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Contribution from the Departments of Chemistry, Rice University, Houston, Texas 77251, The University of Otago, Dunedin, New Zealand, and The State University of New York at Buffalo, Buffalo, New York 14214

Transformations in the Bismuth-Iron Carbonyl Cluster System: Importance of Oxidation/Reduction Reactions. Crystal Structures of $[Me_4N]_3[Bi_2Fe_4(CO)_{13}]Cl$ and $[Et_4N][Bi_2Fe_2Co(CO)_{10}]$

Kenton H. Whitmire,*† Minghuey Shieh,† Craig B. Lagrone,† Brian H. Robinson,‡
Melvyn Rowen Churchill,*§ James C. Fettinger,§ and Ronald F. See§

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The complex anion $[Bi\{Fe(CO)_4\}_4]^{3-}$ reacts instantaneously with $BiCl_3$ in CH_3CN to yield an unknown intermediate that is converted upon refluxing into a mixture of $[BiFe_3(CO)_{10}]^-$, $[Bi_2Fe_4(CO)_{13}]^{2-}$, and $[Bi_4Fe_4(CO)_{13}]^{2-}$. The cluster anion $[Bi_2Fe_4(CO)_{13}]^{2-}$, $[\mathbf{1}]^{2-}$, isolated in 85% yield as the $[Et_4N]^+$ salt from the reaction of $Bi_2Fe_3(CO)_9$ with $[Fe(CO)_4]^{2-}$ reacts with CO in CH_2Cl_2 to yield $[Bi_4Fe_4(CO)_{13}]^{2-}$ and $Fe(CO)_5$. The $[Et_4N]^+$ or Na^+ salt of $[\mathbf{1}]^{2-}$ reacts with $[Cu(CH_3CN)_4][BF_4]$ in CH_2Cl_2 to produce $Bi_2Fe_3(CO)_9$, $Fe(CO)_5$, and $Fe_3(CO)_{12}$. This methodology can be utilized to generate $Bi_2Fe_3(CO)_9$ in high yield by using $[Bi\{Fe(CO)_4\}_4]^{3-}$ as the starting material or in lower yields from the reaction of $[BiFe_3(CO)_{10}]^-$ with $[Cu(CH_3CN)_4][BF_4]$. Reaction of $Bi_2Fe_3(CO)_9$ with $[Co(CO)_4]^-$ yields the cluster anion $[Bi_2Fe_2Co(CO)_{10}]^-$, $[\mathbf{2}]^-$, in which a Bi-Bi bond is formed with elimination of an iron vertex. The $Bi_2Fe_3(CO)_9$ cluster is readily reduced electrochemically ($E_{1/2} = -0.39$ V) or chemically with Na/Hg, yielding sequentially $[Bi_2Fe_3(CO)_9]^-$ and $[Bi_2Fe_3(CO)_9]^{2-}$. The complexes $[Me_4N]_2[\mathbf{1}]\cdot[Me_4N]Cl$ and $[Et_4N][\mathbf{2}]$ have been characterized by X-ray crystallography. The former cocrystallizes with one molecule of $[Me_4N]Cl$ in the centrosymmetric triclinic space group $P\bar{1}$ with $a = 12.642$ (3) Å, $b = 13.215$ (3) Å, $c = 13.589$ (5) Å, $\alpha = 87.343$ (27)°, $\beta = 71.132$ (24)°, $\gamma = 75.592$ (20)°, $V = 2079.3$ (11) Å^3, and $Z = 2$. The structure was refined to $R_F = 6.1\%$ for all 5467 reflections ($R_F = 4.4\%$ for those 4226 reflections with $|F_o| > 6.0\sigma(|F_o|)$). The nucleus of the dianion consists of a square-pyramidal Bi_2Fe_3 cluster (with an apical Fe and trans Bi atoms) with an additional Fe atom bonded to a Bi atom; the pendant Fe atom is linked to four terminal carbonyl ligands, while the other three Fe atoms each bear three such ligands. Intermetallic distances are as follows: Bi···Bi = 3.398 (1), Bi-Fe = 2.592 (2)-2.687 (2), and Fe-Fe = 2.796 (2)-2.808 (2) Å. The compound $[Et_4N][\mathbf{2}]$ crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with $a = 10.205$ (4) Å, $b = 11.250$ (8) Å, $c = 13.125$ (6) Å, $\alpha = 70.30$ (5)°, $\beta = 76.94$ (3)°, $\gamma = 76.89$ (5)°, $V = 1363.1$ (14) Å^3, and $Z = 2$. Diffraction data (Mo K$\bar{\alpha}$, $2\theta = 4-45°$) were collected on a Syntex $P2_1$ four-circle diffractometer, and the structure was refined to $R_F = 8.3\%$ for 2492 reflections with $|F_o| > 3\sigma(|F_o|)$ ($R_F = 6.4\%$ for those 1998 reflections with $|F_o| > 6\sigma(|F_o|)$). The anionic nucleus consists of a tetrahedral Bi_2Fe_2 cluster in which a Co atom bridges the Bi-Bi bond; each Fe atom bears three terminal carbonyl ligands, while the Co is associated with four. Intermetallic distances are as follows: Bi-Bi = 3.092 (2), Bi-Fe = 2.669 (5)-2.693 (5), Bi-Co = 2.868 (5)-2.894 (5), and Fe-Fe = 2.682 (7) Å.

Introduction

From the standpoint of cluster chemistry, bismuth is a very interesting element that forms a variety of cluster cations and anions and for this reason has even been called "the wonder metal".[1] It is, therefore, reasonable that the incorporation of bismuth into transition-metal clusters would produce some unprecedented results. Before our work on iron-bismuth clusters, only three metal carbonyl compounds containing bismuth had been structurally characterized. These included $Bi\{Co(CO)_4\}_3$,[2] $BiIr_3(CO)_9$,[3] and $Bi_2\{W(CO)_5\}_3$.[4] One of the striking features of bismuth is its size, which should have a profound influence on the chemistry of these complexes. Schmid has discussed this steric effect[5] and predicted that the heavier main-group elements would not form closo clusters with the smaller transition metals. For example, $Bi\{Co(CO)_4\}_3$ adopts an open BiX_3-type structure, which could not be induced to form metal-metal bonds as happened easily in the case of $BiIr_3(CO)_9$. Recently, however, we have shown that this steric argument is not completely valid by isolating and characterizing a series of closo $BiFe_3$ clusters that include $[BiFe_3(CO)_{10}]^-$,[6] $Bi_2Fe_3(CO)_9$,[7] $H_3BiFe_3(CO)_9$,[8] and $BiFe_3(CO)_9(COCH_3)$.[8] While the Fe-Fe bonds are long in these molecules, they obviously are not impossible to create, nor are the compounds exceptionally unstable. At the same time the chemistry of the iron-bismuth system is not restricted to the closo geometry as evidenced by the synthesis and characterization[9] of $[Bi\{Fe(CO)_4\}_4]^{3-}$, which adopts an open structure similar to $Bi\{Co(CO)_4\}_3$.

Some bismuth-transition-metal clusters with uncommon bonding patterns have been observed. The compound $Bi_2\{W(CO)_5\}_3$ has already been mentioned and is notable for the short Bi-Bi distance, which is proposed to be a triple bond bridged by three $W(CO)_5$ units, although no Bi-Bi interaction is required by electron-counting considerations. It should be noted that arsenic and antimony form similar $M_2\{W(CO)_5\}_3$ complexes with very short M-M distances.[10] More recently, we have reported the synthesis and structure of the Zintl-metal carbonylate anion $[Bi_4Fe_4(CO)_{13}]^{2-}$, which is based on a tetrahedral array of bismuth atoms capped on three faces by $Fe(CO)_3$ groups with an additional $Fe(CO)_4$ unit attached to the unique bismuth atom.[11] The structure is related to that of cage compounds such as As_7^{3-} and Sb_7^{3-}.[12]

The work described in this paper began as an attempt to create a clean, high-yield synthesis of $Bi_2Fe_3(CO)_9$, which was previously available only from a slow, tedious, low-yield reaction. Our experiments with this compound suggested that it might be a very useful molecule for synthesizing a variety of other cluster materials.[13] Initially, it was thought that reaction of $[Bi\{Fe(CO)_4\}_4]^{3-}$ and $BiCl_3$ would achieve this goal. While we have ultimately developed the desired synthesis, the course of the reaction is not straightforward and unexpected oxidation/reduction chemistry

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† Rice University.
‡ The University of Otago.
§ The State University of New York at Buffalo.

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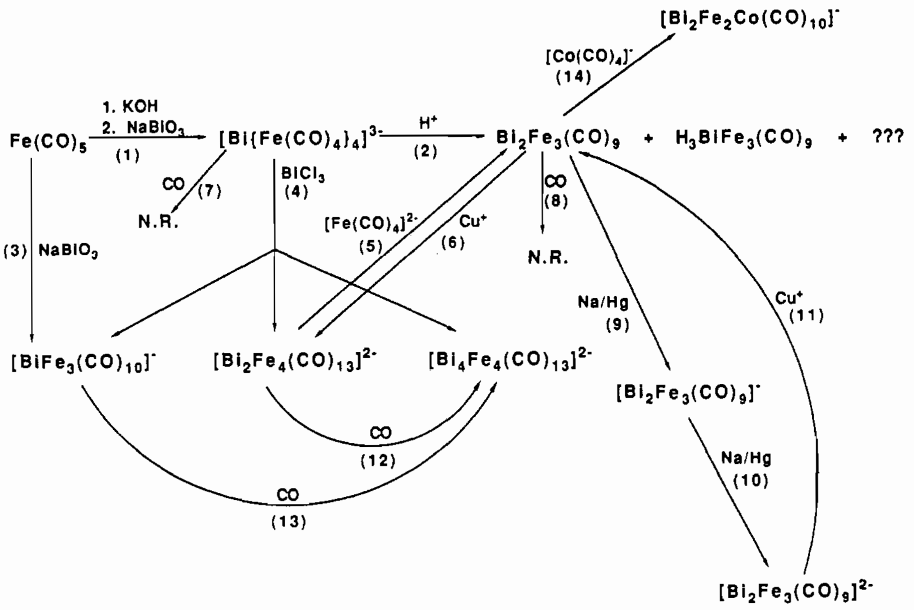
Scheme I



is involved, and so an electrochemical study of the various Bi–Fe carbonyls was undertaken. The chemical transformations reported here are compiled in Scheme I.

Experimental Section

All operations were carried out under air-free nitrogen by using standard Schlenk techniques. Solvents were purified by distillation from standard drying agents and stored under nitrogen: CH_2Cl_2 (P_2O_5), THF (Na/benzophenone), MeOH (Mg/I_2), CH_3CN (CaH_2), hexane (CaH_2). $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$[6,9] and $[Cu(CH_3CN)_4][BF_4]$[14] were synthesized by literature methods. Infrared spectra were obtained on a Perkin-Elmer 1430 spectrophotometer. Elemental analyses were performed by Galbraith Analytical Laboratories, Knoxville, TN.

Reaction of $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ with $BiCl_3$ (1:1). To a mixture of 1.28 g of $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ (1.01 mmol) and 0.32 g of $BiCl_3$ (1.01 mmol) was added 30 mL of CH_3CN. The solution turned immediately from green to brown, after which it was heated to reflux and stirred overnight. The solution was then cooled and the solvent removed under vacuum. The black residue was extracted with toluene and diethyl ether. In these solutions a trace amount of $[BiFe_3(CO)_{10}]^-$ was detected by infrared spectroscopy. The residue was then treated with 20 mL of CH_2Cl_2; the mixture was filtered and the solvent removed under vacuum and washed several times with diethyl ether, yielding 0.49 g of pure $[Et_4N]_2[Bi_2Fe_4(CO)_{13}]$, $[Et_4N]_2[\mathbf{1}]$ (0.39 mmol, 77% based on a 1:2 ratio of $[\mathbf{1}]^{2-}$:$[Bi\{Fe(CO)_4\}_4]^{3-}$). IR (CH_2Cl_2, ν_{CO}): 2020 m, 2010 m, 1978 s, 1959 vs, 1936 s, 1905 m, br cm^{-1}. Anal. Calcd for $C_{29}H_{40}N_2O_{13}Bi_2Fe_4$: Fe, 17.64; Bi, 33.01. Found: Fe, 16.39; Bi, 31.30. The residue was washed with CH_2Cl_2 several times and then dissolved in acetone and filtered. Removal of the solvent gave 0.15 g (0.089 mmol) of the previously known $[Et_4N]_2[Bi_4Fe_4(CO)_{13}]$, which is 18% on the basis of total amount of bismuth available in the reaction. IR (acetone, ν_{CO}): 2010 m, 1960 s, 1905 sh, 1898 w, 1895 w cm^{-1}.

