

## BISMUTH(III) AS A BRIDGING LIGAND IN ORGANOIRON COMPLEXES \*

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### Summary

Bismuth halides  $\text{BiX}_3$  ( $\text{X} = \text{Cl}, \text{Br}$ ) react readily with two equivalents of  $\text{Na}^+ \text{CpFe}(\text{CO})_2^-$  to give the  $\mu$ -halobismuthane complexes  $[\text{CpFe}(\text{CO})_2]_2\text{BiX}$ , which react further with triethylaluminium to give the  $\mu$ -ethylbismuthane  $[\text{CpFe}(\text{CO})_2]_2\text{BiEt}$ . Treatment of  $\text{BiCl}_3$  with three equivalents of  $\text{Na}^+ \text{CpFe}(\text{CO})_2^-$  gives the open cluster compound  $[\text{CpFe}(\text{CO})_2]_3\text{Bi}$ , which undergoes photochemical decarbonylation to the *closo* tetrahedral cluster  $[\text{CpFe}(\mu_2\text{-CO})]_3\text{Bi}$ . The trimeric nature of solid  $\{[\text{CpFe}(\text{CO})_2]_2\text{BiCl}\}_3$  has been shown by single crystal X-ray diffraction. The chlorine atoms provide three bridges between the Bi atoms, forming a six-membered ring, with three  $\text{CpFe}(\text{CO})_2$  units above and three below the planar  $\text{Bi}_3\text{Cl}_3$  ring. (Crystals are monoclinic,  $C2/c$  with  $a$  12.296(1),  $b$  21.398(2),  $c$  37.672(5) Å,  $\beta$  90.07(1)°,  $V$  9911.9 Å<sup>3</sup>,  $D_c$  2.406 g cm<sup>-3</sup> for  $Z = 8$ ,  $R_w = 0.038$  for 592 refined parameters and 5464 observables).

### Introduction

Organometallic complexes of the main group metals are attracting increasing interest [1,2]. Bismuth holds a special position in the Periodic Table as the heaviest stable element, and in view of the size of the bismuth atom and its large atomic mass special behaviour can be expected for its complexes, from both electronic and steric aspects.

Trisubstituted complexes of bismuth, of the form  $[\text{L}_n\text{M}]_3\text{Bi}$ , fall into two major classes, one in which there are no M–M bonds, giving an open cluster, and the other in which three M–M bonds form a tetrahedral framework. Examples of open cluster compounds include  $[\text{Co}(\text{CO})_4]_3\text{Bi}$ ,  $[\text{Co}(\text{CO})_3(\text{PPh}_3)]_3\text{Bi}$  [3], and  $[\text{Fe}(\text{CO})_3(\text{NO})]_3\text{Bi}$  [4]. Three examples of closed clusters have been structurally characterized, viz.  $[\text{Fe}(\text{CO})_3]_3(\mu_3\text{-CO})\text{Bi}$  [5],  $[\text{Ir}(\text{CO})_3]_3\text{Bi}$  [6], and  $[\text{Fe}(\text{CO})_3]_3(\mu_3\text{-Bi})_2$  [7]. Although in

\* Dedicated to Professor G.E. Coates on the occasion of his 70th birthday.

this last example the two Bi atoms do not interact, complexes with a  $\mu_3$ -Bi<sub>2</sub> unit have also been prepared [8,9].

Disubstituted complexes of the bismuth halides are less well-known; Malisch et al. have prepared [CpM(CO)<sub>3</sub>]<sub>2</sub>BiBr and [CpM(CO)<sub>3</sub>]<sub>2</sub>BiMe from the reaction of CpM(CO)<sub>3</sub><sup>-</sup> (M = Cr, Mo, W) with Me<sub>2</sub>BiBr [10]. The unique bismuthinidene dimer {[CpMn(CO)<sub>2</sub>]<sub>2</sub>BiCl}<sub>2</sub> has also been synthesized [11]. We report here the preparation of di- and trisubstituted iron bismuth complexes, their interconversions, and the photochemical conversion of an open Fe<sub>3</sub>Bi ensemble into a *closo* Fe<sub>3</sub>Bi cluster.

