Reactions of [(η-C₅H₅)(CO)FeC(S)SC(Fp)S] (Fp = (η-C₅H₅)Fe(CO)₂) with Group IB and IIB metals; X-ray molecular structure of [(η-C₅H₅)(CO)FeC(SHgBr₂)SC(Fp)S]₂

Luigi Busetto, Silvia Bordoni, Valerio Zanotti *,

Dipartimento di Chimica Fisica ed Inorganica dell'Universita', Viale Risorgimento 4, 40136 Bologna (Italy)

Vincenzo G. Albano, Dario Braga, and Magda Monari *

Dipartimento di Chimica 'G. Ciamician', Via Selmi 2, 40126 Bologna (Italy)

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Abstract

The reactions of the metallacyclic complex [Cp(CO)FeC(S)SC(Fp)S] (1) (Cp = η-C₅H₅) with Group IB and IIB metal compounds have been investigated. Electrophilic addition at the thione sulphur atom has been observed in all cases. The reactions of 1 with the coinage metal complexes [MX(PPh₃)]ₙ (M = Cu, X = I, n = 4; M = Ag, X = Cl, n = 4; M = Au, X = Cl, n = 1) in the presence of TlPF₆ give the adducts [Cp(CO)FeC{SM(PPh₃)}SC(Fp)S]PF₆ (2), which have been characterized spectroscopically. The mercury salt [HgMe]PF₆ reacts similarly with 1 to afford [Cp(CO)FeC(SHgMe)SC(Fp)S]PF₆ (3), whereas mercury dihalides give products that have been shown by an X-ray diffraction study in the case in which X = Br to be halogen-bridged dimers of the type [Cp(CO)FeC(SHgX₂)SC(Fp)S]₂. The bromine-bridged dimer displays C_i symmetry. The coordination around the Hg atoms involves four normal and one weak bonds, and the geometry can be described as a distorted trigonal bipyramid. Zinc chloride reacts with 1 to give an air-sensitive unstable derivative that is tentatively formulated as [Cp(CO)FeC(SZnCl₂)SC(Fp)S].

Introduction

Very few examples are known of coordination of mercury(II) halides at the thione sulphur atom in electron-rich complexes. Of the known compounds, the complexes [Cp₂Fe₂(CO)₃(CSHgX₂)] [1] and [Cp₂Fe₂(CO)₂(CS)(CSHgX₂)] [2], prepared by addition of HgX₂ at the sulphur atom of the bridging CS groups in [Cp₂Fe₂(CO)₃(CS)] and [Cp₂Fe₂(CO)₂(CS)₂], respectively, are the best known. A

report of the addition of HgX_2 to the (μ^3-CS) group in $[Co_3(\eta-C_5H_5)_3(S)(CS)]$ to yield $[Co_3(\eta-C_5H_5)_3(S)(CSHgX_2)]$ has also appeared [3]. All these complexes have been formulated as monomers. Addition of the $[Au(PPh_3)]^+$ fragment at the sulphur atom of bridging or terminal CS groups in transition metal complexes is to the best of our knowledge unknown. The reactions of $[Au(PR_3)Cl]$ (R = Me, Ph) with the anionic thiocarbonyl complex $[\{HB(pz)_3\}(CO)_2W(CS)]^-$ ($HB(pz)_3$ = hydrotris(pyrazol-1-yl)borate) have been reported to give the unusual adduct $[\{HB(pz)_3\}(CO)_2(CS)WAuPR_3]$ [4], despite the observation that alkylation takes place at the CS sulphur atom to yield the mercaptocarbyne complexes $[\{HB(pz)_3\}(CO)_2W(CSR)]$ [5].

We recently reported the synthesis of $[Cp(CO)\overline{FeC(S)SC(Fp)}S]$ (1), which contains the unusual moiety C_2S_3 [6].


(1) $\xrightarrow{\text{E}}$ (I)
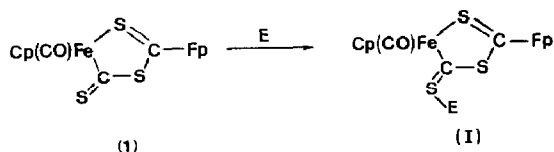
The rich potential chemistry of compound 1, which can function as a nucleophilic ligand through the *exo*-S atom to form adducts of type I not only with organic electrophiles (Me^+, Et^+) but also with Group VI metal carbonyl adducts and Group IIB metal salts ($M(CO)_5(thf)$; M = Cr, Mo, W; HgX_2, X = Cl, Br, I), prompted us to extend the study to reactions with Group IB and other Group IIB metal derivatives.

