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Reaction of $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ with *i*-BuBr. Isolation of the Tetrahedral Anionic Complex $[Et_4N]_2[i\text{-}BuBi\{Fe(CO)_4\}_3]$ and the Ring Complex $(i\text{-}Bu)_2Bi_2Fe_2(CO)_8$

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Transition metal clusters incorporating heavier main group elements have attracted significant attention for several years.[1] Recently, the number of reported transition metal–bismuth clusters increased substantially mainly because of this interest associated with the use of mixed bismuth–transition metal oxide catalysts for acrylonitrile synthesis.[2] Although many bismuth-containing metal carbonyl complexes have been synthesized and structurally characterized, comparatively little is known about their reactivity.[3] Stimulated by the versatile chemistry of Collman's reagent $Na_2Fe(CO)_4$ and tetracarbonylhydridoferrates $MHFe(CO)_4$ in synthesis and catalysis,[4,5] we became interested in the outcome of the reaction of the previously known anionic complex $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$[6] with organic halides. Here we report our initial results concerning the reaction of $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ with *i*-BuBr. Two structurally characterized complexes, $[Et_4N]_2[i\text{-}BuBi\{Fe(CO)_4\}_3]$ (I) and $(i\text{-}Bu)_2Bi_2Fe_2(CO)_8$ (II), have been isolated from the reaction.

Experimental Section

All reactions were performed under an atmosphere of pure nitrogen by using standard Schlenk techniques. Solvents were purified, dried, and distilled under nitrogen prior to use. The compound $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ was prepared according to the published method.[6] Infrared spectra of solutions in CaF_2 cells were recorded on a Jasco 700 IR spectrometer. Mass spectra were obtained on a Finningan MATTSQ-46C mass spectrometer at 30 eV. Elemental analyses were performed on a Perkin-Elmer 2400 analyzer. ^1H NMR spectra were obtained on a JEOL 400 (400 MHz) instrument.

Reaction of $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ with *i*-BuBr. A 2.7-mL sample (24 mmol) of *i*-BuBr was syringed into a green solution of 2.54 g (2 mmol) of $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ in 40 mL of MeCN. The solution was heated at 40 °C for about 40 h, after which it became brownish. The solution was filtered, and the solvent was removed under vacuum. The residue was washed with several 40-mL portions of ether and then extracted into 40 mL of CH_2Cl_2 to give 1.76 g (1.7 mmol) of $[Et_4N]_2[i\text{-}BuBi\{Fe(CO)_4\}_3]$ (I) (85% based on Bi). I is soluble in CH_2Cl_2, CH_3CN, and MeOH but insoluble in hexane and THF. Crystals of I suitable for diffraction were recrystallized from MeOH solution. IR (ν_{CO}, MeOH): 2030 w, 2012 w, 1979 s, 1909 vs cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 3.52 (d, 2H), δ 2.29 (m, 1H), δ 0.95 (d, 6H, $J = 6.3$ Hz) (chemical shifts not given for $[Et_4N]^+$). Anal. Calcd for $[Et_4N]_2[i\text{-}BuBi\{Fe(CO)_4\}_3]$: C, 37.31; H, 4.79; N, 2.72. Found: C, 35.99; H, 4.49; N, 2.62.

Table I. Crystallographic Data for I and II

	I	II
empirical formula	$BiFe_3C_{32}H_{49}O_{12}N_2$	$Bi_2Fe_2C_{16}H_{18}O_8$
fw	1027.23	867.96
crystal system	monoclinic	triclinic
space group (No.)	$P2_1/n$ (14)	$P\bar{1}$ (2)
a, Å	11.340(4)	6.746(1)
b, Å	17.463(4)	9.090(4)
c, Å	21.586(3)	10.388(3)
α, deg		92.42(4)
β, deg	90.57(2)	106.41(2)
γ, deg		105.12(3)
V, Å^3	4274.7(2)	585.2(3)
Z	4	1
D(calc), M gm^{-3}	1.596	2.463
abs coeff, mm^{-1}	5.14	16.20
diffractometer	Nonius CAD-4	Nonius CAD-4
radiation λ(Mo Kα), Å	0.70930	0.70930
temp, °C	25	25
T_{min}/T_{max}	0.64/1.00	0.36/1.00
residuals:[a] R, R_w	0.093, 0.109	0.033, 0.038

[a] The functions minimized during least-squares cycles were $R = \sum(F_o - F_c)/\sum F_o$ and $R_w = [\sum w(F_o - F_c)^2/\sum w(F_o)^2]^{1/2}$.