Reaction of $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ with $BiCl_3$ (2:1). A solution of 0.070 g of $BiCl_3$ (0.22 mmol) mixed with 0.57 g of $[Et_4N]_3[BiFe_4(CO)_{16}]$ (0.45 mmol) in 25 mL of CH_3CN was stirred and refluxed for 2 days, after which the solvent was removed under vacuum and the separation performed as for the 1:1 reaction, yielding 0.37 g of pure Et_4N^+ salt of $[\mathbf{1}]^{2-}$ from the CH_2Cl_2 extract.

Reaction of $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ with $BiCl_3$ (1:1) in the Presence of CH_2Cl_2. A solution of 0.055 g of $BiCl_3$ (0.17 mmol) and 0.43 g of $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ (0.34 mmol) in 20 mL of CH_3CN was heated to reflux. After about 10 min, 3.5 mL of CH_2Cl_2 was added. The solution was refluxed for 2 days, and the color turned from brown to reddish brown. A spectrum characteristic of $[Et_4N]_2[\mathbf{1}]$ was obtained after 24 h of reflux, but further reaction was obvious as refluxing was continued for another day. The solvent was removed under vacuum and the residue extracted into acetone, giving 0.21 g of $[Et_4N]_2[Bi_4Fe_4(CO)_{13}]$ (0.12 mmol, 94% based on total bismuth).

Reaction of $[Et_4N]_2[\mathbf{1}]$ with CO. A solution of 0.29 g of $[Et_4N]_2[\mathbf{1}]$ (0.23 mmol) was dissolved in 20 mL of CH_2Cl_2, and the mixture was placed in a Parr 300-mL magnetically stirred autoclave. The solution was purged with nitrogen and pressurized to 850 psi of CO. After the solution was stirred for 2 days, a black precipitate developed, which was transferred very quickly in air to a Schlenk flask and placed under nitrogen. The solvent and product $Fe(CO)_5$ were removed under vacuum into a trap and analyzed by infrared spectroscopy to confirm the identity of $Fe(CO)_5$. The black residue proved to be $[Et_4N]_2[Bi_4Fe_4(CO)_{13}]$ (0.080 g, 0.047 mmol, 41% based on bismuth).

Synthesis of $Bi_2Fe_3(CO)_9$ from $[\mathbf{1}]^{2-}$. Method 1. To a standard Schlenk flask containing 1.18 g of $[Et_4N]_2[\mathbf{1}]$ (0.93 mmol) and 0.585 g of $[Cu(CH_3CN)_4][BF_4]$ was added 30 mL of CH_2Cl_2. The solution was bubbled with CO and stirred for 1 h as the solution became reddish brown and a precipitate of copper metal developed. The solvent and $Fe(CO)_5$ were removed under vacuum, and the residue was extracted into toluene. The infrared spectrum of the product showed it to be $Bi_2Fe_3(CO)_9$ contaminated with a small amount of $Fe_3(CO)_{12}$. The yield of the crude material was 0.58 g (75%). Purification was achieved by dissolving the mixture in CH_2Cl_2 and pressurizing with 850 psi of CO in the Parr 300-mL autoclave overnight. The volatile $Fe(CO)_5$ and solvent were removed under vacuum to give 85% yield for the purification step. IR (ν_{CO}, acetone): 1980 vs, 1955 m cm^{-1}.

Method 2. To a mixture of 1.05 g of $[Et_4N]_2[\mathbf{1}]$ (0.83 mmol) and excess $[Cu(CH_3CN)_4][BF_4]$ (0.65 g, 2.1 mmol) was added 25 mL of CH_2Cl_2. The solution was treated as above but yielded $Bi_2Fe_3(CO)_9$ that was not contaminated with $Fe_3(CO)_{12}$ (0.56 g, 0.67 mmol, 81%).

Synthesis of $[Et_4N]_2[\mathbf{1}]$ via the Reaction of $Bi_2Fe_3(CO)_9$ and $[Fe(CO)_4]^{2-}$. A solution of $Bi_2Fe_3(CO)_9$ (0.26 mmol) in 10 mL of THF was added dropwise to a solution of $Na_2[Fe(CO)_4]\cdot{}^3/_2$(dioxane) (0.29 mmol) in 10 mL of THF. The color of the solution immediately changed from deep red-brown to yellow-brown. The solvent was removed under vacuum, and the product was dissolved in MeOH and precipitated with deoxygenated, aqueous $[Et_4N]Br$, yielding the Et_4N^+ salt of $[\mathbf{1}]^{2-}$ in 85% yield. The Me_4N^+ salt was prepared similarly but crystallized as a double salt with excess $[Me_4N]Cl$.

Synthesis of $[Et_4N][Bi_2Fe_2Co(CO)_{10}]$, $[Et_4N][\mathbf{2}]$, via the Reaction of $Bi_2Fe_3(CO)_9$ and $[Co(CO)_4]^-$. Excess $Co_2(CO)_8$ (0.16 mmol) dissolved in 10 mL of THF was reduced with 1 mL of 1% Na/Hg. The THF solution was removed via syringe and filtered through Celite onto $Bi_2Fe_3(CO)_9$ (0.24 mmol). The solution was stirred overnight; then the solvent was removed under vacuum. The product was dissolved in methanol, and $[Et_4N]Br$ (0.12 g) was added to the solution followed by addition of water to precipitate the product in yields >45%. Anal. Calcd for $[Et_4N][\mathbf{2}]$: Bi, 41.84; Fe, 11.13; Co, 5.90. Found: Bi, 40.53; Fe, 10.65; Co, 5.12. IR (MeOH): 2030 sh, 2025 w, 2000 s, 1980 vs, 1960 s, 1944 m, 1918 ms cm^{-1}. The complex is unstable in solution and also in the solid state over a period of time. $[Bi_4Fe_4(CO)_{13}]^{2-}$ was noted as one product of that decomposition.

Reaction of $[Et_4N][BiFe_3(CO)_{10}]$ with $[Cu(CH_3CN)_4][BF_4]$. To a flask containing 0.197 g of $[Et_4N][BiFe_3(CO)_{10}]$ (0.25 mmol) and 0.13 g of $[Cu(CH_3CN)_4][BF_4]$ (0.41 mmol) was added 20 mL of CH_2Cl_2. The flask was stirred overnight, developing a clear reddish brown color. The

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solution was filtered, leaving a deposit of metallic copper. The solvent was removed under vacuum and the complex extracted into toluene. The infrared spectrum showed it to be $Bi_2Fe_3(CO)_9$ contaminated with a small amount of $Fe_3(CO)_{12}$. The yield of crude product was 0.051 g (26%).

Reduction of $Bi_2Fe_3(CO)_9$ Using Na/Hg. A tetrahydrofuran solution (30 mL) of $Bi_2Fe_3(CO)_9$ (0.10 g) was added to about 2 mL of a 1% Na/Hg amalgam, and the mixture was stirred. After about 20 s the color of the solution had gone from red-brown to brown, and at this time an aliquot was removed via syringe and filtered through Celite into a Schlenk flask. IR (ν_{CO}, THF): 2008 m, 1993 s, 1959 s, 1938 s, 1900 m, 1680 w, br. After about 10 min of total reaction time, the solution that remained over the amalgam had become greenish brown. At this point it was removed from the amalgam and filtered through Celite into a Schlenk flask [IR (ν_{CO}): 2000 w, 1958 m, 1921 vs, 1904 s, 1877 m, 1860 sh cm^{-1}], and the THF was removed under vacuum. The product was dissolved in water and the solution treated with aqueous tetraethylammonium chloride to precipitate the product. Solutions of both products are more stable when removed from the amalgam. The reversibility of this process was tested by carrying out a reduction–reoxidation cycle in tetrahydrofuran. The dissolved $Bi_2Fe_3(CO)_9$ was treated with 2 mL of 1% Na/Hg for 10 min to reduce it to the dianon, after which time it was filtered through Celite and treated with excess $[Cu(CH_3CN)_4][BF_4]$. After 1 h the infrared spectrum indicated that the only metal carbonyl product present was $Bi_2Fe_3(CO)_9$ in 90% of the original concentration.

Reduction of $Bi_2Fe_3(CO)_9$ with Cobaltocene (1:2) in CH_2Cl_2. A solution of 0.083 g of Cp_2Co in 5 mL of CH_2Cl_2 was added dropwise to 0.186 g of $Bi_2Fe_3(CO)_9$ dissolved in 10 mL of CH_2Cl_2, after which the solution was stirred for 40 min. The precipitate was collected, washed with 20 mL of CH_2Cl_2, and dried under vacuum. The black solid was extracted into acetone, and the mixture was concentrated and cooled, yielding 0.15 g of $[Cp_2Co]_2[Bi_2Fe_3(CO)_9]$. IR ($\nu_{CO}$, acetone): 2000 w, 1958 w, 1923 vs, 1905 s, 1874 m cm^{-1}. Anal. Calcd for $C_{29}H_{20}O_9Bi_2Co_2Fe_3$: Co, 9.69; Bi, 34.37; Fe, 13.78. Found: Co, 9.34; Bi, 33.37; Fe, 13.37.

Reduction of $Bi_2Fe_3(CO)_9$ with Cobaltocene (1:2) in Benzene. To a solution of 0.12 g of $Bi_2Fe_3(CO)_9$ in 10 mL of benzene was added dropwise 0.052 g of Cp_2Co dissolved in 5 mL of benzene. The resultant solution sat at room temperature for ca. 2 h. The precipitate was collected, washed with CH_2Cl_2 several times, and extracted into acetone. The IR spectrum was consistent with this being the one-electron-reduction product. IR (ν_{CO}, acetone): 2005 w, 1983 sh, 1972 sh, 1958 s, 1938 m, 1900 m cm^{-1}.

Electrochemistry. A standard three-electrode cell was used in all polarographic and voltammetric experiments, and coulometry was carried out in a cell with a Pt-basket working electrode.[15] The reference electrode was a Ag/AgCl (saturated LiCl or acetone) electrode isolated from the solution by a Vycor tip or by a solid Ag/AgCl electrode immersed directly in the solution. These reference electrodes were calibrated before each run with a known[16] electrochemically and chemically reversible couple $[PhCCo_3(CO)_9]^{0,-}$ under the same conditions as the test solution. Scan rates were 10 or 20 mV s^{-1} for polarographic and 50 mV s^{-1}–5 V s^{-1} for voltammetric measurements. Solutions were $\sim 10^{-3}$ M in electroactive material and 0.10 M (TEAP, CH_3CN) or 0.08 M (TEAP, CH_2Cl_2) in supporting electrolyte.

Severe poisoning of the electrodes was experienced in this work, and the data discussed in this paper are the result of several runs attained at clean electrodes. The cause is unclear, but there was no satisfactory remedy except to frequently clean the electrodes. Pt electrodes were prepared by anodizing at 2 V for 3 min in 0.1 M perchloric acid and polishing; glassy-carbon electrodes, by washing thoroughly with CH_2Cl_2, acetone, and water and finally polishing the surface. "Ideal" diffusion-controlled parameters for one-electron electrode processes were derived from measurements of $PhCCo_3(CO)_9$ under the same conditions. ESR spectra were recorded by the methods described previously.[17]

Table I. Experimental Data for the X-ray Diffraction Study of $[Me_4N^+]_3[Bi_2Fe_4(CO)_{13}{}^{2-}][Cl^-]$ and $[Et_4N^+][Bi_2Fe_2Co(CO)_{10}{}^-]$

	$[Me_4N]_2$[**1**]·$[Me_4N]$·[Cl]	$[Et_4N]$[**2**]
	A. Crystal Parameters	
cryst syst	triclinic	triclinic
space group	$P\bar{1}$ (C_i^1; No. 2)	$P\bar{1}$ (C_i^1; No. 2)
cell dimens		
a, Å	12.642 (3)	10.205 (4)
b, Å	13.215 (3)	11.250 (8)
c, Å	13.589 (5)	13.125 (6)
α, deg	87.343 (27)	70.30 (5)
β, deg	71.132 (24)	76.94 (3)
γ, deg	75.592 (20)	76.89 (5)
V, Å^3	2079.3 (11)	1363.1 (14)
Z	2	2
formula	$C_{25}H_{36}N_3O_{13}ClFe_4Bi_2$	$C_{18}H_{20}NO_{10}Bi_2Fe_2Co$
mol wt	1263.5	999.0
D(calcd), g cm^{-3}	2.02	2.43
μ(Mo Kα), cm^{-1}	95.3	139.7
	B. Collection of X-ray Data	
temp, K	297	
diffractometer	Syntex $P2_1$	
radiation ($\bar{\lambda}$, Å)	Mo K$\bar{\alpha}$ (0.710 730)	
monochromator	highly oriented (pyrolitic) graphite[a]	
scan type	coupled θ(cryst)–2θ(counter)	
scan width, deg	$[2\theta(K\alpha_1) - 0.9] \rightarrow [2\theta(K\alpha_2) + 0.9]$	
scan speed, deg min^{-1}	4 (in 2θ)	
bkgd measurement	stationary crystal and stationary counter at each end of the 2θ scan each for one-fourth the total scan time	each for one-half the total scan time
reflcns measd	$+h,\pm k,\pm l$	
2θ range, deg	4.5–45.0	4.0–45.0
tot. no. of reflcns	5946	3806
no. of unique data	5467	2492
criteria	none rejected	$\lvert F_o\rvert > 3.0\sigma(\lvert F_o\rvert)$
stdard reflcns	3 collected before every set of 97 reflections	
decay	none	ca. 5%
abs cor	corrected empirically by interpolation (in 2θ and between five Ψ scans of close to axial reflection (within 10° of diffraction vector)	

[a] 2θ(m) = 12.160° for 002 reflection, equatorial mode, assumed to be 50% perfect–50% ideally mosaic for polarization correction.