## Results and discussion

Low temperature reaction of Na<sup>+</sup> CpFe(CO)<sub>2</sub><sup>-</sup> with BiCl<sub>3</sub> or BiBr<sub>3</sub> in 2:1 stoichiometry affords bright green solutions, from which [CpFe(CO)<sub>2</sub>]<sub>2</sub>BiCl, (**1**), or [CpFe(CO)<sub>2</sub>]<sub>2</sub>BiBr, (**2**), may be isolated as dark crystals with a metallic lustre in good yields. These complexes are readily soluble in benzene, tetrahydrofuran, dichloromethane, and less so in diethyl ether; they are insoluble in petroleum ether. The <sup>1</sup>H NMR spectra for **1** and **2** in CDCl<sub>3</sub> show only a singlet for the two equivalent cyclopentadienyl ligands, whereas in the carbonyl region of the infrared spectra there are three bands in each case (see Table 1). These bands lie clearly in the region assignable to terminal CO vibrations, and in view of this, together with the 18-electron environments of the iron centres, we conclude that there is no interaction between the iron atoms.

A molecular weight determination on **1** (cryoscopic in benzene) gave a value of 1439 g mol<sup>-1</sup> (M.W. of monomer 598.34 g mol<sup>-1</sup>) which suggested the presence of oligomers in solution. Hence we undertook a crystallographic investigation to determine the solid state structure. The monoclinic crystals of **1** have three monomeric molecules in the asymmetric unit, which are bound together into a trimer via chlorine atom bridges (see Fig. 1). The Bi and Cl atoms thus form a six-membered ring, which is almost planar; the maximum deviation from the best plane through the six atoms is shown by Bi(3),  $\delta$  0.05 Å (see Fig. 2). The angles Bi–Cl–Bi are close to 90°, as expected for optimal donor ability of the chloride ligands. The average Cl–Bi–Cl angle of 154.2 is extremely large, giving the bismuth atoms a distorted trigonal bipyramidal geometry, with two chloride ligands axial, and two iron atoms as the equatorial ligands; the third equatorial site is presumably filled by the Bi<sup>III</sup> lone pair. This description of the trimer leads to the conclusion that each Bi atom has a lone pair of electrons which is directed towards the centre of the six-membered ring. The average Bi...Bi separation, 3.95 Å, is close to the sum of the Van der Waals radii, and there is no need to invoke Bi–Bi bonds in the molecule. This is also indicated by the results of the molecular weight determination and by the reactivity of the compound, which suggest that the trimeric unit readily dissociates. The Bi–Fe distances (Table 2) are comparable to those found in other FeBi clusters [5,7,13], and the CpFe(CO)<sub>2</sub> units are unexceptional. It is perhaps surprising that the trimeric unit has no crystallographic symmetry, although the structure has approximate *D*<sub>3d</sub> symmetry.

Treatment of [CpFe(CO)<sub>2</sub>]<sub>2</sub>BiBr with one equivalent of triethylaluminium affords a product which dissolves in pentane to give green solutions, and forms dark, metallic shining crystals, **3**. **3** is formulated as [CpFe(CO)<sub>2</sub>]<sub>2</sub>BiEt on the basis of

TABLE 1  
ANALYTICAL AND SPECTROSCOPIC DATA FOR 1-5

Compound	Elemental analysis (%) <sup>a</sup>			other	<sup>1</sup> H NMR <sup>b</sup>	Infrared (Carbonyl region) <sup>c</sup>
	C	H	Fe			
[CpFe(CO) <sub>2</sub> ] <sub>2</sub> BiCl (1)	27.31 (28.10)	1.68 (1.68)	19.58 (18.67)	Cl 6.21 (5.92)	4.96(s)	2005s, 1982s, 1956s, 1948ssh.
[CpFe(CO) <sub>2</sub> ] <sub>2</sub> BiBr (2)	26.68 (26.16)	1.82 (1.57)	18.00 (17.38)	Br 12.34 (12.43)	4.97(s)	2009s, 1984s, 1957s, 1934ssh.
[CpFe(CO) <sub>2</sub> ] <sub>2</sub> BiEt (3)	33.49 (32.46)	2.71 (2.55)	19.98 (18.87)		4.27(s, 10H, Cp), 3.74(q, J 7 Hz, 2H, CH <sub>2</sub> ) 2.18(t, J 7 Hz, 3H, CH <sub>3</sub> ) <sup>d</sup> 5.01(s)	1991s, 1964s, 1926s.
[CpFe(CO) <sub>2</sub> ] <sub>3</sub> Bi (4)	33.40 (34.09)	2.10 (2.04)	22.91 (22.65)			1999s, 1997msh, 1970s, 1929s.
[CpFe(μ-CO)] <sub>3</sub> Bi (5)	32.56 (32.96)	2.33 (2.31)	25.04 (25.55)	O 7.96 (7.32)	4.59(s)	1784s, 1776sh, 1727m, 1718sh.

