Synthesis and Structural Characterisation of some Cyclopentadienyliron–Bismuth Complexes *

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Treatment of $BiCl_3$ with 2 equivalents of $Na[Fe(CO)_2(\eta-C_5H_4Me)]$ in tetrahydrofuran affords the green iron–bismuth complex $[\{[Fe(CO)_2(\eta-C_5H_4Me)]_2BiCl\}_3]$, identified by *X*-ray crystallography and containing a planar Bi_3Cl_3 six-membered ring derived from the cyclotrimerisation of $Fe(BiCl)(CO)_2(\eta-C_5H_4Me)$ units. Similar compounds are formed with C_5H_5 and C_5Me_5 ligands although in the latter case significant amounts of the iron chloro species $[FeCl(CO)_2(\eta-C_5Me_5)]$ are also formed, an *X*-ray structure of which is reported. Treatment of $BiCl_3$ with 3 equivalents of $Na[Fe(CO)_2(\eta-C_5H_4Me)]$ affords the tri-iron–bismuth complex $[Bi\{Fe(CO)_2(\eta-C_5H_4Me)\}_3]$, containing a trigonal-pyramidal bismuth bonded to three $Fe(CO)_2(\eta-C_5H_4Me)$ fragments. Photolysis of this compound leads to loss of three carbonyl groups and formation of the *closo* Fe_3Bi complex $[Fe_3(\eta-C_5H_4Me)_3(\mu-CO)_3(\mu_3-Bi)]$. Both of the tri-iron–bismuth complexes were characterised by *X*-ray crystallography.

The chemistry of transition-metal complexes incorporating atoms or small units of the main-group elements is currently the focus of considerable attention.[1] With particular reference to Group 5, an extensive chemistry involving phosphorus has been developed, most notably by Scherer and Stoppioni.[2] However, examples involving the heavier congeners are less well known, this being particularly the case for antimony and bismuth. While the number of antimony-containing transition-metal complexes remains few, recent work, particularly by Whitmire *et al.*[3] on bismuth–iron carbonyl complexes, has greatly increased the number of such compounds containing bismuth that are known and well characterised. In addition to the iron–bismuth compounds of Whitmire *et al.*, [3] a number of examples are known for different transition metals, which include $[Bi\{Co(CO)_4\}_3]$,[4] $[Ir_3(CO)_9(\mu_3-Bi)]$,[5] $[\{W(CO)_5\}_3(\mu_3-Bi_2)]$,[6,7] $[W_2(CO)_8(\mu-Bi_2)\{\mu-BiMeW(CO)_5\}]$,[7] and $[Bi\{Mn(CO)_5\}_3]$.[8]

In contrast to the above mentioned transition-metal carbonyl complexes, reports dealing with well characterised cyclopentadienyltransition metal–bismuth complexes are scarce. Malisch and co-workers have described the synthesis of $[(\eta-C_5H_5)(OC)_2Fe-BiMe_2]$[9] and $[(\eta-C_5H_5)(OC)_3Mo-BiMe_2]$[10] from $BiMe_2Br$ and the corresponding metal carbonylate anion, and reported additional spectroscopic details and preliminary reactivity studies. Iron–bismuth complexes have also been reported by Cullen *et al.*,[11] involving the reaction of $BiCl_3$ with $[Fe_2(CO)_4(\eta-C_5H_5)_2]$ which affords the bismuth chloro species, $[(\eta-C_5H_5)(OC)_2Fe-BiCl_2]$. Also of interest is a recent report by Wieber *et al.*[12] detailing the synthesis of $[(\eta-C_5H_5)(OC)_2Fe-Bi(S_2CR)_2]$ (R = NEt_2 or OMe), *X*-ray structural data being presented for the dithiocarbamate derivative. It is this latter area which forms the focus of the present work and described herein are the results of a study on the reaction of bismuth(III) chloride with $Na[Fe(CO)_2(\eta-C_5H_4R)]$ (R = H or Me) some aspects of which have been the subject of a preliminary communcation.[13,†]

Results and Discussion

Treatment of a tetrahydrofuran (thf) solution of $BiCl_3$ with 2 equivalents of $Na[Fe(CO)_2(\eta-C_5H_4Me)]$ at room temperature affords a deep emerald green solution. After filtration and recrystallisation from thf–hexane, dark green crystals of $[\{[Fe(CO)_2(\eta-C_5H_4Me)]_2BiCl\}_3]$ (**1a**) can be isolated in good yield. Analogous reactions involving the anions $[Fe(CO)_2(\eta-C_5H_5)]^-$ and $[Fe(CO)_2(\eta-C_5Me_5)]^-$ proceed similarly to give derivatives (**1b**) and (**1c**) respectively, although, in the latter case, significant amounts of the iron chloro complex, $[FeCl(CO)_2(\eta-C_5Me_5)]$, (**2**), are also formed. Formation of such metal chloro species is not uncommon in the reactions of metal carbonylate anions with main-group-element chlorides, such compounds presumably arising as a result of electron-transfer processes occurring in solution in competition with the desired nucleophilic substitution.

Analysis of compounds (**1a**)—(**1c**) by i.r. spectroscopy (Table 1) revealed the presence of terminal carbonyl ligands whilst ^1H and ^{13}C n.m.r. spectra (Table 2) indicated a single cyclopentadienyl environment. Since these data gave little indication as to the nature of (**1a**)—(**1c**) and because meaningful mass spectra (by electron impact or fast atom bombardment) proved difficult to obtain, a single-crystal *X*-ray diffraction study of (**1a**) was undertaken, the results of which are shown in Figures 1 and 2. Selected bond distances and interbond angles are listed in Table 3 and atomic positional parameters in Table 4. The molecule consists of a planar six-membered Bi_3Cl_3 ring in which each bismuth atom is bonded to two chlorine atoms (mean Bi–Cl 2.909 Å) and two $Fe(CO)_2(\eta-C_5H_4Me)$ fragments (mean Bi–Fe 2.680 Å) as shown in Figure 1. Each bismuth atom resides in a tetrahedral co-ordination environment but this is considerably distorted, as evidenced by the large Cl–Bi–Cl angles [153.4(1) and 155.0(1)°], which in turn leads to a small angle at each chlorine [85.8(1) and 84.3(1)°]. These distortions probably result from the presence of a stereochemically active lone pair on each bismuth which presumably lies in the Fe_2Bi plane and bisects the Cl–Bi–Cl angle. An alternative explanation invoking $Bi\cdots Bi$ interactions, which might be expected to result in similar distortions, is considered unlikely due to the large internuclear separations (mean $Bi\cdots Bi$ 3.943 Å). Typical Bi–Bi distances in complexes containing mutually bonded dibismuth fragments range from 2.796 to 3.092 Å,[3e,6,7] while in the cluster $[Bi_4Fe_4(CO)_{13}]^{2-}$,[3f] containing a tetrahedron of bismuth atoms, the $Bi\cdots Bi$ separations range