In a preliminary report of an X-ray structural study of the $HgBr_2$ adduct we revealed the dimeric nature of $[Cp(CO)\overline{FeC(SHgBr_2)SC(Fp)}S]_2$ [6b]. In view of the paucity of crystal structure determinations of halogen-bridged dimeric complexes the results of that study are presented here and discussed in some detail. Furthermore, in order to explore the properties of the thione sulphur atom we have extended our studies towards other metal complexes of the type $[MX(PPh_3)]_n$ (M = Cu, X = I, n = 4; M = Ag, X = Cl, n = 4; M = Au, X = Cl, n = 1).

Results and discussion

The compound $[Cp(CO)\overline{FeC(S)SC(Fp)}S]$ (1) reacts with Group IB complexes $[M(PPh_3)X]_n$ (M = Ag, Au, X = Cl; M = Cu, X = I) in CH_2Cl_2 solution in the presence of $TlPF_6$ to give the stable Lewis acid adducts 2 (eq. 1) (2a: M = Cu, X = I, n = 4; 2b: M = Ag, X = Cl, n = 4; 2c: M = Au, X = Cl, n = 1).

$$\text{(1)}$$

(1) (2)
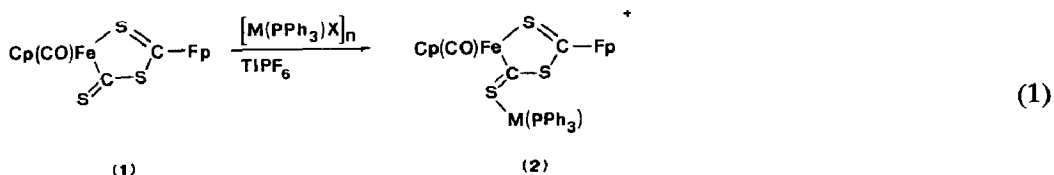
The bright green complexes $[Cp(CO)\overline{FeC\{SM(PPh_3)\}SC(Fp)}S]PF_6$ (2) have been characterised on the basis of their IR and ^1H NMR spectra. Compound 2a shows, as expected, three $\nu(CO)$ frequencies at 2047, 2004 and 1982 cm^{-1}, with the frequency of the band at the lowest wavenumber ca. 16 cm^{-1} higher than that of the lowest band in the precursor $[Cp(CO)\overline{FeC(S)SC(Fp)}S]$ (1) (see Table 1). The IR

Table 1

Infrared data (cm^{-1})

Complex	ν(CO) [a]	ν(CS) [b]
[Cp(CO)FeC(S)SC(Fp)S] (1)	2044s, 1999s, 1962s	996ms, 976m, 819m, 755w
[Cp(CO)FeC{SCu(PPh$_3$)}SC(Fp)S]PF$_6$ (2a)	2047s, 2004s, 1982m	995m, 944m
[Cp(CO)FeC{SAg(PPh$_3$)}SC(Fp)S]PF$_6$ (2b)	2047s, 2004s, 1990(sh)	997m, 943m
[Cp(CO)FeC{SAu(PPh$_3$)}SC(Fp)S]PF$_6$ (2c)	2049s, 2006s	998m, 909m
[Cp(CO)FeC(SHgMe)SC(Fp)S]PF$_6$ (3)	2052s, 2011s	999m, 908m, 804w, 763w
[Cp(CO)FeC(SHgCl$_2$)SC(Fp)S]$_2$ (4a)	2052s, 2012s	997m, 913m, 806m, 764m
[Cp(CO)FeC(SHgBr$_2$)SC(Fp)S]$_2$ (4b)	2051s, 2010s	996m, 911m, 806m, 762m
[Cp(CO)FeC(SZnCl$_2$)SC(Fp)S] (5)	2049s, 2008s	

[a] In CH$_2$Cl$_2$ solutions. [b] In KBr pellets.