<sup>a</sup> Found (calc.)<sup>b</sup> In CDCl<sub>3</sub>, chemical shift in ppm. <sup>c</sup> In CH<sub>2</sub>Cl<sub>2</sub> solution. Abbreviations: s, strong; m, medium; w, weak; sh, shoulder. <sup>d</sup> Solvent C<sub>6</sub>D<sub>6</sub>.

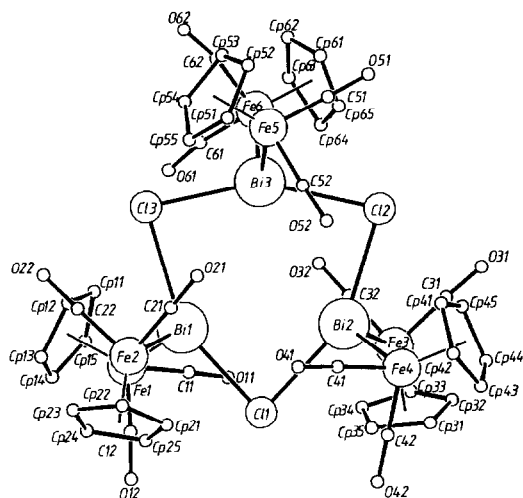


Fig. 1. The trimeric molecular structure of  $\{[\text{CpFe}(\text{CO})_2]_2\text{BiCl}\}_3$  (**1**). Only one alternative is shown for the disordered carbonyl groups C(61)/O(61) and C(62)/O(62).

elemental analysis and spectroscopic data. The  $^1\text{H}$  NMR spectrum shows a 10 hydrogen singlet at  $\delta$  4.27 ppm assignable to two equivalent cyclopentadienyl ligands, and the typical quartet ( $\delta$  3.74 ppm) and triplet ( $\delta$  2.18 ppm) assignable to an ethyl group.

The solution infrared spectrum of **3** is similar to that of **1** and **2**, with three bands in the terminal carbonyl region. The analogous methyl complex  $[\text{CpFe}(\text{CO})_2]_2\text{BiMe}$  has been briefly mentioned by Malisch [12].

The halo complexes **1** and **2** react readily with a further equivalent of  $\text{Na}^+ \text{CpFe}(\text{CO})_2^-$  to form the red crystalline  $[\text{CpFe}(\text{CO})_2]_3\text{Bi}$ , **4**, which is soluble in polar solvents, less so in diethyl ether, and insoluble in pentane. The spectroscopic data are consistent with an "open" cluster, in which there is no interaction between the iron centres. Solution IR studies again show three terminal CO stretches, and

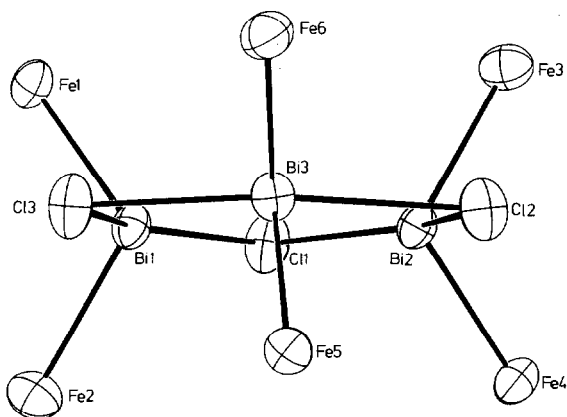


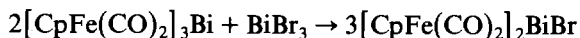
Fig. 2. Side view of the  $[\text{BiFe}_2(\mu\text{-Cl})]_3$  unit in **1**, showing the near planarity of the six-membered  $\text{Bi}_3\text{Cl}_3$  ring (ORTEP, thermal ellipsoids 50%).