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

† While this work was in progress a report appeared describing details of a substantially similar set of reactions.[14]

Table 1. Analytical[a] and physical data for the complexes

Compound	Colour	Yield (%)	$\tilde{\nu}$(CO)[b]/cm^{-1}	Analysis (%) C	Analysis (%) H
(1a) $[\{[Fe(CO)_2(\eta\text{-}C_5H_4Me)]_2BiCl\}_3]$	Green	73	2 041w, 2 006s, 1 973s, 1 948s	28.7 (30.7)	2.1 (2.2)
(1b) $[\{[Fe(CO)_2(\eta\text{-}C_5H_5)]_2BiCl\}_3]$	Green	70	2 046w, 2 008s, 1 976s, 1 952s	26.5 (28.1)	1.5 (1.7)
(1c) $[\{[Fe(CO)_2(\eta\text{-}C_5Me_5)]_2BiCl\}_3]$	Green		[c]2 020m, 1 980s, 1 950m		
(2) $[FeCl(CO)_2(\eta\text{-}C_5Me_5)]$	Orange		[c]2 012s, 1 967s	49.7 (51.0)	5.2 (5.3)
(4) $[Bi\{Fe(CO)_2(\eta\text{-}C_5H_4Me)\}_3]$	Yellow-brown	71	2 001s, 1 963s, 1 924s	36.6 (36.9)	2.6 (2.7)
(9) $[Fe_3(\eta\text{-}C_5H_4Me)_3(\mu\text{-}CO)_3(\mu_3\text{-}Bi)]$	Black	67	1 786s, 1 735m	36.2 (36.1)	2.9 (3.0)

[a] Calculated values are given in parentheses. [b] Measured in thf unless otherwise stated. [c] Nujol mull.

Table 2. Proton and $^{13}C\text{-}\{^1H\}$ n.m.r. data for the complexes[a]

Compound	$^1H(\delta)$[b]	$^{13}C(\delta)$[b,c]
(1a)	1.99 (s, 3 H, C_5H_4Me), 4.84 (s, 2 H, C_5H_4Me), 4.92 (s, 2 H, C_5H_4Me)	13.2 (s, C_5H_4Me), 85.3 and 86.5 (s, C_5H_4Me, ring CH), 103.4 (s, C_5H_4Me, ring CMe), 204.0 (s, CO)
(1b)	5.01 (s, 5 H, C_5H_5)	86.1 (s, C_5H_5), 203.5 (s, CO)
(1c)	1.86 (s, 15 H, C_5Me_5)	9.9 (s, C_5Me_5), 97.0 (s, C_5Me_5), 203.2 and 206.2 (s, CO)
(2)	1.74 (s, 15 H, C_5Me_5)	9.5 (s, C_5Me_5), 97.5 (s, C_5Me_5), 215.9 (s, CO)
(4)[d]	1.95 (s, 3 H, C_5H_4Me), 4.64 (m, 2 H, C_5H_4Me), 4.88 (m, 2 H, C_5H_4Me)	14.4 (s, C_5H_4Me), 84.1 and 84.9 (s, C_5H_4Me, ring CH), 101.1 (s, C_5H_4Me, ring CMe), 215.5 (s, CO)
(9)[e]	1.55 (s, 3 H, C_5H_4Me), 4.47 (m, 2 H, C_5H_4Me), 4.65 (m, 2 H, C_5H_4Me)	13.5 (s, C_5H_4Me), 78.7 and 86.0 (s, C_5H_4Me, ring, CH), 101.6 (s, C_5H_4Me, ring CMe), 228.4 (s, CO)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz; measurements at room temperature. [b] Measured in $[^2H_8]$tetrahydrofuran unless otherwise stated. [c] ^1H Decoupled; chemical shifts are positive to high frequency of $SiMe_4$. [d] Measured in C_6D_6. [e] Measured in CD_2Cl_2.

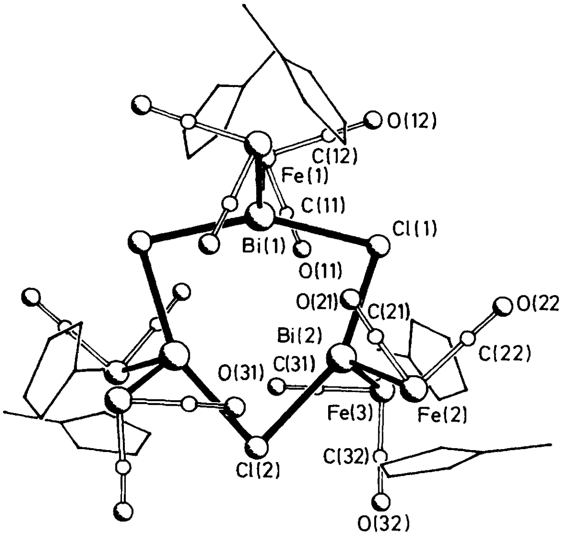


Figure 1. The molecular structure of complex (**1a**) showing the atom-numbering scheme adopted, except for the C_5H_4Me ligands. A crystallographic two-fold axis passes through Bi(1) and Cl(2)

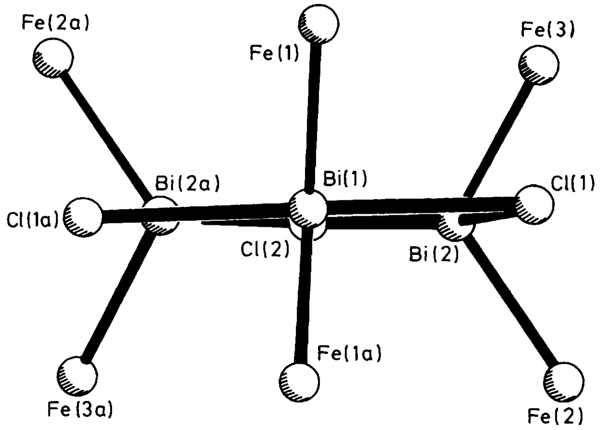


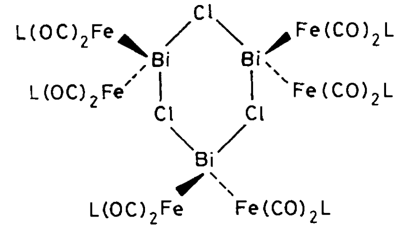
Figure 2. The FeBiCl core of complex (**1a**) viewed along the Bi_3Cl_3 plane and the crystallographic two-fold axis

