Hexa- and Nona-nuclear Heterometallic Clusters based on Mercury-capped MCo_3 (M = Fe or Ru) Tetrahedral Units*

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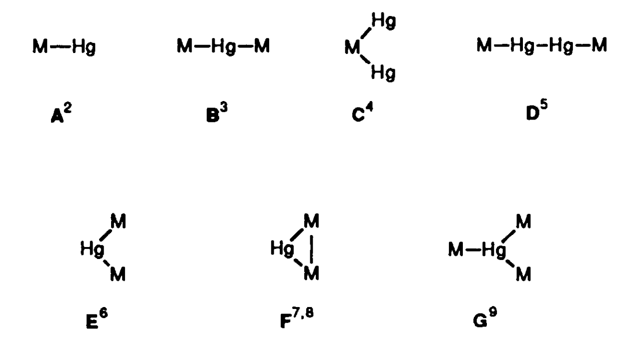
The reactions of tetrahedral mixed-metal clusters $K[MCo_3(CO)_{12}]$ (M = Fe **1a** or Ru **1b**) with $HgBr_2$ afforded the pentanuclear clusters $[MCo_3(CO)_{12}(HgBr)]$ (M = Fe **2a** or Ru **2b**) together with hexanuclear clusters $[MCo_3(CO)_{12}\{\mu_3\text{-}HgCo(CO)_4\}]$ (M = Fe **5a** or Ru **5b**) in which the mercury atom caps the Co_3 face of the precursor. Complexes **5a** and **5b** were most effectively prepared in dichloromethane by the reaction of **2a** or **2b** with $Na[Co(CO)_4]$. The reactions with $Na[Mo(CO)_3(cp)]$ (cp = $\eta\text{-}C_5H_5$) similarly afforded $[MCo_3(CO)_{12}\{\mu_3\text{-}HgMo(CO)_3(cp)\}]$ (M = Fe **6a** or Ru **6b**). The syntheses of the nonanuclear sandwich clusters $[\mu_6\text{-}Hg\{MCo_3(CO)_{12}\}_2]$ (M = Fe **7a** or Ru **7b**) are also described. All the complexes have been characterized by IR and UV/VIS spectroscopy. The crystal structure of $[FeCo_3(\mu\text{-}CO)_3(CO)_9\{\mu_3\text{-}HgMo(CO)_3(cp)\}]$ **6a** has been determined by X-ray diffraction methods. Crystals are monoclinic, space group $P2_1/c$, with a = 28.123(9), b = 8.400(5), c = 25.290(8) Å, β = 114.72(2)° and Z = 8. The structure was solved by direct and Fourier methods and refined by full-matrix least squares to R = 0.0596 for 3016 observed reflections. In the asymmetric unit two crystallographically independent, but essentially identical complexes are present. The complex exhibits a $FeCo_3$ tetrahedron in which the Co_3 face is capped by a $HgMo(CO)_3(cp)$ fragment such that the $FeCo_3Hg$ metal core forms a trigonal bipyramid with the Hg and Fe atoms at the apices. Each Co–Co edge is bridged by an almost symmetrical carbonyl ligand. In addition, three terminal carbonyls are bonded to the Fe atom, and two to each Co atom. The Hg atom has a severely distorted tetrahedral co-ordination involving the three Co atoms and the Mo atom. The structure of **6a** is compared with those of **5b** and **7b**, previously reported.

The isolobal relationship between the proton and some Group 11 complex cations, such as $[Au(PPh_3)]^+$, has now received wide recognition and has been increasingly used for the systematic synthesis of mixed-metal clusters containing these cations.[1a,b] Notwithstanding the more limited use of isoelectronic and isolobal mercury(II) precursors,[1c] a great variety of bonding modes have been encountered for such moieties bonded to metal atoms. These are illustrated in the following examples (see, right) where the references indicate the reported structural characterization. Many complexes of two-, three- or four-co-ordinated mercury containing structural units of types **A–G** have been described in the literature. Only in few clusters is mercury bonded to three or more metal atoms, thus generating core structures of types **H–M** (over page) or higher-nuclearity clusters.[18–27]



