after another 48 h) to $[Fe_6C(CO)_{16}]^{2-}$ as the only anion in solution, evidenced by a single broad carbonyl infrared absorption at 1968 cm^{-1} (CH_3CN).[3] We reasoned that the principal species after 48 h of heating would be one of intermediate nuclearity, i.e., Fe_4 or Fe_5,[4] but the carbonyl IR pattern cited above corresponded to no published spectrum for a carbonylferrate anion.[5] We were thus led to determine its structure.

(1) (a) Presented to the American Crystallographic Association, Calgary, Alberta, Canada, August 1980; *ACA Program Abstr*, Series 2, Vol. 8, No. 1, paper No. PA 19. (b) Taken in part from the Ph.D. Dissertation, van Buskirk, G., UCLA, 1981.
(2) Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7255.
(3) (a) Churchill, M. R.; Wormald, J.; Knight, J.; Mays, M. J. *J. Am. Chem. Soc.* **1971**, *93*, 3073. (b) Stewart, R. P.; Anders, U.; Graham, W. A. G. *J. Organomet. Chem.* **1971**, *32*, C49.
(4) (a) Chini, P.; Heaton, B. T. *Top. Curr. Chem.* **1977**, *71*, 1. (b) Chini, P.; Longoni, G.; Albano, V. G. *Adv. Organomet. Chem.* **1976**, *14*, 285.
(5) Among the various references perused are those containing spectra of tetra- and pentanuclear cations.[4,5a–e] Comparisons between spectra of salts of air-sensitive anions that cannot be purified by chromatographic means is very tenuous. Low-yield preparations are thus susceptible to contamination by impurities, hence the advantage of a high-yield route for spectroscopic characterization. An even better synthesis has become known since the completion of the present work; see ref 10. (a) Hsieh, A. T. T.; Mays, M. J. *J. Organomet. Chem.* **1972**, *37*, C53. (b) Hieber, W.; Lipp, A. *Chem. Ber.* **1959**, *92*, 2075. (c) Edgell, W. F.; Yang, M. T. B.; Bulkin, J.; Bayer, R.; Koizumi, N. *J. Am. Chem. Soc.* **1965**, *87*, 3080. (d) Razuvaev, G. A.; Petukhov, G. G.; Ermolaev, V. I.; Beketov, V. P. *Zh. Obshch. Khim.* **1967**, *37*, 672. (e) Farmery, K.; Kilner, M.; Greatrex, R.; Greenwood, N. N. *J. Chem. Soc. A* **1969**, 2339.

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The $[Et_4N]^+$ salt did not yield good crystals, but those of the title cation were found suitable for crystallographic study described in this work. After identification of the substance by crystallography we recognized that the structure of the anion in our material consisted of a tautomer of that observed in its $[Fe(py)_6]^{2+}$ salt, reported earlier.[6b] The ^{13}C NMR spectrum of the anion has since been examined by Chini, Heaton, and their co-workers who observed a single absorption at room temperature (229.8 ppm, relative to Me_4Si, cf. Table II of ref 4a). We prepared a ^{13}CO-enriched sample of 1 and obtained its ^{13}C NMR at −90 °C (the lowest accessible temperature as determined by sample solubility). The spectrum consisted of a two-line pattern for the carbonyl groups (in the ratio of 14:1),[7] denoting a low barrier for the tautomerism of all but one of the carbonyl groups, consistent with variation of the solid-state structure of the anion observed in the crystallographic study described below.

Experimental Section

$[Et_4N][HFe_3(CO)_{11}]$ was prepared by the method of Case and Whiting.[8] Bis(triphenylphosphine)nitrogen (1+) chloride, [PPN][Cl], was prepared by the method of Ruff and Schlientz[9] and recrystallized from hot water. All manipulations were carried out under nitrogen using Schlenk ware. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl solution. All other solvents were of commercial reagent grade and were used without further purification. Carbonyl infrared spectra were recorded on a Nicolet MX-1 Fourier transform infrared spectrometer. ^{13}C NMR spectra were recorded on a Bruker WP-200 Fourier transform spectrometer and calibrated against internal solvent.

