carbonyl species to give the observed $Fe(CO)_5$. This process may then be the source of an $Fe(CO)_x$ fragment that adds across the Fe–Fe bond of **1** to form **2**, or of **3** to form **4**, and also possibly reacts with $Fe_2(CO)_9$ to form part of the $Fe_3(CO)_{12}$ group. However, the various systems yielded increasing amounts of $Fe_3(CO)_{12}$ on workup, so that the characterized species such as **3** and **4** and, especially, the uncharacterized red species are probably its prime source. Under the reaction conditions of these experiments, $Fe_3(CO)_{12}$ does not form **2** or **4** in direct reaction with the hydrides, and $Fe(CO)_5$ does not react at all. Ge_2H_6 gives enhanced yields of **3b** and **4b** compared with those from GeH_4, showing that the two Ge atoms tend to occur together in the intermediates.

The Sn–Fe system is somewhat richer than the Ge–Fe one, while the Si–Fe one is much more limited. This suggests that Sn is the best match in size to form the critical EFe_2 unit. These comments are only a preliminary rationalization of the observed structures. The reaction systems reported in this and earlier[7,9] papers are complex ones, which are not always fully reproducible and are not yet completely understood. Other species are undoubtedly present and perhaps accessible by modified preparations. Of particular interest would be the replacement of the third μ-CO in **4** and the species related to **3** by the presence of a central four-membered ring, as found for **5**.

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Supplementary Material Available: Tables giving full crystallographic details, thermal parameters, all bond lengths and angles, and equations of least-squares planes (14 pages); tables of calculated and observed structure factors (50 pages). Ordering information is given on any current masthead page.

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Synthesis, Characterization, and Reactivity of Iron Carbonyl Clusters Containing Bismuth or Antimony. Crystal Structures of Isomorphous $[Et_4N][BiFe_3Cr(CO)_{17}]$ and $[Et_4N][SbFe_3Cr(CO)_{17}]$ and the Ring Complex $Bi_2Fe_2(CO)_8Me_2$

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The reaction of $[Et_4N]_2[Fe_2(CO)_8]$ with $BiCl_3$ or $SbCl_3$ forms compounds (Ia, E = Bi; Ib, E = Sb) that are proposed to be the previously characterized $[Et_4N][EClFe_3(CO)_{12}]$ based on elemental analyses and spectroscopic data. Treatment of Ia or Ib with $Cr(CO)_5(THF)$ produces $[Et_4N][EFe_3Cr(CO)_{17}]$ (IIa and IIb, respectively), while the methylation of Ia affords $Bi_2Fe_2(CO)_8Me_2$ (III). Refluxing Ia and Ib in acetonitrile gives the previously known $[Et_4N]_2[Bi_2Fe_4(CO)_{13}]$ and $[Et_4N]_2[Sb_2Fe_5(CO)_{17}]$, respectively. IIa, IIb, and III have been characterized by X-ray crystallography. IIa crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ (no. 2) with $a = 12.297$ (3) Å, $b = 15.154$ (3) Å, $c = 9.791$ (1) Å, $\alpha = 107.60$ (1)°, $\beta = 95.24$ (2)°, $\gamma = 92.02$ (2)°, $V = 1727.9$ (6) Å^3, and $Z = 2$. The structure was refined to $R = 4.5\%$ and $R_w = 5.3\%$ for those 5114 reflections with $I > 3\sigma(I)$. The core framework of IIa consists of a distorted tetrahedral $BiFe_3Cr$ cluster in which a central bismuth atom is bonded to isolated $Fe(CO)_4$ and $Cr(CO)_5$ groups and a metal–metal-bonded $Fe_2(CO)_8$ fragment. The Fe–Fe bond distance is 2.608 (2) Å, and the Fe1–Bi1–Fe2 angle is 56.91 (4)°. IIb is isomorphous with IIa: centrosymmetric triclinic space group $P\bar{1}$ (no. 2), $a = 12.233$ (1) Å, $b = 15.108$ (5) Å, $c = 9.742$ (3) Å, $\alpha = 107.23$ (3)°, $\beta = 94.61$ (2)°, $\gamma = 92.37$ (1)°, $V = 1710.0$ (9) Å^3, and $Z = 2$. Diffraction data were refined to $R = 4.2\%$ and $R_w = 5.7\%$ for those 6100 reflections with $I > 3\sigma(I)$. The Fe–Fe bond distance in IIb is 2.598 (1) Å. III crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ (no. 2) with $a = 7.571$ (4) Å, $b = 8.734$ (4) Å, $c = 7.136$ (3) Å, $\alpha = 107.02$ (4)°, $\beta = 108.41$ (4)°, $\gamma = 79.89$ (4)°, $V = 426.3$ (4) Å^3, and $Z = 1$. Refinement converged at $R = 4.1\%$ and $R_w = 5.3\%$ for those 1355 reflections with $I > 3\sigma(I)$. III consists of a Bi_2Fe_2 parallelogram situated about a crystallographic inversion center. There is one Me group bonded to each bismuth atom. The $Fe(CO)_4$ groups are pseudooctahedral with an average Bi–Fe distance of 2.786 Å. The Bi–C distance is 2.28 (1) Å.

Table I. Crystallographic Data for IIa, IIb, and III

	IIa	IIb	III
empirical formula	$BiFe_3CrC_{25}O_{17}H_{20}N$	$SbFe_3CrC_{25}O_{17}H_{20}N$	$Bi_2Fe_2C_{10}H_6O_8$
fw	1034.95	947.72	391.90
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
b, Å	15.154 (3)	15.108 (5)	8.734 (4)
c, Å	9.791 (1)	9.742 (3)	7.136 (3)
α, deg	107.60 (1)	107.23 (3)	107.02 (4)
β, deg	95.24 (2)	94.61 (2)	108.41 (4)
γ, deg	92.02 (2)	92.37 (1)	79.89 (4)
V, Å^3	1727.9 (6)	1710.0 (9)	426.3 (4)
Z	2	2	1
D (calcd), g cm^{-3}	1.99	1.84	3.05
μ, cm^{-1} (Mo Kα)	64.78	24.59	213.07
T(max)/T(min)	1.0/0.69	1.0/0.71	1.0/0.29
wavelength, Å (Mo Kα)		0.71069	
T, °C		23	
residuals: R; R_w	0.045; 0.053	0.042; 0.057	0.041; 0.053

Introduction

In recent years, heavy main-group atoms bonded to transition-metal fragments have been shown to adopt unexpected structures that range from electron-deficient planar molecules[1,2] to electron-rich environments as found in $[Cp_2Co][Bi\{Co(CO)_4\}_4]$[3] and $(RC_5H_4)MoFe(Te_2X)(CO)_5$[4] (X = Br, S_2CNEt_2). Multiple bonding between the group 15 elements is proposed to occur in $E_2[W(CO)_5]_3$ (E = As, Sb, Bi),[5] and an unusual hybrid cluster

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geometry is observed for $[Et_4N]_2[Bi_4Fe_4(CO)_{13}]$[6] in which adjacent cluster anions have weak Bi···Bi interactions in the solid state. In addition to these remarkable compounds, a number of heavy main-group atom containing molecules exhibiting classical metal carbonyl cluster geometries have been prepared.[7]

We have been exploring the cluster chemistry of Bi and have recently extended this work to the preparation of related antimony-containing compounds.[8] During these studies, an intermediate species that proved difficult to characterize structurally was consistently observed when $BiCl_3$ or $SbCl_3$ and $[Fe_2(CO)_8]^{2-}$ were allowed to react. This paper describes efforts to probe the chemical reactivity of these intermediates in such a way as to clarify their possible structures.