from 3.140 to 3.473 Å, these being associated with some degree of interaction. The Bi–Bi distance in Bi_2Ph_4 is 2.990(2) Å.[15] The $Fe(CO)_2(\eta\text{-}C_5H_4Me)$ fragments are arranged such that the cyclopentadienyl ligands are chemically equivalent, consistent with the observed solution n.m.r. properties of complexes (**1a**)—(**1c**). Figure 1 shows that the carbonyls fall into two sets; six pointing in towards the Bi_3Cl_3 ring and six pointing away. However, in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of (**1a**) and (**1b**) only one carbonyl resonance is observed, indicative of a fluxional process occurring in solution which exchanges the two environments. This most probably involves rotation about the Fe–Bi bonds, but in (**1c**) two resonances are observed consistent with the solid-state structure. The presence of the much bulkier C_5Me_5 ligands in (**1c**) probably leads to hindered rotation (about the Fe–Bi bonds) and accounts for the differences in the ^{13}C n.m.r. spectra of (**1a**), (**1b**), and (**1c**).

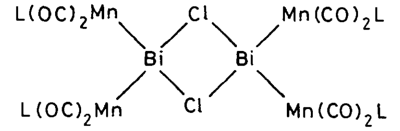
The structure of (**1a**), and inferentially those of (**1b**) and (**1c**), is formally derived from a cyclotrimerisation of $[Fe(CO)_2(\eta\text{-}C_5H_4Me)]_2BiCl$ fragments resulting from a Lewis acid–base interaction between bismuth and a second chlorine. The Lewis acidity of three-co-ordinate bismuth(III) is well known and a similar interaction occurs in the related chlorobismuthinidene complex, (**3**), prepared by von Seyerl and Huttner.[16]

As mentioned previously, the reaction between $BiCl_3$ and $Na[Fe(CO)_2(\eta\text{-}C_5Me_5)]$ affords both (**1c**) and the chloro carbonyl complex (**2**). The structure of (**2**) was determined by *X*-ray crystallography and, although of secondary importance with regard to the main focus of this paper, details are presented herein since it has not been previously reported. A view of the molecule is shown in Figure 3, selected metric parameters are given in Table 5 and atomic positional parameters in Table 6. However, since there are no unusual geometrical features associated with this structure no further discussion is warranted.

The presence of a potentially reactive chloride function in complexes (**1a**)–(**1c**) suggested that further reaction with $Na[Fe(CO)_2(\eta-C_5R_5)]$ might provide access to a tri-iron–bismuth complex. In the particular case of (**1a**) this was found to be the case but a more convenient synthetic route, avoiding the intermediacy of (**1a**), is achieved by dropwise addition of a solution of $BiCl_3$ to a solution of 3 equivalents of $Na[Fe(CO)_2(\eta-C_5H_4Me)]$ both in thf at −50 °C. The initially formed deep red solution becomes black on warming to room temperature and, after filtration and recrystallisation, good yields of $[Bi\{Fe(CO)_2(\eta-C_5H_4Me)\}_3]$, (**4**), can be obtained as dark yellow-brown crystals. Complex (**4**) was characterised by normal spectroscopic and analytical methods (see Tables 1 and 2) and by a single-crystal *X*-ray diffraction study. The molecular structure is shown in Figure 4, bond distance and angle data in Table 7 and atomic positional parameters in Table 8. The structure consists of a single bismuth atom bonded to three $Fe(CO)_2(\eta-C_5H_4Me)$ fragments *via* unbridged bismuth–iron bonds. The co-ordination geometry around the bismuth is trigonal pyramidal with angles Fe(1)–Bi–Fe(2) 108.9(1), Fe(1)–Bi–Fe(3) 109.1(1), and Fe(2)–Bi–Fe(3) 109.8(1)°. These are close to the tetrahedral angle and similar to those found in



	L
(**1a**)	C_5H_4Me
(**1b**)	C_5H_5
(**1c**)	C_5Me_5



	L
(**3**)	C_5H_5

Table 3. Selected bond lengths (Å) and angles (°) for complex (**1a**)

Bi(1)–Cl(1)	2.916(3)	Bi(2)–Cl(1)	2.855(3)
Bi(2)–Cl(2)	2.956(3)	Bi(1)–Fe(1)	2.666(2)
Bi(2)–Fe(2)	2.706(2)	Bi(2)–Fe(3)	2.667(2)
Fe(1)–C(11)	1.726(16)	Fe(1)–C(12)	1.727(15)
Fe(2)–C(21)	1.710(15)	Fe(2)–C(22)	1.752(12)
Fe(3)–C(31)	1.727(14)	Fe(3)–C(32)	1.763(13)
C(11)–O(11)	1.180(20)	C(12)–O(12)	1.180(18)
C(21)–O(21)	1.178(19)	C(22)–O(22)	1.136(15)
C(31)–O(31)	1.176(16)	C(32)–O(32)	1.130(16)
Cl(1)–Bi(1)–Cl(1′)	153.4(1)	Cl(1)–Bi(2)–Cl(2)	155.0(1)
Fe(1)–Bi(1)–Fe(1′)	107.6(1)	Fe(2)–Bi(2)–Fe(3)	110.2(1)
Cl(1)–Bi(1)–Fe(1)	94.2(1)	Cl(1′)–Bi(1)–Fe(1)	101.5(1)
Cl(1)–Bi(2)–Fe(2)	94.0(1)	Cl(2)–Bi(2)–Fe(2)	103.1(1)
Cl(1)–Bi(2)–Fe(3)	99.4(1)	Cl(2)–Bi(2)–Fe(3)	91.7(1)
Bi(1)–Fe(1)–C(11)	85.7(5)	Bi(1)–Fe(1)–C(12)	90.1(5)
C(11)–Fe(1)–C(12)	92.2(6)	Bi(2)–Fe(2)–C(21)	84.3(5)
Bi(2)–Fe(2)–C(22)	92.0(4)	C(21)–Fe(2)–C(22)	93.5(6)
Bi(2)–Fe(3)–C(31)	85.0(5)	Bi(2)–Fe(3)–C(32)	89.3(4)
C(31)–Fe(3)–C(32)	95.8(6)	Fe(1)–C(11)–O(11)	175.9(14)
Fe(1)–C(12)–O(12)	173.5(13)	Fe(2)–C(21)–O(21)	176.5(13)
Fe(2)–C(22)–O(22)	174.4(11)	Fe(3)–C(31)–O(31)	172.6(13)
Fe(3)–C(32)–O(32)	176.4(12)		

Symmetry operator for primed atoms: $1 - x, y, \frac{1}{2} - z$.