Preparation of $[PPN]_2[Fe_4(CO)_{13}]$.[10] A solution of $[Et_4N][HFe_3(CO)_{11}]$ (0.20 g, 33 μmol) in tetrahydrofuran (30 mL) was heated under reflux for 48 h. Upon cooling the solution a black solid precipitates; IR of the supernatant solution showed the presence of $[HFe(CO)_4]^-$ (cm^{-1} in acetonitrile): 1997 (w), 1914 (m), 1883 (s, br) [lit.[11] (as the $[PPN]^+$ salt in THF, cm^{-1}) 1998 (w), 1905 (m), 1876 (s, br)]. This species could be responsible for the further buildup of cluster size as the heating is continued (see introductory statements). The black solid was filtered, washed with 3–10-mL portions of tetrahydrofuran, and dried under vacuum, yielding pure $[Et_4N]_2[Fe_4(CO)_{13}]$ (1), 0.14 g, 74%. Carbonyl absorptions in the infrared spectrum of this material were given in the Introduction. Single crystals of this salt could not be grown. Consequently we sought another derivative and precipitated the anion as the $[PPN]^+$ salt: an equimolar solution of 1 and [PPN][Cl] in acetonitrile was brought to the cloud point by adding 2-butanol/acetonitrile (approximately 60/40). The solution was heated until clear and slowly cooled to −20 °C; this produced dark red opaque crystals of the title compound. The solution infrared spectrum of this was virtually identical with that of the $[Et_4N]^+$ salt mentioned in the Introduction.

Preparation of ^{13}CO-Enriched $[Et_4N]_2[Fe_4(CO)_{13}]$ and Determination of Its ^{13}C NMR. $[Et_4N][HFe_3(CO)_{11}]$ was dissolved in methylene chloride. Carbon monoxide (90% ^{13}C, Merck & Co.) was transferred to the reaction vessel from a storage bulb by using a Toepler pump on a standard chemical vacuum line; the pressure of the gas was below atmospheric and maintained such as to achieve about 45% ^{13}C enrichment assuming complete exchange. The mixture was stirred at 25 °C for 40 h according to the procedure described by Wilkinson and Todd.[11] The ^{13}C enrichment was followed by observing the drop in ^{13}C content of the gas (MS). When exchange had gone to completion, ^{13}C enrichment in the trinuclear anion was estimated to be about 43% by comparing the intensity of the absorption of its bridging CO group (1717 cm^{-1}) with that of its ^{13}C satellite (1684 cm^{-1}). In acetonitrile solution approximately the same enrichment was achieved within 20 days (25 °C).

The synthesis of ^{13}C-enriched 1 was then carried out by using the procedure given above and its ^{13}C NMR spectrum obtained at −90 °C in hexadeuterioacetone (the lowest temperature accessible in this solvent, the best one for this salt). At this temperature signals were observed as follows (ppm relative to Me_4Si): 5.57 and 51.4, CH_3 and CH_2, respectively, of $[(CH_3CH_2)_4N]^+$; multiplet centered at 28.19, $(CD_3)_2C{=}O$; 205.8, $(CD_3)_2C{=}O$; 220.16 (relative intensity 1), μ_3-CO; 226.9 (relative intensity 14),[7] terminal CO of $[Fe_4(CO)_{13}]^{2-}$. At 25 °C we observe an averaged signal at 229 ppm (lit.[4a] 229.8 ppm).

Table I. Crystal, Intensity Collection and Refinement Data for $[\{(C_6H_5)_3P\}_2N]_2[Fe_4(CO)_{13}]$

$a = b = c$/Å	18.039 (7)
$\alpha = \beta = \gamma$/deg	81.51 (3)
V/Å^3	5694 (4)
space group	$R\bar{3}$
formula	$C_{85}H_{60}O_{13}P_4N_2Fe_4$
Z	3
T/K	115
ρ(obsd) at 298 K/g cm^{-3}	1.48 (1)
ρ(calcd) at 115 K/g cm^{-3}	1.46
cryst size/mm	0.23 × 0.23 × 0.23[c]
2θ limits/deg	50
scan rate/deg min^{-1}	2.0
scan range	
below $K\alpha_1$	1.0
above $K\alpha_2$	1.0
radiation source (λ/Å)	0.71073
no. of observed data	2369
no. of parameters	200
R/%[a]	5.94
R_w/%[b]	5.29
abs coeff (μ/cm^{-1})	8.37

[a] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w = 1/\sigma^2(|F_o|)$. [c] First crystal (see text); second crystal: 0.22 × 0.22 × 0.22 mm.