Determination of the Crystal Structure for $[Et_4N]^+[Bi_2Fe_2Co(CO)_{10}]^-$, $[Et_4N]$[2]. The crystal selected for the X-ray diffraction study was a black, somewhat flaky, mass of approximate orthogonal dimensions 0.2 × 0.2 × 0.35 mm. It was inserted into a thin-walled glass capillary, mounted in a eucentric goniometer, and aligned (along its extended direction) on the Syntex $P2_1$ automated four-circle diffractometer at SUNY—Buffalo. All subsequent setup operations (i.e., determination of the crystal's orientation matrix and unit cell parameters) and data collection (Mo Kα radiation; coupled θ(crystal)–2θ(counter scan) were performed as described previously;[18] details appear in Table I. Final unit cell parameters are based upon a least-squares analysis of the unresolved Mo K$\bar{\alpha}$ of 25 reflections, with 2θ = 20–30°, well-dispersed throughout reciprocal space.

The crystal showed only C_i ($\bar{1}$) diffraction symmetry with no systematic absences. It therefore belongs to the triclinic crystal class, possible space groups being the noncentrosymmetric $P1$ (C_1; No. 1) or the centrosymmetric $P\bar{1}$ (C_i^1; No. 2). The distribution of $\lvert E\rvert$ values, volume requirements of the formula unit ($Z = 2$), and successful solution of the structure confirm the latter, centrosymmetric, possibility.

All data were corrected for the effects of absorption and for Lorentz and polarization factors and were converted to unscaled $\lvert F_o\rvert$ values. Data were placed on an approximately absolute scale by means of a Wilson plot.

The structure was solved by direct methods using the SHELX 76 crystallographic program package of G. M. Sheldrick on the CDC Cyber 173 computer at the Computer Center of SUNY—Buffalo; an "*E* map" provided the positions of the two bismuth atoms, while all remaining non-hydrogen atoms were located from difference-Fourier syntheses. Subsequent refinement etc. were performed by using our in-house Syntex XTL interactive crystallographic program package. Hydrogen atoms of the $[Et_4N]^+$ cation were placed in calculated positions based upon a regular tetrahedral geometry and the appropriate "X-ray determined" C–H distance of 0.95 Å.[19] Full-matrix least-squares refinement led to convergence with[20] R_F = 8.1%, R_{wF} = 7.1%, and GOF = 1.87 for those 2492 reflections with $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$ and R_F = 6.4% and R_{wF} = 6.9% for

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(20) R_F (%) = $100[\sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \sum \lvert F_o\rvert]$; R_{wF} (%) = $100[\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \sum w\lvert F_o\rvert^2]^{1/2}$; GOF = $[\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(NO - NV)]^{1/2}$, where NO = number of observations and NV = number of refined variables.

those 1998 reflections with $|F_o| > 6\sigma(|F_o|)$. [For all 3173 reflections (none rejected) $R_F = 10.3\%$ and $R_{wF} = 7.3\%$—indicating the inherently poor diffracting qualities of the crystal.]

A final difference-Fourier synthesis showed no unexpected features; the structure is thus both correct and complete. Final positional parameters are collected in Table IV.

Throughout the analysis we used the scattering factors for neutral atoms in their analytical form; the contributions for all non-hydrogen atoms were corrected for both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion.[21] The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = [(\sigma(|F_o|))^2 + (p|F_o|)^2]^{-1}$ and p, the "ignorance factor", was assigned a value of 0.015.

Determination of the Crystal Structure of $[Me_4N]_2[Bi_2Fe_4(CO)_{13}]\cdot[Me_4N][Cl]$. The crystal chosen for this diffraction study was dark brown with approximate orthogonal dimensions 0.5 × 0.5 × 0.83 mm. Crystal mounting, setup operations, data collection, and treatment of intensity data follow the procedure for the previous structural study, with details being tabulated in Table I. The crystal was found to belong to the centrosymmetric space group $P\bar{1}$.

All calculations were performed on the Syntex XTL system. The positions of the two independent bismuth atoms were determined from a Patterson map. All remaining non-hydrogen atoms were located from difference-Fourier syntheses. Hydrogen atoms of the $[Me_4N]^+$ cations were included in calculated positions. Full-matrix least-squares refinement led to convergence with $R_F = 6.1\%$, $R_{wF} = 5.3\%$, and GOF = 1.95 for all 5467 independent reflections (none rejected) and $R_F = 4.4\%$ and $R_{wF} = 5.0\%$ for those 4226 reflections with $|F_o| > 6\sigma(|F_o|)$. As is clear from these statistics, the diffracting qualities of this crystal were excellent. A final difference-Fourier map was "clean". Final atomic positional parameters are collected in Table II.

Results

Immediately upon addition of CH_3CN to a 1:1 mixture of $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ and $BiCl_3$, a deep brown solution (the starting cluster is dark green) results that gives a very simple infrared spectrum containing two broad bands in the carbonyl stretching region (ν_{CO} = 1996 vs, 1923 s, br cm^{-1}) that are indicative of a negatively charged cluster and definitely not $Bi_2Fe_3(CO)_9$ (ν_{CO} = 2000 s, 1963 m cm^{-1}). Varying the ratios of $BiCl_3$ to $[Bi\{Fe(CO)_4\}_4]^{3-}$ showed that reaction was complete when *2* mol of cluster was treated with 1 mol of bismuth halide. Unfortunately, the intermediate tended to form an oil upon attempts at isolation and purification, and so further characterization has been hindered. It was also noticed that this complex was not stable in solution over a period of several days. Upon refluxing, reaction appears complete in 12–14 h, but the product is still not $Bi_2Fe_3(CO)_9$. Removal of the CH_3CN solvent produces a dark brown solid, but essentially none of this material is soluble in hexane or toluene. Addition of diethyl ether did, however, produce a faintly colored solution that infrared spectroscopy showed to be the known anion $[BiFe_3(CO)_{10}]^-$. The bulk of the material remained undissolved but could be extracted into CH_2Cl_2. The infrared spectrum of this material showed it to be essentially pure $[Et_4N]_2[\mathbf{1}]$. A preliminary report of the structure of this molecule has appeared.[13] Residual, CH_2Cl_2-insoluble solid dissolved in acetone and proved to be $[Et_4N]_2[Bi_4Fe_4(CO)_{13}]$ (Scheme I).

The reaction is sensitive to solvent. When CH_2Cl_2 is added to the reaction mixture as it refluxes, the major product becomes $[Bi_4Fe_4(CO)_{13}]^{2-}$. When monitored by infrared spectroscopy, the reaction appears to proceed to the formation of $[\mathbf{1}]^{2-}$ as before, but continued refluxing yields $[Bi_4Fe_4(CO)_{13}]^{2-}$.

Oxidation of $[Et_4N]_2[\mathbf{1}]$. When treated with a slight excess of $[Cu(CH_3CN)_4][BF_4]$ in CH_2Cl_2, $[\mathbf{1}]^{2-}$ is cleanly converted into $Bi_2Fe_3(CO)_9$, $Fe(CO)_5$, and $Fe_3(CO)_{12}$. $Fe_3(CO)_{12}$ was not conveniently removed from the desired product by solvent separation techniques; however, this problem was partially avoided when the reaction was performed under an atmosphere of CO, which favors the production of $Fe(CO)_5$ over the trinuclear cluster, but this did not completely eliminate $Fe_3(CO)_{12}$. When approximately 30% excess of the copper reagent was employed, however, the production of $Fe_3(CO)_{12}$ was inhibited and pure $Bi_2Fe_3(CO)_9$ was obtained (81% yield). Another purification method involves treatment of the $Bi_2Fe_3(CO)_9$ and $Fe_3(CO)_{12}$ mixture with moderate pressures of CO (850 psi) after workup. This has the effect of converting $Fe_3(CO)_{12}$ into $Fe(CO)_5$ and leaves the $Bi_2Fe_3(CO)_9$ unreacted.

Table II. Final Atomic Positions for $[Me_4N^+]_3[Bi_2Fe_4(CO)_{13}{}^{2-}][Cl^-]$

atom	*x*	*y*	*z*	*B*, Å^2
A. Atoms in the $[Bi_2Fe_4(CO)_{13}{}^{2-}]$ Dianion				
Bi(1)	0.14320 (4)	0.26706 (3)	0.18754 (3)	
Bi(2)	0.15141 (4)	0.38941 (3)	−0.03939 (3)	
Fe(1)	0.15029 (14)	0.18583 (14)	0.36945 (13)	
Fe(2)	0.07010 (13)	0.22351 (12)	0.04048 (13)	
Fe(3)	0.23958 (13)	0.41706 (12)	0.10905 (13)	
Fe(4)	0.30187 (13)	0.22451 (12)	0.00197 (12)	
O(11)	0.0920 (11)	0.4019 (11)	0.4452 (10)	10.41 (34)
O(12)	0.38789 (93)	0.07980 (90)	0.25478 (87)	8.15 (26)
O(13)	0.1729 (12)	0.1088 (12)	0.5656 (12)	11.26 (38)
O(14)	−0.0268 (11)	0.0739 (11)	0.3757 (10)	10.64 (36)
O(21)	0.09847 (75)	0.17396 (74)	−0.17601 (75)	6.34 (21)
O(22)	−0.16897 (89)	0.34214 (85)	0.11347 (81)	7.56 (25)
O(23)	0.05287 (86)	0.01433 (89)	0.11108 (84)	7.81 (26)
O(31)	0.04257 (84)	0.58511 (82)	0.21111 (78)	7.19 (24)
O(32)	0.36945 (80)	0.39987 (77)	0.25580 (77)	6.75 (22)
O(33)	0.38874 (87)	0.52499 (85)	−0.04798 (82)	7.62 (25)
O(41)	0.51598 (80)	0.24343 (74)	0.03087 (72)	6.39 (21)
O(42)	0.33876 (77)	0.00387 (78)	0.05292 (74)	6.56 (22)
O(43)	0.39390 (81)	0.18697 (79)	−0.22361 (78)	6.86 (23)
C(11)	0.1122 (13)	0.3139 (13)	0.4157 (12)	6.92 (36)
C(12)	0.2925 (11)	0.1251 (10)	0.3006 (10)	5.10 (27)
C(13)	0.1653 (14)	0.1378 (14)	0.4850 (14)	7.89 (41)
C(14)	0.0413 (13)	0.1233 (13)	0.3733 (12)	6.75 (35)
C(21)	0.0853 (10)	0.1938 (10)	−0.0897 (10)	4.85 (26)
C(22)	−0.0693 (11)	0.2972 (10)	0.0831 (10)	4.89 (26)
C(23)	0.0596 (11)	0.0995 (11)	0.0833 (10)	5.42 (28)
C(31)	0.1214 (11)	0.5160 (10)	0.1666 (10)	4.96 (27)
C(32)	0.3149 (11)	0.4032 (10)	0.1994 (10)	4.94 (26)
C(33)	0.3291 (11)	0.4822 (10)	0.0144 (10)	5.21 (28)
C(41)	0.4262 (11)	0.2429 (10)	0.0255 (10)	5.35 (28)
C(42)	0.3215 (10)	0.0935 (10)	0.03570 (90)	4.44 (24)
C(43)	0.3538 (10)	0.2094 (10)	−0.1327 (10)	5.08 (27)
B. Atoms in the Three $[Me_4N^+]$ Cations				
N(1)	0.71771 (89)	0.54504 (86)	0.39339 (83)	5.53 (23)
C(1A)	0.6455 (12)	0.5202 (12)	0.3370 (11)	6.56 (34)
C(1B)	0.7446 (14)	0.6474 (14)	0.3652 (13)	8.13 (41)
C(1C)	0.6550 (12)	0.5482 (12)	0.5080 (11)	6.33 (32)
C(1D)	0.8299 (13)	0.4603 (13)	0.3649 (13)	7.62 (39)
N(2)	0.2448 (10)	0.76983 (29)	0.25644 (90)	5.80 (24)
C(2A)	0.2029 (16)	0.7852 (16)	0.1671 (16)	9.84 (51)
C(2B)	0.3429 (21)	0.6758 (21)	0.2319 (20)	13.14 (72)
C(2C)	0.2992 (21)	0.8504 (22)	0.2608 (20)	13.03 (75)
C(2D)	0.1692 (24)	0.7532 (24)	0.3429 (24)	16.26 (91)
N(3)	0.66848 (88)	0.11558 (85)	0.26167 (82)	5.29 (23)
C(3A)	0.7802 (13)	0.1179 (13)	0.2763 (13)	7.51 (38)
C(3B)	0.6893 (16)	0.0628 (16)	0.1584 (16)	10.04 (52)
C(3C)	0.6120 (17)	0.0572 (17)	0.3429 (16)	10.20 (53)
C(3D)	0.5962 (14)	0.2217 (14)	0.2631 (13)	7.96 (40)
C. The Chloride Anion				
Cl	0.38267 (35)	0.71710 (34)	0.48624 (33)	7.64 (10)