Experimental Section

All manipulations were performed by using standard Schlenk and vacuum-line techniques. $[Et_4N]_2[Fe_2(CO)_8]$[10] and $[Cu(MeCN)_4][BF_4]$[11] were prepared by the literature methods. $SbCl_3$ was recrystallized from benzene, and $BiCl_3$ was used as received. All solvents were purified by distillation from the indicated drying agents (CH_2Cl_2, P_2O_5; hexane, CaH_2; acetone, K_2CO_3; THF (tetrahydrofuran), Na/benzophenone; MeOH, Mg/I_2). Solvents were bubbled with nitrogen for 30 min prior to use and stored under nitrogen. UV irradiations were performed upon solutions in Pyrex glassware by using an external high-pressure mercury lamp. Mass spectra were obtained on a Finnegan 3300 GCMS system. NMR spectra were taken on a JEOL FX90Q spectrometer. Galbraith Analytical Laboratories in Knoxville, TN, Texas Analytical Laboratories in Houston, TX, or Desert Analytics in Tucson, AZ, provided the elemental analyses.

Synthesis of Compound Ia from $BiCl_3$ and $[Et_4N]_2[Fe_2(CO)_8]$. An acetone solution of 0.14 g (0.44 mmol) of $BiCl_3$ and 0.39 g (0.65 mmol) of $[Et_4N]_2[Fe_2(CO)_8]$ was stirred for 3 h and filtered to give a greenish brown solution. Removal of solvent under vacuum gave an oily residue, which was then washed with 20 mL of hexane and extracted into 20 mL of CH_2Cl_2. IR (ν_{CO}, acetone) of the CH_2Cl_2 extract: 1990 vs, 1928 m, 1910 m, br cm^{-1}. The product tended to oil in most solvents and decomposed with the formation of $[Et_4N]_2[Bi_4Fe_4(CO)_{13}]$ in concentrated MeOH solution.

Synthesis of $[Et_4N][BiFe_3Cr(CO)_{17}]$ (IIa) from $Cr(CO)_5(THF)$ and Ia. Compound Ia in acetone was prepared from the reaction of 0.10 g (0.32 mmol) of $BiCl_3$ and 0.28 g (0.47 mmol) of $[Et_4N]_2[Fe_2(CO)_8]$ by using the method given above. The acetone was removed and the residue dissolved in 30 mL of THF. After filtering, the THF solution was treated with $Cr(CO)_5(THF)$ prepared from the UV irradiation of 0.14 g (0.64 mmol) of $Cr(CO)_6$ in 25 mL of THF for 5 h. The mixture was stirred overnight, producing a reddish brown solution. The solvent was removed under vacuum, after which the residue was washed quickly with 30 mL of hexane and extracted into 20 mL of CH_2Cl_2. X-ray quality black crystals of IIa were obtained by slow cooling of a concentrated MeOH solution of the CH_2Cl_2 extract. The yield was 79 mg (24% based on Bi). IR (ν_{CO}, MeOH): 2075 w, 2038 s, 2030 s, 2008 vs, 1990 sh, 1940 s, 1915 m, 1825 w, br cm^{-1}. IIa is soluble in CH_2Cl_2, MeOH, THF, and MeCN but not in hexane. Anal. Calcd: C, 29.01; H, 1.93; N, 1.35. Found: C, 28.68; H, 1.83; N, 1.35.

Synthesis of $Bi_2Fe_3(CO)_9$ from $[Cu(MeCN)_4][BF_4]$ and Compound Ia. Ia was prepared by the treatment of 0.11 g (0.35 mmol) of $BiCl_3$ with 0.32 g (0.54 mmol) of $[Et_4N]_2[Fe_2(CO)_8]$ using the method described above. The CH_2Cl_2 extract (25 mL) from that synthesis was filtered and treated with 0.23 g (0.73 mmol) of $[Cu(MeCN)_4][BF_4]$. After the reaction solution was stirred for a couple of hours, a copper precipitate developed. The solution was filtered and the solvent removed under vacuum. Extraction of the residue into 30 mL of hexane followed by chromatography on Florisil (hexane eluent) gave two bands. The first band was identified by infrared spectroscopy and its color (green) as $Fe_3(CO)_{12}$. The infrared spectrum of the second band showed it to be $Bi_2Fe_3(CO)_9$; yield = 30 mg (0.036 mmol, 20% based on Bi).[7f]

Synthesis of $[Et_4N]_2[Bi_2Fe_4(CO)_{13}]$ by Refluxing Ia. Ia was prepared in acetone from 0.10 g (0.32 mmol) of $BiCl_3$ and 0.28 g (0.47 mmol) of $[Et_4N]_2[Fe_2(CO)_8]$ as before. The solvent was removed under vacuum, the solid dissolved in 30 mL of MeCN, and the solution refluxed while purging with N_2 for $1^1/_2$ days. After this the reaction was worked up, and 156 mg $[Et_4N]_2[Bi_2Fe_4(CO)_{13}]$ (0.12 mmol, 78% yield based on Bi) was isolated along with a trace amount of $[Et_4N][BiFe_3(CO)_{10}]$.

Synthesis of $Bi_2Fe_2(CO)_8Me_2$ (III) from Compound Ia and MeI. Ia was prepared from 0.30 g (0.95 mmol) of $BiCl_3$ and 0.85 g (1.4 mmol) of $[Et_4N]_2[Fe_2(CO)_8]$ in acetone. The solvent was removed, and the solid was extracted into 20 mL of CH_2Cl_2. Methyl iodide (0.60 mL, 9.6 mmol) was added, and the solution was stirred for 30 min during which time the color changed from brown to reddish brown. After the solution was filtered, the solvent was removed under vacuum. Iron pentacarbonyl was present in the volatiles as identified by infrared spectroscopy. The solid residue was extracted into 60 mL of hexane, yielding 126 mg of III (0.32 mmol, 34% based on Bi). IR (ν_{CO}, hexane): 2040 s, 1990 vs cm^{-1}. Crystals for X-ray analysis were grown from a concentrated hexane solution. The mass spectrum showed a parent ion (M^+) at m/e 784 with subsequent loss of two Me groups $[M^+ - n(15)]$ and regular loss of CO groups $[M^+ - n(28)]$. Mp: = 142–143 °C dec. ^1H NMR (CD_2Cl_2): δ = 2.53 ppm when the spectrum was obtained on a cold solution freshly prepared. When the solution was allowed to stand at room temperature, a second signal was observed growing in at δ = 2.75 ppm. It has not yet proven possible to determine the identity of the second compound due to instability problems. After a number of days at room temperature in CH_2Cl_2, III was found to have decomposed to give $Bi_2Fe_3(CO)_9$.

Synthesis of Ib from the Reaction of $SbCl_3$ with $[Et_4N]_2[Fe_2(CO)_8]$. To a mixture of 0.11 g (0.48 mmol) of $SbCl_3$ and 0.43 g (0.72 mmol) of $[Et_4N]_2[Fe_2(CO)_8]$ was added 20 mL of acetone. After being stirred for 1 h, the solution was filtered and solvent removed under vacuum to give an oily residue. This residue was washed with 30 mL of hexane, and extracted into 20 mL of CH_2Cl_2. The CH_2Cl_2 was removed and the product dried under vacuum. Two sets of elemental analyses gave 15.60% (15.48%) for Fe, and 11.32% (11.80%) for Sb (Fe:Sb = 3:1). IR (ν_{CO}; acetone): 1995 vs, 1919 vs, 1911 vs cm^{-1}. IR (ν_{CO}; CH_2Cl_2): 1998 vs, 1915 vs, br cm^{-1}. IR (ν_{CO}; THF) 1999 vs, 1910 vs, br cm^{-1}. Black tiny crystals for X-ray diffraction were obtained by slow crystallization of a concentrated MeOH solution at room temperature. X-ray data sets of several of the crystals were obtained, but the crystals were only weakly diffracting, and it has not proven possible to solve the structure. Cell parameters: monoclinic cell with a = 40.13 (4) Å, b = 19.958 (9) Å, c = 8.921 (4) Å, β = 98.49 (5)°, and V = 7067 (8) Å^3. Ultimately, crystals that showed the same unit cell parameters (*C*-centered monoclinic lattice with a = 29.246 (8) Å, b = 18.413 (3) Å, c = 16.855 (5) Å, β = 119.75 (2)°) as those found for $[Et_4N]_2[SbCl\{Fe(CO)_4\}_3]\cdot CH_2Cl_2$ (space group $C2/c$ with a = 29.30 (1) Å, b = 18.500 (6) Å, c = 16.844 (6) Å, β = 119.58 (2)°) were obtained from CH_2Cl_2 solution. Anal. Calcd: Fe, 16.64; Sb, 12.09.