Crystallographic Section

Crystals of the title compound obtained as described above were examined by Weissenberg photographs which indicated no systematic absences. A crystal was glued to a thin glass fiber and mounted on a Syntex P$\bar{1}$ automated diffractometer equipped with scintillation counter, graphite monochromator, and low-temperature capability.[13] The crystal was cooled to 115 K, and some 8526 reflections were collected. Due to an accidental warmup with an attempted recooling, this crystal was lost and another had to be mounted. The data collected on the first crystal were averaged with equivalent data obtained from the second crystal, mentioned below.

The first crystal was nearly equidimensional, having an approximate diameter of 0.23 mm. Fifteen reflections were used as input to the automatic centering, autoindexing, least-squares, and axial photograph routines of the instrument to obtain low-temperature lattice parameters in the space group $P\bar{1}$: a = 18.034 (7) Å, b = 18.045 (7) Å, c = 18.037 (7) Å, α = 81.45 (3)°, β = 81.55 (3)°, and γ = 81.52 (3)°. Recognizing the rhombohedral symmetry, the crystal was recentered by using 15 reflections with 22° < 2θ < 25° collected in a fast scan. An accurate set of rhombohedral lattice parameters was obtained and subsequently used in the refinement of the structure; see Table I.

(6) (a) Hieber, W.; Sonnenkalb, F.; Becker, E. *Chem. Ber.* **1930**, *63*, 1405. (b) Doedens, R. J.; Dahl, L. F. *J. Am. Chem. Soc.* **1966**, *88*, 4847.

(7) This alternatively may be read as 12:0.85; variation in the integrated ratio from that of the formula of the complex is the result of inequivalent relaxation times for the two types of carbonyl groups. For a discussion of this phenomenon see: LaMar, G. N. *J. Am. Chem. Soc.* **1971**, *93*, 1040. Aime, S.; Milone, L. *Prog. Nucl. Magn. Reson. Spectrosc.* **1977**, *11*, 183.

(8) Case, J. R.; Whiting, M. C. *J. Chem. Soc.* **1960**, 4632.

(9) Ruff, J. K.; Schlientz, W. J. *Inorg. Synth.* **1974**, *15*, 84.

(10) After completion of this work we learned of a further improved preparation of $[Fe_4(CO)_{13}]^{2-}$ that can be obtained in almost quantitative yield by reflux of $Fe(CO)_5$ in pyridine solution: Whitmire, K.; Ross, J.; Cooper, D. B.; Shriver, D. F. *Inorg. Synth.* **1982**, *21*, 60.

(11) Darensbourg, M. Y.; Darensbourg, D. J.; Barros, H. L. C. *Inorg. Chem.* **1978**, *17*, 298.

(12) (a) Wilkinson, J. R.; Todd, L. J. *J. Organomet. Chem.* **1976**, *118*, 199. (b) Todd, L. J., private communication.

(13) Strouse, C. E. *Rev. Sci. Instrum.* **1976**, *47*, 871.

Intensity data were collected at low temperature using the conditions given in Table I. The intensities of three reflections, (102), (021), and (210), were recorded after every 97 intensity measurements. These showed no appreciable change during data collection. A total of 8526 reflections were measured on the first crystal, which constitute the entire hemisphere $+h, \pm k, \pm l$ accessible with Mo Kα radiation having $0° < 2\theta < 35°$. Inspection of this data revealed threefold equivalence in the intensities; henceforth rhombohedral symmetry was assumed.