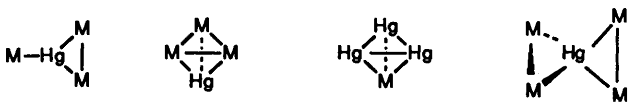
The most widely used synthetic methods for the production of such compounds involve (*a*) the reaction of transition-metal complexes or clusters with mercury or amalgams, (*b*) the reaction of low-valent neutral transition-metal complexes with mercury halides, or (*c*) the reaction of mono- or poly-nuclear carbonylmetalate anions with a mercury halide or pseudohalide. Reactions between nucleophilic metal reagents and mercury(II) salts, such as HgX_2, may lead to (*i*) retention of both chloride atoms to produce simple Lewis-base adducts of HgX_2,[2a,8a,d] (*ii*) displacement of a chloride ion to yield complexes retaining the very versatile HgX unit which, in the case of clusters, may occupy an edge-bridging or face-capping position,[2h,7a] or (*iii*) displacement of both chloride ions with formation of Hg–M bonds only.[3,15] A stepwise access to heterometallic clusters containing a fully metal-substituted Hg atom may utilize the reaction of bimetallic complexes having HgX group(s) with mono- or poly-nuclear carbonylmetalates.

With the aims of synthesising mixed-metal clusters containing mercury that would also provide structural comparisons with their copper-, silver- or gold-containing analogues,[28] we have investigated the reactions of the tetrahedral anionic clusters $K[MCo_3(CO)_{12}]$ (M = Fe **1a** or Ru **1b**) with $HgBr_2$. This has led to clusters in which the mercury atom is bonded to four or six transition-metal atoms. Parts of this work have appeared as preliminary communications.[29,30]

Results and Discussion

(*a*) *Synthesis of the Pentanuclear Clusters* $[MCo_3(CO)_{12}(HgBr)]$ (M = Fe **2a** *or* Ru **2b**).—One equivalent of $K[MCo_3(CO)_{12}]$ (M = Fe **1a** or Ru **1b**) was treated with

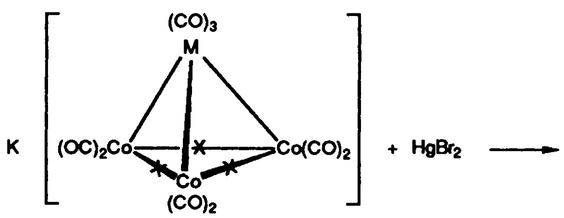
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



H[7,10,11] I[10,12,13] J[14] K[7,15]

L[16] M[17]

$HgBr_2$ in diethyl ether to give $[MCo_3(CO)_{12}(HgBr)]$ (M = Fe **2a** or Ru **2b**) in high yields. In addition, the clusters $[MCo_3(CO)_{12}\{\mu_3\text{-}HgCo(CO)_4\}]$ (M = Fe **5a** or Ru **5b**) were formed in low yield [equation (1)]. Complexes **5** must result



1a M = Fe

1b M = Ru

—✕— = μ-CO

$[MCo_3(CO)_{12}(HgBr)]$ + $[MCo_3(CO)_{12}\{\mu_3\text{-}HgCo(CO)_4\}]$ + ... (1)

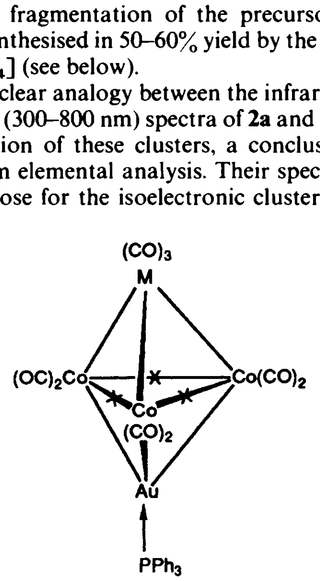
(major) (minor)

2a M = Fe **5a** M = Fe

2b M = Ru **5b** M = Ru

from partial fragmentation of the precursor but were independently synthesised in 50–60% yield by the reactions of **2** with $Na[Co(CO)_4]$ (see below).

There is a clear analogy between the infrared [ν(CO) region] and UV/VIS (300–800 nm) spectra of **2a** and **2b**, consistent with the formulation of these clusters, a conclusion which is also deduced from elemental analysis. Their spectroscopic data are similar to those for the isoelectronic clusters $[MCo_3(\mu\text{-}CO)_3\text{-}$