Synthesis of $[Et_4N][SbFe_3Cr(CO)_{17}]$ (IIb) from $Cr(CO)_5(THF)$ and Ib. Ib was prepared in acetone by the treatment of 0.10 g (0.44 mmol) of $SbCl_3$ with 0.39 g (0.65 mmol) of $[Et_4N]_2[Fe_2(CO)_8]$ using the method described above. The solvent was removed under vacuum to give a solid, which was redissolved in 25 mL of THF. The THF solution was filtered and treated with $Cr(CO)_5(THF)$ from UV irradiation of 0.19 g (0.86 mmol) of $Cr(CO)_6$ in 30 mL of THF for 6 h. The mixture was stirred overnight, and then the solvent was removed under vacuum. The solid residue was washed quickly with 20 mL of hexane and extracted into 20

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Table II. Selected Positional Parameters and B(eq) for IIa

atom	x	y	z	B(eq),[a] Å^2
Bi1	0.74730 (3)	0.25844 (3)	0.18891 (4)	2.76 (1)
Fe1	0.5506 (1)	0.3387 (1)	0.2105 (1)	3.39 (5)
Fe2	0.6606 (1)	0.3268 (1)	0.4443 (1)	3.39 (5)
Fe3	0.7323 (1)	0.0755 (1)	0.0744 (2)	4.30 (6)
Cr1	0.9228 (1)	0.3446 (1)	0.1214 (2)	3.88 (6)
O1	0.6284 (6)	0.5186 (5)	0.4293 (7)	4.8 (3)
O2	0.4454 (6)	0.2206 (6)	0.3585 (8)	5.6 (4)
O11	0.6215 (7)	0.4539 (6)	0.0371 (9)	6.0 (4)
O12	0.4687 (7)	0.1769 (6)	−0.0356 (9)	5.9 (4)
O13	0.3335 (7)	0.4088 (8)	0.234 (1)	7.9 (5)
O21	0.8726 (7)	0.4273 (7)	0.569 (1)	7.1 (4)
O22	0.7155 (8)	0.1514 (6)	0.4980 (9)	6.9 (4)
O23	0.5551 (8)	0.3887 (7)	0.7101 (9)	7.1 (4)
O31	0.684 (1)	0.1148 (8)	−0.199 (1)	8.8 (6)
O32	0.935 (1)	0.0853 (9)	0.255 (1)	12.5 (7)
O33	0.5306 (8)	0.0438 (6)	0.197 (1)	6.8 (4)
O34	0.7487 (9)	−0.1215 (7)	−0.070 (1)	8.8 (5)
O41	0.8578 (8)	0.5322 (6)	0.292 (1)	7.2 (5)
O42	1.0683 (8)	0.3277 (8)	0.377 (1)	9.0 (6)
O43	0.9973 (9)	0.1511 (8)	−0.048 (1)	8.8 (6)
O44	0.7968 (8)	0.3376 (8)	−0.161 (1)	7.9 (5)
O45	1.1147 (8)	0.4342 (8)	0.037 (1)	9.1 (6)
C1	0.6193 (8)	0.4413 (9)	0.385 (1)	4.2 (4)
C2	0.517 (1)	0.2685 (8)	0.344 (1)	4.2 (4)
C11	0.5985 (9)	0.4102 (8)	0.106 (1)	4.2 (4)
C12	0.5042 (8)	0.2375 (7)	0.060 (1)	3.8 (4)
C13	0.419 (1)	0.3842 (8)	0.229 (1)	4.7 (4)
C21	0.7910 (9)	0.3907 (8)	0.518 (1)	4.2 (4)
C22	0.696 (1)	0.2191 (7)	0.474 (1)	4.4 (4)
C23	0.5954 (8)	0.3668 (8)	0.605 (1)	4.4 (4)
C31	0.707 (1)	0.1006 (9)	−0.090 (1)	5.7 (5)
C32	0.855 (1)	0.0804 (9)	0.184 (1)	5.9 (5)
C33	0.609 (1)	0.0574 (7)	0.151 (1)	4.4 (5)
C34	0.741 (1)	−0.043 (1)	−0.015 (1)	6.0 (6)
C41	0.881 (1)	0.4590 (9)	0.224 (1)	4.8 (5)
C42	1.009 (1)	0.3310 (9)	0.278 (1)	5.4 (5)
C43	0.968 (1)	0.222 (1)	0.017 (1)	6.3 (6)
C44	0.8420 (9)	0.3417 (8)	−0.051 (1)	4.5 (4)
C45	1.040 (1)	0.401 (1)	0.071 (1)	5.9 (6)

[a] $B(\mathrm{eq}) = 8\pi^2/_3(U_{11}aa^{*2} + U_{22}bb^{*2} + U_{33}cc^{*2} + 2U_{12}aba^*b^* \cos\gamma + 2U_{13}aca^*c^* \cos\beta + 2U_{23}bcb^*c^* \cos\alpha)$.

Table III. Selected Positional Parameters and B(eq) for IIb

atom	x	y	z	B(eq),[a] Å
Sb1	0.25549 (2)	0.73949 (2)	0.31006 (3)	2.63 (1)
Fe1	0.44636 (5)	0.66149 (5)	0.29217 (7)	3.21 (2)
Fe2	0.26848 (7)	0.91784 (5)	0.42079 (9)	4.30 (3)
Fe3	0.33769 (6)	0.67392 (5)	0.05905 (7)	3.24 (2)
Cr1	0.08271 (6)	0.65527 (7)	0.3752 (1)	3.90 (3)
O11	0.6658 (4)	0.5901 (4)	0.2677 (6)	7.5 (2)
O12	0.3756 (4)	0.5437 (3)	0.4656 (5)	5.7 (2)
O13	0.5303 (4)	0.8217 (3)	0.5374 (5)	5.7 (2)
O14	0.5563 (4)	0.7787 (3)	0.1409 (5)	5.5 (2)
O15	0.3726 (4)	0.4811 (3)	0.0707 (4)	5.1 (2)
O21	0.2502 (5)	1.1145 (4)	0.5678 (7)	8.3 (3)
O22	0.0721 (5)	0.9106 (5)	0.2314 (9)	11.5 (4)
O23	0.3119 (6)	0.8792 (5)	0.6963 (6)	8.9 (3)
O24	0.4732 (4)	0.9540 (4)	0.3042 (6)	6.8 (2)
O31	0.2853 (5)	0.8479 (3)	0.0023 (5)	6.7 (2)
O32	0.4460 (4)	0.6145 (4)	−0.2081 (5)	6.5 (2)
O33	0.1253 (4)	0.5722 (4)	−0.0681 (5)	7.0 (2)
O51	0.1451 (4)	0.4680 (4)	0.2064 (6)	7.2 (3)
O52	−0.0599 (5)	0.6785 (6)	0.1242 (8)	10.2 (4)
O53	0.0060 (5)	0.8520 (5)	0.5438 (6)	8.6 (3)
O54	0.2053 (5)	0.6648 (5)	0.6600 (5)	7.7 (3)
O55	−0.1108 (4)	0.5668 (5)	0.4613 (8)	8.8 (3)
C11	0.5798 (4)	0.6158 (5)	0.2736 (6)	4.6 (2)
C12	0.3988 (5)	0.5901 (4)	0.3980 (6)	3.9 (2)
C13	0.4937 (4)	0.7613 (4)	0.4414 (6)	4.0 (2)
C14	0.4839 (4)	0.7327 (4)	0.1582 (6)	4.0 (2)
C15	0.3785 (5)	0.5603 (4)	0.1159 (6)	4.1 (2)
C21	0.2571 (6)	1.0372 (5)	0.5114 (8)	5.6 (3)
C22	0.1491 (5)	0.9130 (4)	0.3053 (8)	5.6 (3)
C23	0.2934 (6)	0.8929 (5)	0.5891 (7)	5.0 (3)
C24	0.3957 (6)	0.9376 (4)	0.3476 (6)	4.6 (2)
C31	0.3044 (5)	0.7827 (4)	0.0309 (5)	4.2 (2)
C32	0.4047 (5)	0.6344 (4)	−0.1041 (6)	4.2 (2)
C33	0.2067 (5)	0.6125 (4)	−0.0140 (6)	4.0 (2)
C51	0.1244 (5)	0.5404 (4)	0.2719 (7)	4.5 (2)
C52	−0.0022 (6)	0.6730 (6)	0.2217 (9)	5.9 (3)
C53	0.0352 (6)	0.7787 (6)	0.4780 (9)	6.4 (3)
C54	0.1608 (5)	0.6605 (5)	0.5505 (7)	4.9 (2)
C55	−0.0345 (5)	0.5994 (5)	0.4263 (8)	5.7 (3)