TABLE 2  
SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR 1

Bi(1)–Cl(1)	2.803(4)	Bi(1)–Fe(1)	2.677(2)	Fe(1)–Cp(1) <sup>a</sup>	1.744
Bi(1)–Cl(3)	3.018(4)	Bi(1)–Fe(2)	2.704(2)	Fe(2)–Cp(2) <sup>a</sup>	1.724
Bi(2)–Cl(2)	2.874(3)	Bi(2)–Fe(3)	2.680(2)	Fe(3)–Cp(3) <sup>a</sup>	1.722
Bi(2)–Cl(1)	2.931(3)	Bi(2)–Fe(4)	2.678(2)	Fe(4)–Cp(4) <sup>a</sup>	1.740
Bi(3)–Cl(3)	2.833(4)	Bi(3)–Fe(5)	2.675(2)	Fe(5)–Cp(5) <sup>a</sup>	1.734
Bi(3)–Cl(2)	2.983(4)	Bi(3)–Fe(6)	2.710(2)	Fe(6)–Cp(6) <sup>a</sup>	1.724
Cl(1)–Bi(1)–Cl(3)	154.2(1)	Fe(1)–Bi(1)–Cl(1)	95.1(1)		
Cl(2)–Bi(2)–Cl(1)	153.9(1)	Fe(1)–Bi(1)–Cl(3)	101.2(1)		
Cl(3)–Bi(3)–Cl(2)	154.5(1)	Fe(2)–Bi(1)–Cl(1)	98.7(1)		
		Fe(2)–Bi(1)–Cl(3)	94.4(1)		
Fe(1)–Bi(1)–Fe(2)	109.7(1)	Fe(3)–Bi(2)–Cl(2)	94.8(1)		
Fe(3)–Bi(2)–Fe(4)	109.7(1)	Fe(3)–Bi(2)–Cl(1)	99.2(1)		
Fe(5)–Bi(3)–Fe(6)	110.0(1)	Fe(4)–Bi(2)–Cl(2)	101.6(1)		
		Fe(4)–Bi(2)–Cl(1)	94.3(1)		
Bi(1)–Cl(1)–Bi(2)	86.3(1)	Fe(5)–Bi(3)–Cl(3)	99.1(1)		
Bi(2)–Cl(2)–Bi(3)	85.6(1)	Fe(5)–Bi(3)–Cl(2)	90.7(1)		
Bi(3)–Cl(3)–Bi(1)	85.1(1)	Fe(6)–Bi(3)–Cl(3)	96.2(1)		
		Fe(6)–Bi(3)–Cl(2)	102.4(1)		

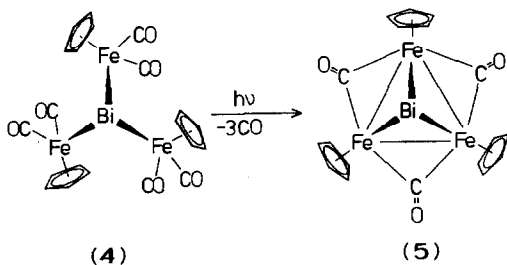
<sup>a</sup> Perpendicular distance of iron atom from the best plane through Cp<sub>n</sub>1 - Cp<sub>n</sub>5.

the <sup>1</sup>H NMR spectrum gives a singlet, indicating the equivalence of the three Cp ligands. The mass spectrum of **4** shows a molecular ion at *m/e* 740, as well as peaks at *m/e* 563 and 386 corresponding to *M*<sup>+</sup> – CpFe(CO)<sub>2</sub> and *M*<sup>+</sup> – 2(CpFe(CO)<sub>2</sub>), respectively. **4** can also be readily prepared from the reaction of BiX<sub>3</sub> (X = Cl, Br) with three equivalents of Na<sup>+</sup> CpFe(CO)<sub>2</sub><sup>–</sup>. Although **4** is stable in solution, treatment with 0.5 equivalent of BiBr<sub>3</sub> causes an immediate colour change from deep red to green as a result of a redistribution reaction:

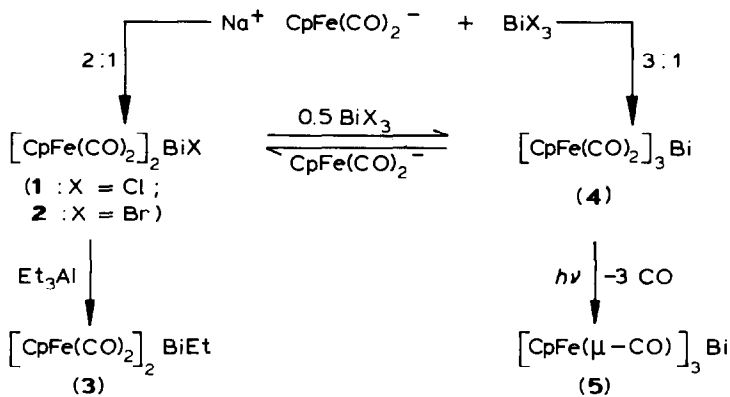


If a solution of **4** in benzene is irradiated with UV light a smooth reaction occurs in which three equivalents of carbon monoxide gas are liberated. The product **5**, which is formed in high yield and may be crystallized from dichloromethane, differs from **4** in that its solutions are red-brown, and that it is less soluble in benzene. In stark contrast to **4**, which shows three terminal C=O stretches in the IR spectrum, dichloromethane solutions of **5** have no C=O absorption bands above 1800 cm<sup>–1</sup>, but have two strong bands at 1784 and 1727 cm<sup>–1</sup>, with shoulders at 1776 and 1718 cm<sup>–1</sup>. The <sup>1</sup>H NMR spectrum of **5** shows a singlet Cp resonance, indicating the equivalence of the three iron environments. On the basis of these data, together with the elemental analysis (particularly the O analysis), we suggest that **5** is the *closo* tetrahedral cluster tris[cyclopentadienyl(μ<sub>2</sub>-carbonyl)ferrio]bismuthane, [CpFe(CO)]<sub>3</sub>Bi, containing three Fe–Fe single bonds\*.

\* Note added in proof. The structure of **5** has now been confirmed by X-ray diffraction: J.M. Wallis, G. Müller, and H. Schmidbaur, *J. Organomet. Chem.*, to be submitted.



Compounds 1–5 (see Scheme 1 for a summary of their syntheses) are stable in air for several hours, but their solutions decompose immediately on exposure to air. It was initially suggested that first row transition metals were unable to form *closo* clusters with a  $\mu_3$ -Bi atom present, because of the strain that this would place on the M–M bonds [3]. The synthesis and structural characterisation of the two iron clusters  $[\text{Fe}(\text{CO})_3]_3(\mu_3\text{-CO})\text{Bi}$  [5] and  $[\text{Fe}(\text{CO})_3]_3(\mu_3\text{-Bi})_2$  [7] have shown that *closo* species are accessible, although the mechanism of formation of these two clusters is far from clear. In the present work we have demonstrated the facile conversion of an open  $\text{Fe}_3\text{Bi}$  unit into a *closo* tetrahedral cluster. We are examining further the reactions of the above complexes in order to gain more information on the effects of the presence of a Bi atom in organometallic compounds.



SCHEME 1. Summary of the syntheses of 1–5.

## Experimental

All reactions were carried out under nitrogen, using solvents which had been freshly distilled after drying by standard techniques and storage over molecular sieves.  $^1\text{H}$  NMR spectra were recorded for  $\text{CDCl}_3$  solutions on a JEOL JNM-PMX 60 spectrometer, the residual protio-solvent being used as reference. Infrared spectra of  $\text{CH}_2\text{Cl}_2$  solutions were recorded on a Perkin–Elmer 283 B spectrophotometer with NaCl cells.

### *Bis(cyclopentadienyldicarbonylferrio)chlorobismuthane (1)*

An orange solution of sodium cyclopentadienyldicarbonylferrate (5.66 mmol) in THF (100 ml) was prepared from cyclopentadienyldicarbonyliron dimer (1.00 g,

2.83 mmol) and sodium amalgam (0.15%), and cooled to  $-30^{\circ}\text{C}$ . Anhydrous bismuth trichloride (0.89 g, 2.83 mmol) was dissolved in THF (25 ml) and added dropwise to the stirred solution of the anion during 20 min. The colour of the solution gradually changed to red, brown, and finally bright green. The mixture was stirred at room temperature for 2 h, then the solvent was removed in vacuo. Extraction with benzene (100 ml) and filtration gave a bright green solution, which on concentration gave very deep red, metallic crystals of **1**. Yield 1.00 g (60%). M.p.  $160^{\circ}\text{C}$  dec.