spectra of **2b** and **2c**, on the other hand, exhibit only two bands (see Table 1), with the lowest energy carbonyl stretching superimposed to the bands at 2004 cm^{-1} in **2b** and 2006 cm^{-1} in **2c**, respectively. Therefore the band at 1962 cm^{-1} in complex **1**, which has been assigned to the endocyclic iron carbonyl, is shifted towards higher wavenumbers. The electron-withdrawing ability of the [M(PPh$_3$)]$^+$ fragments seems to increase in the order [Cu(PPh$_3$)]$^+ <$ [Ag(PPh$_3$)]$^+ <$ [Au(PPh$_3$)]$^+$ and consequently the band for the CO bonded to the Fe$_{endo}$ is superimposed on the lower-frequency carbonyl bonded to the Fe$_{exo}$ in complexes **2b** and **2c**. As is generally found, formation of sulphur-bound Lewis adducts in thione derivatives of transition metals [1,2,7] and in the thioanhydride-like derivatives of type I [6] results in a shift to lower wavenumbers of the ν(CS) band from the thione group. Similar behaviour is also observed for the complexes [Cp(CO)FeC{SM(PPh$_3$)}SC(Fp)S]PF$_6$ (**2**), which exhibit a lowering of the highest and most intense ν(CS) stretching mode in compound **1** of ca. 50 cm^{-1} for **2a** and **2b** and ca. 90 cm^{-1} for **2c**; this further lowering is due to the high electronegativity of the gold atom. In the ^{1}H NMR spectra of **2** (see Table 2), in addition to the two singlets attributed to the non-equivalent cyclopentadienyl rings, there is a multiplet in the phenyl region. Complex [Cp(CO)FeC{SAg(PPh$_3$)}SC(Fp)S]PF$_6$ (**2b**) can be compared with the related dimeric [Cp(CO)FeC(SAg$_{0.5}$)SC(Fp)S]$_2$PF$_6$ (**3**) formed in the reaction of the silver ion Ag$^+$ with **1** [6], the main difference being that a PPh$_3$ ligand in **2b** replaces a [Cp(CO)FeC(S)SC(Fp)S] ligand. The ν(CO) absorptions in the IR spectra of the two complexes are very similar, suggesting that the donor properties of triphenylphoshine and the sulphur atom in **1** are comparable.

The methylmercury salt [HgMe]PF$_6$ reacts with **1** to give [Cp(CO)FeC(SHgMe)SC(Fp)S]PF$_6$ (**3**), characterized from its IR and ^{1}H NMR spectra. The IR spectrum of **3** shows two terminal carbonyl absorptions at 2052 and 2011 cm^{-1}. In the ^{1}H NMR spectrum the methyl protons give a singlet resonance at δ 1.31 ppm; this

Table 2

^{1}H NMR data ^{a} (CDCl$_3$)

Compound	δ(Cp)	Other δ
[Cp(COFeC(S)SC(Fp)S] (1)	5.13, 4.75	
[Cp(CO)FeC{SCu(PPh$_3$)}SC(Fp)S]PF$_6$ (2a)	4.95, 4.84	7.47 (m, Ph)
[Cp(CO)FeC{SAg(PPh$_3$)}SC(Fp)S]PF$_6$ (2b)	4.90, 4.77	7.38 (m, Ph)
[CP(CO)FeC{SAu(PPh$_3$)}SC(Fp)S]PF$_6$ (2c) ^{b}	5.31, 5.17	7.67 (m, Ph)
[Cp(CO)FeC(SHgMe)SC(Fp)S]PF$_6$ (3)	5.21, 5.08	1.31 (s, Me)
[Cp(CO)FeC(SHgCl$_2$)SC(Fp)S]$_2$ (4a)	5.53, 5.29	
[Cp(CO)FeC(SHgBr$_2$)SC(Fp)S]$_2$ (4b)	5.55, 5.30	

^{a} Chemical shifts (δ, ppm) from TMS. ^{b} In (Cd$_3$)$_2$CO.

value falls close to that reported for the thiocarbonyl complex [Cp$_2$Fe$_2$(CO)$_3$CS-HgMe]PF$_6$ [8] (δ 1.33), but is downfield with respect to the methyl signal from [(μ-MeHgS)$_2$Fe$_2$(CO)$_6$] (δ (CH$_3$HgS) 0.86) in which the sulphur atoms bridge two iron atoms [9].