Table 5. Selected bond lengths (Å) and angles (°) for complex (**2**)

Fe–Cl	2.291(2)	Fe–C(1)	1.774(4)
Fe–C(2)	1.802(4)	Fe–C(10)	2.141(3)
Fe–C(11)	2.116(3)	Fe–C(12)	2.086(4)
Fe–C(13)	2.097(4)	Fe–C(14)	2.100(3)
C(1)–O(1)	1.132(5)	C(2)–O(2)	1.055(5)
Cl–Fe–C(1)	88.9(2)	Cl–Fe–C(2)	92.6(2)
C(1)–Fe–C(2)	94.4(2)	Fe–C(1)–O(1)	178.0(3)
Fe–C(2)–O(2)	177.2(5)		

Table 4. Atomic co-ordinates (× 10^4) for complex (**1a**)

Atom	*x*	*y*	*z*
Bi(1)	5 000	4 909(1)	2 500
Bi(2)	5 925(1)	2 191(1)	2 671(1)
Cl(1)	6 327(1)	4 371(2)	2 676(2)
Cl(2)	5 000	435(3)	2 500
Fe(1)	5 120(1)	6 171(1)	1 459(1)
Fe(2)	6 556(1)	1 733(1)	3 849(1)
Fe(3)	6 550(1)	1 449(1)	1 686(1)
C(11)	5 425(6)	5 055(14)	1 101(7)
O(11)	5 656(5)	4 335(11)	835(5)
C(12)	5 850(7)	6 571(11)	1 798(7)
O(12)	6 357(4)	6 884(7)	1 970(5)
C(13)	4 721(6)	6 801(11)	576(6)
C(14)	4 271(6)	6 167(10)	884(7)
C(15)	4 186(7)	6 663(12)	1 512(7)
C(16)	4 573(6)	7 534(10)	1 581(6)
C(17)	4 898(6)	7 655(9)	994(6)
C(18)	5 334(9)	8 527(13)	838(10)
C(21)	6 089(6)	2 700(12)	4 146(7)
O(21)	5 789(5)	3 368(10)	4 380(6)
C(22)	7 154(5)	2 641(10)	3 708(6)
O(22)	7 553(4)	3 230(8)	3 671(5)
C(23)	6 988(6)	258(10)	3 684(6)
C(24)	6 316(7)	105(9)	3 698(6)
C(25)	6 155(6)	436(12)	4 302(7)
C(26)	6 699(6)	782(12)	4 715(7)
C(27)	7 209(6)	668(10)	4 326(6)
C(28)	7 874(6)	834(15)	4 558(8)
C(31)	5 829(7)	1 456(10)	1 235(7)
O(31)	5 373(4)	1 432(10)	868(5)
C(32)	6 483(6)	141(10)	2 001(6)
O(32)	6 472(5)	−707(7)	2 195(5)
C(33)	6 959(5)	2 877(10)	1 393(6)
C(34)	7 303(5)	2 521(11)	1 973(6)
C(35)	7 535(5)	1 505(13)	1 826(7)
C(36)	7 344(6)	1 222(12)	1 174(6)
C(37)	6 996(5)	2 057(12)	878(6)
C(38)	6 720(8)	2 158(19)	162(8)

Table 6. Atomic co-ordinates (× 10^4) for complex (**2**)

Atom	*x*	*y*	*z*
Fe	1 537(1)	3 616(1)	2 695(1)
Cl	190(2)	2 059(2)	1 898(1)
C(1)	1 534(5)	2 046(5)	3 951(3)
O(1)	1 590(5)	1 025(5)	4 748(3)
C(2)	−761(6)	5 264(5)	3 148(4)
O(2)	−2 083(5)	6 280(5)	3 393(4)
C(10)	3 256(4)	3 978(4)	1 108(3)
C(11)	2 459(4)	5 638(4)	1 590(3)
C(12)	3 089(4)	5 331(4)	2 666(3)
C(13)	4 306(4)	3 468(5)	2 831(3)
C(14)	4 371(4)	2 608(4)	1 892(3)
C(15)	3 018(6)	3 732(6)	−38(3)
C(16)	1 264(6)	7 472(5)	1 027(3)
C(17)	2 705(7)	6 780(6)	3 416(4)
C(18)	5 419(6)	2 590(7)	3 813(4)
C(19)	5 521(6)	660(5)	1 694(4)

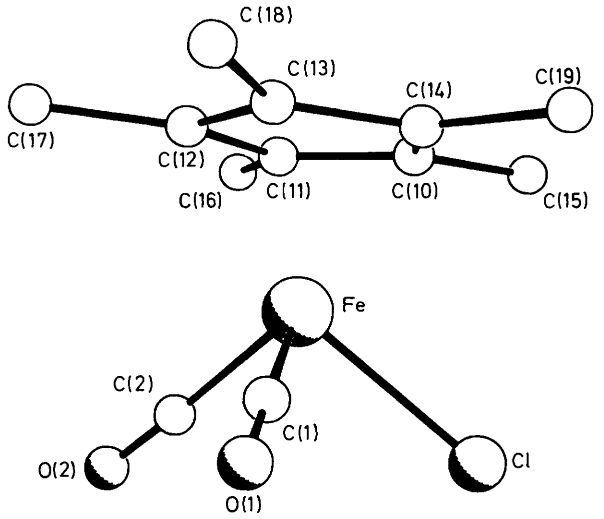


Figure 3. The molecular structure of complex (**2**) showing the atom-numbering scheme adopted

the related trimetalbismuth complexes [Bi{$Mn(CO)_5$}$_3$], (**5**) [av. Mn–Bi–Mn 108.2(1)°],[8] and [Bi{$Co(CO)_4$}$_3$], (**6**) [av. Co–Bi–Co 106.8(1)°].[4] However, such values are unusually large for three-co-ordinate bismuth. In $BiPh_3$ the C–Bi–C angles are 92(1), 94(1), and 96(1)°,[17] whilst in $BiMe_3$ an angle of 96.7(10)° has been obtained from electron-diffraction studies.[18] When larger substituents are present, these angles increase as found for example in $Bi(C_6H_2Me_3\text{-}2,4,6)_3$[17] (av. C–Bi–C 102.6°) and $Bi[CH(SiMe_3)_2]_3$[19] [av. C–Bi–C 102.9(5)°]. The reason for this variation in angle has been attributed to steric effects[19] with increasing steric bulk resulting in larger angles. Thus in the case of complexes (**4**)—(**6**), all of which contain three bulky transition-metal fragments, angles in the region of 108° may be presumed to result primarily from intramolecular steric crowding.

