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Synthesis and Characterization of an Iron Carbonyl Cluster Containing Lead: Crystal and Molecular Structure of $[\text{Et}_4\text{N}]_2[\text{Pb}\{\text{Fe}(\text{CO})_4\}_2\{\text{Fe}_2(\text{CO})_8\}]$

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Lead(II) acetate and lead(II) chloride react with $\text{Fe}(\text{CO})_5$, dissolved in methanolic KOH (lead:iron ratio of 1.33:1) to produce $[\text{Et}_4\text{N}]_2[\text{Pb}\{\text{Fe}(\text{CO})_4\}_2\{\text{Fe}_2(\text{CO})_8\}]$ (85%) and metallic lead. The same cluster was obtained from the reaction of lead(II) acetate with $[\text{Et}_4\text{N}]_2[\text{Fe}_2(\text{CO})_8]$ in methanol. If the lead(II) chloride reaction is carried out with a larger proportion of iron, a different product is obtained which is proposed to be $[\text{Et}_4\text{N}]_2[\text{Pb}\{\text{Fe}(\text{CO})_4\}_2]$ on the basis of its elemental analysis and spectral characterization. This same complex along with $\text{Fe}(\text{CO})_5$ is obtained when $[\text{Et}_4\text{N}]_2[\text{Pb}\{\text{Fe}(\text{CO})_4\}_2\{\text{Fe}_2(\text{CO})_8\}]$ is treated with 1000 psi of CO in CH_2Cl_2 for several days. The complex $[\text{Et}_4\text{N}]_2[\text{Pb}\{\text{Fe}(\text{CO})_4\}_2\{\text{Fe}_2(\text{CO})_8\}]$ crystallizes in the noncentrosymmetric monoclinic space group Cc (C_2^2 ; No. 9) with $a = 11.614$ (5) Å, $b = 22.608$ (6) Å, $c = 17.082$ (6) Å, $\beta = 103.24$ (3)°, $V = 4366$ (2) Å³, and $Z = 4$. Single-crystal X-ray diffraction data (Mo K α ; $2\theta = 4-40^\circ$) were collected on a Syntex P2₁ four-circle diffractometer, and the structure was refined to $R_F = 6.7\%$ and $R_{wF} = 5.6\%$ for all 2182 independent reflections (none rejected) and $R_F = 4.4\%$ and $R_{wF} = 4.7\%$ for those 1501 reflections with $|F_o| > 6\sigma(|F_o|)$. The $[\text{Pb}\{\text{Fe}(\text{CO})_4\}_2\{\text{Fe}_2(\text{CO})_8\}]^{2-}$ dianion is centered by a lead atom that is in a highly distorted tetrahedral environment, being bonded to four iron atoms. Two of these iron atoms belong to discrete $\text{Fe}(\text{CO})_4$ units (Pb-Fe(1) = 2.651 (5) Å, Pb-Fe(2) = 2.659 (5) Å, Fe(1)-Pb-Fe(2) = 115.95 (14)°), while the other two belong to a $(\text{OC})_3\text{Fe}(\mu\text{-CO})_2\text{Fe}(\text{CO})_3$ moiety (Pb-Fe(3) = 2.832 (4) Å, Pb-Fe(4) = 2.823 (4) Å, Fe(3)-Fe(4) = 2.617 (5) Å, Fe(3)-Pb-Fe(4) = 55.13 (12)°).

Introduction

We have recently been exploring the effect of incorporating a large main-group atom into transition-metal carbonyl clusters. These studies, which have concentrated on bismuth to date, have produced a number of clusters including ones exhibiting traditional bonding patterns such as $\text{Bi}_2\text{Fe}_3(\text{CO})_9$ and $[\text{Et}_4\text{N}][\text{BiFe}_3(\text{CO})_{10}]$.² Treatment of $[\text{Et}_4\text{N}][\text{BiFe}_3(\text{CO})_{10}]$ with CO, however, led to an unusual hybrid cluster of formula $[\text{Et}_4\text{N}]_2[\text{Bi}_4\text{Fe}_4(\text{CO})_{13}]$.³ We have termed this cluster type a "Zintl-metal carbonylate" to emphasize its relationship to the main-group cluster Zintl ions. This paper represents our attempts to extend the Zintl-metal carbonylate analogy to the group-14 elements.

Well-characterized clusters containing a single group-14 heteroatom include $\text{Sn}[\text{Fe}_2(\text{CO})_8]_2$,⁴ from the reaction of pentacarbonyliron with tri-*n*-butyltin chloride, and $\text{Ge}[\text{Fe}_2(\text{CO})_8]_2$,⁵ which is formed from reactions involving iron carbonyls and vinylgermanes. The compound $\text{Si}[\text{Fe}_2(\text{CO})_8]_2$ has also been reported.⁶ Schmid and Etzrodt⁷ produced $\text{M}[\text{Co}(\text{CO})_4]_4$ ($\text{M} = \text{Pb}, \text{Sn}$) by reacting the metals with $\text{Co}_2(\text{CO})_8$, while tertiary arsine, phosphine, and phosphite substituted compounds of this type were produced by Hackett and Manning.⁸ Several oligomeric compounds containing group-14 metals have been reported.⁹ Most of the compounds containing only a single group-14 metal atom and more than one transition-metal atom are neutral species. We wish to report here the preparation, structure, and some of the reactivity of $[\text{Et}_4\text{N}]_2[\text{Pb}\{\text{Fe}(\text{CO})_4\}_2\{\text{Fe}_2(\text{CO})_8\}]$, a monomeric, anionic cluster containing lead.

Experimental Section

All solvents used were reagent grade and were prepared as follows: Methanol was distilled from magnesium methoxide, while methylene chloride and acetonitrile were distilled from phosphorus pentoxide.¹⁰ All solvents were bubbled with nitrogen for 30 min before use and stored under nitrogen. All manipulations were performed under an atmosphere of prepurified nitrogen using standard Schlenk methods. Infrared spectra were obtained on a Perkin-Elmer 1430 spectrophotometer. Carbon-13 NMR spectra were obtained on a JEOL FX90Q using samples prepared from $\text{Fe}(\text{CO})_5$ enriched to approximately 25% in ¹³CO. The compound $[\text{Et}_4\text{N}]_2[\text{Fe}_2(\text{CO})_8]$ was prepared by the method of Pettit and co-workers.¹¹ Lead(IV) acetate was prepared by the method of Bailar.¹² Elemental analyses were performed by NUS laboratories located in Houston, TX.