The mercury(II) salts HgX$_2$ (X = Cl, Br) react smoothly in CH$_2$Cl$_2$ solutions with 1 to give the dark-green complexes [Cp(CO)FeC(SHgX$_2$)SC(Fp)S]$_2$ (4) (4a: X = Cl; 4b: X = Br) in 52 and 81% yields, respectively. It has been shown previously that for 1/1 adducts of mercuric halides with monodentate two-electron donors there are several possible geometries [10]. Even the related complexes [HgCl$_2$ · PR$_3$] (R = Me, Et, Ph, etc.) that have been investigated by X-ray studies have been found not to be isostructural [11]. In order to establish the geometry of these complexes far infrared spectroscopy has commonly been used, but it has been shown to be unsatisfactory in several cases because of the difficulty of assigning ν(HgCl) frequencies to bridging or terminal mercury–halogen bonds [11]. We have found that the compounds [Cp(CO)FeC(SHgX$_2$)SC(Fp)S]$_2$ (4) give spectra similar to those reported for the related Lewis acid adducts [Cp(CO)FeC(SE)SC(Fp)S] [6] for the electron-rich thiocarbonyl complexes [Cp$_2$Fe$_2$(CO)$_2$(L)(CSHgCl$_2$)] (L = CO, CS) [1,2] and [Co$_3$(η-C$_5$H$_5$)$_3$(CSHgX$_2$)(S)] (X = Cl, Br, I) [3], which were formulated as monomers on the basis of their analytical and spectroscopic data. In order to assign the correct geometry to compounds 4 crystals of 4b were grown from CH$_2$Cl$_2$ solutions at −20°C and an X-ray crystal structure study was undertaken (see next section).

Further evidence of the ability of [Cp(CO)FeC(S)SC(Fp)S] (1) to function as a ligand through the thione sulphur atom was provided by its reaction with zinc chloride. Compound 1 reacts with ZnCl$_2$ in a few minutes in THF solution under nitrogen to give the dark-green air-sensitive [Cp(CO)FeC(SZnCl$_2$)SC(Fp)S] (5), which shows the characteristic ν(CO) band pattern of this type of complex. The instability of complex 5, which decomposes to its precursor 1 when kept in solution in chlorinated solvents, prevented further spectroscopic characterization.

*The molecular structure of **4b***

The dimeric nature of the molecule is the most important feature revealed by the crystallographic study. The geometry of the complex is shown in Fig. 1 and selected bond lengths and angles are listed in Table 3. Two mercury atoms are linked through two bridging bromide ligands, and their seemingly tetrahedral coordination involves two terminal ligands, a bromide ion, and the thione sulphur of the [Cp(CO)FeC(S)SC(Fp)S] unit. The molecule adopts a centrosymmetric conformation and lies around inversion centres in the crystal. The dimeric arrangement of mercury(II) complexes of general formula $[HgX_2L]$ is a common feature, as is a degree of bond asymmetry for the bridging halogens [10,11].

The Hg–(μ-Br) distances are slightly but significantly different (2.702(2), 2.836(2) Å), probably in order to optimize bond angles and contacts in the Hg_2Br_2 ring. This effect is even more marked in the recently reported dimer $[Hg_2Br_4(PPr_3)_2]$ [11b] (2.667(2), 3.015(2) Å), and in that case is accompanied by a further narrowing of the (μ-Br)–Hg–(μ-Br) angle (90.9(1)°). A similar deformation pattern is exhibited by the molecule $[Hg_2Br_4\{PPh_2(CH_2COOH)\}_2]$ [12].

The Hg–S(1) distance of 2.450(5) Å is in the range previously observed; e.g. 2.467(2) Å in $[\{C_6H_5C(NH_2)S\}HgI_2]_2$ [13], 2.42(1) Å in $[Hg(tu)_2Cl]Cl$ (tu = thiourea) [14], and 2.506(8) Å in $(Hg(tu)_4]Cl_2$ [15].