The Bi–Fe bond lengths (av. Bi–Fe 2.738 A) are similar to those found in (**1a**) and are consistent with Bi–Fe single bonding (required by electron-counting procedures) as derived from the sum of the covalent radii of the respective elements, 2.67 Å. Values ranging between 2.6 and 2.8 Å are observed in a range of bismuth–iron carbonyl complexes reported by Whitmire *et al.*[3] and in [$(\eta\text{-}C_5H_5)(OC)_2Fe\text{–}Bi(S_2CNEt_2)_2$] a value of 2.641(2) Å has been reported.[12]

Table 7. Selected bond lengths (Å) and angles (°) for complex (**4**)

Bi–Fe(1)	2.727(1)	Bi–Fe(2)	2.751(1)
Bi–Fe(3)	2.737(1)	Fe(1)–C(11)	1.749(11)
Fe(1)–C(12)	1.769(8)	Fe(2)–C(21)	1.744(11)
Fe(2)–C(22)	1.753(9)	Fe(3)–C(31)	1.728(10)
Fe(3)–C(32)	1.741(9)	C(11)–O(11)	1.147(13)
C(12)–O(12)	1.136(10)	C(21)–O(21)	1.158(13)
C(22)–O(22)	1.136(11)	C(31)–O(31)	1.159(12)
C(32)–O(32)	1.146(11)		
Fe(1)–Bi–Fe(2)	108.9(1)	Fe(1)–Bi–Fe(3)	109.1(1)
Fe(2)–Bi–Fe(3)	109.8(1)	Bi–Fe(1)–C(11)	91.9(3)
Bi–Fe(1)–C(12)	88.4(3)	C(11)–Fe(1)–C(12)	93.9(4)
Bi–Fe(2)–C(21)	92.7(3)	Bi–Fe(2)–C(22)	88.5(3)
C(21)–Fe(2)–C(22)	93.6(4)	Bi–Fe(3)–C(31)	92.0(3)
Bi–Fe(3)–C(32)	90.2(3)	C(31)–Fe(3)–C(32)	94.5(4)
Fe(1)–C(11)–O(11)	174.1(8)	Fe(1)–C(12)–O(12)	175.9(8)
Fe(2)–C(21)–O(21)	175.8(10)	Fe(2)–C(22)–O(22)	176.4(8)
Fe(3)–C(31)–O(31)	175.0(8)	Fe(3)–C(32)–O(32)	176.0(8)

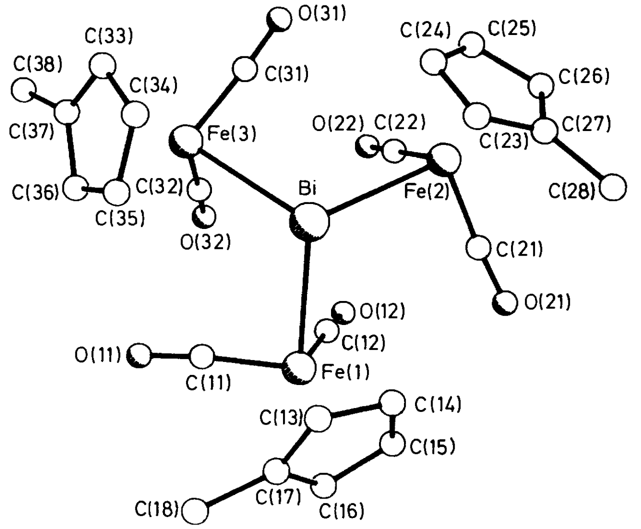
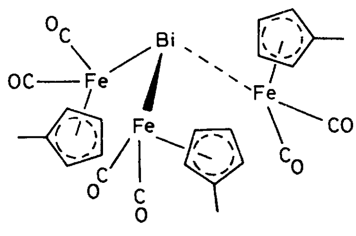


Figure 4. The molecular structure of complex (**4**) showing the atom-numbering scheme adopted



(**4**)

Each iron atom is also bonded to a methylcyclopentadienyl group and two terminal carbonyl ligands of normal geometry. These $Fe(CO)_2(\eta\text{-}C_5H_4Me)$ fragments are oriented such that the molecule has approximate C_3 symmetry.

As mentioned above, complex (**4**) can be considered as a trimetal bismuthine, BiX_3 where X = $Fe(CO)_2(\eta\text{-}C_5H_4Me)$, and it is therefore closely related to the manganese and cobalt carbonyl complexes (**5**) and (**6**), where X = $Mn(CO)_5$ and $Co(CO)_4$ respectively. As such these complexes contain an open trigonal-pyramidal M_3Bi core with bismuth at the apex and no

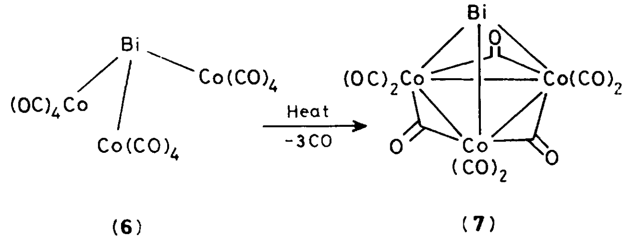
Table 8. Atomic co-ordinates (× 10^4) for complex (**4**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Bi	2 650(1)	7 466(1)	6 699(1)	C(23)	879(8)	8 934(10)	7 504(7)
Fe(1)	4 399(1)	8 026(1)	6 100(1)	C(24)	388(9)	8 250(11)	7 006(11)
C(11)	4 674(6)	6 761(8)	5 789(7)	C(25)	−66(9)	8 720(16)	6 328(11)
O(11)	4 935(5)	5 958(6)	5 583(6)	C(26)	122(11)	9 770(13)	6 324(10)
C(12)	3 883(6)	8 316(7)	4 965(6)	C(27)	735(9)	9 861(8)	7 137(8)
O(12)	3 602(5)	8 526(6)	4 221(4)	C(28)	1 133(15)	10 854(12)	7 464(17)
C(13)	4 791(7)	8 330(8)	7 550(7)	Fe(3)	2 187(1)	5 596(1)	5 926(1)
C(14)	4 370(6)	9 197(7)	7 151(6)	C(31)	1 062(7)	6 009(7)	5 610(7)
C(15)	4 896(7)	9 505(7)	6 368(6)	O(31)	298(5)	6 218(6)	5 363(6)
C(16)	5 669(6)	8 842(7)	6 295(6)	C(32)	2 680(6)	5 959(6)	4 845(6)
C(17)	5 594(7)	8 115(8)	7 018(7)	O(32)	2 986(5)	6 145(6)	4 110(4)
C(18)	6 316(10)	7 294(8)	7 234(11)	C(33)	1 696(7)	4 292(7)	6 620(8)
Fe(2)	1 355(1)	8 918(1)	6 095(1)	C(34)	2 152(8)	4 940(8)	7 300(7)
C(21)	2 236(8)	9 802(8)	5 825(7)	C(35)	3 077(8)	5 028(7)	7 028(7)
O(21)	2 780(6)	10 437(6)	5 652(6)	C(36)	3 184(7)	4 453(7)	6 228(7)
C(22)	1 362(6)	8 353(7)	4 954(6)	C(37)	2 332(7)	3 984(6)	5 948(6)
O(22)	1 355(5)	8 037(6)	4 195(4)	C(38)	2 211(12)	3 234(10)	5 146(10)