A second nearly equidimensional crystal with an approximate diameter of 0.22 mm was mounted, cooled, and centered as described above. A total of 4596 independent reflections were measured, which constitute those with $h < k < l$ accessible with Mo Kα radiation having $35° < 2\theta < 50°$. Again, the reflections showed no appreciable intensity change during data collection. The intensities of this data set were treated with a scale factor so as to equalize overlapping data from the set collected with the first crystal. In the unique data set, 4395 reflections showed $I < 3\sigma(I)$; these were considered unobserved and were omitted from the refinement. The 2369 remaining reflections were corrected for Lorentz and polarization effects and converted to $|F_o|$ and $\sigma(|F_o|)$ by means of the equations $I = SC - t(B_1 + B_2)$, $\sigma(I) = [SC + t^2(B_1 + B_2) + p^2I^2]^{1/2}$, $|F_o| = k[I/(Lp)]^{1/2}$, and $\sigma(|F_o|) = (k/2)[\sigma(I)]/[I(Lp)]^{1/2}$, where SC is the count during the scan, t is the ratio of scan time to background time (= 1 here), B_1 and B_2 are the two background counts, p is the "ignorance factor" (set to 0.04 here), and Lp is the Lorentz and polarization factors. Because the first crystal was lost, faces were not indexed. Fortunately the effect of absorption was negligible (μ = 8.37 cm^{-1}, maximum, minimum, and mean transmission factors of 0.9).[14] No absorption correction was applied.

Solution and Refinement of the Structure

Calculations for the structure analysis[15] were performed on the IBM 360/91 and 3033 computers at the UCLA Office of Academic Computing. The scattering factors for neutral iron, phosphorus, oxygen, nitrogen, and carbon were taken from Cromer and Mann[16a] while those of hydrogen were from Stewart et al.[16b] Both real and imaginary components of anomalous dispersion were employed.[16c] The function minimized during least-squares refinement was $\sum w[|F_o| - |F_c|]^2$ where $w = 1/\sigma^2(|F_o|)$. The discrepancy indices are defined in Table I.

Direct methods were used for location of the heavy atoms.[17] The sign determination of 499 reflections with $E > 1.87$ was accomplished by use of MULTAN74.[15] Statistical analysis showed the unit cell contents to be centrosymmetric, consistent with the space group $R\bar{3}$. The solution with the maximum combined figure of merit (2.4185) was chosen; this factor was obtained from the highest absolute figure of merit (ABS FOM = 1.4357), the lowest residual (RESID = 33.65), and lowest psi zero (PSI ZERO = 0.8208 × 10^{-3}).[17] The positions of four unique iron atoms (the two unique Fe_4 tetrahedra) and two unique phosphorus atoms were located on the E map based on this solution. These positions were chemically reasonable and thus consistent with the assigned space group.

A Fourier map phased on the iron atoms revealed the carbonyls on one of the tetrahedra, the nitrogen, and most of the phenyl carbons. The latter were used to determine the orientation of the rigid phenyl group; these were constrained to be hexagons with C–C = 1.395 and C–H = 1.008 Å. The carbonyl groups of the other tetrahedron proved more difficult to find due to overlap as explained below; only the triply bridging carbonyl group could be found unambiguously by using ORFLS and JBFOUR;[15] full-matrix refinement converged at R_f = 12.0% and R_{wF} = 15.4% by using SHELX 76.[15] The positions of the disordered carbonyl group atoms were allowed to refine given fixed bond length restraints (Fe–C = 1.785 Å, esd 0.013; C–O = 1.150 Å, esd 0.015). This led to a convergence at R_F = 7.46%. Three more cycles of least-squares refinement with anomalous dispersion included for iron and anisotropic thermal parameters included for all iron, phosphorus, nitrogen, and ordered carbonyl group atoms led to convergence at R_F = 6.31%. The temperature factors of the phenyl carbons were then refined, constrained to being equal at equivalent ring positions. Temperature factors of the hydrogen atoms were set to 1.67 times those of the ring carbons to which they were attached. Two more cycles of least-squares refinement converged as shown