The coordination tetrahedron around the Hg atoms is substantially distorted. One source of distortion is the ring constraint, which reduces the Br(2)–Hg–Br(2^i) angle to 97.0(1)°. The ring effect can account for some widening of the S(1)–Hg–Br(1) angle, but this angle is wider than expected (138.6(1)°) and so there must be some other source of deformation. In fact the S(2)...Hg contact (3.16 Å) is shorter than the sum (ca. 3.5 Å) of the Van der Waals radii (1.8 Å for S [16] and ca. 1.7 Å for Hg [17]) and indicates a significant bonding interaction. This view is supported by a slight reduction of the relevant angles S(2)–C(1)–S(1) and C(1)–S(1)–Hg (114(1)° and 106.1(6)°, respectively) with respect to the corresponding values in the cation $[Cp(CO)FeC(SEt)SC(Fp)S]^+$ [6b] (116.0(3) and 110.1(3)°, respectively). Fur-
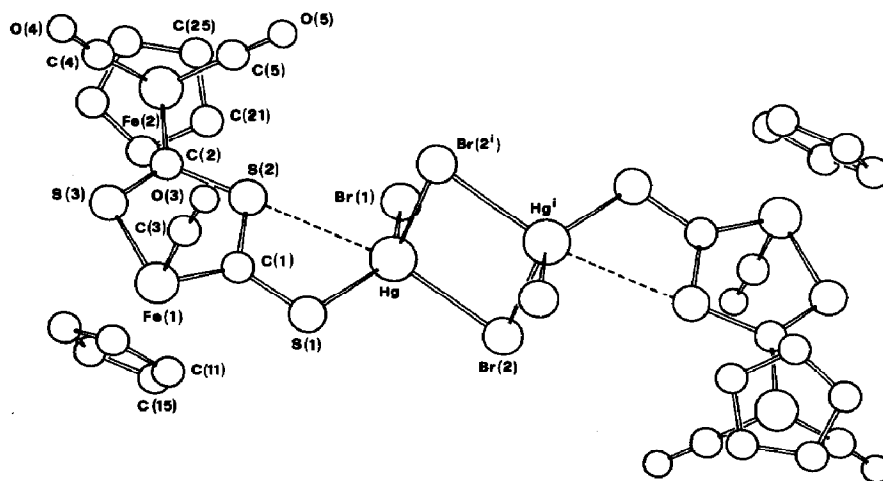

Fig. 1. Molecular drawing of **4b** showing the atom labelling scheme. The H atoms have been omitted for clarity.

Table 3

Selected bond lengths (Å) and angles (°) for [Cp(CO)FeC(SHgBr$_2$)SC(Fp)S]$_2$ (**4b**) with e.s.d.'s in parentheses[a]

Fe(1)–S(3)	2.202(6)	Fe(2)–C(4)	1.79(3)
Fe(1)–C(1)	1.88(2)	C(4)–O(4)	1.12(3)
Fe(2)–C(2)	1.93(2)	Fe(2)–C(5)	1.75(2)
C(1)–S(1)	1.68(2)	C(5)–O(5)	1.15(2)
C(2)–S(2)	1.75(2)	Fe(1)–C(cp1)(av.)	2.11(1)
C(1)–S(2)	1.71(2)	Fe(2)–C(cp2)(av.)	2.08(1)
C(2)–S(3)	1.62(2)	C(cp1)–C(cp1)(av.)	1.43(2)
Hg–Br(1)	2.496(3)	C(cp2)–C(cp2)(av.)	1.40(1)
Hg–Br(2)	2.702(2)	S(2)...Hg	3.16
Hg–Br(2^i)	2.836(2)	S(2)...Br(1)	4.01
Hg–S(1)	2.450(5)	Br(2)...Br(2^i)	4.15
Fe(1)–C(3)	1.75(2)	Hg...Hg^i	3.67
C(3)–O(3)	1.15(2)		
C(1)–Fe(1)–S(3)	89.1(5)	S(1)–Hg–Br(2^i)	103.1(1)
Fe(1)–S(3)–C(2)	108.9(7)	S(1)–Hg–Br(1)	138.6(1)
S(3)–C(2)–S(2)	115(1)	S(1)–Hg–Br(2)	102.7(1)
C(2)–S(2)–C(1)	104.5(9)	Hg–Br(2)–Hg^i	83.0(1)
S(2)–C(1)–Fe(1)	120(1)	S(2)–Hg–Br(2)	161.8(1)
S(2)–C(1)–S(1)	114(1)	S(3)–C(2)–Fe(2)	132(1)
Fe(1)–C(1)–S(1)	125(1)	S(2)–C(2)–Fe(2)	113(1)
C(1)–S(1)–Hg	106.1(6)	Fe(1)–C(3)–O(3)	177(2)
Br(1)–Hg–Br(2)	107.5(1)	Fe(2)–C(4)–O(4)	175(2)
Br(1)–Hg–Br(2^i)	103.1(1)	Fe(2)–C(5)–O(5)	178(3)
Br(2)–Hg–Br(2^i)	97.0(1)		

[a] Symmetry code: (i) $1 - x$, $- y$, $2 - z$.

thermore, the metallacyclic ring containing S(2) is close to coplanar with the C(1)–S(1)–Hg plane (dihedral angle 7.1°), clearly in order to optimize the S(2)...Hg contact. In conclusion the coordination polyhedron around mercury can be described as a distorted trigonal bipyramid in which the metallacyclic complex acts as a bidentate ligand. This bonding mode resembles that observed in the dithiocarbamate complexes of mercury, in which long and short Hg–S bonds have been noticed [18]. The presence of short and long coordination interactions is commonly seen in the crystal structures of mercury compounds [19].