Synthesis of $[\text{Et}_4\text{N}]_2[\text{Pb}\{\text{Fe}(\text{CO})_4\}_2\{\text{Fe}_2(\text{CO})_8\}]$. Method I. Pentacarbonyliron (0.95 mL) was added to a degassed solution of 1.0 g of KOH dissolved in 20 mL of methanol in an ice bath. Next, 2.0 g of lead(II) acetate trihydrate dissolved in 10 mL of methanol was added dropwise through

a pressure-equalizing addition funnel. An immediate color change to dark brown occurred and within 10 min deposition of a metal mirror on the walls of the flask was noted. The solution was stirred for approximately 20 h and filtered through a medium frit. A concentrated solution of tetraethylammonium bromide in methanol was added slowly followed by slow addition of excess water, producing a precipitate of crude $[\text{Et}_4\text{N}]_2[\text{Pb}\{\text{Fe}(\text{CO})_4\}_2\{\text{Fe}_2(\text{CO})_8\}]$. The product was filtered and washed with water and then dried under vacuum overnight. The compound was purified by dissolution in dichloromethane, filtration, and precipitation with hexane. The final yield is 1.42 g (71% yield based on Fe). The product decomposes rapidly upon exposure to air and is soluble in methanol, methylene chloride, tetrahydrofuran, and acetonitrile but insoluble in hexane, toluene, and water. A sample for elemental analysis by atomic absorption was prepared by ashing 0.10 g of the compound, which was then boiled in 5 mL of concentrated HNO_3 , transferred to a volumetric flask, and diluted to 100 mL. Anal. Calcd Fe, 19.67; Pb, 18.2. Found: Fe, 18.22; Pb, 19.2. Analysis for iron by titrating with cerium(IV) after the technique of Fischer and Peters¹³ gave 18.8% iron. IR (CH_2Cl_2 , cm^{-1}): 2042 m, 1999 s, 1990 s, 1975 s, 1900 s, 1777 m, br. Single crystals suitable for X-ray diffraction were grown by cooling a concentrated solution of the product in methanol overnight. Qualitative analysis of the metal mirror¹⁴ was negative for iron but positive for lead.

Method II. The procedure was the same as outlined above, except 1.0 mL of $\text{Fe}(\text{CO})_5$ was employed and a slurry of lead(II) chloride in methanol was added in place of the lead(II) acetate solution. The color change and elemental lead precipitate were noted as before. Workup of the reaction proceeded as above to yield 1.82 g of $[\text{Et}_4\text{N}]_2[\text{Pb}\{\text{Fe}(\text{CO})_4\}_2\{\text{Fe}_2(\text{CO})_8\}]$ (85% based on Fe).

Method III. $[\text{Et}_4\text{N}]_2[\text{Fe}_2(\text{CO})_8]$ (0.3 g) was placed in a Schlenk flask containing 10 mL of methanol to which a pressure-equalizing dropping funnel was attached. A solution of 1.2 g of lead(II) acetate trihydrate was placed in the dropping funnel and degassed and then added dropwise

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Table I. Experimental Data for the X-ray Diffraction Study of $[\text{Et}_4\text{N}]_2[\text{PbFe}_4(\text{CO})_{16}]$

(A) Crystallographic Parameters at 24 °C (297 K)			
cryst syst	monoclinic	$V, \text{Å}^3$	4366 (2)
space group	$Cc[C_2^2; \text{No. } 9]$	formula	$\text{C}_{32}\text{H}_{40}\text{N}_2\text{O}_{16}\text{Fe}_4\text{Pb}$
$a, \text{Å}$	11.614 (5)	mol wt	1139.3
$b, \text{Å}$	22.608 (6)	Z	4
$c, \text{Å}$	17.082 (6)	$D(\text{calcd}), \text{g cm}^{-3}$	1.73
β, deg	103.24 (3)	$\mu(\text{Mo K}\alpha), \text{cm}^{-1}$	51.8

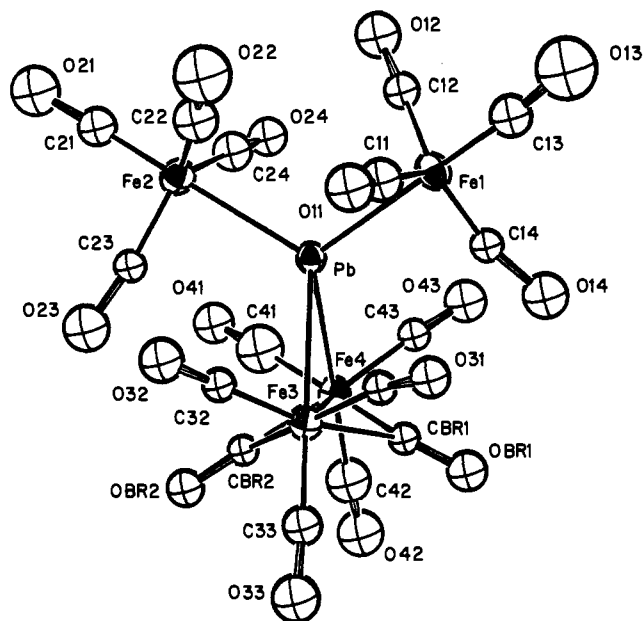
(B) Collection of X-Ray Diffraction Data	
diffractometer	Syntax P2 ₁
radiation	Mo K α ($\lambda = 0.710730 \text{ Å}$)
monochromator	pyrolytic graphite in equatorial mode; $2\theta(m) = 12.160^\circ$ for 002 refln; assumed 50% perfect/50% ideally mosaic for polarization cor
reflens measd	$h, \pm k, \pm l$ for $2\theta = 4.0\text{--}40.0^\circ$; 4504 reflens colld and merged to 2182 point-group independent data; none rejected
scan type	coupled $\theta(\text{crystal})\text{--}2\theta(\text{counter})$ from $[2\theta(\text{Mo K}\alpha_1) - 0.9]^\circ$ through $[2\theta(\text{Mo K}\alpha_2) + 0.9]^\circ$ at a scan rate of $3.0^\circ/\text{min}$ in 2θ
bkgd	measd with stationary counter and stationary crystal at each extreme of the 2θ scan; each for one-fourth total scan time
stds	3 approximately mutually orthogonal check reflens remeasd after each batch of 97 reflens; no significant fluctuation or decay obsd
abs	corrected empirically by interpolation (in 2θ and ϕ) between ψ scans of close-to-axial reflens

to the flask, in which the solution was stirred magnetically. An immediate color change to dark brown occurred, and the solution was filtered after about 1 h. The solvent was removed under vacuum and the solid dried overnight. The final yield was 0.152 g (53.0% based on Fe) of $[\text{Et}_4\text{N}]_2[\text{Pb}[\text{Fe}(\text{CO})_4]_2[\text{Fe}_2(\text{CO})_8]]$. The infrared spectrum of this compound upon dissolution in methylene chloride was identical with that of the product described in Method I.

Reaction of $[\text{Et}_4\text{N}]_2[\text{PbFe}_4(\text{CO})_{16}]$ with CO. $[\text{Et}_4\text{N}]_2[\text{PbFe}_4(\text{CO})_{16}]$ (0.60 g) was dissolved in 50 mL of CH_2Cl_2 and placed in a 300-mL Parr minireactor under a flush of nitrogen. The solution was purged with 500 psi of CO, pressurized to 1000 psi of CO, and stirred for 1 week. The solution was transferred rapidly in air to a Schlenk flask and filtered. The volatile components were removed under vacuum and collected in a liquid-nitrogen-cooled trap. The infrared spectrum and yellow color of this solution indicated that pentacarbonyliron was produced in the reaction. The infrared spectrum of the remaining solid redissolved in CH_2Cl_2 showed only two bands, at 1973 and 1895 cm^{-1} . The solid product is completely soluble in acetonitrile, sparingly soluble in methylene chloride and THF, but insoluble in hexane and diethyl ether. The reaction may be done in acetonitrile with similar results. The final yield was 0.11 g. A sample of this compound was prepared for atomic absorption analysis by ashing 0.10 g of the compound, boiling it for 30 min in concentrated HNO_3 , and diluting it to 100 mL with deionized water. Anal. Found: Fe, 15.8; Pb, 24.9. The ^{13}C NMR of this compound in Me_2SO showed a single peak at $\delta = 220$.