Table IIa. Positional Parameters for Nongroup Atoms[a]

atom	x	y	z
Fe1	0.3615 (1)	0.2480 (1)	0.3498 (1)
Fe2	0.3804 (1)	0.3804 (1)	0.3804 (1)
C11	0.3087 (5)	0.2239 (5)	0.4402 (6)
C12	0.4537 (6)	0.2366 (6)	0.3738 (5)
C13	0.3747 (6)	0.1588 (7)	0.3165 (6)
O11	0.2809 (4)	0.2013 (4)	0.4993 (4)
O12	0.5152 (4)	0.2192 (4)	0.3898 (4)
O13	0.3851 (4)	0.1007 (4)	0.2962 (5)
C21	0.3900 (6)	0.3489 (6)	0.4779 (7)
O21	0.3983 (4)	0.3301 (5)	0.5404 (4)
CFAC	0.2797 (5)	0.2797 (5)	0.2797 (5)
OFAC	0.2458 (3)	0.2458 (3)	0.2458 (3)
Fe1D	−0.0852 (1)	0.0396 (2)	−0.0328 (1)
Fe2D	0.0338 (1)	0.0338 (1)	0.0338 (1)
C11D	−0.0535 (10)	0.0986 (9)	−0.1157 (8)
C12D	−0.1151 (10)	0.1069 (8)	0.0332 (9)
C13D	−0.1774 (9)	0.0366 (17)	−0.0562 (19)
O11D	−0.0419 (7)	0.1445 (7)	−0.1656 (7)
O12D	−0.1382 (8)	0.1560 (7)	0.0696 (7)
O13D	−0.2323 (6)	0.0313 (7)	−0.0722 (7)
C21D	0.0503 (10)	0.1293 (7)	−0.0045 (10)
O21D	0.0608 (21)	0.1904 (11)	−0.0239 (18)
CBRD	−0.0644 (10)	−0.0644 (10)	−0.0644 (10)
OBRD	−0.0983 (6)	−0.0983 (6)	−0.0983 (6)
P1	0.0145 (1)	0.4109 (1)	0.7395 (2)
P2	0.0962 (1)	0.5310 (1)	0.7690 (2)
N	0.0423 (4)	0.4914 (4)	0.7291 (4)

[a] Positions are given in fractional coordinates followed in parentheses by the estimated standard deviation of the least significant digit.

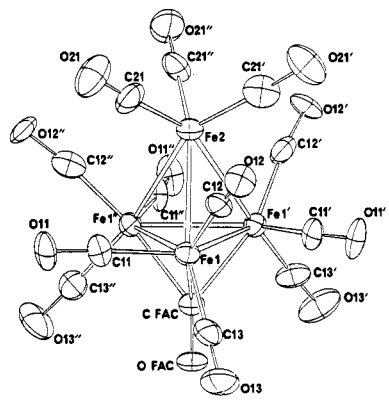

Figure 1. Overall view of the ordered title anion $[Fe_4(CO)_{13}]^{2-}$ (thermal ellipsoids at 50% probability level).

(14) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1975; Vol. 2, p 302.

(15) Programs used during the structural analysis included the data reduction program PIBAR by Bell and Murphy, for the Syntex diffractometer, MULTAN74 by Main, Woolfson, Lessinger, Germain, and Declerq for direct methods phase solution, JBFOUR and PKLIST, by Blount, modified versions of Fourier programs, RBANG by Watkins for calculation of rigid group constants, a local version of ORFLS by Busing, Martin, and Levy for full-matrix least-squares refinement, SHELX76 by Sheldrick for Fourier maps, full-matrix least-squares refinement, and constrained refinement, ORTEPII by Johnson for structure plots, and PUBLIST by Hoel for structure factor table listing.