4a M = Fe

4b M = Ru

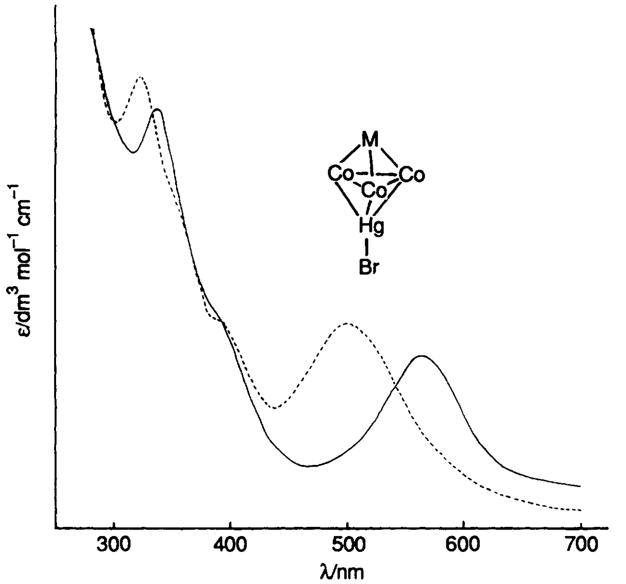
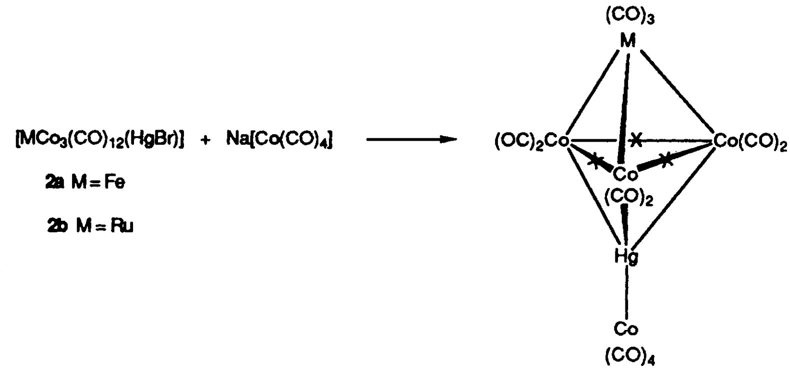


Fig. 1 Comparison of the UV/VIS spectra in CH_2Cl_2 for the clusters **2a** (M = Fe, full line) and **2b** (M = Ru, dotted line)

$(CO)_9\{\mu_3\text{-}M'(PPh_3)\}]$ (M = Fe, M′ = Cu **3a** or Au **4a**; M = Ru, M′ = Cu **3b** or Au **4b**) which have been prepared recently and structurally characterized by X-ray diffraction.[31,32] In all cases, the highest-wavenumber IR absorption band is shifted by *ca.* 10 cm^{-1} to higher frequency when replacing M = Fe with Ru. The UV/VIS absorption bands between *ca.* 550 and 570 nm (Fig. 1) may be attributed to transitions between orbitals involved in the metal–metal bonds.[33] The spectral blue shift of *ca.* 60–70 nm observed when replacing Fe by Ru is consistent with an increase in energy as the strength of the metal–metal bonds increases. Similar shifts have been previously observed in the UV/VIS spectra of the homologous clusters $[Fe_3(CO)_{12}]$, $[Fe_2Ru(CO)_{12}]$, $[FeRu_2(CO)_{12}]$, $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$,[34] as well as of the series $[FeRu_3H_2(CO)_{13}]$, $[FeRu_2OsH_2(CO)_{13}]$ and $[FeRuOs_2H_2(CO)_{13}]$.[35] This behaviour, which is also observed within the family of clusters **2**–**7** (see below), strongly indicates a close structural relationship between the analogous iron- and ruthenium-containing clusters. We therefore suggest that the HgBr group in **2a** or **2b** is bonded to the cluster in a similar way, probably triply bridging the Co_3 face,[27] although this could not be confirmed by an X-ray crystallographic study as it has not yet been possible to obtain suitable crystals. The presence of a dimeric structure involving a $Hg(\mu\text{-}Br)_2Hg$ unit, as encountered *e.g.* in $[\{Ru_3(CO)_9(\mu\text{-}C_2Bu^t)(\mu\text{-}HgBr)\}_2]$,[7a] is ruled out by the lack of absorptions in the far-IR region corresponding to bridging ν(Hg–Br) vibrations.