*Bis(cyclopentadienyldicarbonylferrio)bromobismuthane (2)*

**2** was prepared analogously to **1** from cyclopentadienyl-dicarbonyliron dimer (1.00 g, 2.83 mmol) and bismuth tribromide (1.27 g, 2.83 mmol). (Note that solutions of  $\text{BiBr}_3$  in THF are light-sensitive.) Yield of deep red, metallic crystals 1.06 g (58%). M.p.  $160^{\circ}\text{C}$  dec.

*Bis(cyclopentadienyldicarbonylferrio)ethylbismuthane (3)*

A green suspension of **2** (0.30 g, 0.47 mmol) in toluene (25 ml) was cooled to  $-50^{\circ}\text{C}$  and triethylaluminium (0.30 ml of a 25% solution in hexane, 0.54 mmol) was added dropwise. The stirred mixture was allowed to warm to room temperature during 2 h, and a brown solution resulted. Addition of methanol (0.4 ml) gave a green solution, which was evaporated to dryness. Repeated extractions with pentane followed by concentration of the combined extracts and cooling to  $-20^{\circ}\text{C}$  afforded the product as deep red, metallic crystals. Yield 0.09 g, 32%.

*Tris(cyclopentadienyldicarbonylferrio)bismuthane (4)*

*Method A.* A green solution of **1** (0.27 g, 0.45 mmol) in THF (20 ml) was added dropwise to a cooled ( $-30^{\circ}$ ) solution of sodium cyclopentadienyldicarbonylferrate (0.45 mmol) in THF (25 ml) during 15 min. The resulting deep red solution was stirred at room temperature for one hour, and the solvent then removed under reduced pressure. Extraction with benzene (30 ml) gave a deep red solution, from which deep red crystals of **4** were obtained after concentration of the solution. The product was recrystallized from diethyl ether (50 ml). Yield 0.24 g (72%). M.p.  $195^{\circ}\text{C}$  dec.

*Method B.* Cyclopentadienyldicarbonyliron dimer (1.00 g, 2.83 mmol) was used to prepare a solution of sodium cyclopentadienyldicarbonylferrate (5.66 mmol) in THF (100 ml), which was then filtered and cooled to  $-30^{\circ}\text{C}$ . A solution of bismuth trichloride (0.58 g, 1.84 mmol) in THF (25 ml) was added dropwise, and the solution immediately turned deep red. It was warmed to room temperature and evaporated to dryness. The solid was extracted with benzene (100 ml) and the extract filtered. Concentration of the filtrates gave deep red crystals of **4**, which were washed with diethyl ether ( $2 \times 20$  ml) and dried in vacuo. Yield 0.69 g (51%).

*Tris[cyclopentadienyl( $\mu_2$ -carbonyl)ferrio]bismuthane (5)*

**4** (0.41 g, 0.55 mmol) was dissolved in benzene (150 ml), giving a deep red, translucent solution. The solution was photolyzed using a water-cooled 150 W low pressure Hg vapour lamp until the evolution of gas ceased (3.5 h). The deeper red solution was evaporated under reduced pressure to leave a dark solid. Extraction with dichloromethane (30 ml) and filtration afforded a red-brown solution, which

TABLE 3

ATOMIC FRACTIONAL COORDINATES AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS FOR (1);  $U_{eq} = (U_1U_2U_3)^{1/3}$ , WHERE  $U_i$  ARE THE EIGENVALUES OF THE  $U_{ij}$  MATRIX.