Reaction of $Bi_2Fe_3(CO)_9$ with Metal Carbonyl Anions. When $Bi_2Fe_3(CO)_9$ and $[Fe(CO)_4]^{2-}$ are mixed in tetrahydrofuran solution at room temperature, an instantaneous reaction occurs producing $[\mathbf{1}]^{2-}$ quantitatively as seen by infrared spectroscopy. The product can be isolated as tetraalkylammonium salts in >85% yields. Thus, reaction of $Bi_2Fe_3(CO)_9$ with $[Fe(CO)_4]^{2-}$ takes place stoichiometrically with retention of the Bi_2Fe_3 unit, addition of a pendant $[Fe(CO)_4]^{2-}$, and no loss of carbonyl ligands.

The reaction of $[Co(CO)_4]^-$ and $Bi_2Fe_3(CO)_9$ also proceeds in a 1:1 ratio but the product is a cluster of considerably different geometry showing loss of an iron vertex and incorporation of cobalt. The presence of Co was confirmed by elemental analyses. The structure of $[Et_4N][\mathbf{2}]$ was determined by X-ray crystallography.[13]

Molecular Structure of $[Me_4N]_2[\mathbf{1}]\cdot[Me_4N][Cl]$. The crystal consists of an ordered arrangement of $[Me_4N]^+$, $[\mathbf{1}]^{2-}$, and Cl^- ions with a 3:1:1 stoichiometry; there are no abnormally short

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

Table III. Selected Interatomic Separations (Å) and Angles (deg) for $[Me_4N^+]_3[Bi_2Fe_4(CO)_{13}{}^{2-}][Cl^-]$

	Metal–Metal Separations		
Bi···Bi	3.398 (1)	Bi(1)–Fe(4)	2.645 (2)
Bi(1)–Fe(1)	2.668 (2)	Bi(2)–Fe(2)	2.687 (2)
Bi(1)–Fe(2)	2.597 (2)	Bi(2)–Fe(3)	2.678 (2)
Bi(1)–Fe(3)	2.592 (2)	Bi(2)–Fe(4)	2.683 (2)
Fe(2)–Fe(4)	2.808 (2)	Fe(3)–Fe(4)	2.796 (2)
	Fe–C(Carbonyl) Distances		
Fe(1)–C(11)	1.729 (17)	Fe(3)–C(31)	1.709 (14)
Fe(1)–C(12)	1.736 (14)	Fe(3)–C(32)	1.760 (14)
Fe(1)–C(13)	1.716 (18)	Fe(3)–C(33)	1.766 (14)
Fe(1)–C(14)	1.761 (17)	Fe(4)–C(41)	1.776 (15)
Fe(2)–C(21)	1.769 (13)	Fe(4)–C(42)	1.747 (13)
Fe(2)–C(22)	1.711 (14)	Fe(4)–C(43)	1.735 (13)
Fe(2)–C(23)	1.735 (14)		
	C–O Distances within Carbonyl Ligands		
C(11)–O(11)	1.186 (22)	C(31)–O(31)	1.184 (17)
C(12)–O(12)	1.179 (19)	C(32)–O(32)	1.178 (17)
C(13)–O(13)	1.169 (24)	C(33)–O(33)	1.167 (17)
C(14)–O(14)	1.194 (23)	C(41)–O(41)	1.162 (19)
C(21)–O(21)	1.162 (16)	C(42)–O(42)	1.177 (16)
C(22)–O(22)	1.193 (18)	C(43)–O(43)	1.194 (17)
C(23)–O(23)	1.186 (18)		
	Bi···Bi–Fe Angles		
Bi(2)···Bi(1)–Fe(1)	173.43 (4)	Bi(1)···Bi(2)–Fe(2)	48.82 (4)
Bi(2)···Bi(1)–Fe(2)	51.15 (4)	Bi(1)···Bi(2)–Fe(3)	48.74 (4)
Bi(2)···Bi(1)–Fe(3)	50.96 (4)	Bi(1)···Bi(2)–Fe(4)	49.88 (4)
Bi(2)···Bi(1)–Fe(4)	50.86 (4)		
	Fe–Bi–Fe Angles		
Fe(1)–Bi(1)–Fe(2)	135.40 (6)	Fe(1)–Bi(1)–Fe(3)	122.48 (6)
Fe(1)–Bi(1)–Fe(4)	128.63 (5)	Fe(2)–Bi(1)–Fe(3)	101.91 (5)
Fe(2)–Bi(1)–Fe(4)	64.78 (5)	Fe(3)–Bi(1)–Fe(4)	64.52 (5)
Fe(2)–Bi(2)–Fe(3)	97.38 (5)	Fe(2)–Bi(2)–Fe(4)	63.06 (5)
Fe(3)–Bi(2)–Fe(4)	62.87 (5)		
	Bi–Fe–Bi Angles		
Bi(1)–Fe(2)–Bi(2)	80.03 (5)	Bi(1)–Fe(3)–Bi(2)	80.30 (5)
	Bi–Fe–Fe Angles		
Bi(1)–Fe(2)–Fe(4)	58.44 (5)	Bi(2)–Fe(3)–Fe(4)	58.65 (5)
Bi(2)–Fe(2)–Fe(4)	58.40 (5)	Bi(1)–Fe(4)–Fe(2)	56.78 (5)
Bi(1)–Fe(3)–Fe(4)	58.66 (5)	Bi(2)–Fe(4)–Fe(2)	58.54 (5)
Bi(1)–Fe(4)–Fe(3)	56.81 (5)	Bi(2)–Fe(4)–Fe(3)	58.47 (5)
Fe(2)–Fe(4)–Fe(3)	91.96 (7)		
	Bi–Fe–C(Carbonyl) Angles		
Bi(1)–Fe(1)–C(11)	85.7 (6)	Bi(1)–Fe(3)–C(32)	92.2 (4)
Bi(1)–Fe(1)–C(12)	84.8 (5)	Bi(1)–Fe(3)–C(33)	157.2 (5)
Bi(1)–Fe(1)–C(13)	174.9 (6)	Bi(2)–Fe(3)–C(31)	90.7 (5)
Bi(1)–Fe(1)–C(14)	90.6 (5)	Bi(2)–Fe(3)–C(32)	166.1 (4)
Bi(1)–Fe(2)–C(21)	154.2 (4)	Bi(2)–Fe(3)–C(33)	85.8 (5)
Bi(1)–Fe(2)–C(22)	100.4 (5)	Bi(1)–Fe(4)–C(41)	102.3 (5)
Bi(1)–Fe(2)–C(23)	94.4 (5)	Bi(1)–Fe(4)–C(42)	86.3 (4)
Bi(2)–Fe(2)–C(21)	84.6 (4)	Bi(1)–Fe(4)–C(43)	156.2 (5)
Bi(2)–Fe(2)–C(22)	92.5 (5)	Bi(2)–Fe(4)–C(41)	119.7 (5)
Bi(2)–Fe(2)–C(23)	163.5 (5)	Bi(2)–Fe(4)–C(42)	143.8 (4)
Bi(1)–Fe(3)–C(31)	95.6 (5)	Bi(2)–Fe(4)–C(43)	82.3 (5)
	Fe–Fe–C Angles		
Fe(4)–Fe(2)–C(21)	95.8 (4)	Fe(2)–Fe(4)–C(41)	159.0 (5)
Fe(4)–Fe(2)–C(22)	144.8 (5)	Fe(2)–Fe(4)–C(42)	85.8 (4)
Fe(4)–Fe(2)–C(23)	105.4 (5)	Fe(2)–Fe(4)–C(43)	100.6 (5)
Fe(4)–Fe(3)–C(31)	141.1 (5)	Fe(3)–Fe(4)–C(41)	72.4 (5)
Fe(4)–Fe(3)–C(32)	107.5 (4)	Fe(3)–Fe(4)–C(42)	135.7 (4)
Fe(4)–Fe(3)–C(33)	98.6 (5)	Fe(3)–Fe(4)–C(43)	123.6 (5)
	C–Fe–C Angles		
C(11)–Fe(1)–C(12)	121.0 (7)	C(21)–Fe(2)–C(22)	100.9 (6)
C(11)–Fe(1)–C(13)	92.4 (8)	C(21)–Fe(2)–C(23)	94.6 (6)
C(11)–Fe(1)–C(14)	119.4 (8)	C(22)–Fe(2)–C(23)	103.9 (7)
C(12)–Fe(1)–C(13)	92.2 (8)	C(31)–Fe(3)–C(32)	101.7 (6)
C(12)–Fe(1)–C(14)	118.9 (7)	C(31)–Fe(3)–C(33)	102.7 (6)
C(13)–Fe(1)–C(14)	94.5 (8)	C(32)–Fe(3)–C(33)	97.3 (6)
C(41)–Fe(4)–C(42)	95.7 (6)	C(42)–Fe(4)–C(43)	100.1 (6)
C(41)–Fe(4)–C(43)	99.8 (6)		
	Fe–C–O Angles		
Fe(1)–C(11)–O(11)	176.6 (15)	Fe(3)–C(31)–O(31)	175.8 (12)
Fe(1)–C(12)–O(12)	177.2 (13)	Fe(3)–C(32)–O(32)	174.7 (12)
Fe(1)–C(13)–O(13)	177.4 (17)	Fe(3)–C(33)–O(33)	179.7 (12)
Fe(1)–C(14)–O(14)	175.1 (15)	Fe(4)–C(41)–O(41)	170.5 (12)
Fe(2)–C(21)–O(21)	178.2 (12)	Fe(4)–C(42)–O(42)	176.3 (11)
Fe(2)–C(22)–O(22)	175.4 (12)	Fe(4)–C(43)–O(43)	172.4 (12)
Fe(2)–C(23)–O(23)	179.0 (13)		

interionic contacts. The labeling of atoms in the dianion is provided by Figure 1, while a stereoview is shown in Figure 2 (supplementary material). Crystallographic data collection parameters are given in Table I with final atomic coordinates in Table II. Distances and angles are collected in Table III. The bimetallic dianion is based upon a square-pyramidal Bi_2Fe_3 cluster (with an apical Fe and trans Bi atoms) with an additional Fe atom bonded to a Bi atom in a pendant fashion. The bismuth–bismuth distance of 3.398 (1) Å is regarded formally as nonbonding. Internal bismuth–iron distances show some variation. Those involving the four-coordinate Bi(1) are Bi(1)–Fe(2) = 2.597 (2), Bi(1)–Fe(3) = 2.592 (2), and Bi(1)–Fe(4) = 2.645 (2) Å within the square-pyramidal cluster, with the pendant Bi–Fe(CO)$_4$ bond being slightly longer, having Bi(1)–Fe(1) = 2.668 (2) Å. Rather surprisingly, Bi–Fe distances involving the three-coordinate Bi(2) are longer than those to Bi(1), with Bi(2)–Fe(2) = 2.687 (2), Bi(2)–Fe(3) = 2.678 (2), and Bi(2)–Fe(4) = 2.683 (2) Å. These bond lengths are consistent with previous observations (vide supra), perhaps as a result of Fe(4) being seven-coordinate. The iron atoms of the square pyramidal Bi_2Fe_3 cluster each bear three terminal carbonyl ligands while the pendant iron atom bears four. Fe–CO distances range from 1.709 (14) to 1.776 (15) Å, with C-O distances lying in the range 1.162 (19)–1.194 (17) Å.