The ligand molecule [Cp(CO)FeC(S)SC(Fp)S], the geometry of which we previously determined in [Cp(CO)FeC{SW(CO)$_5$}SC(Fp)S] and in the related cation [Cp(CO)FeC(SEt)SC(Fp)S]$^+$, does not differ significantly in the three species. It is noteworthy that the C–S$_{exo}$ distance of 1.68(2) Å is closely similar for all these species, and indicates multiple bond character.

Experimental

All reactions were routinely carried out under nitrogen by standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents: CH$_2$Cl$_2$ from CaH$_2$, tetrahydrofuran from sodium benzophenone ketyl, petroleum ether (b.p. 40–60°C) from sodium wire. Infrared spectra were recorded on a Perkin Elmer 983-G in solution or as KBr pellets. ^{1}H

NMR spectra were recorded on a Varian XL100 spectrometer with $SiMe_4$ as internal standard. Conductivities were measured with a LKB 5300B conductivity bridge (1×10^{-4} mol dm^{-3} solutions in acetone). Melting points were determined with a Büchi instrument and are uncorrected. The compounds [Cp(CO)FeC(S)SC(Fp)S] [6], [Ag(PPh$_3$)Cl]$_4$ [20a] and [Cu(PPh$_3$)I]$_4$ [20b] were prepared by published methods.

Synthesis of [Cp(CO)FeC{SCu(PPh$_3$)}SC(Fp)S]PF$_6$ (2a)

Complex 1 (0.14 g, 0.31 mmol) was added to a CH$_2$Cl$_2$ suspension (20 ml) of [CuI(PPh$_3$)]$_4$ (0.14 g, 0.08 mmol) and TlPF$_6$ (0.11 g, 0.33 mmol) and the mixture was stirred for 5 h. The solution was filtered through Celite under N$_2$ and evaporated to dryness under vacuum. The black residue was washed with Et$_2$O to remove some residual starting material. The crude product was crystallised three times from a CH$_2$Cl$_2$/Et$_2$O mixture at −20°C to give black-green microcrystals of [Cp(CO)FeC{SCu(PPh$_3$)}SC(Fp)S]PF$_6$ (2a). Yield: 0.20 g (71%). M.p. 145–147°C. Molar conductivity in acetone Λ_m 86.2 Ω^{-1} mol^{-1} cm^2.

Synthesis of [Cp(CO)FeC{SAg(PPh$_3$)}SC(Fp)S]PF$_6$ (2b)

[AgCl(PPh$_3$)]$_4$ (0.10 g, 0.06 mmol) was added to a CH$_2$Cl$_2$ solution containing [Cp(CO)FeC(S)SC)Fp)S] (1) (0.11 g, 0.25 mmol) and an excess of TlPF$_6$ (0.09 g). The mixture was stirred at room temperature for 2 h, then worked-up as above to give [Cp(CO)FeC{SAg(PPh$_3$)}SC(Fp)S]PF$_6$ (2b) as dark-green microcrystals. Yield: 0.18 g (77%). M.p. 147–150°C (dec.). Molar conductivity in acetone Λ_m 94.0 Ω^{-1} mol^{-1} cm^2.

Synthesis of [Cp(CO)FeC{SAu(PPh$_3$)}SC(Fp)S]PF$_6$ (2c)

This reaction was carried out in two ways involving slightly different methods for generating the salt [Au(PPh$_3$)]PF$_6$: (a) One equivalent of [AuCl(PPh$_3$)] (0.13 g, 0.26 mmol) was added to a CH$_2$Cl$_2$ solution of 1 (0.11 g, 0.26 mmol) and the mixture was stirred for 2.5 h in the presence of a large excess of TlPF$_6$. The solution was filtered through Celite under N$_2$ and the solvent evaporated under vacuum. The dark-green residue was washed with several portions of Et$_2$O then redissolved in CH$_2$Cl$_2$, and Et$_2$O was added. The solution was kept at −20°C to give the black-green microcrystalline solid [Cp(CO)FeC{SAu(PPh$_3$)}SC(Fp)S]PF$_6$ (2c). Yield: 0.22 g (82%). M.p. 121–125°C (dec.). Molar conductivity in acetone Λ_m 115.9 Ω^{-1} mol^{-1} cm^2.