Reaction of PbCl_2 with $\text{Fe}(\text{CO})_5/\text{OH}^-$. Pentacarbonyliron (1.0 mL) was added to a solution of 1.0 g of potassium hydroxide in an ice bath. Lead(II) chloride (0.41 g) was added dropwise as a slurry to the reaction flask through a pressure-equalizing dropping funnel. A dark brown color appeared almost immediately. The reaction was allowed to proceed for 1 h. Slow addition of aqueous tetraethylammonium bromide caused precipitation of the product. The solvent was removed by filtration and the product washed several times with water and then dried under vacuum overnight. The total yield was 1.18 g, and the compound has an infrared spectrum in methylene chloride identical with that of the product of the CO reaction described above.

Collection of X-ray Diffraction Data for $[\text{Et}_4\text{N}]_2[\text{PbFe}_4(\text{CO})_{16}]$. A black opaque crystal of approximate dimensions $0.1 \times 0.2 \times 0.2 \text{ mm}^3$ was sealed into a thin-walled capillary under an argon atmosphere. The crystal was accurately aligned and centered on a Syntax P2₁ automated four-circle diffractometer. All subsequent setup operations (i.e., determination of the crystal's lattice parameters, its orientation matrix, and the Bravais lattice) and data collection (via a coupled $\theta(\text{crystal})\text{--}2\theta(\text{counter})$ scan routine) were performed as described previously.¹⁵ De-

**Figure 1.** ORTEP diagram showing the molecular geometry of $[\text{Pb}\{\text{Fe}(\text{CO})_4\}_2\{\text{Fe}_2(\text{CO})_8\}]^{2-}$.**Table II.** Intensity Statistics of $[\text{Et}_4\text{N}]_2[\text{PbFe}_4(\text{CO})_{16}]$

	obsd	ideal acentric	ideal centric
$\langle E \rangle$	0.889	0.886	0.798
$\langle E ^2 \rangle$	1.001	1.000	1.000
$\langle E^2 - 1 \rangle$	0.700	0.736	0.968
$ E > 1.0$	40.25%	36.79%	31.73%
$ E > 1.2$	26.27%	23.69%	23.01%
$ E > 1.4$	14.38%	14.09%	16.15%
$ E > 1.6$	6.82%	7.73%	10.96%
$ E > 1.8$	2.44%	3.92%	7.19%
$ E > 2.0$	0.68%	1.89%	4.55%
$ E > 2.5$	0.00%	0.19%	1.24%
$ E > 3.0$	0.00%	0.01%	0.27%

tails are provided in Table I. The final unit cell parameters were determined by a least-squares analysis of the setting angles of the unresolved Mo K α peaks of 25 reflections with $2\theta = 20\text{--}30^\circ$. All data were corrected for absorption and for Lorentz and polarization effects and were averaged and converted to an approximately absolute scale by means of a Wilson plot. No data were rejected. Any reflection with $I(\text{net}) < 0$ was assigned the value $|F_o| = 0$.

The systematic absences hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$ ($h0l$ for $h = 2n + 1, 0k0$ for $k = 2n + 1$) are consistent with either the noncentrosymmetric monoclinic space group Cc (C_2^2 ; No. 9) or the centrosymmetric monoclinic space group $C2/c$ (C_2h^2 ; No. 15). With $Z = 4$, the crystallographic asymmetric unit is one formula unit in Cc or half a formula unit (with crystallographic C_2 or C_i symmetry imposed upon the $[\text{PbFe}_4(\text{CO})_{16}]^{2-}$ ion) in $C2/c$. The distinction between these is not straightforward (see below).

Solution of the Crystal Structure. The structure was solved initially by using MULTAN and assuming the noncentrosymmetric space group Cc . The lead atom was assigned the coordinates $x = 1/2$ and $z = 1/4$; all other atoms were located from subsequent difference-Fourier syntheses. Full-matrix least-squares¹⁶ refinement led smoothly to convergence with $R_F = 6.7\%$,¹⁶ $R_{wF} = 5.6\%$, and $\text{GOF} = 0.94$ for all 2182 reflections (all hydrogen atoms in calculated positions with $\text{C-H} = 0.95 \text{ Å}$ ¹⁷ and only the five metal atoms refined anisotropically). For those 1872 reflections with $|F_o| > 3\sigma(|F_o|)$, discrepancy indices were $R_F = 5.0\%$ and $R_{wF} = 5.1\%$; for those 1501 reflections with $|F_o| > 6\sigma(|F_o|)$, $R_F = 4.4\%$, and $R_{wF} = 4.7\%$.

(16) Discrepancy indices are defined as follows:

$$R_F = [\sum (|F_o| - |F_c|) / \sum |F_o|] \times 100$$

$$R_{wF} = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} \times 100$$

$$\text{GOF} = [\sum w(|F_o| - |F_c|)^2 / (\text{NO} - \text{NV})]^{1/2}$$

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(15) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* 1977, 16, 265.

Since the crystal is chiral, we now reversed the polarity (i.e., all atomic coordinates inverted) and refined to convergence once again. The resulting discrepancy indices were substantially higher, with $R_F = 8.3\%$, $R_{wF} = 7.6\%$, and $GOF = 1.24$; these results were discarded and we reverted to our original (correct) choice of crystal chirality. The geometry of the $PbFe_4(CO)_{16}^{2-}$ ion thus derived is shown in Figure 1. A careful study of the structure, however, gave us some cause for alarm—the $[PbFe_4(CO)_{16}]^{2-}$ ion is really very close to being bisected by a C_2 axis at $x = 1/2$ and $z = 1/4$, which would be consistent with the higher space group $C2/c$. However, after a considerable amount of effort we have convinced ourselves that the true space group is indeed Cc , although it is quite close to the higher group $C2/c$. The following points should be noted.

(1) Intensity statistics are in keeping with the acentric case (see Table II).

(2) The midpoint of Fe(1)–Fe(2) is at 0.478 47, $-0.114\ 06$, 0.245 67 rather than at exactly $1/2, y, 1/4$; the y coordinates of these atoms also differ by about 0.03. Also, the midpoint of Fe(3)–Fe(4) is at 0.543 36, 0.055 90, 0.262 83 rather than at exactly $1/2, y, 1/4$.

(3) The change in R_F ($6.7 \rightarrow 8.3\%$), R_{wF} ($5.6 \rightarrow 7.6\%$), and GOF ($0.94 \rightarrow 1.24$) upon inversion of coordinates is consistent with that expected for an acentric structure, since the components of anomalous dispersion for lead are huge ($\Delta f' = -4.133\ e^-$ and $\Delta f'' = 10.102\ e^-$ for Mo $K\alpha$ radiation).

(4) Bond lengths determined for the “wrong” chirality of crystal are less internally consistent than for the “correct” chirality (e.g., Pb–Fe(1) = 2.727 Å and Pb–Fe(2) = 2.601 Å for the “wrong” chirality, as compared with values of 2.651 (5) and 2.659 (5) Å for the “correct” chirality).