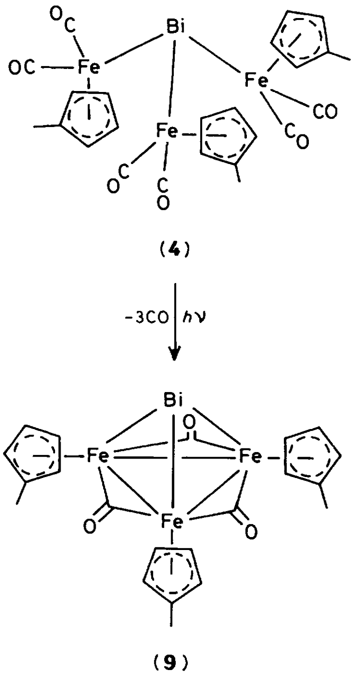
Table 9. Selected bond lengths (Å) and angles (°) for complex (**9**)

Bi–Fe(1)	2.584(1)	Bi–Fe(2)	2.582(1)
Fe(1)–Fe(2)	2.600(1)	Fe(2)–Fe(2′)	2.620(2)
Fe(1)–C(1)	1.920(5)	Fe(2)–C(1)	1.937(4)
Fe(2)–C(2)	1.928(5)	C(1)–O(1)	1.166(5)
C(2)–O(2)	1.166(9)		
Fe(1)–Bi–Fe(2)	60.4(1)	Fe(2)–Bi–Fe(2′)	61.0(1)
Bi–Fe(1)–Fe(2)	59.7(1)	Bi–Fe(1)–Fe(2′)	59.7(1)
Bi–Fe(2)–Fe(1)	59.8(1)	Bi–Fe(2)–Fe(2′)	59.5(1)
Fe(2)–Fe(1)–Fe(2′)	60.5(1)	Fe(1)–Fe(2)–Fe(2′)	59.8(1)
Bi–Fe(1)–C(1)	107.1(1)	Bi–Fe(2)–C(1)	106.7(2)
Bi–Fe(2)–C(2)	105.6(1)	Fe(2)–Fe(1)–C(1)	47.9(1)
Fe(2′)–Fe(1)–C(1)	89.1(1)	Fe(2)–Fe(1)–C(1′)	89.1(1)
Fe(1)–Fe(2)–C(1)	47.3(1)	Fe(1)–Fe(2)–C(2)	90.3(2)
Fe(2′)–Fe(2)–C(1)	88.2(1)	Fe(2′)–Fe(2)–C(2)	47.2(1)
C(1)–Fe(1)–C(1′)	81.1(3)	C(1)–Fe(2)–C(2)	83.9(2)
Fe(1)–C(1)–Fe(2)	84.8(2)	Fe(2)–C(2)–Fe(2′)	85.6(3)
Fe(1)–C(1)–O(1)	138.6(4)	Fe(2)–C(1)–O(1)	136.6(4)
Fe(2)–C(2)–O(2)	137.2(2)		

Symmetry operator for primed atoms: *x*, $\frac{1}{2} - y$, *z*.



(**6**) (**7**)



(**4**)

(**9**)

M–M bonding. In principle it should be possible for the above complexes to lose carbon monoxide with concomitant M–M bond formation, resulting in *closo* tetrahedral clusters. This has recently been described by Whitmire *et al.*[20] in the case of (**6**) which on heating loses three molecules of CO affording the *closo* Co_3Bi cluster (**7**). The cluster (**7**) is interesting as it is representative of a rare class of compounds in which a heavy main-group element caps a mutually bonded triangle of first-row transition-metal atoms. Indeed, it was originally suggested by the authors who synthesised (**6**)[4] that a *closo* species such as (**7**), and analogous to the known iridium complex [$Ir_3(CO)_9(\mu_3\text{-Bi})$] (**8**),[5] would be too strained to exist primarily as a result of the large relative difference in size between cobalt and bismuth. The synthesis of (**7**), however, clearly demonstrates that such complexes can exist and in addition a number of compounds containing a *closo* Fe_3Bi core have also recently been synthesised.[3a,b,g]

With this information available, it was anticipated that (**4**) might lose CO to afford a cyclopentadienyl-substituted Fe_3Bi cluster. Accordingly a solution of (**4**) was irradiated with a u.v. source and this led, after work up, to the isolation of black shiny crystals of [$Fe_3(\eta\text{-}C_5H_4Me)_3(\mu\text{-CO})_3(\mu_3\text{-Bi})$] (**9**). The complex was characterised by normal spectroscopic methods (Tables 1 and 2) and by an *X*-ray diffraction study, the results of which are shown in Figure 5. Selected bond distances and angles are given in Table 9 and atomic positional parameters in Table 10.

The molecule consists of a tetrahedron of three iron atoms and one bismuth all within bonding distance. The bismuth–iron (av. 2.583 Å) and iron–iron bond lengths (av. 2.607 Å) are both similar to each other and to those found in other *closo* Fe_3Bi clusters[3a,b,g] and in neither case is their length indicative of any substantial strain. This is particularly the case for the bismuth–iron bond lengths which in complex (**9**) are similar to those

Table 10. Atomic co-ordinates (× 10^4) for complex (**9**)

Atom	*x*	*y*	*z*
Bi	3 554(1)	2 500	3 818(1)
Fe(1)	6 999(1)	2 500	5 651(1)
Fe(2)	6 244(1)	3 369(1)	3 117(1)
C(1)	8 483(6)	3 328(3)	4 870(5)
O(1)	9 978(5)	3 678(3)	5 261(4)
C(2)	7 638(9)	2 500	2 316(7)
O(2)	8 754(7)	2 500	1 626(6)
C(11)	5 677(9)	2 971(5)	7 306(7)
C(12)	7 598(9)	3 244(4)	7 650(6)
C(13)	8 799(11)	2 500	7 880(8)
C(14)	10 974(14)	2 500	8 362(11)
C(21)	5 506(8)	4 001(4)	997(6)
C(22)	3 929(7)	4 082(3)	1 607(7)
C(23)	4 556(8)	4 552(3)	2 966(7)
C(24)	6 517(8)	4 760(3)	3 215(6)
C(25)	7 106(8)	4 437(3)	1 976(6)
C(26)	9 039(9)	4 571(4)	1 737(10)