[a] $B(\mathrm{eq}) = 8\pi^2/_3(U_{11}aa^{*2} + U_{22}bb^{*2} + U_{33}cc^{*2} + 2U_{12}aba^*b^* \cos\gamma + 2U_{13}aca^*c^* \cos\beta + 2U_{23}bcb^*c^* \cos\alpha)$.

mL of CH_2Cl_2. X-ray quality crystals of IIb were obtained in 22% yield (based on Sb) by slow cooling of a concentrated MeOH solution of the CH_2Cl_2 extract. IIb is soluble in MeOH, MeCN, CH_2Cl_2, and THF but not in hexane. IR (ν_{CO}, MeOH): 2080 w, 2040 vs, 2010 s, 1940 s, 1918 m, 1830 w cm^{-1}. Anal. Calcd for $[Et_4N][SbFe_3Cr(CO)_{17}]$: Sb, 12.85; Fe, 17.68; Cr, 5.49. Found: Sb, 12.07; Fe, 16.99; Cr, 4.69.

Synthesis of $[Et_4N]_2[Sb_2Fe_5(CO)_{17}]$ by Refluxing Ib. Ib was made in situ from 0.10 g (0.44 mmol) of $SbCl_3$ and 0.39 g (0.65 mmol) of $[Et_4N]_2[Fe_2(CO)_8]$ in acetone. The solvent was removed under vacuum, affording a residue, which was dissolved in 30 mL of MeCN. The MeCN solution was heated to reflux and purged with N_2 periodically for 14 days, producing 0.17 g (0.13 mmol) of $[Et_4N]_2[Sb_2Fe_5(CO)_{17}]$ (60% based on Sb).

Attempted Reaction of Ib with CO. Ib was prepared in acetone from the reaction of 0.059 g (0.26 mmol) of $SbCl_3$ with 0.23 g (0.38 mmol) of $[Et_4N]_2[Fe_2(CO)_8]$. The solvent was removed under vacuum, and the solid was dissolved in 30 mL of CH_2Cl_2. The solution was pressurized with 800 psi of CO for 8 days, after which Ib was recovered unreacted with no evidence for formation of other clusters.

Crystal Structure Determination for IIa. The crystal selected for the X-ray diffraction study was a black, cut parallelepiped plate of dimensions 0.30 × 0.40 × 0.50 mm. It was mounted with epoxy on the tip of a glass fiber. Data were collected by using the Rigaku CRYSTAN/TEXTL (3:2:1) Automatic Data Collection Series (Molecular Structure Corp., College Station, TX). Final unit cell parameters are based upon a least-squares analysis of the angular setting of 24 reflections ($34° \leq 2\theta \leq 39°$). The crystallographic data collection parameters are listed in Table I. The crystal system was shown to be triclinic, and the more common centrosymmetric setting was chosen and shown to be correct by subsequent structural solution and refinement. The data were corrected for decay, absorption (ψ scans), and Lorentz and polarization factors. The analytical form of the scattering factors for the appropriate neutral atoms were corrected for both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion.[12]

Table IV. Positional Parameters and B(eq) for III

atom	x	y	z	B(eq),[a] Å
Bi1	0.96431 (6)	0.55570 (5)	0.25245 (7)	2.93 (2)
Fe1	0.8123 (2)	0.6970 (2)	−0.0741 (3)	2.99 (6)
O1	0.536 (1)	0.459 (2)	−0.213 (2)	6.4 (6)
O2	1.166 (2)	0.847 (2)	0.056 (2)	6.5 (6)
O3	0.669 (2)	0.826 (2)	−0.440 (2)	6.1 (6)
O4	0.616 (2)	0.945 (2)	0.187 (2)	6.9 (6)
C1	0.645 (2)	0.549 (2)	−0.163 (2)	4.4 (6)
C2	1.027 (2)	0.785 (2)	0.010 (2)	4.0 (6)
C3	0.725 (2)	0.773 (2)	−0.302 (2)	4.0 (5)
C4	0.695 (2)	0.849 (2)	0.089 (2)	4.6 (6)
C5	1.170 (2)	0.736 (2)	0.468 (2)	5.2 (7)

[a] $B(\mathrm{eq}) = 8\pi^2/_3(U_{11}aa^{*2} + U_{22}bb^{*2} + U_{33}cc^{*2} + 2U_{12}aba^*b^* \cos\gamma + 2U_{13}aca^*c^* \cos\beta + 2U_{23}bcb^*c^* \cos\alpha)$.

The structure was solved by direct methods using SHELX-86, which indicated the presence of the bismuth, iron, and chromium atoms. The remaining non-hydrogen atoms were found by using successive least-squares cycles and difference maps. The hydrogen atoms were not located or calculated. Refinement was performed by using the TEXSAN (2.0) structure solution and refinement package (Molecular Structure Corp.). All non-hydrogen atoms were refined with anisotropic thermal parameters. Full-matrix least-squares refinement led to convergence with $R = 4.5\%$, $R_w = 5.3\%$, and GOF = 1.28 for those 5114 reflections with $I > 3\sigma(I)$. Final positional and thermal parameters are listed in Table II and selected bond distances and angles in Table V.