(5) Attempts to solve the structure in space group $C2/c$ were unsuccessful. The lead atom was well-behaved, but each of the now two independent iron atoms was ill-behaved with an isotropic thermal parameter greater than $B = 15\ \text{Å}^2$; difference-Fourier maps were not readily interpretable.

(6) In space group Cc the structure refines smoothly with no asymmetry in “equivalent” bond lengths and no difficulty with matrix inversion.

In summary, the true space group appears to be the noncentrosymmetric space group Cc , even though the $[PbFe_4(CO)_{16}]^{2-}$ ion comes close to lying on a crystallographic C_2 axis, which would be consistent with the higher centrosymmetric space group $C2/c$.

All crystallographic calculations were performed on the SUNY—Buffalo Syntex XTL system.¹⁸ The analytical form of the scattering factor for the appropriate neutral atoms were used in calculating F_c values; these were corrected both for the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion for all non-hydrogen atoms.¹⁹

A final difference-Fourier synthesis was “clean”; the structure is thus both correct and complete. Final positional and thermal parameters are collected in Table III.

Results and Discussion

Mechanism for Formation of the Clusters. When lead(II) acetate or lead(II) chloride is allowed to react with $[HFe(CO)_4]^-$ generated from $Fe(CO)_5$ in basic media in a mole ratio of lead:iron of 1.33, $[Et_4N]_2[Pb\{Fe(CO)_4\}_2\{Fe_2(CO)_8\}]$ is formed and the majority of the lead is reduced to a metallic state that deposits as a mirror on the reaction flask. In turn, the lead atom in the cluster is formally in the +4 state and is coordinated formally by one $[Fe_2(CO)_8]^{2-}$ ion and two $[Fe(CO)_4]^{2-}$ ions. A phenomenon of this type has been previously reported in a lead-cobalt system, although no confirmation was made that the mirror was lead.⁸ An interesting observation is the production of the $PbFe_4^{2-}$ cluster directly from Pb^{2+} and two $[Fe_2(CO)_8]^{2-}$ anions. The charge balance is appropriate for the formation of the cluster, and no external redox is required, so lead metal is not produced. An internal redox process, however, seems apparent to generate a formal lead(IV) oxidation state by breaking a Fe–Fe bond of an original $Fe_2(CO)_8$ fragment. This overall structure has suggested a possible cyclic redox process involving reversible metal–metal bond breaking and formation, especially in light of the known neutral complexes $M[Fe_2(CO)_8]_2$ ($M = Si, Ge, Sn$).

In the case of lead(II) chloride, a different product is obtained when excess iron is employed, which we propose to be $[Et_4N]_2-$

Table III. Final Atomic Coordinates for $[Et_4N]_2[PbFe_4(CO)_{16}]$

atom	x	y	z	$B_{iso}, \text{Å}^2$
Pb	0.50000 (0)	-0.05273 (5)	0.25000 (0)	
Fe(1)	0.30113 (38)	-0.09867 (22)	0.27436 (25)	
Fe(2)	0.65581 (38)	-0.12944 (23)	0.21697 (24)	
Fe(3)	0.57392 (38)	0.05074 (20)	0.34115 (21)	
Fe(4)	0.51280 (38)	0.06106 (20)	0.18450 (21)	
C(11)	0.3866 (28)	-0.1139 (17)	0.3733 (19)	5.43 (75)
O(11)	0.4381 (21)	-0.1224 (11)	0.4409 (13)	6.48 (53)
C(12)	0.3081 (23)	-0.1529 (15)	0.2044 (15)	3.93 (58)
O(12)	0.3158 (19)	-0.1906 (12)	0.1542 (13)	6.66 (53)
C(13)	0.1777 (27)	-0.1268 (16)	0.2855 (17)	5.38 (70)
O(13)	0.0884 (29)	-0.1521 (19)	0.2983 (17)	11.69 (92)
C(14)	0.2505 (23)	-0.0334 (14)	0.2536 (15)	3.44 (54)
O(14)	0.1849 (19)	0.0146 (12)	0.2394 (12)	6.76 (53)
C(21)	0.7512 (26)	-0.1773 (16)	0.1938 (16)	4.92 (65)
O(21)	0.8253 (23)	-0.2112 (14)	0.1706 (15)	8.30 (63)
C(22)	0.6124 (31)	-0.1757 (19)	0.2843 (20)	6.38 (82)
O(22)	0.5890 (27)	-0.2103 (18)	0.3273 (16)	10.31 (85)
C(23)	0.7583 (24)	-0.0757 (15)	0.2443 (15)	3.27 (61)
O(23)	0.8448 (22)	-0.0404 (13)	0.2623 (13)	7.20 (55)
C(24)	0.5635 (30)	-0.1266 (17)	0.1160 (20)	5.34 (74)
O(24)	0.5029 (17)	-0.1245 (11)	0.0568 (12)	5.26 (47)
C(31)	0.4636 (23)	0.0283 (13)	0.3963 (14)	3.10 (55)
O(31)	0.3964 (17)	0.0218 (10)	0.4374 (11)	4.67 (45)
C(32)	0.6821 (23)	0.0018 (14)	0.3919 (14)	3.23 (52)
O(32)	0.7525 (18)	-0.0302 (12)	0.4271 (11)	5.76 (48)
C(33)	0.6185 (24)	0.1147 (16)	0.3929 (16)	4.58 (63)
O(33)	0.6559 (20)	0.1588 (13)	0.4290 (13)	6.93 (54)
C(41)	0.5999 (37)	0.0249 (24)	0.1237 (25)	8.1 (11)
O(41)	0.6559 (19)	0.0043 (11)	0.0800 (12)	5.85 (50)
C(42)	0.5228 (33)	0.1345 (21)	0.1488 (22)	7.03 (88)
O(42)	0.5240 (22)	0.1805 (14)	0.1282 (14)	7.66 (61)
C(43)	0.3705 (25)	0.0410 (14)	0.1202 (16)	3.54 (57)
O(43)	0.2791 (20)	0.0306 (12)	0.0795 (13)	6.28 (50)
C(BR1)	0.4365 (22)	0.0919 (13)	0.2624 (14)	3.08 (51)
O(BR1)	0.3606 (18)	0.1240 (10)	0.2716 (11)	5.18 (43)
C(BR2)	0.6686 (21)	0.0737 (13)	0.2658 (13)	2.91 (49)
O(BR2)	0.7654 (16)	0.0928 (10)	0.2635 (10)	4.48 (40)
N(5)	0.0461 (20)	0.1083 (13)	0.4749 (14)	5.13 (55)
C(51)	0.0018 (25)	0.0603 (15)	0.4100 (16)	4.79 (63)
C(52)	0.1832 (25)	0.1174 (16)	0.4828 (17)	4.78 (64)
C(53)	0.0436 (26)	0.0860 (15)	0.5608 (16)	4.58 (64)
C(54)	-0.0367 (34)	0.1596 (23)	0.4421 (22)	7.5 (10)
C(55)	0.0569 (33)	0.0025 (20)	0.4243 (20)	7.07 (84)
C(56)	0.2103 (28)	0.1397 (18)	0.4056 (18)	5.95 (76)
C(57)	-0.0779 (31)	0.0706 (21)	0.5704 (20)	7.28 (89)
C(58)	-0.0116 (78)	0.2056 (47)	0.4919 (54)	19.6 (30)
N(6)	-0.5141 (20)	-0.3182 (13)	0.0393 (13)	4.74 (55)
C(61)	-0.4174 (37)	-0.3482 (24)	0.0177 (25)	8.2 (10)
C(62)	-0.5347 (35)	-0.2621 (23)	-0.0105 (24)	8.2 (10)
C(63)	-0.6177 (31)	-0.3603 (19)	0.0245 (20)	6.71 (84)
C(64)	-0.4849 (34)	-0.3001 (23)	0.1250 (24)	8.1 (10)
C(65)	-0.3019 (35)	-0.3169 (22)	0.0246 (21)	8.1 (10)
C(66)	-0.5731 (31)	-0.2702 (19)	-0.0970 (20)	6.61 (84)
C(67)	-0.7283 (44)	-0.3363 (31)	0.0413 (27)	10.9 (14)
C(68)	-0.4702 (43)	-0.3482 (29)	0.1814 (29)	10.9 (13)