(16) (a) Cromer D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321. (b) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175. (c) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(17) MULTAN: P. Main, M. M. Woolfson, and G. Germain, University of York, Monograph, Heslington, York, Great Britain, May 1971.

$$\text{ABS FOM} = \frac{\sum_h \alpha_h - \sum_h (\alpha_h^2)_r^{1/2}}{\sum (\alpha_h^2)_e^{1/2} - \sum (\alpha_h^2)_r^{1/2}}$$

$$\text{RESID} = \frac{\sum_{h_r} ||E_h|_{obsd} - |E_h|_{calcd}|}{\sum_{h_r} |E_h|_{obsd}}$$

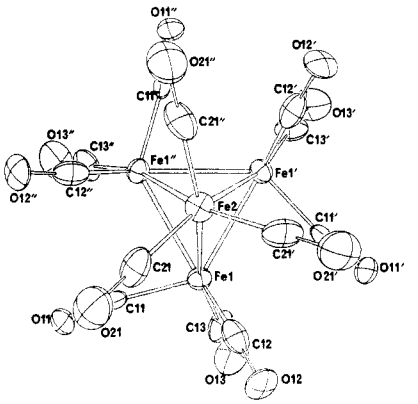

Figure 3. Top view of the ordered anion $[Fe_4(CO)_{13}]^{2-}$ (thermal ellipsoids at 50% probability level).

Table IV. Interatomic Distances (Å) for Nongroup Atoms[a]

Fe1-Fe2	2.610 (2)	Fe1D-Fe2D	2.592 (5)
-Fe1'	2.545 (2)	-Fe1D'	2.556 (5)
-C11	1.792 (11)	-C11D	1.775 (10)
-C12	1.757 (12)	-C12D	1.796 (10)
-C13	1.771 (12)	-C13D	1.786 (10)
-CFAC	2.046 (13)	-CBRD	2.007 (24)
Fe2-C21	1.791 (12)	Fe2D-C21D	1.810 (10)
C11-O11	1.153 (10)	C11D-O11D	1.148 (11)
C12-O12	1.173 (11)	C12D-O12D	1.172 (11)
C13-O13	1.142 (11)	C13D-O13D	1.093 (11)
C21-O21	1.154 (11)	C21D-O21D	1.140 (13)
CFAC-OFAC	1.205 (18)	CBRD-OBRD	1.205 (34)

[a] The numbers given in parentheses are the estimated standard deviations in the least significant digit(s).

in Table I. Positional and thermal parameters are given in Tables II and III.

Results and Discussion

The crystal consists of discrete cations and anions. The overall geometry of the ions and the system used in labeling are shown in Figures 1–4. Selected bond distances and angles are presented in Tables IV and V, respectively.

The PPN Cation. The six $[PPN]^+$ cations are all symmetry related. The average P–N bond length is 1.587 Å with an average P–N–P angle of 136.2°; these fall within the range of known values, i.e., 1.53–1.59 Å and 135–142° (for the bent form), respectively.[18] The bent form is understood to possess sp^2 hybridization on nitrogen, one lone pair being in an sp^2 orbital, with the other in a p orbital that is engaged in π-bonding with each phosphorus.

The Iron Atoms. Two tetrahedra of iron atoms are symmetry related and ordered. The crystallographic center of symmetry lies within the third tetrahedron, which thus contains symmetry-induced disorder. Each tetrahedron is situated on the three fold axis such that an apical iron atom lies on the axis with the basal iron atoms symmetrically disposed about the axis. All iron interactions are bonding. The separations are as follows (Å): apical–basal 2.610 (2) and 2.592 (5); basal–basal 2.545 (2) and 2.556 (5). The shortening of the basal–basal lengths compared to the apical–basal lengths could be due to the presence of the triply bridging carbonyl group on the basal face. The apical–basal separations are close to those observed in the earlier structure of $[Fe_4(CO)_{13}]^{2-}$ (2.57, 2.58, 2.60 ± 0.005 Å).[6] The basal–basal separation, however, is perceptibly longer compared to that (2.50 (1) Å) in the previous structure. This change is connected with the reduction of semibridging by the basal carbonyl groups in the present structure. Similar differences between bridged, semibridged, and nonbridged edges may be seen in such structures as $Fe_3(CO)_{12}$,[19] $[HFe_3(CO)_{11}]^-$,[20] or $[FeC(CO)_{16}]^{2-}$.[21]

The Carbonyl Groups. The triply bridging carbonyl group lies directly on the threefold axis. In addition three terminal carbonyl groups are bonded to each iron atom, symmetrically disposed about the threefold axis. This is the feature by which this structure differs from the earlier work,[6b] discussed more fully below. The disposition of the carbonyl groups in the disordered anion do not differ significantly from that of the ordered anion; see Tables IV and V for bond distances and angles.