Crystal Structure Determination for IIb. A black, cut parallelpiped crystal of dimensions 0.50 × 0.50 × 0.50 mm was selected for X-ray

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

Table V. Selected Bond Distances (Å) and Angles (deg) for IIa

(A) Distances			
Bi–M and M–M			
Bi1–Fe1	2.742 (2)	Bi1–Cr1	2.718 (2)
Bi–Fe2	2.732 (1)	Fe1–Fe2	2.608 (2)
Bi1–Fe3	2.651 (2)		
Carbonyl Ranges			
Fe–C(term)	1.76 (1)–1.82 (1)	Fe–C(br)	1.98 (1)–2.06 (1)
Cr–C	1.84 (1)–1.96 (2)	C–O	1.12 (1)–1.17 (1)
(B) Angles			
Fe3–Bi1–Cr1	114.28 (6)	Cr1–Bi1–Fe1	120.50 (5)
Fe3–Bi1–Fe2	116.18 (5)	Fe2–Bi1–Fe1	56.91 (4)
Fe3–Bi1–Fe1	114.77 (5)	Fe2–Fe1–Bi1	61.33 (4)
Cr1–Bi1–Fe2	122.33 (5)	Fe1–Fe2–Bi1	61.75 (4)
Fe–C–O(term)	175 (1)–178 (1)	Fe–C–O(br)	138.5 (9)–141.0 (9)
Cr–C–O	175 (1)–178 (1)		

Table VI. Selected Bond Distances (Å) and Angles (deg) for IIb

(A) Distances			
Sb–M and M–M			
Sb1–Fe1	2.6538 (8)	Sb1–Cr1	2.6382 (9)
Sb1–Fe2	2.581 (1)	Fe1–Fe3	2.598 (1)
Sb1–Fe3	2.649 (1)		
Carbonyl Ranges			
Fe–C(term)	1.755 (7)–1.813 (7)	Fe–C(br)	1.990 (6)—2.023 (6)
Cr–C	1.821 (6)–1.974 (9)	C–O	1.117 (8)–1.163 (8)
(B) Bond Angles			
Fe2–Sb1–Cr1	113.91 (4)	Cr1–Sb1–Fe1	120.18 (3)
Fe2–Sb1–Fe3	116.40 (4)	Fe3–Sb1–Fe1	58.67 (3)
Fe2–Sb1–Fe1	115.32 (3)	Fe3–Fe1–Sb1	60.56 (3)
Cr1–Sb1–Fe3	121.52 (4)	Fe1–Fe3–Sb1	60.77 (3)
Fe–C–O(term)	174.5 (5)–179.5 (7)	Fe–C–O(br)	139.3 (5)–140.6 (5)
Cr–C–O	175.3 (7)–177.8 (8)		

analysis. The crystal mounting, data collection, treatment of intensity, data correction, and the solution of the structure followed the procedures for the previous study. The final unit cell parameters were derived from a least-squares analysis of the angular setting of 24 reflections (47° $\leq 2\theta \leq$ 51°). All non-hydrogen atoms were refined anisotropically. The refinement converged with R = 4.2%, R_w = 5.7%, and GOF = 1.63 for those 6100 reflections with $I > 3\sigma(I)$. The crystallographic data are listed in Table I. Final positional and thermal parameters are listed in Table III. Selected bond distances are bond angles appear in Table VI.

Determination of the Crystal Structure for III. The crystal selected for X-ray analysis was a black, somewhat flaky, diamond-shaped plate of approximate dimensions 0.20 × 0.40 × 0.30 mm. Data collection and refinement followed the procedures for the previous structural studies. The crystallographic data are given in Table I. Final unit cell parameters are based upon a least-squares analysis of the angular setting of 19 reflections (22° $\leq 2\theta \leq$ 25°). The data were corrected for absorption using ψ scans.

The structure was solved by direct methods using the program MITHRIL, which indicated the positions of the unique bismuth and iron atoms. The refinement cycles and difference maps were used to locate the rest of the non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms could not be located and their contributions were ignored. Full-matrix least-squares refinement led to convergence with R = 4.1%, R_w = 5.3%, and GOF = 1.28 for those 1355 reflections with $I > 3\sigma(I)$. Final positional and thermal parameters are listed in Table IV. Selected bond distances and bond angles are given in Table VII.

Results

Syntheses of I–III. The treatment of ECl_3 (E = Bi, Sb) with $[Et_4N]_2[Fe_2(CO)_8]$ produces compounds I, which have simple infrared spectra. In acetone solution, the spectra contain three prominent bands with the two at lower energy being barely separated, while in CH_2Cl_2 the lower two bands are not resolved. Ia tends to form an oil upon cooling in most solvents and decomposes gradually to $[Et_4N]_2[Bi_4Fe_4(CO)_{13}]$ in MeOH. Attempts to obtain single-crystal X-ray data have not, therefore, been successful. Crystallographic problems also plague the antimony system when the crystals are grown from solutions containing MeOH, but weakly diffracting crystals were obtained. The data set, however, has not yet yielded to numerous attempts at solution. The unit cell constants found for crystals grown from CH_2Cl_2 solutions of samples that had never been exposed to MeOH were found to be to those of $[Et_4N]_2[SbCl\{Fe(CO)_4\}_3]$.[13] The infrared spectra of products Ia and Ib in CH_2Cl_2 are identical with those found for $[Et_4N]_2[ECl\{Fe(CO)_4\}_3]$ (E = Bi; E = Sb).

Table VII. Selected Bond Distances (Å) and Angles (deg) for III

(A) Distances			
Bi1–Fe1	2.785 (2)	Fe1–C3	1.82 (2)
Bi1–Fe1*	2.787 (2)	C1–O1	1.15 (2)
Bi1–C5	2.28 (1)	C2–O2	1.18 (2)
Fe1–C2	1.77 (2)	C3–O3	1.14 (2)
Fe1–C4	1.80 (2)	C4–O4	1.13 (2)
Fe1–C1	1.81 (2)		
(B) Angles			
Fe1–Bi1–Fe1*	98.56 (6)	Fe1*–Bi1–C5	100.7 (4)
Bi1–Fe1–Bi1*	81.44 (6)	C2–Fe1–C4	97.1 (7)
Bi1–Fe1–C2	79.5 (5)	C2–Fe1–C1	161.3 (6)
Bi1*–Fe1*–C2	85.3 (4)	C2–Fe1–C3	94.0 (7)
Bi1–Fe1–C4	168.2 (4)	C4–Fe1–C1	97.9 (7)
Bi1*–Fe1*–C4	87.0 (4)	C4–Fe1–C3	98.6 (6)
Bi1–Fe1–C1	83.5 (5)	C1–Fe1–C3	94.6 (7)
Bi1*–Fe1*–C1	84.5 (5)	Fe1–C1–O1	177 (1)
Bi1–Fe1–C3	92.9 (4)	Fe1–C2–O2	176 (1)
Bi1*–Fe1*–C3	174.4 (4)	Fe1–C3–O3	178 (1)
Fe1–Bi1–C5	104.1 (5)	Fe1–C4–O4	178 (1)

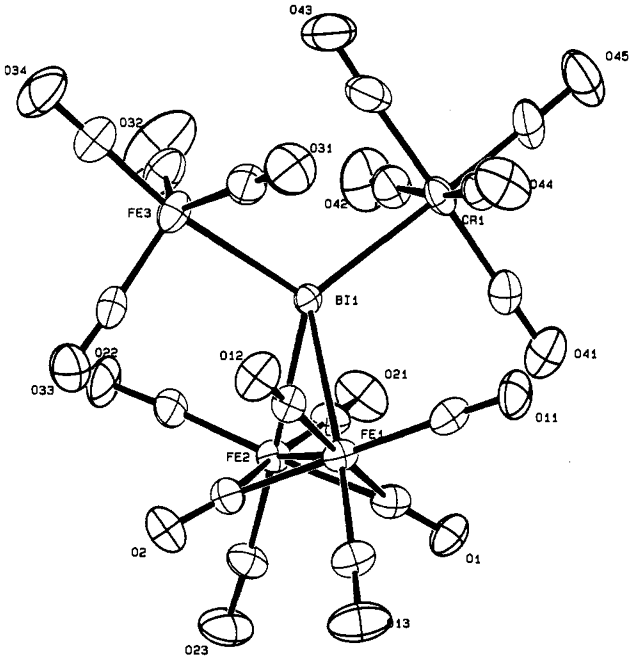

Figure 1. ORTEP diagram of the molecular structure (50% probability ellipsoids) and labeling scheme for IIa. Carbon atoms are labeled according to the oxygen atom to which they are attached.

Ia and $Cr(CO)_5(THF)$ react to produce IIa, which has been crystallographically characterized (Figure 1). Crystals of IIb prepared from the analogous reaction of Ib and $Cr(CO)_5(THF)$ are isomorphous with those of IIa, the only difference being the replacement of the bismuth by antimony.