$[Pb\{Fe(CO)_4\}_2]$ on the basis of the following information. First, this compound is generated along with $Fe(CO)_5$ when $[Et_4N]_2-[PbFe_4(CO)_{16}]$ is treated with CO. The calculated analysis for the species $[Et_4N]_2[Pb\{Fe(CO)_4\}_2]$ is 13.8% Fe and 25.8% Pb, while the actual results of the analysis showed 15.8% Fe and 24.9% Pb (Fe:Pb = 2.2:1). The simple infrared spectrum is consistent with a product containing identical trigonal-bipyramidal $Fe(CO)_4$ groups as is the presence of only one peak in the ^{13}CO NMR spectrum since such units are known to be highly fluxional. It is probable that this compound is an intermediate in the reaction of lead(II) acetate with $[Fe(CO)_4]^{2-}$, although it has not been possible to isolate it from that reaction.

Analogous compounds of the type $[M\{Fe(CO)_4\}_2]^{2-}$ ($M = Zn, Cd, Hg$) have been reported.²⁰ These compounds are similar to the proposed structure in that they contain a post transition element as the central atom between two $Fe(CO)_4$ moieties. An

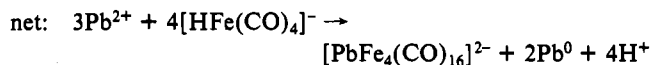
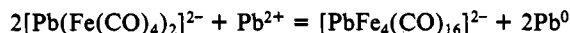
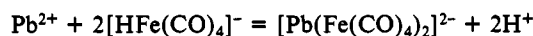
(18) *Syntex XTL Operations Manual*; 2nd ed.; Syntex Analytical Instruments: Cupertino, CA, 1976.

(19) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4, pp 99–101, 149–150.

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interesting feature of these compounds is that the tetracarbonyliron groups are distorted from an ideal trigonal-bipyramidal arrangement, with the distortion increasing as the size of the central atom decreases. The infrared spectra of these compounds in THF show a decrease in the number of clearly resolved bands as the metal size increases. Lead is a slightly larger element than mercury, so that the distortion may not be present and would account for the simpler infrared spectrum.

On the basis of the results obtained from the lead system, it appears that the reaction of lead(II) acetate with $[\text{HFe}(\text{CO})_4]^-$ in base proceeds as outlined.



The first step is proposed to be the formation of a $[\text{PbFe}_2]^{2-}$ intermediate, in which oxidation has not yet occurred. In agreement with this, the precipitate of metallic lead is not observed when an excess of iron is present. This step is followed by subsequent reactions in which the lead of the cluster is formally oxidized to Pb(IV) by external lead(II) that is reduced to Pb(0). Adequate lead is recovered to support this type of process. The stoichiometry of the reaction was varied and the reaction found to proceed to completion only if the requisite amount of lead(II) salt was present. If not, IR bands due to the $[\text{PbFe}_2]^{2-}$ intermediate persisted. When lead(II) acetate was used, it was not possible to observe the intermediate complex, which may be a function of the greater availability of lead in the more weakly bound acetate salt. The protons produced would be rapidly consumed in the basic media to form water.

Structural Discussion of the $\text{PbFe}_4(\text{CO})_{16}^{2-}$ Anion. The crystal contains well-separated, discrete $[\text{Et}_4\text{N}]^+$ and $[\text{PbFe}_4(\text{CO})_{16}]^{2-}$ ions; there are no unusually short interionic contacts. Interatomic distances and angles are collected in Tables IV and V, respectively. This anion is not the symmetrical $[\text{Pb}(\text{Fe}(\text{CO})_4)_4]^{2-}$ anion but is, instead, correctly represented as $[\text{Pb}(\text{Fe}(\text{CO})_4)_2(\text{Fe}_2(\text{CO})_8)]^{2-}$.

It can thus properly be termed a very distorted tetrahedral complex of Pb(IV) with two monodentate $[\text{Fe}(\text{CO})_4]^{2-}$ ligands (centered on Fe(1) and Fe(2)) and one bidentate $[\text{Fe}_2(\text{CO})_8]^{2-}$ ligand (centered by Fe(3) and Fe(4)). The two $[\text{Fe}(\text{CO})_4]^{2-}$ groups are linked to the Pb(IV) center via the equivalent bonds $\text{Pb}-\text{Fe}(1) = 2.651(5) \text{ \AA}$ and $\text{Pb}-\text{Fe}(2) = 2.659(5) \text{ \AA}$ and are separated by a slightly expanded tetrahedral angle of $115.95(14)^\circ$. The bidentate $[\text{Fe}_2(\text{CO})_8]^{2-}$ ion is linked to the Pb(IV) center with longer Pb-Fe bonds ($\text{Pb}-\text{Fe}(3) = 2.832(4) \text{ \AA}$ and $\text{Pb}-\text{Fe}(4) = 2.823(4) \text{ \AA}$) and an acute intermetallic angle of $\text{Fe}(3)-\text{Pb}-\text{Fe}(4) = 55.13(12)^\circ$. The extremely distorted tetrahedral environment of the center Pb(IV) atom is further defined by the monodentate-bidentate ligand angles of $\text{Fe}(1)-\text{Pb}-\text{Fe}(3) = 113.74(13)^\circ$, $\text{Fe}(1)-\text{Pb}-\text{Fe}(4) = 123.11(13)^\circ$, $\text{Fe}(2)-\text{Pb}-\text{Fe}(3) = 121.34(13)^\circ$, and $\text{Fe}(2)-\text{Pb}-\text{Fe}(4) = 114.22(13)^\circ$.

Atoms Fe(1) and Fe(2) each have a fairly regular trigonal-bipyramidal coordination environment with axial-axial angles being $\text{Pb}-\text{Fe}(1)-\text{C}(13) = 177.8(12)^\circ$ and $\text{Pb}-\text{Fe}(2)-\text{C}(21) = 178.5(11)^\circ$ and with $\text{Pb}-\text{Fe}-\text{CO}(\text{eq})$ angles ranging from $83.9(10)$ through $89.4(10)^\circ$.