ATOM	x	y	z	$U$ (eq.)
Bi(1)	0.2751(1)	0.4564(1)	0.3784(1)	0.034
Fe(1)	0.3179(2)	0.5399(1)	0.3274(1)	0.041
Fe(2)	0.3632(2)	0.4952(1)	0.4404(1)	0.048
Cl(1)	0.0609(3)	0.4967(1)	0.3896(1)	0.045
Cp(11)	0.4333(16)	0.4923(10)	0.2935(6)	0.071
Cp(12)	0.4792(13)	0.5076(9)	0.3262(6)	0.038
Cp(13)	0.4759(12)	0.5748(9)	0.3310(5)	0.035
Cp(14)	0.4269(13)	0.5948(9)	0.2992(6)	0.046
Cp(15)	0.3964(16)	0.5511(11)	0.2766(5)	0.074
Cp(21)	0.2431(19)	0.5352(8)	0.4730(5)	0.052
Cp(22)	0.3457(21)	0.5338(10)	0.4922(6)	0.074
Cp(23)	0.4193(20)	0.5697(9)	0.4726(6)	0.067
Cp(24)	0.3645(17)	0.5935(6)	0.4401(5)	0.057
Cp(25)	0.2535(15)	0.5718(6)	0.4417(5)	0.050
C(11)	0.1962(17)	0.5191(9)	0.3058(5)	0.064
C(12)	0.2568(16)	0.5975(6)	0.3509(5)	0.071
C(21)	0.3422(15)	0.4192(8)	0.4571(5)	0.065
C(22)	0.4910(15)	0.4801(9)	0.4225(5)	0.061
O(11)	0.1177(12)	0.5077(8)	0.2914(4)	0.099
O(12)	0.2166(11)	0.6394(5)	0.3674(4)	0.082
O(21)	0.3305(13)	0.3702(5)	0.4687(4)	0.094
O(22)	0.5789(10)	0.4675(6)	0.4134(4)	0.089
Bi(2)	-0.0022(1)	0.3657(1)	0.3801(1)	0.034
Fe(3)	-0.1309(2)	0.3780(1)	0.3230(1)	0.047
Fe(4)	-0.1238(2)	0.3620(1)	0.4389(1)	0.041
Cl(2)	0.0411(3)	0.2352(2)	0.3685(1)	0.050
Cp(31)	-0.2601(18)	0.4312(10)	0.3412(5)	0.057
Cp(32)	-0.2885(15)	0.4065(8)	0.3056(6)	0.062
Cp(33)	-0.2177(20)	0.4269(11)	0.2816(6)	0.084
Cp(34)	-0.1426(24)	0.4643(12)	0.2969(8)	0.077
Cp(35)	-0.1656(20)	0.4696(6)	0.3348(9)	0.052
Cp(41)	-0.1242(16)	0.2699(8)	0.4581(6)	0.061
Cp(42)	-0.1846(22)	0.3071(10)	0.4824(6)	0.072
Cp(43)	-0.2707(17)	0.3309(8)	0.4626(6)	0.055
Cp(44)	-0.2681(13)	0.3132(8)	0.4270(5)	0.059
Cp(45)	-0.1752(16)	0.2719(6)	0.4244(5)	0.043
C(31)	-0.1729(17)	0.3001(8)	0.3257(6)	0.080
C(32)	-0.0118(19)	0.3588(10)	0.2994(5)	0.070
C(41)	-0.0032(15)	0.3883(6)	0.4614(4)	0.053
C(42)	-0.1660(13)	0.4392(6)	0.4336(4)	0.042
O(31)	-0.2045(13)	0.2501(6)	0.3280(5)	0.121
O(32)	0.0656(13)	0.3468(8)	0.2835(4)	0.102
O(41)	0.0704(11)	0.4053(6)	0.4761(4)	0.089
O(42)	-0.1927(9)	0.4914(5)	0.4319(3)	0.069
Bi(3)	0.2731(1)	0.2738(1)	0.3612(1)	0.037
Fe(5)	0.3302(2)	0.1983(1)	0.4146(1)	0.044
Fe(6)	0.3300(2)	0.2219(1)	0.2983(1)	0.054
Cl(3)	0.4484(3)	0.3595(2)	0.3646(1)	0.053
Cp(51)	0.4272(15)	0.1965(9)	0.4623(5)	0.071
Cp(52)	0.4361(15)	0.1377(9)	0.4435(5)	0.075
Cp(53)	0.4783(13)	0.1519(6)	0.4094(6)	0.048
Cp(54)	0.4978(12)	0.2193(6)	0.4050(4)	0.050



TABLE 3 (continued)