Ia reacts readily with MeI to form III in 34% yield but does not react with PhBr under the same conditions. In solution, III slowly is converted into another compound. When the compound is first dissolved at low temperature, only one Me signal is observed (2.53 ppm) in the NMR, but when the solution is warmed, a second resonance also attributable to a methyl attached to Bi grows in at 2.75 ppm. The structural characterization of this compound has been hindered by decomposition.

The oxidation of Ia produces $Bi_2Fe_3(CO)_9$ in 20% yield, but refluxing Ia in MeCN forms $[Et_4N]_2[Bi_2Fe_4(CO)_{13}]$ in high yield. On the other hand, the oxidation of Ib produces $Sb_2Fe_6(CO)_{22}$. A report of the structure of this molecule has already appeared.[8a]

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(13) Luo, S.; Whitmire, K. H. *Inorg. Chem.* **1989**, *28*, 1424.

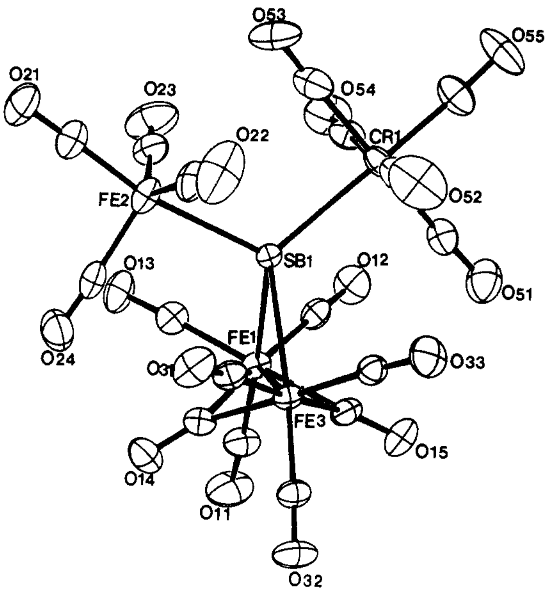

Figure 2. ORTEP diagram of the molecular structure (50% probability ellipsoids) and labeling scheme for IIb. Carbon atoms are labeled according to the oxygen atom to which they are attached.

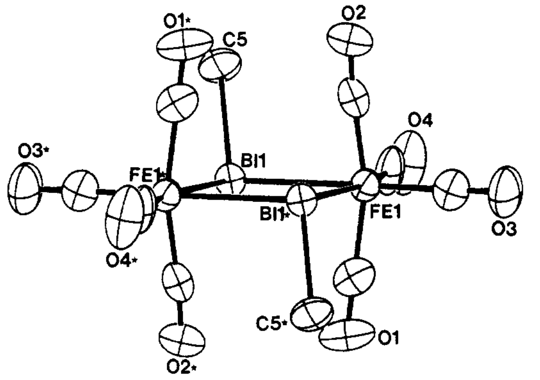

Figure 3. ORTEP diagram of the molecular structure (50% probability ellipsoids) and labeling scheme for III.

Refluxing Ib in MeCN at 75 °C for 2 days produces the previously characterized $[Et_4N]_2[Sb_2Fe_5(CO)_{17}]$.[8b] Ib does not react with CO at moderate pressures.

Structures of Compounds IIa and IIb. The molecular structures and labeling schemes for IIa and IIb are shown in Figures 1 and 2, respectively. Bond distances and angles are given in Tables V (IIa) and VI (IIb). The core framework of II (a or b) can be viewed as a distorted tetrahedron in which the central main group atom is bonded to four transition metals, one chromium atom and three iron atoms. Two iron atoms are bonded to each other and are bridged by three groups—the Bi or Sb and two carbonyls. That fragment is similar to $Fe_2(CO)_9$[14] and $Fe_2(CO)_6(\mu\text{-}GeMe_2)_3$,[15] which also show Fe-Fe bonds bridged by three ligands. The isolated $Fe(CO)_4$ group is trigonal bipyramidal with the bismuth atom occupying an axial site and with the chromium atom in an octahedral environment.

Structure of III. Crystallographic characterization of III shows it to be composed of an Fe_2Bi_2 parallelogram that lies on a crystallographic inversion center (Figure 3). Bond angle and distance data are supplied in Table VII. Each iron is pseudooctahedral with the axial carbonyls strongly bent toward the center of the molecule. The bismuth atoms are pyramidal with one coordination site evidently occupied by a lone pair of electrons. The methyl groups are oriented trans to each other with respect to the Fe_2Bi_2 ring in the solid state.

Discussion

Syntheses of Ia, Ib, IIa, IIb, and III. The reactions of $[Et_4N]_2[Fe_2(CO)_8]$ and ECl_3 (E = Bi, Sb) result in a compounds Ia and Ib, respectively, which have simple infrared spectra. These spectra are similar to a number of other iron carbonyl compounds that contain only isolated $Fe(CO)_4$ groups. The spectra obtained in acetone show three bands (although the lower energy pair is barely resolved), which are similar to the three-band patterns obtained for $[Et_4N]_3[E\{Fe(CO)_4\}_4]$ (E = Bi, Sb) while the spectra in CH_2Cl_2 look almost identical with those found for trigonal-planar $[Et_4N]_2[E\{Fe(CO)_4\}_3]$ (E = Sn, Pb), whose structures are known.[9] In the latter cases the lower energy band is broad and slightly asymmetric and appears to be a composite of two bands. The analytical data for Ib gave a Sb:Fe ratio of 1:3, suggesting that the compounds I could contain the $[E\{Fe(CO)_4\}_3]^-$ ions, which would be isoelectronic with trigonal-planar $[Et_4N]_2[E\{Fe(CO)_4\}_3]$ (E = Sn, Pb). The Fe and Sb values, however, were low compared to those expected for a monoanion. Initially, it was believed that this discrepancy was attributable to solvent occlusion, which has been seen in other compounds of this type. Analyses were repeated and gave results consistent with the first fitting better those for dianionic $[Et_4N]_2[SbCl\{Fe(CO)_4\}_3]$, whose infrared spectrum is identical with that of Ib.[13] The analytical data are not exact for that formulation either, but this may be expected since the crystals of $[Et_4N]_2[SbCl\{Fe(CO)_4\}_3]$ have been shown to retain solvent CH_2Cl_2, which is slowly lost after the crystals are removed from the mother liquor. The unit cell parameters of crystals of Ib grown from MeOH solution were considerably different from those of $[Et_4N]_2[SbCl\{Fe(CO)_4\}_3]$, and so the immediate connection between this compound and Ib was not made. The unit cell constants of crystals of Ib grown from CH_2Cl_2 with no exposure to MeOH, however, are very close to those found for $[Et_4N]_2[SbCl\{Fe(CO)_4\}_3]$. MeOH reacts slowly with both Ia and Ib, producing as yet unidentified complexes, and thus the crystals of Ib isolated from MeOH/acetone are probably of different formulation.