It is interesting that pure compound **2a** or **2b** is insoluble in non-polar solvents such as hexane, and transforms slowly in dichloromethane to **7a** and **7b**, respectively (see below). In contrast, in a polar solvent such as tetrahydrofuran (thf), **2a** and **2b** are rapidly transformed into the corresponding anionic clusters $[MCo_3(CO)_{12}]^-$ (M = Fe or Ru, respectively), as a result of deco-ordination of the HgBr fragment. A similar solvent-induced heterolytic cleavage has been observed previously for the related clusters $[MCo_3H(CO)_{12}]$ (M = Fe or Ru)[36] and $[RuCo_3(CO)_{12}\{\mu_3\text{-}M'(PPh_3)\}]$ (M′ = Cu or Au).[31,32b]

(*b*) *Synthesis of the Hexanuclear Clusters* $[MCo_3(CO)_{12}\{\mu_3\text{-}HgCo(CO)_4\}]$ (M = Fe **5a** *or* Ru **5b**) *and* $[MCo_3(CO)_{12}\{\mu_3\text{-}HgMo(CO)_3(cp)\}]$ (M = Fe **6a** *or* Ru **6b**; cp = $\eta\text{-}C_5H_5$).—Clusters **5a** or **5b** are best prepared by the reactions of **2a** or **2b**, respectively, with 1 equivalent of $Na[Co(CO)_4]$ in dichloromethane [equation (2)]. Complex **5b** has been isolated as black



(2)

5a M = Fe

5b M = Ru

needles (characterized by X-ray diffraction [29]) or red crystals, which can only be distinguished from each other by their solid-state IR spectra (see Fig. 2). In solution, both give rise to a common species since identical spectroscopic properties are observed (see Experimental section). We cannot state whether these solids correspond to polymorphic forms or to isomers. We have previously observed a similar phenomenon with the $[Au(PPh_3)]^+$ adduct **4b**.[31] The crystal structure of one of the two forms also showed a bipyramidal geometry of the metal core.[32b] It is interesting that two structural isomers have been observed for the $[HgMe]^+$ adduct [12] and the $[HgMo(CO)_3(cp)]^+$ adduct [10] of $[N(PPh_3)_2]_2[Fe_4(CO)_{13}]$. In the former case the solid-state structure of one isomer consists of a Fe_4 tetrahedron with the Lewis acid capping a face. In the latter adduct the Lewis acid metalloligand $Hg{-}Mo(CO)_3(cp)$ bridges the Fe–Fe hinge of a Fe_4 butterfly through the mercury atom and a π-CO connects the wing-tip Fe atoms. We have no indication of a similar behaviour in our case, and can presently only tentatively suggest that different packing of the same compound in the crystalline solids occurs.

Formation of compound **5a** or **5b** in equation (1) presumably

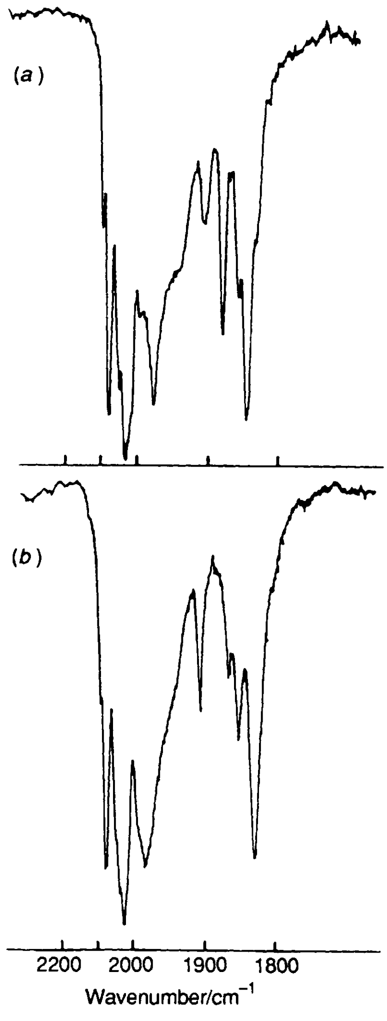


Fig. 2 The IR spectra (KBr pellets) of the forms A (*a*) and B (*b*) for cluster **5b**