The square-pyramidal core of the molecule shows systematic distortions as a result of its heteronuclear character. Within the "square" base, angles at bismuth are obtuse [Fe(2)–Bi(1)–Fe(3) = 101.91 (5) and Fe(2)–Bi(2)–Fe(3) = 97.38 (5)°] while those at iron are acute [Bi(1)–Fe(2)–Bi(2) = 80.03 (5) and Bi(1)–Fe(3)–Bi(2) = 80.30 (5)°]. This base is not precisely planar; hinge angles are Bi(1)–Fe(2)–Bi(2)/Bi(1)–Fe(3)–Bi(2) = 5.96 and Fe(2)–Bi(1)–Fe(3)/Fe(2)–Bi(2)–Fe(3) = 7.08°. Angles at the apical iron atom show slight irregularities reflecting the shorter Bi(1)–Fe (vs. Bi(2)–Fe) intracluster angles; thus we have Bi(1)–Fe(4)–Fe(3) = 56.81 (5) and Bi(1)–Fe(4)–Fe(2) = 56.78 (5)°

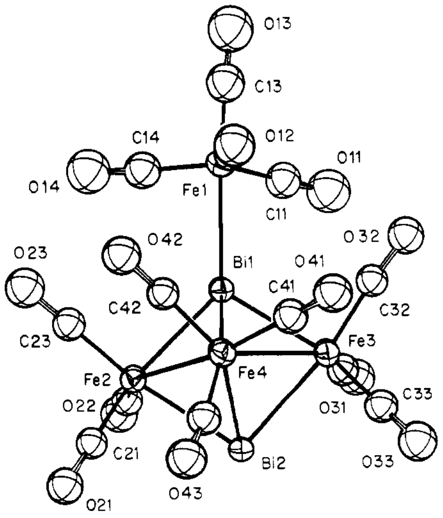


Figure 1. ORTEP diagram showing labeling of atoms within the $[Bi_2Fe_4(CO)_{13}]^{2-}$ dianion, $[1]^{2-}$. Thermal ellipsoids are drawn to 50% probability.

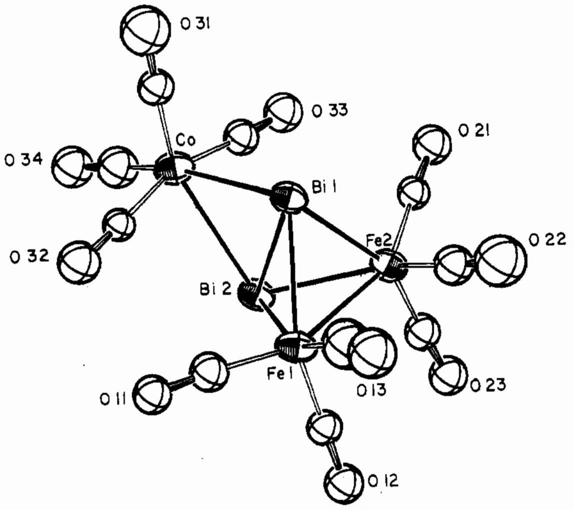


Figure 3. ORTEP drawing showing the labeling of atoms within the $[Bi_2Fe_2Co(CO)_{10}]^-$ anion, $[\mathbf{2}]^-$. Thermal ellipsoids are drawn to 50% probability. Note that the relative identity of Co (vs. Fe(1) or Fe(2)) is based upon chemical evidence (see text) but is not *crystallographically* definitive.

Table IV. Final Atomic Positions for $[Et_4N^+][Bi_2Fe_2Co(CO)_{10}^-]$

atom	*x*	*y*	*z*	B_{iso}, Å^2
Bi(1)	0.04896 (12)	0.66204 (13)	0.83398 (10)	
Bi(2)	−0.01367 (13)	0.85879 (14)	0.61342 (10)	
Fe(1)	0.23284 (42)	0.77927 (51)	0.67255 (35)	
Fe(2)	0.03811 (46)	0.91535 (48)	0.78261 (36)	
Co	−0.14827 (44)	0.64003 (49)	0.71651 (38)	
C(11)	0.3003 (32)	0.6606 (35)	0.6033 (27)	4.97 (75)
C(12)	0.2882 (33)	0.9131 (36)	0.5773 (28)	5.25 (77)
C(13)	0.3497 (43)	0.7292 (45)	0.7597 (35)	7.7 (11)
C(21)	−0.1180 (31)	0.9475 (31)	0.8531 (25)	4.37 (70)
C(22)	0.1455 (45)	0.8938 (48)	0.8769 (39)	8.7 (12)
C(23)	0.0605 (33)	1.0636 (38)	0.6990 (28)	5.50 (81)
C(31)	−0.1813 (40)	0.5030 (46)	0.8332 (35)	7.3 (10)
C(32)	−0.0088 (33)	0.5623 (35)	0.6428 (27)	5.01 (77)
C(33)	−0.2681 (37)	0.7540 (39)	0.7681 (29)	5.94 (87)
C(34)	−0.2613 (41)	0.6587 (42)	0.6244 (34)	7.4 (10)
O(11)	0.3515 (22)	0.5921 (24)	0.5544 (19)	6.15 (56)
O(12)	0.3295 (22)	1.0087 (24)	0.5149 (18)	6.10 (56)
O(13)	0.4330 (32)	0.6943 (34)	0.8176 (28)	10.26 (87)
O(21)	−0.2253 (23)	0.9722 (24)	0.9037 (19)	6.16 (56)
O(22)	0.2150 (36)	0.8792 (38)	0.9449 (31)	12.2 (10)
O(23)	0.0672 (25)	1.1745 (29)	0.6488 (22)	7.68 (66)
O(31)	−0.2102 (29)	0.4133 (33)	0.8952 (25)	9.21 (79)
O(32)	0.0832 (25)	0.5073 (26)	0.5940 (20)	7.35 (65)
O(33)	−0.3408 (27)	0.8285 (29)	0.8070 (22)	8.26 (71)
O(34)	−0.3317 (30)	0.6662 (32)	0.5613 (26)	9.84 (83)
N	0.5596 (24)	0.7423 (27)	0.2037 (20)	4.74 (59)
C(1)	0.6947 (35)	0.6728 (36)	0.2213 (28)	5.83 (83)
C(2)	0.5402 (39)	0.7539 (44)	0.0924 (33)	7.7 (10)
C(3)	0.4607 (41)	0.6683 (42)	0.2902 (32)	7.5 (10)
C(4)	0.5395 (37)	0.8834 (40)	0.1983 (31)	6.67 (92)
C(5)	0.8108 (40)	0.7201 (42)	0.1475 (33)	7.7 (10)
C(6)	0.5543 (44)	0.6232 (49)	0.0697 (37)	9.1 (12)
C(7)	0.3102 (43)	0.7262 (46)	0.2853 (35)	8.5 (11)
C(8)	0.5507 (49)	0.8927 (54)	0.3080 (42)	11.0 (14)

vs. Bi(2)–Fe(4)–Fe(2) = 58.54 (5) and Bi(2)–Fe(4)–Fe(3) = 58.47 (5)°. The remaining two, pseudotrans, angles are Bi(1)–Fe(4)–Bi(2) = 79.26 (5) and Fe(2)–Fe(4)–Fe(3) = 91.96 (7)°.

The pendant iron atom, Fe(1), lies only 0.002 (2) Å from the least-squares plane through the Bi(1)–Fe(2)–Bi(2)–Fe(4) base of the square pyramid, but it is not in a perfectly externally bisecting position since Fe(1)–Bi(1)–Fe(2) = 135.40 (6)°—some 13° greater than Fe(1)–Bi(1)–Fe(3) = 122.48 (6)°. Finally we note that the carbonyl ligands on Fe(4) and those on Fe(1) are arranged so as to "mesh" with the minimum intramolecular CO···CO repulsions. All other distances and angles in $[Bi_2Fe_4(CO)_{13}]^{2-}$ and $[Et_4N]^+$ are normal.

Table V. Bond Angles (deg) and Distances (Å) for $[Et_4N^+][Bi_2Fe_2Co(CO)_{10}^-]$

Metal–Metal Bond Lengths			
Bi(1)–Bi(2)	3.092 (2)	Bi(2)–Fe(2)	2.693 (5)
Bi(1)–Fe(1)	2.682 (5)	Bi(1)–Co	2.894 (5)
Bi(1)–Fe(2)	2.680 (6)	Bi(2)–Co	2.868 (5)
Bi(2)–Fe(1)	2.669 (5)	Fe(1)–Fe(2)	2.682 (7)
Fe–CO Bond Lengths			
Fe(1)–C(11)	1.79 (4)	Fe(2)–C(21)	1.68 (3)
Fe(1)–C(12)	1.72 (4)	Fe(2)–C(22)	1.76 (5)
Fe(1)–C(13)	1.71 (5)	Fe(2)–C(23)	1.69 (4)
Co–CO Bond Lengths			
Co–C(31)	1.80 (5)	Co–C(33)	1.76 (4)
Co–C(32)	1.76 (4)	Co–C(34)	1.79 (4)
C–O (Carbonyl) Bond Lengths			
C(11)–O(11)	1.13 (5)	C(23)–O(23)	1.21 (5)
C(12)–O(12)	1.21 (5)	C(31)–O(31)	1.11 (6)
C(13)–O(13)	1.18 (6)	C(32)–O(32)	1.19 (5)
C(21)–O(21)	1.17 (4)	C(33)–O(33)	1.16 (5)
C(22)–O(22)	1.21 (6)	C(34)–O(34)	1.18 (5)
Angles within the Bi_2Fe_2Co Cluster			
Bi(2)–Bi(1)–Fe(1)	54.51 (11)	Bi(1)–Bi(2)–Fe(1)	54.89 (11)
Bi(2)–Bi(1)–Fe(2)	55.06 (11)	Bi(1)–Bi(2)–Fe(2)	54.67 (11)
Fe(1)–Bi(1)–Fe(2)	60.03 (15)	Bi(1)–Fe(1)–Bi(2)	70.60 (13)
Fe(1)–Bi(1)–Co	102.98 (15)	Bi(1)–Fe(1)–Fe(2)	59.95 (15)
Fe(2)–Bi(1)–Co	103.56 (15)	Bi(2)–Fe(1)–Fe(2)	60.43 (15)
Fe(1)–Bi(2)–Fe(2)	60.02 (15)	Bi(1)–Fe(2)–Bi(2)	70.27 (13)
Fe(1)–Bi(2)–Co	104.01 (15)	Bi(1)–Fe(2)–Fe(1)	60.02 (15)
Fe(2)–Bi(2)–Co	103.94 (15)	Bi(2)–Fe(2)–Fe(1)	59.55 (15)
Bi(1)–Co–Bi(2)	64.92 (11)	Co–Bi(1)–Bi(2)	57.13 (11)
Co–Bi(2)–Bi(1)	57.96 (11)		
Bi–Fe–CO Angles			
Bi(1)–Fe(1)–C(11)	101.2 (12)	Bi(1)–Fe(2)–C(21)	97.3 (12)
Bi(2)–Fe(1)–C(11)	100.2 (12)	Bi(2)–Fe(2)–C(21)	103.3 (12)
Bi(1)–Fe(1)–C(12)	152.2 (13)	Bi(1)–Fe(2)–C(22)	91.4 (17)
Bi(2)–Fe(1)–C(12)	90.1 (13)	Bi(2)–Fe(2)–C(22)	149.8 (17)
Bi(1)–Fe(1)–C(13)	90.2 (16)	Bi(1)–Fe(2)–C(23)	155.6 (13)
Bi(2)–Fe(1)–C(13)	156.8 (16)	Bi(2)–Fe(2)–C(23)	89.7 (13)
Bi–Co–CO Angles			
Bi(1)–Co–C(31)	84.7 (15)	Bi(1)–Co–C(33)	89.8 (13)
Bi(2)–Co–C(31)	149.3 (15)	Bi(2)–Co–C(33)	80.4 (13)
Bi(1)–Co–C(32)	86.0 (12)	Bi(1)–Co–C(34)	167.7 (15)
Bi(2)–Co–C(32)	84.4 (12)	Bi(2)–Co–C(34)	102.8 (15)
Fe–Fe–CO Angles			
Fe(1)–Fe(2)–C(21)	154.2 (12)	Fe(2)–Fe(1)–C(11)	155.6 (12)
Fe(1)–Fe(2)–C(22)	90.6 (17)	Fe(2)–Fe(1)–C(12)	93.4 (13)
Fe(1)–Fe(2)–C(23)	98.3 (13)	Fe(2)–Fe(1)–C(13)	99.0 (16)
Terminal Fe–C–O Angles			
Fe(1)–C(11)–O(11)	174 (3)	Fe(2)–C(21)–O(21)	178 (3)
Fe(1)–C(12)–O(12)	176 (3)	Fe(2)–C(22)–O(22)	177 (4)
Fe(1)–C(13)–O(13)	178 (4)	Fe(2)–C(23)–O(23)	172 (3)
Terminal Co–C–O Angles			
Co–C(31)–O(31)	170 (4)	Co–C(33)–O(33)	175 (4)
Co–C(32)–O(32)	178 (3)	Co–C(34)–O(34)	177 (4)