The $[\text{Fe}_2(\text{CO})_8]^{2-}$ moiety has an $\text{Fe}(3)-\text{Fe}(4)$ bond length of $2.617(5) \text{ \AA}$; each iron atom is associated with three terminal carbonyl groups; the iron-iron bond is bridged by a Pb(IV) atom and two mutually compensating asymmetrically bridging carbonyl groups ($\text{Fe}(3)-\text{C}(\text{br}2) = 1.945(24) \text{ \AA}$, $\text{Fe}(3)-\text{C}(\text{br}1) = 2.059(26) \text{ \AA}$, $\text{Fe}(4)-\text{C}(\text{br}1) = 1.893(25) \text{ \AA}$, $\text{Fe}(4)-\text{C}(\text{br}2) = 2.034(24) \text{ \AA}$).

The geometry of the "Pb $\text{Fe}_2(\text{CO})_8$ " (I) moiety is closely related to that of $\text{Fe}_2(\text{CO})_9$ (II).²¹ However, the Fe-Fe distance of $2.617(5) \text{ \AA}$ in I is increased markedly relative to the Fe-Fe distance

Table IV. Interatomic Distances (\AA) (with Esd's) for $[\text{Et}_4\text{N}]_2[\text{PbFe}_4(\text{CO})_{16}]$

(A) Metal-Metal Bond Lengths			
Pb-Fe(1)	2.651 (5)	Pb-Fe(3)	2.832 (4)
Pb-Fe(2)	2.659 (5)	Pb-Fe(4)	2.823 (4)
Fe(3)-Fe(4)	2.617 (5)		
(B) Terminal Fe-CO Bond Lengths			
Fe(1)-C(11)	1.79 (3)	Fe(2)-C(21)	1.66 (3)
Fe(1)-C(12)	1.73 (3)	Fe(2)-C(22)	1.71 (4)
Fe(1)-C(13)	1.62 (3)	Fe(2)-C(23)	1.69 (3)
Fe(1)-C(14)	1.60 (3)	Fe(2)-C(24)	1.81 (3)
Fe(3)-C(31)	1.83 (3)	Fe(4)-C(41)	1.80 (5)
Fe(3)-C(32)	1.75 (3)	Fe(4)-C(42)	1.78 (5)
Fe(3)-C(33)	1.71 (3)	Fe(4)-C(43)	1.82 (3)
(C) Bridging Fe-CO Bond Lengths			
Fe(3)-C(br1)	2.059 (26)	Fe(4)-C(br1)	1.893 (25)
Fe(3)-C(br2)	1.945 (24)	Fe(4)-C(br2)	2.034 (24)
(D) Terminal and Bridging C-O Bond Lengths			
C(11)-O(11)	1.19 (4)	C(21)-O(21)	1.28 (4)
C(12)-O(12)	1.23 (4)	C(22)-O(22)	1.15 (5)
C(13)-O(13)	1.25 (5)	C(23)-O(23)	1.27 (4)
C(14)-O(14)	1.32 (4)	C(24)-O(24)	1.09 (4)
C(31)-O(31)	1.17 (3)	C(41)-O(41)	1.19 (5)
C(32)-O(32)	1.15 (4)	C(42)-O(42)	1.10 (6)
C(33)-O(33)	1.20 (4)	C(43)-O(43)	1.15 (4)
C(br1)-O(br1)	1.18 (4)	C(br2)-O(br2)	1.21 (3)
(E) N-C Distances in $[\text{Et}_4\text{N}]^+$ Cations			
N(5)-C(51)	1.55 (4)	N(6)-C(61)	1.43 (5)
N(5)-C(52)	1.58 (4)	N(6)-C(62)	1.52 (6)
N(5)-C(53)	1.56 (4)	N(6)-C(63)	1.51 (5)
N(5)-C(54)	1.53 (5)	N(6)-C(64)	1.48 (5)
(F) C-C Distances in $[\text{Et}_4\text{N}]^+$ Cations			
C(51)-C(55)	1.45 (6)	C(61)-C(65)	1.50 (6)
C(52)-C(56)	1.51 (4)	C(62)-C(66)	1.45 (5)
C(53)-C(57)	1.50 (5)	C(63)-C(67)	1.48 (7)
C(54)-C(58)	1.33 (11)	C(64)-C(68)	1.44 (8)

of $2.523(1) \text{ \AA}$ in $\text{Fe}_2(\text{CO})_9$; this presumably simply reflects the greater size of the Pb(IV) atom as compared to a carbon atom of a μ -CO ligand. It is interesting to note that a free $[\text{Fe}_2(\text{CO})_8]^{2-}$ ion has only terminal carbonyl ligands.²² All other features of the structure are normal.

The structure of $[\text{Et}_4\text{N}]_2[\text{PbFe}_4(\text{CO})_{16}]$ is consistent with the spectroscopic and analytical data obtained. The presence of an IR band at 1777 cm^{-1} in solution indicates that the bridging carbonyls are retained in solution. The average length in the C-O bonds in the "Pb $\text{Fe}_2(\text{CO})_8$ " moiety (1.195 \AA) is slightly greater than those in $\text{Fe}_2(\text{CO})_9$ (1.176 \AA).²³ This change in bond length could be due to the anionic nature of the lead cluster.

The compound $[\text{BiFe}_4(\text{CO})_{16}]^{3-}$ has been previously reported¹ and recently structurally characterized.²⁴ This compound contains no iron-iron bonds. Comparing the compound electronically to $[\text{PbFe}_4(\text{CO})_{16}]^{2-}$ and assuming the charges are distributed as in $[\text{Fe}_2(\text{CO})_8]^{2-}$, $[\text{Fe}(\text{CO})_4]^{2-}$, Pb^{4+} , and Bi^{5+} , we see that the lead complex has two fewer electrons than the bismuth cluster, as lead has one less electron than bismuth and the cluster charge is one less, so that the lead complex needs the iron-iron bond. Furthermore, the compounds $\text{Sn}[\text{Fe}_2(\text{CO})_8]_2^{4-}$ and $\text{Ge}[\text{Fe}_2(\text{CO})_8]_2^{5-}$ both neutral, differ electronically from the lead cluster by having two less electrons. Thus, these compounds need an additional iron-iron bond, and this is indeed the case in their crystal structures.

The iron-iron bond distance in $[\text{PbFe}_4(\text{CO})_{16}]^{2-}$ (2.62 \AA) is shorter than that of the iron-iron bonds in $\text{Sn}[\text{Fe}_2(\text{CO})_8]_2$ (2.87 \AA)⁴ and $\text{Ge}[\text{Fe}_2(\text{CO})_8]_2$ (2.82 \AA).⁵ This difference could be due to the presence of the bridging carbonyl groups in the lead com-

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Table V. Interatomic Angles (deg) for $[\text{Et}_4\text{N}]_2[\text{PbFe}_4(\text{CO})_{16}]$