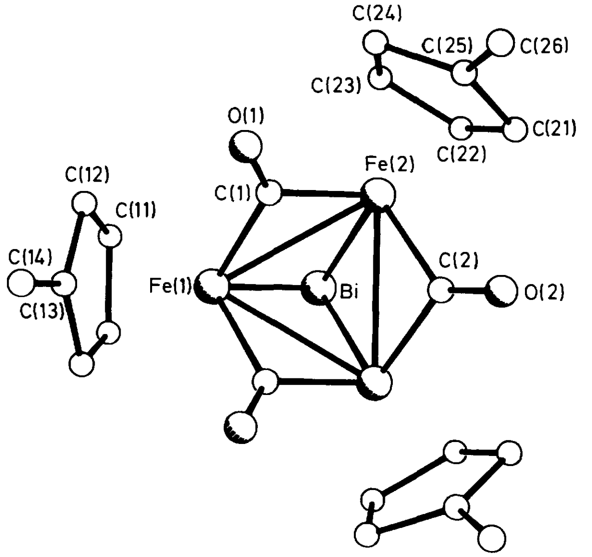


Figure 5. The molecular structure of complex (**9**) showing the atom-numbering scheme adopted. A crystallographic mirror plane passes through Bi(1), Fe(1) and the midpoint of the Fe(2)–Fe(2′) vector

observed in (**1a**), (**4**), and $[(C_5H_5)(OC)_2Fe-Bi(S_2CNEt_2)_2]$. These latter complexes may be assumed to possess much less potential strain and thus the Fe–Bi bond lengths should represent normal single-bond values. The iron–iron bond lengths are somewhat longer than typical values, *e.g.* 2.534(2) Å in $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$[21] and 2.52 Å in $[Fe_2(CO)_9]$[22] both of which contain bridging carbonyls. However in the strained di-iron stibinidene complex, $[Fe_2(CO)_8\{\mu\text{-}SbCH(SiMe_3)_2\}]$,[23] a much longer bond length of 2.801(1) Å is observed and it is values in this region that are generally associated with bond strain. Since all bond lengths are similar, the interbond angles in the Fe_3Bi tetrahedron are all close to the ideal angle of 60° (Table 9).

In addition each iron carries a methylcyclopentadienyl group and each iron–iron vector is bridged by a carbonyl ligand. These ligands are disposed such that the overall symmetry of the molecule is C_{3v}. This is not crystallographically imposed but the molecule does reside on a mirror plane which passes through Bi, Fe(1), and the midpoint of the Fe(2)–Fe(2′) vector.

Conclusions

These studies indicate that a range of cyclopentadienyl-substituted iron–bismuth complexes can readily be synthesised according to the general equations (1)—(3), where cp = η-cyclopentadienyl.

$$BiCl_3 + 2Na[Fe(CO)_2(cp)] \longrightarrow \tfrac{1}{3}[\{[Fe(CO)_2(cp)]_2BiCl\}_3] + 2NaCl \quad (1)$$

$$BiCl_3 + 3Na[Fe(CO)_2(cp)] \longrightarrow [Bi\{Fe(CO)_2(cp)\}_3] + 3NaCl \quad (2)$$

$$[Bi\{Fe(CO)_2(cp)\}_3] \xrightarrow{h\nu} [Fe_3(cp)_3(\mu\text{-}CO)_3(\mu_3\text{-}Bi)] + 3CO \quad (3)$$

In equations (1) and (2) nucleophilic substitution of chloride occurs in high yield affording the desired iron–bismuth complexes, although in the case of C_5Me_5 substantial amounts of the iron chloro complex, (**2**), are formed by competing electron-transfer processes in solution. Equations (2) and (3) together provide a facile route to a class of *closo* Fe_3Bi clusters.

Further studies on the synthesis of other transition-metal bismuth clusters are in progress.

Experimental

All experiments were performed using standard Schlenk techniques under an atmosphere of dry oxygen-free dinitrogen. All solvents were freshly distilled over appropriate drying agents immediately prior to use. Proton and ^{13}C n.m.r. spectra were recorded on a Bruker WP200 spectrometer operating at 200.13 and 50.324 MHz respectively, i.r. spectra on a Nicolet 20 SXB FTIR spectrophotometer. Bismuth trichloride and the cyclopentadienyliron dicarbonyl dimers, $[Fe_2(CO)_4L_2]$ (L = η-C_5H_5, η-C_5H_4Me, or η-C_5Me_5) were procured commercially and used without further purification. Analytical and other data for all new compounds are given in Tables 1 and 2.

Preparations.—$[\{[Fe(CO)_2(\eta\text{-}C_5H_4Me)]_2BiCl\}_3]$, (**1a**). A sample of $BiCl_3$ (0.425 g, 1.35 mmol) was dissolved in thf (20 cm^3) and stirred at room temperature. To this a solution of 2 equivalents of $Na[Fe(CO)_2(\eta\text{-}C_5H_4Me)]$, prepared by sodium amalgam reduction of the dimer, $[Fe_2(CO)_4(\eta\text{-}C_5H_4Me)_2]$ (0.515 g, 1.35 mmol) in thf (20 cm^3), was added with continued stirring over a period of 2—3 min. This caused an immediate colour change to deep emerald green and after complete addition the mixture was allowed to stir for a further 30 min. After two successive filtrations through Celite, to remove dispersed NaCl, and removal of all volatiles *in vacuo*, a dark green solid remained. The crude solid was redissolved in the minimum of fresh thf (about 3—4 cm^3) over which was layered approximately 20 cm^3 of hexane. Solvent diffusion over a period of 24 h at −20 °C afforded shiny dark green crystals of complex (**1a**) (0.62 g, 73% isolated yield based on $BiCl_3$). A second recrystallisation by the same method produced single crystals suitable for *X*-ray diffraction.

The derivatives (**1b**) and (**1c**) were produced in a similar manner to that for (**1a**). In the case of (**1c**) appreciable quantities of complex (**2**) are also formed. Filtration and recrystallisation led to intimate mixtures of (**1c**) and (**2**) making reliable estimates of the yields of each difficult and, in the case of (**1c**), preventing satisfactory analytical data from being obtained. Attempted purification by column chromatography was unsuccessful due to the facile decomposition of (**1c**) on the supports used. This is also the case for (**1a**) and (**1b**).