The M–C–O angles for all but the triply bridging CO group are found in the range 169–178°. This is a significant departure from that in the previous structure in which semibridging CO groups are found in the basal plane: the semibridging CO groups were characterized by M–C–O angles in the range 151–158°.[6b,22,23] Also characteristic of these groups are the contacts between the carbon atom of a carbonyl group and the adjacent metal atom. In the present structure these are in the following ranges (Å): C–M(bonded) = 1.76–1.81 and C–M(adjacent) = 2.67–2.82. By contrast the ranges of the corresponding data in the previous structure are as follows (Å): C–M(bonded) = 1.66–1.85 and C–M(adjacent) = 2.24–2.33.[6b]

Although we see a distinct departure from the semibridging mode for the basal carbonyl groups, they are not purely terminal. Few tetrahedral metal carbonyls are known that possess all-terminal ligands. The best comparison we found is $H_4Re_4(CO)_{12}$ in which the M–C–O bond angles for CO groups fall in the range 171–178°, while the C–M contacts are (Å) C–M(bonded) = 1.85–1.96 and C–M(adjacent) = 3.44–3.58.[24] Scaled to iron these are 1.67–1.78 and 3.26–3.47 Å, respectively.

These three structures and that of a complex with symmetrically bridging carbonyl groups in the basal plane, e.g., $HFeCo_3(CO)_9(P(OMe)_3)_3$,[25] constitute members of a series defining a reaction coordinate like that discussed by Cotton for intramolecular tautomerism of $M_4(CO)_{12}$.[22,26] The earlier structure in fact was described by Cotton in just such a manner.[22] The relationship in the complexes discussed here is best illustrated by comparison of the projections of these structures onto the plane containing the basal triangle of metal atoms (see Figure 5).

The difference in conformation of the carbonyl ligands between the present and former crystals, which was ef-

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Table V. Interatomic Angles (deg) for Nongroup Atoms[a]

Fe1-Fe2-Fe1′	58.4 (1)	Fe1D-Fe2D-Fe1D′	59.1 (1)
-Fe2-C21	94.7 (3)	-Fe2D-C21D	93.9 (6)
-C11-O11	172.1 (9)	-C11D-O11D	169.6 (17)
-C12-O12	171.4 (9)	-C12D-O12D	172.2 (16)
-C13-O13	177.9 (10)	-C13D-O13D	176.2 (25)
-CFAC-Fe1′	76.9 (6)	-CBRD-Fe1D′	79.1 (11)
-CFAC-OFAC	134.1 (4)	-CBRD-OBRD	132.7 (8)
Fe2-Fe1-C11	93.4 (3)	Fe2D-Fe1D-C11D	96.4 (6)
-Fe1-C12	75.0 (3)	-Fe1D-C12D	77.4 (6)
-Fe1-C13	164.1 (3)	-Fe1D-C13D	166.2 (11)
-Fe1-CFAC	99.8 (4)	-Fe1D-CBRD	98.0 (8)
-C21-O21	177.6 (11)	-C21D-O21D	175.6 (22)
C11-Fe1-C12	101.1 (5)	C11D-Fe1D-C12D	101.6 (10)
-Fe1-C13	99.1 (5)	-Fe1D-C13D	96.6 (13)
-Fe1-CFAC	103.4 (3)	-Fe1D-CBRD	103.6 (6)
C12-Fe1-C13	92.8 (5)	C12D-Fe1D-C13D	95.5 (12)
-Fe1-CFAC	155.3 (3)	-Fe1D-CBRD	154.8 (6)
C13-Fe1-CFAC	86.9 (5)	C13D-Fe1D-CBRD	83.4 (11)
C21-Fe2-C21	97.2 (5)	C21D-Fe2D-C21D	98.6 (7)

[a] The numbers given in parentheses are the estimated standard deviations in the least significant digit(s).