Synthesis of $(i\text{-}Bu)_2Bi_2Fe_2(CO)_8$, II. To a sample of 0.88 g (0.85 mmol) of I was added about 5 mL of HOAc. The mixed solution was allowed to stir for 40 h to give a reddish brown solution. The solvent was removed under vacuum, and the residue was extracted into several portions of 40 mL of hexane to give 0.072 g (0.083 mmol) of $(i\text{-}Bu)_2Bi_2Fe_2(CO)_8$ (II) (20% based on Bi). Upon cooling, reddish black crystals formed in the hexane solution. IR (ν_{CO}, hexane): 2034 vs, 1986 vs cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 223 K): δ 3.80 (d, 2H, $J = 6.8$ Hz), δ 2.22 (m, 1H), δ 0.99 (d, 6H, $J = 6.6$ Hz). Mass spectrum (EI): $M^+ = 868$ and the regular loss of CO groups $[M^+ - n(28)]$. Anal. Calcd for $(i\text{-}Bu)_2Bi_2Fe_2(CO)_8$: C, 22.01; H, 2.08. Found: C, 21.93; H, 1.82. Mp: 140 °C dec. The residue was then extracted into CH_2Cl_2, yielding 0.32 g of the previously reported complex $[Et_4N]_2[Bi_2Fe_4(CO)_{13}]$.[7]

X-ray Structural Characterization of I and II. A summary of selected crystallogaphic data for I and II is given in Table I. Data collection was carried out on a Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation at 25 °C. All crystals were mounted on glass fibers with Epoxy cement. Atomic scattering factors were taken from ref 8, and data reduction and structural refinement were performed using the NRCC-SDP-VAX packages.[9]

A reddish black crystal of I with dimensions 0.08 × 0.35 × 0.40 mm^3 was selected for X-ray analysis. Cell parameters of I were obtained from 25 reflections with 2θ in the range 12.24–19.08°. Systematic absences and intensity statistics indicated that the space group was $P2_1/n$. A 5% decay occurred in the three standard reflections over the course of the data collection. A total of 5576 unique reflections were collected and corrected for absorption and decay. Because of the poor quality of the crystal, only 1616 reflections with $I > 2.0\sigma(I)$ were used for refinement. The structure of I was solved by the heavy-atom method and refined by least-squares cycles and by fixed refinement for the two $[Et_4N]$ cations due to the disorder problem. The Bi and Fe atoms were refined with anisotropic temperature factors, and the other non-hydrogen atoms were refined with isotropic temperature factors. Full-matrix least-squares refinement led to convergence with $R = 9.3\%$ and $R_w = 10.9\%$ for those reflections with $I > 2.0\sigma(I)$.

A reddish black crystal of II was selected for analysis with dimensions 0.20 × 0.30 × 0.50 mm^3. Cell parameters of II were obtained from 25

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Table II. Selected Positional Parameters for I

atom	*x*	*y*	*z*
Bi	0.29588(22)	0.77591(14)	0.09409(10)
Fe(1)	0.5143(8)	0.7362(6)	0.1288(4)
Fe(2)	0.2360(9)	0.7474(5)	–0.0242(4)
Fe(3)	0.1333(8)	0.7357(8)	0.1773(4)
C(1)	0.473(6)	0.757(4)	0.199(3)
C(2)	0.575(5)	0.798(5)	0.076(3)
C(3)	0.648(7)	0.710(5)	0.158(4)
C(4)	0.487(7)	0.649(5)	0.107(4)
C(5)	0.362(6)	0.778(5)	–0.044(3)
C(6)	0.192(7)	0.723(5)	–0.108(3)
C(7)	0.240(8)	0.657(5)	–0.004(4)
C(8)	0.117(6)	0.804(4)	–0.017(3)
C(9)	0.194(8)	0.664(5)	0.187(4)
C(10)	0.041(10)	0.717(7)	0.115(5)
C(11)	0.024(10)	0.695(7)	0.240(5)
C(12)	0.161(8)	0.812(5)	0.223(4)
C(13)	0.323(8)	0.907(5)	0.102(4)
C(14)	0.251(13)	0.968(9)	0.124(7)
C(15)	0.330(15)	1.042(10)	0.098(7)
C(16)	0.136(17)	0.944(12)	0.080(9)
O(1)	0.452(5)	0.792(3)	0.2477(24)
O(2)	0.620(4)	0.841(3)	0.0433(22)
O(3)	0.736(5)	0.693(4)	0.179(3)
O(4)	0.449(5)	0.585(3)	0.081(3)
O(5)	0.456(5)	0.814(3)	–0.0612(23)
O(6)	0.188(7)	0.691(5)	–0.155(4)
O(7)	0.181(6)	0.602(4)	0.019(3)
O(8)	0.044(4)	0.848(3)	–0.0177(22)
O(9)	0.274(6)	0.611(4)	0.201(3)
O(10)	–0.049(5)	0.758(4)	0.086(3)
O(11)	–0.028(7)	0.706(5)	0.273(3)
O(12)	0.181(5)	0.876(3)	0.237(3)