Because of the lack of certainty about the identity of Ia and Ib at the time of study, attempts were made to structurally characterize derivatives obtained from their reactions with $Cr(CO)_5(THF)$. The originally postulated cluster formulation $[EFe_3(CO)_{12}]^-$ (E = Bi, Sb) could exist in the same trigonal-planar configuration found for $[E\{Fe(CO)_4\}_3]^{2-}$ (E = Sn, Pb)[9] with which they would be isoelectronic, or they could exist as pyramidal species with one metal–metal bond. In the latter form, the main-group atom would possess a lone pair of electrons that could be used to ligate an additional metal fragment such as the $Cr(CO)_5$ group. Compounds Ia and Ib were treated with $Cr(CO)_5(THF)$ as the coordinated THF in $Cr(CO)_5(THF)$ is easily replaced with other two-electron donors, forming simple $Cr(CO)_5$ adducts.[16] Examples of group 15 element containing clusters where this is known to happen include $As_2[Co(CO)_3]_2$, which reacts with $M(CO)_5(THF)$ (M = Cr, Mo, W) to generate the heteronuclear complexes $(CO)_5MAs_2[Co(CO)_3]_2$,[17] and $As_2[Co(CO)_2(PR_3)]_2$, which is more basic and readily reacts with $M(CO)_5(THF)$ (R = OMe; M = Cr, Mo, W) to afford $[(CO)_5M]_2As_2[Co(CO)_2(PR_3)]_2$.[17] Fortuitously in spite of the erroneous assumption about the nature of Ia and Ib, the expected products $[Et_4N][E\{Fe_2(CO)_8\}\{Fe(CO)_4\}\{Cr(CO)_5\}]$ were obtained. This suggests that compounds $[Et_4N]_2[ECl\{Fe(CO)_4\}_3]$ (E = Bi, Sb) could function as sources of $[E\{Fe(CO)_4\}_3]^-$. Initial attempts to confirm this by treatment of $[Et_4N]_2[SbCl\{Fe(CO)_4\}_3]$ with $Ag[BF_4]$ unfortunately have led to oxidation and not halide abstraction. Reaction of an authentic sample of $[Et_4N]_2[SbCl\{Fe(CO)_4\}_3]$ with $Cr(CO)_5(THF)$ did produce IIb, but the yield was low and freshly prepared solutions from the reaction $SbCl_3$ with $[Et_4N]_2[Fe_2(CO)_8]$ seem to be more active. Further studies to determine if halide ions can be removed from $[Et_4N]_2[SbCl\{Fe(CO)_4\}_3]$ are in progress.

A similar motivation prompted the study of the reaction of Ia with MeI. The expected product was the hypothetical $BiMe\{Fe_2(CO)_8\}\{Fe(CO)_4\}$, which has not been seen. Obviously the

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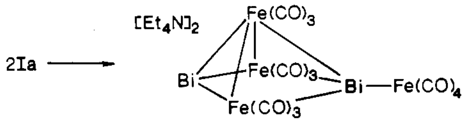
(14) Cotton, F. A.; Troup, J. M. *J. Chem. Soc., Dalton Trans.* **1974**, 800.
(15) Elder, M.; Hall, D. *Inorg. Chem.* **1969**, *8*, 1424.
(16) Scherer, O. J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 924.
(17) Müller, M.; Vahrenkamp, H. *J. Organomet. Chem.* **1983**, *252*, 95.

reaction must be more complicated than a simple alkylation of a lone pair on the bismuth atom. III, however, is observed and could be considered to result from dimerization of reactive, intermediate $Fe(CO)_4BiMe$ fragments. Similar reactions with Ib have not proven successful.

The oxidation reactions of Ia and Ib yield $Bi_2Fe_3(CO)_9$ (20% yield) and $Sb_2Fe_6(CO)_{22}$ (8.5% yield), respectively. Both these reactions might be thought to occur through dimerization of radical species formed upon oxidation of the original EFe_3 clusters. A very dramatic rearrangement coupled with loss of iron carbonyl groups would need to take place for Ia, but the process for building up $Sb_2Fe_6(CO)_{22}$ is more readily envisaged since the metals ratio in the product is the same as that in the starting material.

Neither Ia nor Ib is stable in refluxing MeCN under a purge of N_2. $[Et_4N]_2[Bi_2Fe_4(CO)_{13}]$[7n] and $[Et_4N]_2[Sb_2Fe_5(CO)_{17}]$[8b] have been identified as products in the respective reactions. These two thermally stable products can again be considered dimerization products of Ia and Ib and show very similar structures (eq 1 and 2). The difference in the products obtained highlights the tendency for the antimony atom's lone pair to coordinate to metal fragments, while that property of bismuth is somewhat diminished.



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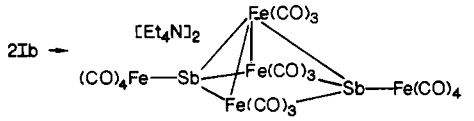

(2)

Discussion of the Structures of IIa and IIb. Compound IIa can be envisaged as a derivative of $Fe_2(CO)_9$, in which a bridging $[Bi\{Fe(CO)_4\}\{Cr(CO)_5\}]^-$ fragment replaces one bridging CO group. It is isoelectronic with $[Et_4N]_2[PbFe_4(CO)_{16}]$ and has virtually the same arrangement of metals around the main-group element.[18] The $Fe_2(CO)_8$ groups in these anions both have two bridging carbonyls. The Fe1–Fe2 bond lengths of 2.608 (2) Å in IIa and 2.598 (1) Å in IIb can be compared to those in $Fe_2(CO)_9$ (2.523 (1) Å),[14] $[Et_4N]_2[PbFe_4(CO)_{16}]$ (2.617 (5) Å),[18] $[PPN]_2[Fe_2(CO)_8]$ (2.787 (2) Å),[19] $Sn[Fe_2(CO)_8]_2$ (2.87 Å),[20] $Ge[Fe_2(CO)_8]_2$ (2.825 (1) and 2.821 (1) Å),[21] $[Fe_2\{\mu\text{-}SbC(H)(SiMe_3)_2\}]$ (2.801 (1) Å),[22] $Pb\{Fe_2(CO)_8\}_2$ (2.890 (4) and 2.911 (4) Å),[23] and $Si[Fe_2(CO)_8]_2$ (2.792 (3) Å).[24] That the iron–iron bond lengths are on the short end of this range of values is probably due to the presence of the bridging CO groups. The infrared spectra show moderate bands in the bridging CO region (CH_2Cl_2) at 1825 (IIa) and 1830 (IIb) cm^{-1} which indicate that the bridging CO's are retained in solution (cf. $\nu_{CO\text{-bridging}}$ for $Fe_2(CO)_9$ = 1828 cm^{-1} in the solid state).[25]

The average Bi–Fe bond distance in IIa is 2.708 (50) Å[26] but individual values fall into two distinct groups with the Bi–Fe distances within the $BiFe_2$ triangle (2.742 (2) and 2.732 (1) Å) being significantly longer than that to the lone $Fe(CO)_4$ group (2.651 (2) Å). Average distances in other bismuth–iron clusters include 2.750 (2) Å in $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$,[7a] 2.650 (2) Å in $[Et_4N][BiFe_3(CO)_{10}]$,[7g] 2.628 (14) Å in $Bi_2Fe_3(CO)_9$,[7f] 2.650 (40) Å in $[Et_4N]_2[Bi_2Fe_4(CO)_{13}]$,[7l] and 2.725 (33) Å in $[Et_4N]_2[Bi_4Fe_4(CO)_{13}]$.[4] The angle Fe1–Bi–Fe2 (56.91 (4)°) is slightly greater than the value (55.13 (12)°) in $[Et_4N]_2[PbFe_4(CO)_{16}]$[18] but much smaller than that of 73° in $Si[Fe_2(CO)_8]_2$,[24] 72° in $Sn[Fe_2(CO)_8]_2$,[20] and 72.07 (18)° in $Ge[Fe_2(CO)_8]_2$.[21]

Compound IIb is isomorphous with IIa. The average Sb–Fe bond length in this cluster is 2.628 (41) Å. The Sb–Fe distances exhibit variations between those bonds within the $SbFe_2$ triangle (2.6538 (8) and 2.649 (1) Å) and that to the lone $Fe(CO)_4$ group (2.581 (1) Å) in a fashion similar to the Bi–Fe bonding trends noted above. Comparisons can be made to other known Sb–Fe distances such as 2.715 Å (average) in $[Fe(\eta^2\text{-}\{(Me_3Si)_2CH\}_2Sb)_2(CO)_4]$,[22] and 2.637 (6) Å in $[Fe_2\{\mu\text{-}SbC(H)(SiMe_3)_2\}]$.[22] The Sb–Cr distance (2.6382 (9) Å) is in good agreement with that found in $(Sb^tBu)_2[Cr(CO)_5]_3$ (average 2.6935 (7) Å).[2b]