Molecular Structure of $[Et_4N][\mathbf{2}]$. The crystal consists of an ordered arrangement of $[Et_4N]^+$ and $[\mathbf{2}]^-$ anions separated by normal van der Waals distances. The labeling of atoms in the anion is shown in Figure 3, while a stereoscopic view of the cation and anion is provided in Figure 4 (supplementary material). Atomic coordinates are given in Table IV. Distances and angles are collected in Table V. The heteronuclear anion is based upon a tetrahedral Bi_2Fe_2 cluster with a Co atom bridging the Bi–Bi edge. The Bi–Bi bond distance is short, 3.092 (2) Å. Distances between the Bi atoms and the metals that make up the tetrahedron are normal, ranging from 2.669 (5) to 2.693 (5) Å, while those to the external metal are somewhat longer (2.868 (5) and 2.894 (5) Å).

Oxidation/Reduction Chemistry of $Bi_2Fe_3(CO)_9$ and Related Compounds

Neutral Cluster. The closo cluster $Bi_2Fe_3(CO)_9$ undergoes a diffusion-controlled, chemically reversible one-electron reduction on Pt in CH_2Cl_2 ($E_{1/2}$ = −0.39 V, slope $(i_d - i)/i$ = 60 mV, i_{pc}/i_{pa} = 1.0); an irreversible reduction occurs at more negative potentials (E_{pc} = −1.1 V; Scheme I (9–11)). A one-electron transfer was confirmed by coulometry at −0.40 V, and controlled reduction at this potential in CH_2Cl_2 in an ESR cavity produced a paramagnetic species ($\langle g \rangle$ = 2.0034; half-peak width of 0.44 mT); no coupling to Bi was evident.

Anionic Clusters. Complex polarographic and voltammetric responses in CH_3CN on Pt or Hg were found with the anionic clusters $[\mathbf{1}]^{2-}$, $[BiFe_3(CO)_{10}]^-$, $[Bi\{Fe(CO)_4\}_4]^{3-}$, and $[Bi_4Fe_4(CO)_{13}]^{2-}$; Hg was not an "innocent" electrode, and only the Pt data are quoted. In no instance did oxidation produce $Bi_2Fe_3(CO)_9$.

Oxidation of $[BiFe_3(CO)_{10}]^-$ at 0.78 V precipitated a brown solid immediately on the electrode surface and rapidly in the bulk solution. This solid was also produced during electrochemical investigation of the other anions (vide infra).

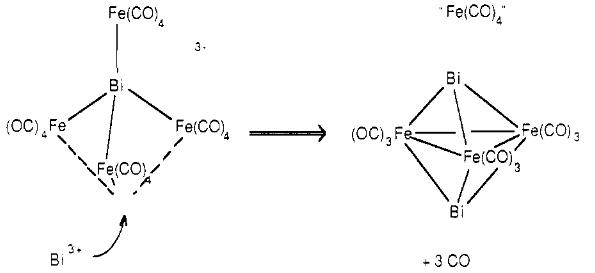
For $[Bi_4Fe_4(CO)_{13}]^{2-}$ under argon, successive oxidation at E_{pa} = ~0.18 and 0.48 V is followed by a partially reversible couple at E_{pa} = 0.64 V, E_{pc} = 0.54 V, and $i_{pc}/i_{pa} \simeq 0.5$ and on the reverse scan an oxidation process occurs at −0.02 V (200 mV s^{-1}). On repeat scans at slow scan speed (<100 mV s^{-1}) this pattern is repeated; at scan rates >500 mV s^{-1} the waves at 0.18 and 0.48 V decrease in i_{pa} at the expense of a new wave at E_{pa} = ~0.55 V ($[BiFe_3(CO)_{10}]^-$) and the wave at ~0.64 V. Under CO the initial wave at 0.18 V is followed by the wave at 0.55 V, and on the second scan $[BiFe_3(CO)_{10}]^-$ is the only feature indicating that the couple $E_{1/2}$ = ~0.6 V and the wave at E_{pa} = −0.02 V (probably $[Fe(CO)_4]^{2-}$) represent species arising from CO-dissociative equilibria.

The first irreversible oxidation step for $[\mathbf{1}]^{2-}$ occurs at 0.33 V, followed by features at E_{pa} = 0.55 and 0.68 V (E_{pc} = 0.52 V); on the repeat scan the −0.02-V wave appears and that at 0.33 V is lost. For $[Bi\{Fe(CO)_4\}_4]^{3-}$ the initial irreversible step is at 0.48 V, followed by a small wave at ~0.80 V and on repeat scans −0.02, 0.34, and 0.55 V.

Chemical Oxidation and Reduction of Bi/Fe Carbonyls. When $Bi_2Fe_3(CO)_9$ is treated with Na/Hg in tetrahydrofuran, two distinct cluster products are observed, which are proposed to be the one- and two-electron-reduction products. After the solution has been stirred for approximately 20 s, the color has noticeably changed from reddish brown to brown and the infrared spectrum is as follows: ν_{CO} = 2008 m, 1993 s, 1959 s, 1938 s, 1900 m, 1680 w, br cm^{-1}. If the solution is removed from the amalgam at this point, the product is stable for days at −20 °C; however, if it is left over Na/Hg, then it is converted to a greenish brown solution within 10 min and gives an infrared spectrum (ν_{CO} = 2003 w, 1956 m, 1920 vs, 1903 s, 1873 m cm^{-1}) that is shifted to lower energy. The second product is stable in solution for several days after removal from the amalgam. If the product is not removed from the amalgam, then the cluster continues to react with complete decomposition. The two products can also be generated by treating $Bi_2Fe_3(CO)_9$ with cobaltocene in benzene or methylene chloride. The elemental analyses of the second material support its formulation as $[Cp_2Co]_2[Bi_2Fe_3(CO)_9]$. Unfortunately to date, attempts at obtaining X-ray-quality crystals have not succeeded. Slow decomposition of both of these products to $[Bi_4Fe_4(CO)_{13}]^{2-}$ in solution has been observed, and both appear to react slowly with water.

Discussion

Reaction of $BiCl_3$ with $[Bi\{Fe(CO)_4\}_4]^{3-}$. The strategy of this synthetic work was to produce $Bi_2Fe_3(CO)_9$ from $[Bi\{Fe(CO)_4\}_4]^{3-}$ and $BiCl_3$ in a rational, high-yield synthesis. It was postulated that a Bi^{3+} cation could easily attack one face of the $[BiFe_4]^{3-}$ tetrahedron as shown in eq 1.



(1)

It was thought that the addition of Bi^{3+} would promote the formation of Fe–Fe bonds and consequent CO loss. The resultant neutral cluster could then lose the terminal $Fe(CO)_4$ moiety because the lack of charge on the cluster would render the lone pair on bismuth less effective for donation to an external metal. We were already aware of the existence of $[\mathbf{1}]^{2-}$, as it had been isolated and characterized as a minor product of the reaction of $NaBiO_3$ with $Fe(CO)_5$/KOH/MeOH (i.e. the reaction to produce $[Bi\{Fe(CO)_4\}_4]^{3-}$) upon accidental oxidation by excess $NaBiO_3$,[22] but we had not expected it to be the major product of this reaction. The formation of $[\mathbf{1}]^{2-}$ from $BiCl_3$ and $[Bi\{Fe(CO)_4\}_4]^{3-}$ can be rationalized by proposing the involvement of complex redox disproportionation processes. This is apparent when one considers that $[\mathbf{1}]^{2-}$ could be derived formally from $[Bi\{Fe(CO)_4\}_4]^{3-}$ by addition of Bi^+ as opposed to Bi^{3+}.

Some insight into this can be gained by examining the reaction stoichiometry, which was determined to be 2 mol of $[Bi\{Fe(CO)_4\}_4]^{3-}$/mol of $BiCl_3$. It is not unreasonable that an intermediate composed of two $BiFe_4{}^{3-}$ clusters and a Bi^{3+} ion could dissociate heterolytically into fragments, ultimately yielding $[\mathbf{1}]^{2-}$ and $[BiFe_3(CO)_{10}]^-$. Such an intermediate could be structurally similar to $Sb_2Fe_6(CO)_{22}$, which we have recently isolated from Cu^+ oxidation of dichloromethane solutions of $SbCl_3$ and $[Fe_2(CO)_8]^{2-}$.[23]

The production of $[Bi_4Fe_4(CO)_{13}]^{2-}$ is readily explained since it is a known product of the reaction of $[BiFe_3(CO)_{10}]^-$ with CO (Scheme I(13)), both of which are products of this reaction. The anion $[\mathbf{1}]^{2-}$ is also converted into $[Bi_4Fe_4(CO)_{13}]^{2-}$ and $Fe(CO)_5$ by CO (850 psi) in CH_2Cl_2 (Scheme I(12)). On the basis of 1:2 stoichiometry, the yields of $[Et_4N]_2[\mathbf{1}]$ are consistently greater than 75%, although the yields of $[Bi_4Fe_4(CO)_{13}]^{2-}$ and $[BiFe_3(CO)_{10}]^-$ are variable. Considering the high yields of $[Et_4N]_2[\mathbf{1}]$ and the low yields of $[BiFe_3(CO)_{10}]^-$, it is more likely that $[Bi_4Fe_4(CO)_{13}]^{2-}$ arises from the reaction of CO with $[BiFe_3(CO)_{10}]^-$ than with $[\mathbf{1}]^{2-}$ under these conditions.

The reaction of $BiCl_3$ with $[Bi\{Fe(CO_4\}_4]^{3-}$ was not completely satisfying from the standpoint that the desired product was $Bi_2Fe_3(CO)_9$. Having obtained $[Et_4N]_2[\mathbf{1}]$ in reasonable yield, however, we questioned whether or not that cluster could be converted into the desired product by oxidation. It was apparent that $[\mathbf{1}]^{2-}$ is related structurally to $Bi_2Fe_3(CO)_9$ and that an oxidation route might afford a viable synthetic route. This was indeed observed upon addition of $[Cu(CH_3CN)_4]^+$ to $[Et_4N]_2[\mathbf{1}]$ (Scheme I(6)). The external $Fe(CO)_4$ fragment is lost as $Fe(CO)_5$ or $Fe_3(CO)_{12}$. This process is essentially the reverse of the addition of $[Fe(CO)_4]^{2-}$ to $Bi_2Fe_3(CO)_9$ (Scheme I(5)) to be discussed shortly. The iron pentacarbonyl is easily removed because of its volatility while $Fe_3(CO)_{12}$ is more troublesome, although its presence can be avoided by using an excess of the copper reagent.

Purification of the product can also be achieved by pressurizing it with CO. $Bi_2Fe_3(CO)_9$ does not react with pressures of CO even after many days of stirring, whereas the $Fe_3(CO)_{12}$ reacts readily. This behavior is in marked contrast to that of the $Te_2Fe_3(CO)_9$ cluster,[24,25] which readily adds CO and other ligands in an Fe–Fe bond-breaking process. It is believed that the steric requirements of the Te induce strain on the Fe–Fe framework and facilitate this conversion. The Fe–Fe framework in $Bi_2Fe_3(CO)_9$ ($d_{Fe-Fe,av}$ = 2.745 Å)[7] should be at least as strained as that for the tellurium compound, for which no X-ray structural data have been reported. It is, therefore, very surprising that the bismuth complex does not react with CO. This is furhter emphasized by

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[22] Whitmire, K. H., unpublished results.