(A) M-M-M Angles			
Pb-Fe(3)-Fe(4)	62.25 (13)	Pb-Fe(4)-Fe(3)	62.62 (13)
Fe(1)-Pb-Fe(2)	115.95 (14)	Fe(2)-Pb-Fe(3)	121.34 (13)
Fe(1)-Pb-Fe(3)	113.74 (13)	Fe(2)-Pb-Fe(4)	114.22 (13)
Fe(1)-Pb-Fe(4)	123.11 (13)	Fe(3)-Pb-Fe(4)	55.13 (12)
(B) M-M-CO Angles			
Pb-Fe(1)-C(11)	84.8 (11)	Pb-Fe(2)-C(21)	178.5 (11)
Pb-Fe(1)-C(12)	89.4 (10)	Pb-Fe(2)-C(22)	86.3 (13)
Pb-Fe(1)-C(13)	177.8 (12)	Pb-Fe(2)-C(23)	86.8 (10)
Pb-Fe(1)-C(14)	83.9 (10)	Pb-Fe(2)-C(24)	84.0 (11)
Pb-Fe(3)-C(31)	83.9 (8)	Pb-Fe(4)-C(41)	84.4 (15)
Pb-Fe(3)-C(32)	81.0 (9)	Pb-Fe(4)-C(42)	176.8 (14)
Pb-Fe(3)-C(33)	177.8 (11)	Pb-Fe(4)-C(43)	83.6 (9)
Pb-Fe(3)-C(br1)	85.6 (7)	Pb-Fe(4)-C(br1)	89.0 (8)
Pb-Fe(3)-C(br2)	90.2 (8)	Pb-Fe(4)-C(br2)	88.7 (7)
Fe(4)-Fe(3)-C(31)	119.6 (9)	Fe(3)-Fe(4)-C(41)	119.5 (15)
Fe(4)-Fe(3)-C(32)	124.0 (9)	Fe(3)-Fe(4)-C(42)	114.2 (14)
Fe(4)-Fe(3)-C(33)	115.6 (11)	Fe(3)-Fe(4)-C(43)	126.2 (10)
Fe(4)-Fe(3)-C(br1)	45.9 (7)	Fe(3)-Fe(4)-C(br1)	51.3 (8)
Fe(4)-Fe(3)-C(br2)	50.4 (8)	Fe(3)-Fe(4)-C(br2)	47.4 (7)
(C) C-Fe-C Angles			
C(11)-Fe(1)-C(12)	114.5 (15)	C(21)-Fe(2)-C(22)	94.4 (17)
C(11)-Fe(1)-C(13)	97.4 (16)	C(21)-Fe(2)-C(23)	93.9 (15)
C(11)-Fe(1)-C(14)	119.0 (15)	C(21)-Fe(2)-C(24)	94.5 (16)
C(12)-Fe(1)-C(13)	89.2 (15)	C(22)-Fe(2)-C(23)	123.3 (16)
C(12)-Fe(1)-C(14)	125.1 (14)	C(22)-Fe(2)-C(24)	117.4 (17)
C(13)-Fe(1)-C(14)	95.6 (16)	C(23)-Fe(2)-C(24)	117.6 (15)
C(31)-Fe(3)-C(32)	94.5 (13)	C(41)-Fe(4)-C(42)	97.8 (20)
C(31)-Fe(3)-C(33)	97.7 (14)	C(41)-Fe(4)-C(43)	95.2 (18)
C(31)-Fe(3)-C(br1)	86.1 (11)	C(41)-Fe(4)-C(br1)	170.7 (17)
C(31)-Fe(3)-C(br2)	169.9 (12)	C(41)-Fe(4)-C(br2)	85.9 (17)
C(32)-Fe(3)-C(33)	100.4 (14)	C(42)-Fe(4)-C(43)	98.5 (16)
C(32)-Fe(3)-C(br1)	166.4 (12)	C(42)-Fe(4)-C(br1)	88.5 (16)
C(32)-Fe(3)-C(br2)	92.7 (12)	C(42)-Fe(4)-C(br2)	89.1 (15)
C(33)-Fe(3)-C(br1)	93.0 (13)	C(43)-Fe(4)-C(br1)	90.6 (12)
C(33)-Fe(3)-C(br2)	88.0 (13)	C(43)-Fe(4)-C(br2)	172.1 (12)
C(br1)-Fe(3)-C(br2)	85.3 (11)	C(br1)-Fe(4)-C(br2)	87.4 (11)
(D) Fe-C-Fe Angles			
Fe(3)-C(br1)-Fe(4)	82.8 (10)	Fe(3)-C(br2)-Fe(4)	82.2 (10)
(E) Fe-C-O Angles			
Fe(1)-C(11)-O(11)	176.0 (30)	Fe(2)-C(21)-O(21)	174.8 (28)
Fe(1)-C(12)-O(12)	178.2 (25)	Fe(2)-C(22)-O(22)	174.2 (36)
Fe(1)-C(13)-O(13)	174.5 (31)	Fe(2)-C(23)-O(23)	172.3 (26)
Fe(1)-C(14)-O(14)	166.0 (25)	Fe(2)-C(24)-O(24)	176.3 (32)
Fe(3)-C(31)-O(31)	170.0 (24)	Fe(4)-C(41)-O(41)	175.5 (39)
Fe(3)-C(32)-O(32)	178.3 (25)	Fe(4)-C(42)-O(42)	176.4 (38)
Fe(3)-C(33)-O(33)	176.5 (28)	Fe(4)-C(43)-O(43)	177.2 (27)
Fe(3)-C(br1)-O(br1)	133.1 (21)	Fe(4)-C(br1)-O(br1)	143.6 (22)
Fe(3)-C(br2)-O(br2)	141.8 (20)	Fe(4)-C(br2)-O(br2)	135.6 (20)
(F) C-N-C Angles in $[\text{Et}_4\text{N}]^+$ Cations			
C(51)-N(5)-C(52)	108.4 (22)	C(61)-N(6)-C(62)	106.6 (30)
C(51)-N(5)-C(53)	111.9 (22)	C(61)-N(6)-C(63)	107.4 (28)
C(51)-N(5)-C(54)	101.0 (25)	C(61)-N(6)-C(64)	111.7 (30)
C(52)-N(5)-C(53)	101.4 (22)	C(62)-N(6)-C(63)	114.7 (27)
C(52)-N(5)-C(54)	118.0 (26)	C(62)-N(6)-C(64)	107.2 (29)
C(53)-N(5)-C(54)	116.4 (26)	C(63)-N(6)-C(64)	109.4 (27)
(G) N-C-C Angles in $[\text{Et}_4\text{N}]^+$ Cations			
N(5)-C(51)-C(55)	116.7 (27)	N(6)-C(61)-C(65)	119.8 (37)
N(5)-C(52)-C(56)	112.1 (25)	N(6)-C(62)-C(66)	116.0 (34)
N(5)-C(53)-C(57)	113.5 (26)	N(6)-C(63)-C(67)	115.4 (34)
N(5)-C(54)-C(58)	109.3 (51)	N(6)-C(64)-C(68)	114.8 (38)

plex. The average length of the lead-iron bonds in this compound (2.74 Å) compare well with the value of 2.71 Å reported for $\text{Me}_2\text{Pb}[\text{Fe}(\text{CO})_2\text{Cp}]_2$.²⁵ We also find that the iron(3)-lead-iron(4) bond angle is an extremely acute 55°, as stated previously. This is in comparison to values of 72° for $\text{Sn}[\text{Fe}_2(\text{CO})_8]_2$ and 69° for $\text{Ge}[\text{Fe}_2(\text{CO})_8]_2$. This is less than the average angle at the bismuth atom in $[\text{BiFe}_3(\text{CO})_{10}]^-$ of 59.8°.² In this compound a

bismuth atom caps a triangle of iron atoms, with three iron-iron bonds present. The structure of $[\text{BiFe}_4(\text{CO})_{16}]^{3-}$ is basically a slightly distorted tetrahedron by comparison.²⁴ The strain implied by the geometry of the PbFe_2 triangle may be in part responsible for the cluster's reactivity with CO to eliminate $\text{Fe}(\text{CO})_5$.