Structure of III. III contains a Bi_2Fe_2 parallelogram with average Bi–Fe distances of 2.786 (1) Å. This value is comparable to other known Bi–Fe separations listed earlier. The cross-ring distances of 3.787 (2) Å for Bi···Bi and greater than 4.10 Å for Fe···Fe are considered nonbonding. The important structural features are the presence of a stereochemically active lone pair of electrons and a methyl group on each bismuth atom. Very few structurally characterized examples of Bi–alkyl complexes are known. The bismuth–carbon distance of 2.28 (1) Å is consistent with the sum of the covalent radii (2.23 Å) and compares well with the reported value of 2.263 (4) Å for $BiMe_3$[27] but is somewhat shorter than the value of 2.339 (1) Å reported for $Bi_2W_2(CO)_8(\mu\text{-}BiMe\{W(CO)_5\})$.[28] There do not appear to be any unfavorable steric interactions between the methyl groups and the axial carbonyls as indicated by an essentially perpendicular angle between the Bi_2Fe_2 plane and the plane containing the two iron atoms and the four axial carbonyls. The electron counting for this compound is conventional for each atom, and one lone pair is left on each of the two bismuth atoms.

At low temperature, a single ^1H NMR signal is observed for freshly dissolved III at 2.53 ppm in CD_2Cl_2, which is in the same range as the value of 2.70 ppm reported for only one other known compound in which an alkylbismuth is connected to two metal fragments, $[Cp(CO)_2Fe]_2BiMe$.[29] Upon warming, another peak at 2.75 ppm grows in very slowly. Elucidation of the identity of this compound has been hampered by decomposition although there are a couple of obvious suggestions for its identity. One possibility is conversion to the cis form in solution. Another possibility is loss of CO with formation of a metal–metal bond to give $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}BiMe)_2$. Unfortunately, III is very sensitive as may be expected for Bi–alkyl complexes in general and is slowly converted into $Bi_2Fe_3(CO)_9$. More work will be necessary to answer this question.

Conclusions

Reaction of EX_3 (E = Bi, Sb) with $[Et_4N]_2[Fe_2(CO)_8]$ leads to production of compounds believed to be $[Et_4N]_2[ECl\{Fe(CO)_4\}_3]$ (E = Bi, Sb) previously prepared from $[Et_4N]_3[Sb\{Fe(CO)_4\}_4]$ and $SbCl_3$ or $TlCl_3$. These compounds are starting materials for the production of mixed-metal bismuth- and antimony-containing cluster compounds. X-ray analyses of the products II from the reaction of I with $Cr(CO)_5(THF)$ show them to be similar structurally to $[Et_4N]_2[Pb\{Fe_2(CO)_8\}\{Fe(CO)_4\}_2]$ containing one iron–iron bond. Alkylation of Ia with MeI leads to a rare example

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$$\sigma = \left[\sum_{i=1}^{i=N}(d_i - d)^2/(N-1)\right]^{1/2}$$

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of a metalated bismuth alkyl complex.

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Supplementary Material Available: Tables of complete crystallographic data collection parameters, positional parameters and isotropic thermal parameters for the $[Et_4N]^+$ cations in IIa and IIb, anisotropic thermal parameters for IIa, IIb, and III, and additional bond parameters for IIa and IIb (16 pages); tables of observed and calculated structure factors for IIa, IIb, and III (86 pages). Ordering information is given on any current masthead page.

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Magnetism of Alternating Bimetallic Chains: Application to $MnCu(obzp)(H_2O)_3 \cdot H_2O$ (obzp = Oxamido-*N*-benzoato-*N'*-propionato)

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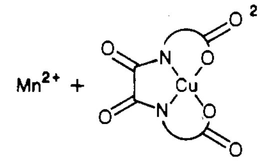
Two new alternating bimetallic chain compounds have been synthesized. Their formulas are $MnCu(obzp)(H_2O)_3 \cdot H_2O$ (**1**), with obzp = oxamido-*N*-benzoato-*N'*-propionato, and $MnCu(ophp) \cdot 5H_2O$ (**2**), with ophp = oxamido-*N*-phenolato-*N'*-propionato. **1** and **2** have been obtained by reaction of the Mn(II) ion with the dissymmetrical copper(II) brick $[Cu(obzp)]^{2-}$ or $[Cu(ophp)]^{2-}$. The crystal structure of **1** has been determined. It crystallizes in the monoclinic system, space group $P2_1/n$, with a = 7.814 (1) Å, b = 10.3375 (7) Å, c = 19.981 (1) Å, β = 98.43 (1)°, and Z = 4 (MnCu units). The structure consists of $Mn^{II}Cu^{II}$ chains with octahedral Mn(II) and square-planar Cu(II) bridged by oxamido (Mn···Cu = 5.4376 (6) Å) and carboxylato (Mn···Cu = 5.3670 (4) Å) groups. The configuration around the carboxylato bridge is of the anti–syn type, whereas it is of the anti–anti type in the previously reported alternating bimetallic chain compound $MnCu(obp)(H_2O)_3 \cdot H_2O$, with obp = oxamido-*N*,*N'*-bis-propionato). The $\chi_M T$ versus T plot, χ_M being the molar magnetic susceptibility per MnCu unit and T the temperature, has been measured in the 300–2 K temperature range. In spite of the chain structure, **1** does not behave as a ferrimagnetic chain but as an isolated $Mn^{II}Cu^{II}$ pair with an oxamido bridge. The quintet–septet energy gap was found equal to $3J = -82.2$ cm^{-1}. The interaction parameter through the carboxylato bridge is negligible. This unexpected result is attributed to the anti–syn configuration around this bridge; the $d_{x^2-y^2}$ and d_{z^2} type magnetic orbitals on Mn(II), and the $d_{x^2-y^2}$ type magnetic orbital on Cu(II), are unfavorably oriented to interact. The magnetic behavior of **2** is very similar to that of **1**.

Introduction

For a couple of years, a new type of molecular-based materials has emerged, namely the molecular-based ferromagnets.[2,3] The first compounds of this kind have been reported. To our knowledge, three research teams have synthesized and fully characterized molecular-based compounds exhibiting a spontaneous magnetization below a critical temperature T_c.[4–10] Our specific strategy along this line consists of assembling ferrimagnetic chains within the crystal lattice in a ferromagnetic fashion.[6,9] This strategy led us to describe a new family of regular bimetallic chains, in which the nearest-neighbor metal centers are equally spaced[11] and then the first alternating bimetallic chains.[12,13] Alternating in the context means that there is alternation not only of the magnetic centers but also of the exchange pathways. Our synthetic approach to obtain $Mn^{II}Cu^{II}$ alternating bimetallic chains is schematized as



The Mn(II) ion reacts with a dianionic copper(II) precursor containing both oxamido and carboxylato groups capable of bridging the metal centers. So far, we have synthesized and utilized two copper(II) precursors of this kind, namely $[Cu(obp)]^{2-}$ and $[Cu(obbz)]^{2-}$ with obp = oxamido-*N*,*N'*-bis(propionato) and obbz = oxamido-*N*,*N'*-bis(benzoato). These two copper(II) dianions are symmetrical in the sense that, in addition to the molecular plane, there is a mirror plane perpendicular to the molecular plane. Their symmetry is expected to be close to C_{2v}. The former compound when reacting with Mn(II) gives $MnCu(obp)(H_2O)_3 \cdot H_2O$, which magnetically behaves as a ferrimagnetic

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