[23] Shieh, M. S.; Whitmire, K. H.; Rheingold, A. L. *Inorg. Chem.*, in press.

[24] Lesch, D. A.; Rauchfuss, T. B. *Inorg. Chem.* **1981**, *20*, 3583.

[25] Lesch, D. A.; Rauchfuss, T. B. *Organometallics* **1982**, *1*, 499.

the ease with which the cluster is chemically reduced to $[Bi_2Fe_3(CO)_9]^{2-}$. The differences may be due to the lack of a suitable location for a carbonyl in the hypothetical product $Bi_2Fe_3(CO)_{10}$, which would be expected to contain two Fe–Fe bonds. The tellurium cluster begins as a square-pyramidal cluster possessing two electrons more than our bismuth compound, and addition of phosphines or CO produces the symmetrical adducts $[Fe_2(CO)_6Te_2\{\mu\text{-}Fe(CO)_3L\}]$, which have only one Fe–Fe bond.

Reaction of $Bi_2Fe_3(CO)_9$ with Metal Carbonyl Anions. The production of $[\mathbf{1}]^{2-}$ from the $NaBiO_3/Fe(CO)_5/KOH/MeOH$ solutions is a complex reaction and does not offer an adequate method of making $[Et_4N]_2[\mathbf{1}]$. When this product was first characterized, the $BiCl_3/[Bi\{Fe(CO)_4\}_4]^{3-}$ reaction was unknown, and consequently a rational synthesis was desired. In examining the structure of this cluster, it seemed reasonable that it could be separated into $[Bi_2Fe_3(CO)_9]$ and $[Fe(CO)_4]^{2-}$ fragments. The reaction between $[Bi_2Fe_3(CO)_9]$ and $[Fe(CO)_4]^{2-}$ was successful and essentially quantitative, as seen by infrared spectroscopy, giving an 85% isolated yield of $[Et_4N]_2[\mathbf{1}]$ (Scheme I(5)). It is interesting to speculate that hypervalency of the main-group atom may play a key role in the formation of this cluster. This idea is suggested by the recent observation of hypervalency in some related tellurium compounds.[26] Thus, one can envisage the $[Fe(CO)_4]^{2-}$ group attacking bismuth initially to give a hypervalent main-group atom, which then transfers the excess electrons into the cluster core. Such a process may also be possible for the cobalt reaction described next.

Via analogy to the above reaction of $Bi_2Fe_3(CO)_9$ with $[Fe(CO)_4]^{2-}$, it was hoped that similar heterometal systems could be produced by using other metal carbonyl anions, such as $[Co(CO)_4]^-$. Treatment of $Bi_2Fe_3(CO)_9$ with $[Co(CO)_4]^-$ (Scheme I(14)) leads to replacement of an iron vertex with concurrent formation of a Bi–Bi bond—collapsing a trigonal-bipyramidal cluster to an edge-bridged tetrahedral cluster.

Discussion of the Structures of $[\mathbf{1}]^{2-}$ and $[\mathbf{2}]^-$. The core geometry of this cluster anion $[\mathbf{1}]^{2-}$ is consistent with Wade's rules for a five-vertex nido cluster containing seven skeletal electron pairs. It is structurally related to other triiron clusters containing $AsPh$,[27] S,[28] Se,[29] Te,[24,30] NCH_3,[31] or SO[32] in place of the bismuth atoms. The product is easily derived from $Bi_2Fe_3(CO)_9$, which has the appropriate electron count for the observed trigonal-bipyramidal geometry. Addition of the $[Fe(CO)_4]^{2-}$ group formally transfers two electrons to the cluster core of $Bi_2Fe_3(CO)_9$, which results in the breakage of an Fe–Fe bond, as might be expected. The leftover "$Fe(CO)_4$" group is then available for coordination to a Bi atom.

The "edge-bridged tetrahedron" observed for $[\mathbf{2}]^-$ is not such a common cluster shape but has been observed previously in $Te_2Fe_3(CO)_9(PPh_3)$[25] and $(\eta\text{-}C_5H_5)_2Mo_2FeTe_2(CO)_7$.[33] Treatment of $Bi_2Fe_3(CO)_9$ with $[Co(CO)_4]^-$ thus leads to replacement of an iron vertex with concurrent formation of a Bi–Bi bond—collapsing a trigonal-bipyramidal cluster to an edge-bridged tetrahedral cluster. It is not possible to determine the position of the cobalt and iron atoms from the X-ray crystal data. ^{13}C NMR spectroscopy could help resolve this issue, but to date the ^{13}C spectra obtained have not been interpretable, partially owing to the instability of this complex in solution. In Figure 3 we have placed the cobalt atom in the bridging position, which we felt is reasonable on the basis of the observation that the cluster decomposes to $[Bi_4Fe_4(CO)_{13}]^{2-}$ in solution and the bridging metal appears to be the most weakly bonded. It is not too difficult to see how loss of $Co(CO)_4$ could result in the formation of $Fe_2Bi_2^-$ fragments, which would dimerize to form $[Bi_4Fe_4(CO)_{13}]^{2-}$. Obviously, the decomposition reaction is more complicated than this, and the definitive distribution of the cobalt and iron atoms in the structure will have to await further study.

The Bi(1)–Bi(2) bond length of 3.092 (2) Å in $[\mathbf{2}]^-$ is characteristic of a Bi–Bi single bond. Thus, the closest Bi–Bi contacts in the crystalline element are 3.07 and 3.53 Å;[34] Bi–Bi distances in $[Bi_8^{2+}][AlCl_4^-]_2$ range from 3.072 to 3.126 Å, averaging 3.100 Å;[35] Bi–Bi distances within the Bi_9^{5+} cation of $[Bi_9^{5+}]_2[Bi_2Cl_8^{2-}][BiCl_5^{2-}]_4$, "$Bi_{24}Cl_{28}$", separate into groups averaging 3.103 (6), 3.202 (11), and 3.796 (7) Å;[36] Bi–Bi distances within the Bi_9^{5+} cation in $[Bi_9^{5+}][Bi^+][HfCl_6^{2-}]_3$ separate into groups averaging 3.094 (3), 3.241 (3), and 3.747 (7) Å;[37] Bi–Bi distances in the $[Bi_4Fe_4(CO)_{13}^{2-}]$ anion of $[Et_4N^+]_2[Bi_4Fe_4(CO)_{13}^{2-}]$ separate into groups of 3.140 (2)–3.168 (2) and 3.453 (2)–3.473 (2) Å.[11,38] (We note that the Bi–Bi distances for the six-π-electron system Bi_4^{2-} are shorter at 2.936 (2)–2.941(2)Å.[39]) The bismuth–iron distances are Bi(1)–Fe(1) = 2.682 (5), Bi(1)–Fe(2) = 2.680 (6), Bi(2)–Fe(1) = 2.669 (5), and Bi(2)–Fe(2) = 2.693 (5) Å and are in the normal range. Corresponding distances in closely related species include Bi–Fe = 2.648 (2)–2.652 (1) Å in $[Et_4N^+][BiFe_3(CO)_9(\mu_3\text{-}CO)^-]$,[6] 2.617 (2)–2.643 (2) Å in $(\mu_3\text{-}Bi)_2Fe_3(CO)_9$,[7] 2.699 (6)–2.753 (6) Å in $[Et_4N^+]_2[Bi_4Fe_4(CO)_{13}^{2-}]$,[11,38] and 2.748 (2)–2.753 (3) Å in $[Et_4N^+]_3[BiFe_4(CO)_{16}^{3-}]$.[9] The bismuth–cobalt distances are quite long, with Bi(1)–Co = 2.894 (5) and Bi(2)–Co = 2.868 (5) Å; these may be compared with Bi–Co distances of 2.760 (2)–2.770 (2) Å in $Bi[Co(CO)_4]_3$. Finally, the Fe(1)–Fe(2) distance of 2.682 (7) Å is typical of such distances within bismuth–iron clusters, comparable with Fe–Fe distances of 2.634 (2)–2.646 (2) Å in the $[BiFe_3(CO)_9(\mu_3\text{-}CO)^-]$ anion[6] and 2.735 (5)–2.757 (5) Å in $(\mu_3\text{-}Bi)_2Fe_3(CO)_9$.[7] All other distances and angles in this complex have normal values but are of limited precision (see Table V).

The molecule is similar to recent Te_2 metal cluster complexes synthesized by Rauchfuss and co-workers, which are now believed to possess Te–Te bonding.[25,33,40] We hypothesize that part of the driving force for this reaction is the low charge on the cluster. In all the known cases where a four-coordinate bismuth is observed, the charge on the cluster is 2– or greater. We have not been able to detect appreciable basicity at bismuth in clusters of lower charge. For example, $[BiFe_3(CO)_{10}]^-$ is alkylated at the μ_3-CO rather than at Bi,[8] and the oxidation of $[\mathbf{1}]^{2-}$ results in the loss of the external $Fe(CO)_4$ unit. This effect coupled with the main group–main group interaction could provide suitable driving force for the formation of the observed product. Rauchfuss has proposed main group–main group bond formation to be a significant influence in determining the chemistry of the tellurium cluster series.[33]

In the comparison of $Te_2(CpMo)_2Fe(CO)_7$[33] and $Te_2Fe_3(CO)_9PPh_3$[25] to **2**, there are some obvious differences in structure and electron-counting schemes. First, the $[Te_2MoFe]^+$ and Te_2Fe_2 cores are electron precise for the expected tetrahedral arrangement of atoms, and consequently the Te–Te bond is considered a donor to the external, lone bridging metal fragment. In the bismuth cluster, however, the Bi_2Fe_2 core possesses only five skeletal electron pairs and is electron deficient. The extra electron pair, which would be necessary for Bi–Bi bond formation, is then thought to be donated by the external $[Co(CO)_4]^-$ unit. There

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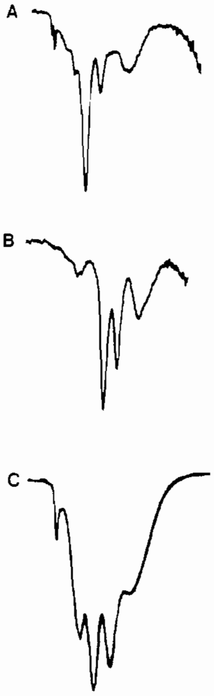
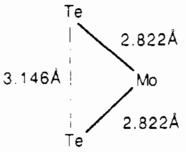
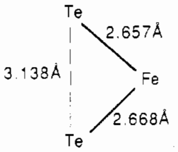
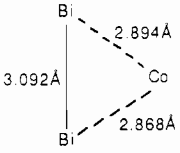


Figure 5. Infrared spectra (THF): (A) proposed $[BiFe_3(CO)_9]^{\bullet-}$ ion; (B) proposed $[BiFe_3(CO)_9]^{2-}$ ion; (C) $[Et_4N]_2[\mathbf{1}]$.

are also some structural differences in the association of the lone metal to the main group–main group bond, as can be seen here:







In the tellurium examples, it has been estimated that the bond order is approximately $^2/_3$, while in the Bi cluster the Bi–Bi separation is consistent with a bond order of 1. In fact, the Bi–Bi distance is as short as the Te–Te distances seen in the other clusters! On the other hand, the Bi–Co distances are quite long, about 0.1 Å longer than in $Bi\{Co(CO)_4\}_3$. This same lengthening is observed in the Te_2Fe_3 case and, to a lesser extent, in the Te_2FeMo_2 compound.

The observation of a main group–main group interaction in these compounds is significant and helps to bridge the gap between the transition-metal carbonyl clusters and the Zintl cluster anions. This observation in the cobalt case suggests the possibility of the involvement of the unknown but structurally and electronically reasonable $[Bi_2Fe_2(CO)_6]^{2-}$ anion in the formation of $[Bi_4Fe_4(CO)_{13}]^{2-}$ and implies that other Zintl-metal carbonylates may be accessible from similar routes.