(b) Silver hexafluorophosphate (0.02 g, 0.1 mmol) was added to a solution of [AuCl(PPh$_3$)] (0.05 g, 0.11 mmol) in CH$_2$Cl$_2$ (20 ml) at 0°C and the mixture was stirred for 15 min. Complex 1 (55 mg, 0.12 mmol) was added to the solution and the mixture was stirred for 1 h at room temperature. Work-up as above afforded [Cp(CO)FeC{SAu(PPh$_3$)}SC(Fp)S]PF$_6$ (2c). Yield: 0.09 g (69%).

Synthesis of [Cp(CO)FeC(SHgMe)SC(Fp)S]PF$_6$ (3)

Silver hexafluorophosphate (0.04 g, 0.16 mmol) was added to a CH$_2$Cl$_2$ solution (20 ml) containing methylmercuric chloride (0.05 g, 0.14 mmol) at 0°C. The mixture was stirred for 15 min and then 1 (0.05 g, 0.11 mmol) was added. After 30 min stirring at room temperature the solution was filtered to remove AgI and evaporated under vacuum. The residue was recrystallised from a CH$_2$Cl$_2$/Et$_2$O mixture at

$-20\,^{\circ}$C to afford dark-green crystals of $[Cp(CO)\overline{FeC(SHgMe)SC(Fp)S}]PF_6$ (3). Yield 0.06 g (70%). M.p. 90–94$\,^{\circ}$C (dec.). Molar conductivity in acetone Λ_m 139 Ω^{-1} mol^{-1} cm^2.

Synthesis of $[Cp(CO)\overline{FeC(SZnCl_2)SC(Fp)S}]$ (5)

$[Cp(CO)\overline{FeC(S)SC(Fp)S}]$ (1) (0.15 g, 0.34 mmol) was added to a solution of $ZnCl_2 \cdot 2H_2O$ (0.06 g, 0.34 mmol) in tetrahydrofuran (25 ml) and the mixture stirred for 30 min. The solution was filtered through Celite under N_2 and evaporated to dryness under vacuum. Attempted crystallisation from CH_2Cl_2/Et_2O or acetone/ Et_2O gave the unstable oily $[Cp(CO)\overline{FeC(SZnCl_2)SC(Fp)S}]$ (5).

Data collection and structure determination of (4b)

Crystal data and details of the data collection for compound **4b** are listed in Table 5. Diffraction data were collected at room temperature with an Enraf–Nonius CAD4 diffactometer using graphite-monochromated Mo-K_α radiation (λ 0.71067 Å). The unit cell was determined from a least squares fit of 25 reflections. Data were

Table 4

Fractional atomic coordinates for **4b**

Atom	x	y	z
Hg	0.33368(10)	$-0.01109(8)$	0.86448(9)
Br(1)	0.2927(3)	$-0.1776(2)$	0.6885(2)
Br(2)	0.3487(2)	$-0.1315(2)$	1.0686(2)
Fe(1)	0.1723(3)	0.4014(2)	0.7721(2)
Fe(2)	0.2914(3)	0.2218(3)	0.4103(3)
S(1)	0.2328(7)	0.1631(5)	0.9061(5)
S(2)	0.2940(6)	0.1930(5)	0.6779(5)
S(3)	0.1750(6)	0.3917(5)	0.5796(5)
C(1)	0.2271(19)	0.2484(16)	0.7858(15)
C(2)	0.2498(20)	0.2811(20)	0.5548(16)
C(3)	0.3662(28)	0.4978(19)	0.8273(19)
O(3)	0.4943(19)	0.5584(17)	0.8674(16)
C(5)	0.4742(28)	0.2233(27)	0.4996(22)
O(5)	0.5924(21)	0.2198(25)	0.5584(19)
C(4)	0.3442(29)	0.3863(29)	0.3769(20)
O(4)	0.3805(24)	0.4863(18)	0.3491(17)
C(11)	0.0867(44)	0.4147(39)	0.9188(29)
C(12)	0.1181(41)	0.5368(32)	0.8712(30)
C(13)	0.0313(43)	0.5265(33)	0.7431(31)
C(14)	$-0.0570(36)$	0.3902(35)	0.7139(29)
C(15)	$-0.0317(42)$	0.3221(29)	0.8191(38)
C(21)	0.1796(23)	0.0192(21)	0.3863(21)
C(22)	0.0725(23)	0.0860(18)	0.3528(18)
C(23)	0.0942(25)	0.1581(21)	0.2562(19)
C(24)	0.2185(24)	0.1385(21)	0.2279(22)
C(25)	0.2650(27)	0.0507(21)	0.3049(20)
C(11')	$-0.0613(47)$	0.3466(43)	0.7598(53)
C(12')	0.0277(47)	0.3510(43)	0.8849(53)
C(13')	0.1301(47)	0.4805(43)	0.9286(53)
C(14')	0.1045(47)	0.5561(43)	0.8305(53)
C(15')	$-0.0138(47)$	0.4734(43)	0.7261(53)