ATOM	x	y	z	U (eq.)
Cp(55)	0.4638(13)	0.2464(6)	0.4377(5)	0.052
Cp(61)	0.2663(34)	0.1329(9)	0.2965(9)	0.104
Cp(62)	0.3297(26)	0.1412(13)	0.2659(8)	0.107
Cp(63)	0.2844(23)	0.1853(12)	0.2484(6)	0.076
Cp(64)	0.1896(25)	0.2109(11)	0.2677(8)	0.090
Cp(65)	0.1866(23)	0.1731(15)	0.2982(8)	0.074
C(51)	0.2506(13)	0.1395(6)	0.3983(5)	0.058
C(52)	0.2226(15)	0.2314(8)	0.4401(5)	0.066
O(51)	0.1973(12)	0.0993(5)	0.3856(4)	0.090
O(52)	0.1531(12)	0.2495(8)	0.4571(4)	0.098
C(61)	0.3907(26)	0.2886(9)	0.2803(9)	0.080
C(62)	0.4467(21)	0.1800(18)	0.3102(13)	0.154
O(61)	0.4102(22)	0.3372(6)	0.2687(6)	0.104
O(62)	0.5346(13)	0.1758(13)	0.3208(8)	0.118
C(61)'	0.3258(33)	0.2982(6)	0.2817(10)	0.094
C(62)'	0.4647(10)	0.2224(13)	0.3133(8)	0.058
O(61)'	0.3317(21)	0.3502(5)	0.2735(6)	0.095
O(62)'	0.5564(9)	0.2307(13)	0.3181(8)	0.124

upon concentration and cooling produced black, metallic shining crystals of **5**. Yield 0.28 g (78%). M.p. 147°C dec.

#### Crystal structure determination of **1**

Enraf–Nonius CAD4 diffractometer;  $C_{42}H_{30}Bi_3Cl_3Fe_6O_{12}$ ,  $M_r = 1795.08$ , monoclinic,  $C2/c$ ,  $a$  12.296(1),  $b$  21.398(2),  $c$  37.672(5) Å,  $\beta$  90.07(1)°,  $V$  9911.87 Å<sup>3</sup>,  $D_c$  2.406 g cm<sup>-3</sup> for  $Z = 8$ ,  $F(000) = 6671$ ,  $\mu(Mo-K_\alpha)$  125.05 cm<sup>-1</sup>. 9367 measured reflections of which 8694 were unique ( $R_{int} = 0.02$ ) and 5464 regarded as “observed” with  $I \geq 2.0\sigma(I)$  ( $\omega$  scan,  $\Delta\omega = 0.85 + 0.35 \tan\theta$ ,  $(\sin\theta/\lambda)_{max} = 0.593$ ,  $hkl$ : +14, +25,  $\pm 44$ , Mo- $K_\alpha$  radiation,  $\lambda$  0.71069 Å, graphite monochromator). Corrections for decay, Lp and absorption effects (empirical, rel. transmission 0.38–1.00). No indication for symmetry higher than monoclinic was provided by reduced cell calculations, nor was an orthorhombic  $C$ -centered cell, which was suggested by the angle  $\beta$  of 90.07(1)°, confirmed by the Laue symmetry. The structure solution was by a novel random start multiresolution direct methods program (SHELXS-86 [14]) with completion by Fourier syntheses. A disorder in the carbonyl groups C(61)/O(61) and C(62)/O(62) was modelled by giving these atoms half occupancy (C(61)'/O(61)' and C(62)'/O(62)'), and refining each pair in separate blocks isotropically with the Fe–C and C–O bonds constrained to 1.749(5) and 1.154(5) Å, respectively. All other atoms were refined anisotropically in two large blocks, with the H-atoms neglected; refinement converged at  $R = 0.039$ ,  $R_w = 0.038$ ,  $w = 1/\sigma^2(F_o)$ , 592 refined parameters,  $\Delta\rho_{fin} = +1.12/-0.94$  e/Å<sup>3</sup> with maxima at Bi(2) (SHELX-76).

Further details of intensity data collection, data reduction and refinement procedures were as described elsewhere [15]. Table 2 lists selected bond distances and angles and Table 3 the atomic coordinates. Figures 1 and 2 show the molecular structure. Complete tables of atomic and thermal parameters and observed and calculated structure factors have been deposited [16].

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