Redox Chemistry of the Bi/Fe Carbonyl Clusters. The reaction of $Bi_2Fe_3(CO)_9$ with metal carbonyl anions suggested that it might be possible to add electrons to this cluster directly. This proved to be possible by both chemical and electrochemical methods. Chemical reduction by Na/Hg amalgam (Scheme I(9,10)) proceeds very quickly, and one must work fast to isolate the one-electron-reduction product, which is not exceedingly stable. Continued reduction produces a species thought to be the two-electron-reduction product $[Bi_2Fe_3(CO)_9]^{2-}$. The same anion can be obtained by addition of cobaltocene to $Bi_2Fe_3(CO)_9$, which elemental analyses support as the given formulation. In addition, the infrared spectra of the one- and two-electron-reduction products are similar to each other and to the spectrum of $[Et_4N]_2[\mathbf{1}]$ (Figure 5). This suggests that the two reduction products have similar square-pyramidal geometries, as is intuitively reasonable. The shift to lower energy of the ν_{CO} bands on going from $[Bi_2Fe_3(CO)_9]^{\bullet-}$ to $[Bi_2Fe_3(CO)_9]^{2-}$ is consistent with the additional charge. The reduction to the dianion can be reversed chemically by addition of $[Cu(NCCH_3)_4]^+$, giving the starting material is high spectroscopic yield.

Two reductions, the first being both chemically and electrochemically reversible, are also seen at an electrode surface. Controlled-potential reduction at the first reduction potential (with the passage of 1 $\mathcal{F}$ mol^{-1}) gives a paramagnetic species having an ESR signal with a g value typical of radical anions where the electron has entered a LUMO centered on the metal framework[41] and shows no coupling to Bi ($I = {}^9/_2$). The g value is comparable to $\langle g \rangle = 2.0043$ for $[Fe_3(CO)_{12}]^{\bullet-}$ ($E_{1/2} = -0.44$ V).[42,43] Conproportionation 2, which is fast for the $Fe_3(CO)_{12}$ system,[43] plays

$$Fe_3(CO)_{12} + [Fe_3(CO)_{12}]^{2-} \leftrightarrow 2[Fe_3(CO)_{12}]^{\bullet-} \qquad (2)$$

no role in the redox chemistry of $Bi_2Fe_3(CO)_9$, and the kinetic stability of $[Bi_2Fe_3(CO)_9]^{\bullet-}$ is greater than that of $[Fe_3(CO)_{12}]^{\bullet-}$ (which fragments at room temperature) but similar to that of the capped cluster $[RCCo_3(CO)_9]^{\bullet-}$.[16] $[Bi_2Fe_3(CO)_9]^{\bullet-}$ is best described as a bicapped Fe_3 cluster where the extra electron occupies an antibonding a_2 orbital centered on the Fe_3 framework.

The electrochemical studies of the other Bi/Fe carbonyl cluster anions were not so straightforward; however, for the Bi_nFe_4 clusters a common pattern emerged from these data suggesting rapid structural rearrangement following the primary oxidation step. The ultimate electrochemically active species from oxidation of all $Bi_nFe_4^{2-}$ clusters are that oxidized at $E_{pa} = \sim 0.55$ V and that giving rise to the partially chemically reversible couple $E_{pa} = 0.64$ V. We have not identified these species. There is no indication from the electrochemical data that neutral Bi_nFe_4 clusters would have a finite existence, and this has been borne out by attempts to carry out these transformations chemically. Furthermore, oxidation of $[\mathbf{1}]^{2-}$ (or indeed any Bi_nFe_4 cluster) at an electrode surface does not produce $Bi_2Fe_3(CO)_9$, indicating that the Cu^+ reaction shown in Scheme I(6) is not a simple electron-transfer reaction.

It is interesting to note that $[Bi_4Fe_4(CO)_{13}]^{2-}$ is the most easily oxidized of the anionic clusters. We have recently discussed the bonding in this molecule from consideration of Wade's rules and from a molecular orbital analysis.[38] One scheme derives the molecular structure from a tetrahedron of Bi atoms. The number of skeletal electron pairs required for a tetrahedron is 6; however, the $Bi_4Fe_3^{2-}$ core contains ten pair. Three of these pair are accounted for by placement in Bi–Bi antibonding orbitals. The basal to apical distances are substantially longer than the other three and probably do not represent bonding distances (3.45 Å vs. 3.15 Å). The tenth electron pair was found by extended Hückel calculations to reside in an orbital centered on the three irons, which is of inappropriate symmetry to interact with the Bi orbitals so that it is essentially nonbonding. It is not surprising, therefore, that these two electrons should be so readily lost.

Concluding Remarks. The redox chemistry of the bismuth-containing iron carbonyl clusters is interesting and exhibits a variety of unexpected processes. Thus the reaction of $[Bi\{Fe(CO)_4\}_4]^{3-}$ with $BiCl_3$ produces $[\mathbf{1}]^{2-}$, which upon mild oxidation yields $Bi_2Fe_3(CO)_9$. This method affords a reasonable synthesis of $Bi_2Fe_3(CO)_9$, which has only been available previously from a slow, low-yield process. This oxidation/metal elimination reaction can be reversed if $Bi_2Fe_3(CO)_9$ is treated with $[Fe(CO)_4]^{2-}$. In this reaction $[Fe(CO)_4]^{2-}$ acts as a reducing agent to the cluster and an Fe–Fe bond in $Bi_2Fe_3(CO)_9$ is broken to accommodate the added electrons. The resultant "$Fe(CO)_4$" then is ligated by a bismuth atom of the cluster. Electrochemically and chemically it is easy to add electrons to this cluster core in the absence of stabilizing metal centers to coordinate to the bismuth atom. Thus $[Bi_2Fe_3(CO)_9]^{2-}$ can be easily generated and can be reversibly

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oxidized to the parent cluster. The cluster acts as an electron storage site through the reversible breakage and formation of metal–metal bonds, although the cycle is not 100% efficient. In general, the electrochemical results indicate that the rearrangement of the Bi–Fe clusters is very rapid on the electrode surface.

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Registry No. $[Et_4N]_2[\mathbf{1}]$, 101858-51-9; $[Me_4N]_2[\mathbf{1}]\cdot[Me_4N][Cl]$, 101834-85-9; $[Et_4N][\mathbf{2}]$, 101997-75-5; $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$, 92763-37-6; $[Et_4N]_2[Bi_4Fe_4(CO)_{13}]$, 94483-21-3; $Fe(CO)_5$, 13463-40-6; $Bi_2Fe_3(CO)_9$, 96525-96-1; $[Cu(CH_3CN)_4][BF_4]$, 15418-29-8; $[Fe(CO)_4]^{2-}$, 22321-35-3; $[Co(CO)_4]^-$, 14971-27-8; $Co_2(CO)_8$, 15226-74-1; $[Et_4N][BiFe_3(CO)_{10}]$, 92786-73-7; Cp_2Co, 1277-43-6; $[Cp_2Co]_2[Bi_2Fe_3(CO)_9]$, 109243-26-7; $(Bi_2Fe_3(CO)_9)^-$, 109243-27-8; Bi, 7440-69-9; Co, 7440-48-4; Fe, 7439-89-6.

Supplementary Material Available: For $[Me_4N]_2[\mathbf{1}]\cdot[Me_4N][Cl]$ and $[Et_4N][\mathbf{2}]$ listings of anisotropic thermal parameters, Figures 2 and 4 (stereoviews of the anions $[\mathbf{1}]^{2-}$ and $[\mathbf{2}]^-$), and tables of bond length and angle parameters for the cations of $[Me_4N]_2[\mathbf{1}]\cdot[Me_4N][Cl]$ and $[Et_4N][\mathbf{2}]$ (5 pages); tables of calculated and observed structure factors for both compounds (43 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of South Carolina, Columbia, South Carolina 29208

Cluster Syntheses. 14. The Syntheses and Structural Characterizations of the High-Nuclearity Sulfidoruthenium Carbonyl Cluster Compounds $Ru_5(CO)_{14}(\mu_4\text{-}S)_2$, $Ru_6(CO)_{17}(\mu_4\text{-}S)_2$, and $Ru_7(CO)_{20}(\mu_4\text{-}S)_2$

Richard D. Adams,* James E. Babin, and Miklos Tasi

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The reaction of $Ru_3(CO)_9(\mu_3\text{-}S)_2$ (**2**) with $Ru_3(CO)_{12}$ under UV irradiation has yielded the higher nuclearity cluster compounds $Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}S)_2$ (**3**), 38%, $Ru_5(CO)_{14}(\mu_4\text{-}S)_2$ (**4**), 20%, and $Ru_6(CO)_{17}(\mu_4\text{-}S)_2$ (**5**), 3%. Thermal decarbonylation of $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ (**1**) at 100 °C has yielded **3**, 47%, **5**, 10%, and $Ru_7(CO)_{20}(\mu_4\text{-}S)_2$ (**6**), 26%. The large clusters are decomposed to **2** and **3** by reaction with CO at 1 atm. Compounds **4**–**6** have been characterized by single-crystal X-ray diffraction analyses. For **4**: space group $P2_1/n$, $a = 8.787$ (2) Å, $b = 14.550$ (3) Å, $c = 19.741$ (3) Å, $\beta = 98.09$ (1)°, $Z = 4$, $\rho_{calcd} = 2.56$ g/cm^3. The structure was solved by direct methods and was refined (3023 reflections) to the final residuals $R_F = 0.033$ and $R_{wF} = 0.036$. The cluster consists of an approximately square arrangement of four ruthenium atoms with quadruply bridging sulfido ligands on each face. An $Ru(CO)_4$ unit bridges one Ru–Ru edge of the cluster. By the EAN rule the molecule is unsaturated, and one of the Ru–Ru bonds was found to be unusually short, 2.704 (1) Å. For **5**: space group $P2_12_12_1$, $a = 11.211$ (2) Å, $b = 14.666$ (4) Å, $c = 17.611$ (4) Å, $Z = 4$, $\rho_{calcd} = 2.63$ g/cm^3. Compound **5** is isomorphous and isostructural with the known osmium homologue. The structure was refined (2482 reflections) to the final values of the residuals $R_F = 0.033$ and $R_{wF} = 0.039$. The molecule consists of a pentagonal-bipyramidal cluster of five ruthenium atoms with two sulfido ligands. A $Ru(CO)_4$ group bridges one apical–equatorial edge of the cluster. For **6**: space group $P2_12_12_1$, $a = 11.226$ (3) Å, $b = 14.320$ (4) Å, $c = 21.217$ (5) Å, $Z = 4$, $\rho_{calcd} = 2.59$ g/cm^3. Compound **6** is isomorphous and isostructural with the known osmium homologue. The structure was refined (2296 reflections) to the final values of the residuals $R_F = 0.041$ and $R_{wF} = 0.044$. The molecule consists of a pentagonal-bipyramidal cluster of five ruthenium atoms and two sulfido ligands. Two $Ru(CO)_4$ groups bridge symmetrically adjacent apical–equatorial edges of the cluster. The chemistry of the ruthenium clusters is compared to that of the corresponding osmium system.

Introduction

A number of methods have now been developed for the systematic synthesis of transition-metal cluster compounds.[1,2] Bridging ligands have been shown to be especially useful by facilitating metal atom addition reactions and by stabilizing the products.[1-4] Bridging ligands appear to play an important role in the chemistry of high-nuclearity clusters of ruthenium.[5] No neutral binary carbonyls containing more than three ruthenium atoms are known.[6]

We have had considerable success in our efforts to prepare high-nuclearity cluster compounds of osmium containing sulfido ligands[3] and have now begun to apply this knowledge to the development of the chemistry of sulfidoruthenium carbonyl clusters. We have recently reported high-yield syntheses of the sulfidotriruthenium carbonyl clusters $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ (**1**) and $Ru_3(CO)_9(\mu_3\text{-}S)_2$ (**2**) from the reaction of $Ru_3(CO)_{12}$ with ethylene sulfide.[7]

Experimental Section

General Information. Reagent grade solvents were stored over 4-Å molecular sieves. THF was freshly distilled from sodium diphenylketyl before use. $Ru_3(CO)_{12}$ was purchased from Strem Chemical Co. and was used as received. Ethylene sulfide was purchased from Aldrich Chemical Co. and was distilled before use. CP grade carbon monoxide was purchased from Linde Co. and was used without further purification. $Ru(CO)_5$ was prepared by the literature methods.[8] $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ (**1**), $Ru_3(CO)_9(\mu_3\text{-}S)_2$ (**2**), and $Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}S)_2$ (**3**) were prepared as previously reported.[7]

All reactions were performed under a nitrogen atmosphere. All chromatographic separations were performed in air. TLC separations were performed on plates (0.25-mm Kieselgel 60 F_{254}, E. Merck) purchased from Bodman Chemicals. UV irradiation experiments were performed by using an external high-pressure mercury lamp on reaction solutions contained in Pyrex glassware. IR spectra were recorded on a Nicolet 5 DXB FT IR spectrometer. Elemental analyses were performed by MicAnal, Tucson, AZ.

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