Table III. Selected Positional Parameters for II

atom	*x*	*y*	*z*
Bi	0.21926(7)	0.03670(5)	0.15164(5)
Fe	–0.09138(23)	–0.23807(16)	0.02789(15)
C(1)	–0.2564(18)	–0.1726(12)	0.1129(12)
C(2)	0.0163(21)	–0.3386(13)	0.1654(12)
C(3)	–0.3082(18)	–0.3909(13)	–0.0795(11)
C(4)	0.1037(19)	–0.2454(13)	0.0597(13)
C(5)	0.1005(22)	0.0985(15)	0.3272(12)
C(6)	0.243(3)	0.2499(15)	0.4091(13)
C(7)	0.461(4)	0.246(3)	0.4781(22)
C(8)	0.141(4)	0.3012(23)	0.5100(19)
O(1)	–0.3665(14)	–0.1359(12)	0.1652(9)
O(2)	0.0772(19)	–0.4055(12)	0.2493(10)
O(3)	–0.4449(15)	–0.4897(10)	–0.1455(10)
O(4)	0.2299(14)	–0.2526(10)	–0.1100(9)

Table IV. Selected Bond Distances (Å) and Angles (deg) for I

(A) Distances			
Bi–Fe(1)	2.673(9)	Bi–Fe(2)	2.681(8)
Bi–Fe(3)	2.681(9)	Bi–C(13)	2.32(9)
Carbonyl Ranges (Disorder)			
Fe–C	1.44(9)–1.98(12)	C–O	0.94(14)–1.34(11)
Carbon-Carbon Range			
C–C	1.42(17)–1.67(22)		
(B) Angles			
Fe(1)–Bi–Fe(2)	116.4(3)	Fe(1)–Bi–Fe(3)	112.7(3)
Fe(1)–Bi–C(13)	96.7(22)	Fe(2)–Bi–Fe(3)	114.8(3)
Fe(2)–Bi–C(13)	106.3(21)	Fe(3)–Bi–C(13)	107.7(22)

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

(A) Distances			
Bi–Fe	2.7856(21)	Bi–Fe′	2.7884(20)
Bi–C(5)	2.292(13)	Fe–C(1)	1.797(11)
Fe–C(2)	1.809(13)	Fe–C(3)	1.790(11)
Fe–C(4)	1.812(12)	C(1)–O(1)	1.140(14)
C(2)–O(2)	1.128(15)	C(3)–O(3)	1.133(13)
C(4)–O(4)	1.130(15)	C(5)–C(6)	1.46(3)
C(6)–C(8)	1.523(25)		
(B) Angles			
Fe–Bi–Fe′	100.70(6)	Fe–Bi–C(5)	101.5(3)
Fe–Bi′–C(5)	101.3(3)	Bi–Fe–Bi′	79.30(5)
Bi–Fe–C(1)	84.9(3)	Bi–Fe–C(2)	91.2(4)
Bi–Fe–C(3)	167.9(4)	Bi–Fe–C(4)	81.3(4)
Bi–Fe′–C(1)	82.3(4)	Bi–Fe′–C(2)	169.9(4)
Bi–Fe′–C(3)	88.6(4)	Bi–Fe′–C(4)	86.2(4)
C(1)–Fe–C(2)	93.6(6)	C(1)–Fe–C(3)	94.8(5)
C(1)–Fe–C(4)	163.5(5)	C(2)–Fe–C(3)	100.9(5)
C(2)–Fe–C(4)	95.8(6)	C(3)–Fe–C(4)	96.8(5)
Bi–C(5)–C(6)	111.6(9)	C(5)–C(6)–C(7)	113.2(15)
C(5)–C(6)–C(8)	110.6(13)	C(7)–C(6)–C(8)	110.3(16)
Fe–C–O range	177.1(11)–178.5(11)		