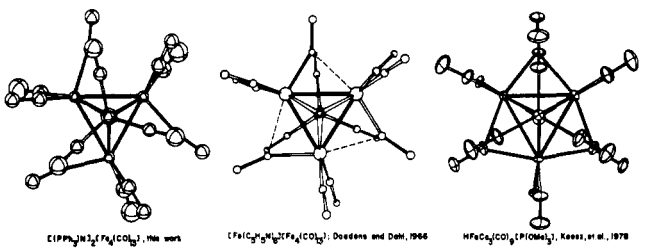

Figure 5. Comparison of carbonyl ligand configurations in $[PPN]_2[Fe_4(CO)_{13}]$, left (this work), $[Fe(L)_6][Fe_4(CO)_{13}]$,[6b] center, and $HFeCo_3(CO)_9L_3$,[25a] right.

fected merely by changing cations, deserves some comment. First, it is not likely that the energy difference between these two conformers is very large. We may anticipate a low-energy process equilibrating all but the triply bridging carbonyl groups. Such low barriers are not unique; one must go to −60 °C to obtain a limiting spectrum for $Co_4(CO)_{12}$.[27] Indeed in the classical example of $Fe_3(CO)_{12}$,[19,28] a limiting spectrum has never been frozen out; the energy difference between terminal and bridging configurations is estimated to be less than 5 kcal/mol.

Very minor effects could thus be responsible for the change associated with changing the cation. It is well-known that equilibria between terminal and bridging carbonyl groups can be affected by environment, such as complex formation with a Lewis acid[29,30] or merely changing the solvent polarity.[30b] As this environment places a stress on the complex, either by directly withdrawing negative charge or by breaking up ion pairs that could relieve the charge density, the carbonyl groups become bridging.[28-30] The effect of the cation (a Lewis acid) is undoubtedly predominant in this instance, though at present we have no means of quantifying it.

The Lattice of Carbonyl Ligands. As in the case of the earlier structure,[6b] the 12 nonbridging carbonyl groups lie approximately at the vertices of a polyhedron intermediate to an icosahedron (the form found for a purely bridging structure) and a cubooctahedron (the form found for a purely terminal structure).[4b,6b,31] This suggested to us that an overlay of our structure on that of Dahl and Doedens,[6b] as well as on that of the isoelectronic $HFeCo_3(CO)_9(P(OMe)_3)_3$[25] should show the carbonyl lattice to be essentially unaltered; the overlays are shown in Figure 6 and seem to bear this out to a satisfying degree.

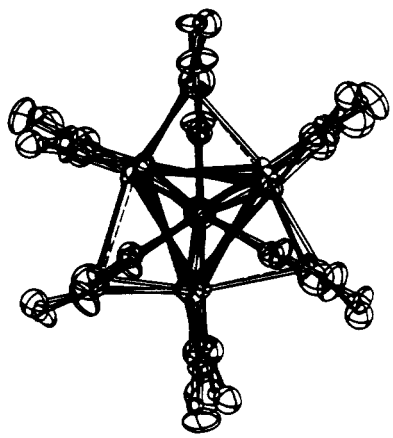

Figure 6. Overlay of structures of $[PPN]_2[Fe_4(CO)_{13}]$, $[Fe(L)_6][Fe_4(CO)_{13}]$, and $HFeCo_3(CO)_9L_3$.

Summary

The present study is the first elucidation of a metal carbonyl cluster whose ligand conformation in the solid state is altered by a change in counterion. This parallels observation of structural tautomers in the solid state for geometries where the barrier for exchange is low, such as in salts of the $[Ni(CN)_5]^-$ anion[32] or structural tautomers in binuclear complexes of cobalt.[33]

Registry No. 1, 26024-89-5; $[PPN]_2[Fe_4(CO)_{13}]$, 69665-30-1; $[Et_4N][HFe_3(CO)_{11}]$, 55976-22-2; [PPN][Cl], 21050-13-5.

Supplementary Material Available: Table IIb, thermal parameters for nongroup atoms, Table III, positional and thermal parameters for rigid-group atoms, a listing of calculated and observed structure factors, and Figures 2 and 4, stereoviews (18 pages). Ordering information is given on any current masthead page.

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