Table 5

Crystal data and intensity collection parameters for **4b**

Formula	$C_{30}H_{20}Br_4Fe_4Hg_2O_6S_6$
M	1613.06
Crystal size (mm)	$0.1 \times 0.05 \times 0.1$
System	triclinic
Space group	$P\bar{1}$
a(Å)	9.629(1)
b(Å)	10.822(3)
c(Å)	11.399(2)
α (°)	92.45(2)
β (°)	107.28(1)
γ (°)	107.17(1)
U (Å^3)	1072.6
Z	1
D_c (g cm^{-3})	2.50
$F(000)$	748
Radiation (graphite monochromated) (λ, Å)	Mo-K_α (0.71067)
μ(Mo-K_α) (cm^{-1})	124.6
Diffractometer	Enraf–Nonius CAD-4
Scan mode	$\omega/2\theta$
θ range (°)	2.5–28
ω scan width (°)	$0.8 + 0.35\text{tg}\theta$
Prescan rate (° min^{-1})	5
Prescan acceptance $\sigma(I)/I$	0.3
Required $\sigma(I)/I$	0.01
Maximum scan time (s)	150
Standard reflections	3 remeasured periodically no decay
Reflections collected	5416 ($\pm h, \pm k, l$)
Unique observed reflections $[F_o > 4\sigma(F_o)]$	1478
No. of refined parameters	196
R, R_w	0.045, 0.045

$R = \Sigma(|F_o| - |F_c|)/\Sigma F_o$
$R_w = \Sigma(|F_o| - |F_c|)w^{1/2}/\Sigma F_o w^{1/2}$

corrected for Lorentz-polarization effects. Empirical absorption corrections were applied by using the Walker and Stuart method [19]. All calculations were performed by use of the SHELX 76 system of programs [20].

The structure was solved by direct methods, which allowed location of Hg, Fe and S atoms of the molecule, which has a crystallographically imposed inversion centre located in the middle of the [HgBr$_2$Hg] bridging unit. All additional non-hydrogen atoms were located in Fourier maps phased with the heavy atoms. The structure was refined by full-matrix least-squares calculations in the space group $P\bar{1}$ (No. 2). The weighting factor used in the least-squares calculations was $w = k/[\sigma^2(F) + |g|F^2]$. Hydrogen atoms were included in calculated positions (d(CH) 1.08 Å) and their coordinates were not refined but continuously adjusted in line with those of their carbon atoms. Bond-lengths constraints for the C–C distances in the cyclopentadienyl rings were introduced (distances equal within an estimated

error of 0.01 Å). The cyclopentadienyl ligand bonded to the endocyclic iron atom showed a weak second image indicating disorder over two sites and was refined as rigid group. The second image gave an occupancy factor of ca. 30%. The final refinement of all positional and thermal parameters involved anisotropic thermal parameters except in the case of the cyclopentadienyl atoms, which were refined isotropically with the thermal parameters of the hydrogens fixed at U 0.08 Å^2. The final Fourier difference map showed peaks in the range ± 1 e Å^{-3} adjacent to the Hg atom, but no chemically signicant feature. The final positional parameters are listed in Table 4. A complete list of bond lengths and angles, and a table of thermal parameters and a list of observed and calculated structure factors are available from the authors.

Acknowledgements

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