Final Remarks

Lead(II) acetate reacts with $[\text{HFe}(\text{CO})_4]^-$ in alkaline medium to produce metallic lead and $[\text{PbFe}_4(\text{CO})_{16}]^{2-}$. This compound differs from the previously described compound $[\text{Bi}(\text{Fe}(\text{CO})_4)_4]^{3-}$ in that it contains an iron-iron bond as well as bridging carbonyl

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groups. X-ray crystallography indicates that the compound displays a severely distorted and strained tetrahedral geometry about lead, which is supported by the fact that the compound reacts with CO to eliminate $\text{Fe}(\text{CO})_5$. Efforts are continuing to establish the structure of the $[\text{PbFe}_2]^{2-}$ intermediate.

The original goal of producing group-14 Zintl-metal carbonylates has unfortunately not yet been achieved by the same methodology applicable to the bismuth system. The $[\text{PbFe}_4(\text{CO})_{16}]^{2-}$ cluster, however, does possess some interesting features. First, it represents a clean, high-yield synthesis, which is rare for clusters of this type. Second, it has sites of potential reactivity in the bridging carbonyls and in the two terminal $\text{Fe}(\text{CO})_4$ units. These latter metal sites could act as centers for addition of further main-group fragments, which could ultimately give access to the desired Zintl-type clusters. The cluster also possesses potential for undergoing reversible redox cycles involving the formation/breaking of metal-metal bonds as implicated by the known

structures of neutral $\text{M}[\text{Fe}_2(\text{CO})_8]_2$ ($\text{M} = \text{Sn}, \text{Ge}$). In keeping with this idea, the cluster is found to be oxidized by a variety of reagents including Cu^+ , H^+ , and CH_3^+ . These results and an electrochemical study of the molecule will be presented elsewhere.

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Supplementary Material Available: Tables of hydrogen atom positions and anisotropic thermal parameters as well as a stereoview of $[\text{PbFe}_4(\text{CO})_{16}]^{2-}$ (2 pages). According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (11 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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Nitrosyl Complexes of Technetium: Synthesis and Characterization of $[\text{Tc}^{\text{I}}(\text{NO})(\text{CNCMe}_3)_5](\text{PF}_6)_2$ and $\text{Tc}(\text{NO})\text{Br}_2(\text{CNCMe}_3)_3$ and the Crystal Structure of $\text{Tc}(\text{NO})\text{Br}_2(\text{CNCMe}_3)_3$

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Reaction of $[\text{Tc}^{\text{I}}(\text{CNCMe}_3)_6]^+$ with NOPF_6 or with nitric acid in glacial acetic acid leads to the formation of $[\text{Tc}^{\text{I}}(\text{NO})(\text{CNCMe}_3)_5](\text{PF}_6)_2$ in high yield. The complex has been characterized by elemental analysis, infrared and ^1H NMR spectroscopy, cyclic voltammetry, and fast-atom-bombardment mass spectrometry. Attempts to form the manganese nitrosyl congener by reaction of $[\text{Mn}(\text{CNCMe}_3)_6]^+$ with NOPF_6 or NO yielded only the oxidation product $[\text{Mn}(\text{CNCMe}_3)_6]^{2+}$. Reaction of *tert*-butyl isocyanide with $[\text{Tc}(\text{NO})\text{Br}_4]^-$ did not yield $[\text{Tc}(\text{NO})(\text{CNCMe}_3)_5]^{2+}$; instead, $\text{Tc}^{\text{I}}(\text{NO})\text{Br}_2(\text{CNCMe}_3)_3$ was isolated in 30% yield. A crystal structure of this material reveals an approximately octahedral array of ligands. The three isocyanide ligands are meridional with respect to one another and one isocyanide is *trans* to the nearly linear NO^+ ligand. Crystal data are as follows: space group $P2_1cn$, with $a = 10.985$ (2) Å, $b = 14.250$ (2) Å, $c = 14.677$ (2) Å, $V = 2297.5$ Å³, $\rho(\text{calcd}) = 1.556$ g cm⁻³ for $Z = 4$ and mol wt 538.29. Final $R_1 = 0.060$ and $R_2 = 0.048$.

Introduction

Several preparations for the manganese isonitrile dications $[\text{Mn}(\text{CNR})_6]^{2+}$ ($\text{R} = \text{alkyl}, \text{aryl}$) have been reported in the literature. These compounds can be prepared by the oxidation of the corresponding monocations $[\text{Mn}(\text{CNR})_6]^+$ with nitric acid in glacial acetic acid^{1,2} or bromine in ethanol³ and can also be electrochemically generated.⁴ Cyclic voltammetry of the Tc(I)-isonitrile complex $[\text{Tc}(\text{CNCMe}_3)_6]^+$ in acetonitrile reveals a quasi-reversible one-electron-oxidation wave at +0.83 V vs. SCE, indicating that the corresponding Tc(II) complex $[\text{Tc}(\text{CNCMe}_3)_6]^{2+}$ is potentially accessible under highly oxidizing conditions. During our attempts^{6,7} at the preparation of $[\text{Tc}(\text{CNCMe}_3)_6]^{2+}$, several routes used to prepare $[\text{Mn}(\text{CNCMe}_3)_6]^{2+}$ were explored. However, in most instances where a potential NO^+ source was used as the "oxidant", the new complex $[\text{Tc}^{\text{I}}(\text{NO})(\text{CNCMe}_3)_5]^{2+}$ was the major product isolated. The synthesis and characterization of this new nitrosyl complex of technetium are reported in this paper and the differences in reactivity of $[\text{Mn}(\text{CNCMe}_3)_6]^+$ and $[\text{Tc}(\text{CNCMe}_3)_6]^+$ are discussed.

An alternative synthesis of $[\text{Tc}(\text{NO})(\text{CNCMe}_3)_5]^{2+}$ via the reaction of *tert*-butyl isocyanide with labile $\text{TBA}[\text{Tc}^{\text{II}}(\text{NO})\text{Br}_4]^\ddagger$ was attempted. However, only two of the four halides were displaced in this reaction. The resulting Tc(I) complex, $\text{Tc}(\text{NO})\text{Br}_2(\text{CNCMe}_3)_3$ was crystallographically characterized to determine the disposition of the isonitrile ligands in the molecule.

The synthesis, characterization, and crystal structure of this new compound are reported here.

Experimental Section

Technetium, as $\text{NH}_4^{99}\text{TcO}_4$ in aqueous solution, was obtained as a gift from NEN Products/DuPont, Billerica, MA. ^{99}Tc is a weak β -emitter (0.29 keV, half-life 2.12×10^5 years); therefore, all manipulations were carried out in laboratories approved for the use of low-level radioactivity, following precautions detailed elsewhere.⁹ The complex $[\text{Tc}(\text{CNCMe}_3)_6]^+$ was prepared from TcO_4^- as either the chloride or PF_6^- salt, using the procedure of Abrams et al.;⁵ $\text{TBA}[\text{TcNOBr}_4]$ was pre-

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