$[Bi\{Fe(CO)_2(\eta\text{-}C_5H_4Me)\}_3]$, (**4**). A sample of $[Fe_2(CO)_4(\eta\text{-}C_5H_4Me)_2]$ (0.414 g, 1.08 mmol) was dissolved in thf (20 cm^3) and stirred over a sodium amalgam for 12 h. The resulting solution of Na[Fe(CO)$_2$(η-C$_5$H$_4$Me)] was decanted into a separate nitrogen-filled flask, stirred, and cooled to -50 °C. Dropwise addition of a solution of BiCl$_3$ (0.228 g, 0.722 mmol, Fe:Bi = 3:1) in thf (20 cm^3) over a period of 10 min led to an initial red solution which, on warming to room temperature, became dark brown. Stirring was maintained for a further hour after which time all volatiles were removed by vacuum. Extraction of the crude dark solid with 3 × 20 cm^3 portions of Et$_2$O followed by filtration through Celite gave a dark yellow-brown solution. The solvent volume was reduced to approximately 5 cm^3 over which hexane (20 cm^3) was layered. Solvent diffusion at -20 °C over a period of 24 h afforded dark brown needles of complex (**4**) (0.40 g, 71% yield) which were suitable for *X*-ray diffraction.

[Fe$_3$(η-C$_5$H$_4$Me)$_3$(μ-CO)$_3$(μ_3-Bi)], (**9**). A sample of complex (**4**) (0.1 g, 0.13 mmol) was dissolved in toluene (50 cm^3) and photolysed using a water-cooled 100-W medium-pressure mercury u.v. lamp for 4 h. The solution was purged with dinitrogen throughout this time although little colour change was observed, from dark yellow-brown to dark brown-black. After photolysis the toluene was removed under reduced pressure and the resulting black solid was redissolved in thf (20 cm^3) and filtered through Celite. After filtration, the thf was reduced in volume from 20 to about 5 cm^3. Hexane (20 cm^3) was layered over the thf solution and solvent diffusion at -20 °C over a period of 4 d afforded shiny black crystals of complex (**9**) (0.06 g, 67% yield).

X-*Ray Crystallographic Studies.—Crystal data.* (**1a**), C$_{48}$H$_{42}$Bi$_3$Cl$_3$Fe$_6$O$_{12}$, M_r = 1 879.2, monoclinic, space group $C2/c$, a = 21.440(7), b = 12.480(4), c = 20.315(6) Å, β = 95.00(4)°, U = 5 415.0 Å^3 (from 2θ values of 32 reflections measured at $\pm\omega$, λ = 0.710 73 Å for graphite-monochromated Mo-K_α radiation), Z = 4, D_c = 2.305 g cm^{-3}, F(000) = 3 528, μ = 11.5 mm^{-1}, crystal dimensions 0.31 × 0.42 × 0.65 mm.

(**2**), C$_{12}$H$_{15}$ClFeO$_2$, M_r = 282.6, triclinic, space group $P\bar{1}$, a = 7.583(1), b = 7.880(1), c = 12.155(2) Å, α = 79.11(1), β = 78.67(1), γ = 68.32(1)°, U = 656.36 Å^3 (from 32 reflections), Z = 2, D_c = 1.429 g cm^{-3}, F(000) = 292, μ(Mo-K_α) = 1.3 mm^{-1}, crystal dimensions 0.12 × 0.27 × 0.38 mm.

(**4**), C$_{24}$H$_{21}$BiFe$_3$O$_6$, M_r = 782.0, monoclinic, space group $P2_1/c$, a = 14.142(1), b = 13.020(1), c = 13.948(1) Å. β = 91.266(8)°, U = 2 567.6 Å^3 (from 32 reflections), Z = 4, D_c = 2.023 g cm^{-3}, F(000) = 1 496, μ(Mo-K_α) = 8.5 mm^{-1}, crystal dimensions 0.17 × 0.17 × 0.38 mm.

(**9**), C$_{21}$H$_{21}$BiFe$_3$O$_3$, M_r = 697.9, monoclinic, space group $P2_1/m$, a = 7.255(1), b = 15.068(1), c = 9.242(1) Å, β = 106.720(7)°. U = 967.5 Å^3 (from 32 reflections), Z = 2, D_c = 2.395 g cm^{-3}, F(000) = 664, μ(Mo-K_α) = 11.3 mm^{-1}, crystal dimensions 0.1 × 0.2 × 0.35 mm.

Data collection and processing. Siemens AED2 diffractometer, Mo-K_α radiation, ω—θ scan mode, on-line profile fitting for complexes (**4**) and (**9**).[24] For (**1a**) [in square brackets for (**2**), (**4**), and (**9**) if different]: 5 622 [4 616, 5 479, 5 009] reflections measured with 2$\theta \leqslant 45°$ [50, 50, 50], 3 792 [2 309, 4 530, 1 769] unique reflections, 3 142 [1 932, 2 967, 1 654] with $F > 4\sigma_c(F)$ (σ_c based on counting statistics only), R_{int} = 0.037 [0.083, 0.034, 0.020], data corrected for Lorentz and polarisation effects, decay of intensity of standard reflections for (**1a**) only, and absorption (semi-empirically); extinction insignificant.

Structure solution and refinement. Patterson and difference syntheses, blocked-cascade least-squares refinement on F, weighting $w^{-1} = \sigma^2(F) = \sigma_c{}^2(F) + f(G,S)$, where $f(G,S)$ is an empirical second-order function of $G = F_o/F_{max.}$ and $S = \sin\theta/\sin\theta_{max.}$ giving optimum analysis of variance:[25] $f(G,S) = 501 - 1907G + 6995G^2 - 782S + 727S^2 - 2122GS$ [$4.1G - 0.5G^2 + 0.9S - 0.3S^2 - 8.7GS$, $-6 + 104G - 31G^2 + 10S + 5S^2 - 152GS$, $7 + 39G + 161G^2 - 25S + 26S^2 - 115GS$]. Anisotropic thermal parameters, H-atoms constrained with C–H 0.96 Å, H–C–H 109.5°, U(H) = 1.2U_{eq}(C), U_{eq} = 1/3 (trace of orthogonalised U_{ij} matrix) [no H atoms for (**1a**)]. 327 [160, 317, 140] Parameters, R = 0.057 [0.040, 0.032, 0.034], R' = 0.039 [0.032, 0.034, 0.029], S = 1.39 [1.03, 1.00, 1.26], all shift/error values <0.1, largest features in final difference syntheses close to heavy atoms. Scattering factors from ref. 26; SHELXTL[27] and local computer programs.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

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