reflections with 2θ in the range 14.50–25.54°. A total of 2051 unique reflections were collected and corrected for absorption, Lorentz, and polarization factors. The structure was solved by direct methods, which indicated the presence of the bismuth and iron atoms. The light atoms were found using successive least-squares cycles and difference maps. All non-hydrogen atoms were refined with anisotropic thermal parameters. The structure was refined by full-matrix least-squares procedures using 1745 reflections with $I > 2.0\sigma(I)$ to $R = 3.3\%$ and $R_w = 3.8\%$. The selected atomic coordinates of I and II are given in Tables II and Table III, respectively. Selected bond distances and angles for I are presented in Table IV, and those for II are listed in Table V. Additional crystallographic data are available as supplementary material.

Results

The reaction of $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ with *i*-BuBr in acetonitrile produces compound I in high yield. Further oxidation of I with HOAc yields two major products, II and the previously reported $[Et_4N]_2[Bi_2Fe_4(CO)_{13}]$.[7] By use of this methodology, II can be generated in reasonable yield from $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$. II also can be obtained by careful oxidation of I with CH_3I, but the isolation is difficult because of the formation of $Me_2Bi_2Fe_2(CO)_8$[10] as a side product.

Complexes I and II are fully characterized by spectroscopic methods and elemental analysis. The IR spectra of I and II show the absorptions characteristic of the terminal carbonyl ligands. The ^1H NMR spectra of I and II exhibit three resonances corresponding to the absorptions of the isobutyl group in each case.[10,11] Mass spectroscopy shows the molecular ion peak for II, and elemental analysis confirms the molecular formulas for I and II. In addition, the structures of I and II are further confirmed by X-ray analysis. I consists of two disordered $[Et_4N]^+$ cations and one $[i\text{-}BuBi\{Fe(CO)_4\}_3]$ anion, with a central bismuth atom tetrahedrally coordinated to one isobutyl group and three $Fe(CO)_4$ fragments. The core geometry of II can be viewed as a Bi_2Fe_2 parallelogram. Each pyramidal bismuth atom is bonded to an isobutyl group, and the iron atoms are pseudooctahedrally coordinated. The structure of the anion of I and its atomic numbering scheme are presented in Figure 1, and the molecular structure of compound II is shown in Figure 2.

Discussion

The anion of I can be considered as a central 5+ bismuth ion bonded to one one-electron-donor $i\text{-}Bu^-$ group and three two-electron-donor $Fe(CO)_4^{2-}$ groups. Basically, I is structurally similar to $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ except for one $Fe(CO)_4^{2-}$ group being replaced by one $i\text{-}Bu^-$ group. Compound II exhibits a ring core geometry structurally similar to those of $Me_2Bi_2Fe_2(CO)_8$ and $Ph_2Bi_2Fe_2(CO)_8$,[12] which have been synthesized by the other two methods. The electron counting for each atom in I and II is conventional and obeys the EAN rule.

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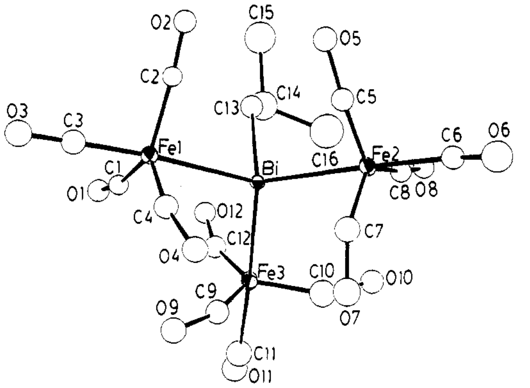

Figure 1. ORTEP diagram showing the structure and atom labeling for the anion of I.

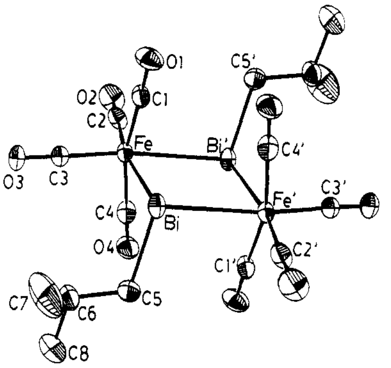

Figure 2. Molecular structure and labeling scheme for II. The thermal ellipsoids are at 30% probability.

The reaction of [Et$_4$N]$_3$[Bi{Fe(CO)$_4$}$_4$] with *i*-BuBr is believed to occur via loss of one Fe(CO)$_4$ fragment followed by the attack of the central Bi atom on the isobutyl group. Compound II can be considered to result from dimerization of *i*-BuBiFe(CO)$_4$ derived from I. Interestingly, we observed that the reaction of [Et$_4$N]$_3$[Bi{Fe(CO)$_4$}$_4$] with MeI or EtI directly produces Me$_2$Bi$_2$Fe$_2$(CO)$_8$ and Et$_2$Bi$_2$Fe$_2$(CO)$_8$, respectively.[13] This suggests that the reactivity of the alkyl halide may play an important role in the reaction with [Et$_4$N]$_3$[Bi{Fe(CO)$_4$}$_4$]. Compound I may represent an analogue of the intermediate or transition state in these alkylation reactions.

In the anion of I, the average Bi–Fe bond length of 2.678(9) Å is close to those seen in [Et$_4$N]$_3$[Bi{Fe(CO)$_4$}$_4$] (2.750(2) Å), [PPN][Ph$_2$BiFe(CO)$_4$] (2.676(4) Å),[12] [Et$_4$N][BiFe$_3$Cr(CO)$_{17}$] (2.708(5) Å),[10] [Et$_4$N]$_2$[Bi$_2$Fe$_4$(CO)$_{13}$] (2.650(40) Å),[7] [Et$_4$N]-[BiFe$_3$(CO)$_{10}$] (2.650(2) Å),[14] and [Et$_4$N]$_2$[Bi$_4$Fe$_4$(CO)$_{13}$] (2.725(33) Å).[15] The Fe–Bi–Fe angles about bismuth are 116.4(3), 112.7(3), and 114.8(3)°; and the three Fe–Bi–C angles are 96.7(2), 106.3(2), and 107.7(2)°. The extremely distorted tetrahedral angles about bismuth are due to the steric hindrance of the Fe(CO)$_4$ groups. The bismuth–carbon distance is 2.32 Å, which is somewhat longer than the sum of the covalent radii (2.23 Å) and comparable to 2.339(1) Å reported for Bi$_2$W$_2$(CO)$_8$(μ-BiMe{W(CO)$_5$})[16] and 2.33(4) Å (average) for [Bi{CH(SiMe$_3$)$_2$}$_3$].[17]

In II, the Bi–Fe (2.787(4) Å) and Bi–C (2.292(13) Å) distances are comparable to those in Me$_2$Bi$_2$Fe$_2$(CO)$_8$ and Ph$_2$Bi$_2$Fe$_2$(CO)$_8$. Each Bi atom displays a pyramidal geometry, and the iron atom is pseudooctahedrally coordinated to four carbonyls and two Bi atoms. Similarly, the cross-ring distances 3.557 Å for Bi···Bi and 4.292 Å for Fe···Fe are considered nonbonding. The respective Fe–Bi–Fe and Bi–Fe–Bi angles in II are 100.70(6) and 79.30(5)°, close to 98.56(6) and 81.44(6)° in Me$_2$Bi$_2$Fe$_2$(CO)$_8$ and 98.33(5) and 81.67(5)° in Ph$_2$Bi$_2$Fe$_2$(CO)$_8$. This suggests that the presence of different organo groups has no significant influence on the parallelogram owing to the trans orientations of the organo groups and the little steric interaction between the organo groups and the carbonyl ligands.

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Supplementary Material Available: A complete listing of crystallographic data and tables of positional parameters, anisotropic thermal parameters, and bond distances and angles for I and II (9 pages). Ordering information is given on any current masthead page.

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