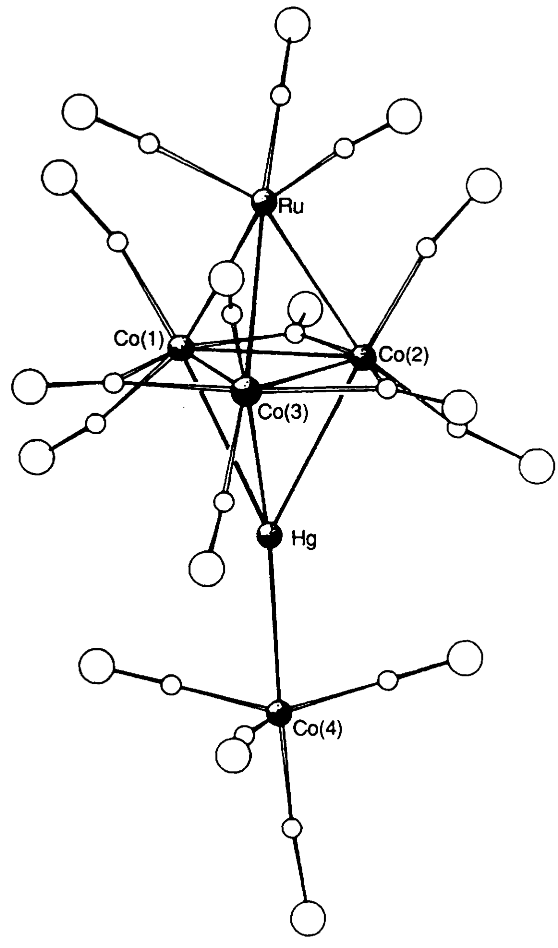
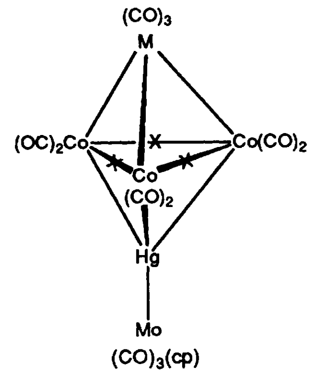


Fig. 3 View of the molecular structure of form A of cluster **5b** [29]

[$MCo_3(CO)_{12}(HgBr)$] + Na[$Mo(CO)_3(cp)$] ⟶  (3)

2a M = Fe

2b M = Ru

6a M = Fe

6b M = Ru

occurs by partial fragmentation of **1a** or **1b**, respectively, releasing $[Co(CO)_4]^-$ which in turn reacts according to equation (2). The formulation of **5a** and **5b** was deduced from mass, IR and UV/VIS spectroscopic results and elemental analysis and confirmed by an X-ray study[29] of one of the forms (called A) of **5b**. It revealed an unprecedented bonding mode for the Hg–$Co(CO)_4$ fragment (see Fig. 3).

Similarly, the reaction of **2a** or **2b** with Na[$Mo(CO)_3(cp)$] afforded the new (deep) violet microcrystalline clusters [$MCo_3(CO)_{12}\{\mu_3$-$HgMo(CO)_3(cp)\}$] (M = Fe **6a** or Ru **6b**), respectively [equation (3)]. Preliminary studies also indicate that K[$Fe(CO)_3(NO)$] reacts quantitatively with **2a** to give [$FeCo_3(CO)_{12}\{\mu_3$-$HgFe(CO)_3(NO)\}$] [IR (hexane): ν(CO) 2075m, 2063s, 2040vs, 2011m, 1982m and 1883s; ν(NO) 1777m cm^{-1}] which is isoelectronic with **5a**.

During the synthesis of compound **6a** by reaction (3) some [$Hg\{Mo(CO)_3(cp)\}_2$] was also formed and isolated together with [μ_6-$Hg\{FeCo_3(CO)_{12}\}_2$] **7a** (see below), as a result of the redistribution reaction (4). Mass spectra, IR and UV/VIS

$$2\,\mathbf{6a} \longrightarrow [Hg\{Mo(CO)_3(cp)\}_2] + \underset{\mathbf{7a}}{[\mu_6\text{-}Hg\{FeCo_3(CO)_{12}\}_2]} \quad (4)$$

spectroscopy and elemental analyses are consistent with the formulation given for clusters **6** and the results of an X-ray diffraction study on a single crystal of **6a** are discussed below. The UV/VIS spectra of **6a** and **6b** are very similar to those found for clusters **5a** and **5b**, respectively. The IR spectra show carbonyl stretching frequencies at 1919 and 1939 cm^{-1}, which are assigned to the $Mo(CO)_3(cp)$ group by comparison with the IR spectra of **2a** and **2b**, respectively.

(*c*) *Synthesis of the Nonanuclear Sandwich Clusters* [μ_6-$Hg\{MCo_3(CO)_{12}\}_2$] (M = Fe **7a** *or* Ru **7b**).—We found initially that slow recrystallization of compound **2b** in dichloromethane afforded black-green single crystals, whose spectroscopic properties differed from those of the initial product. We believe that this new compound is formed by reaction (5). Related ligand-redistribution reactions involving

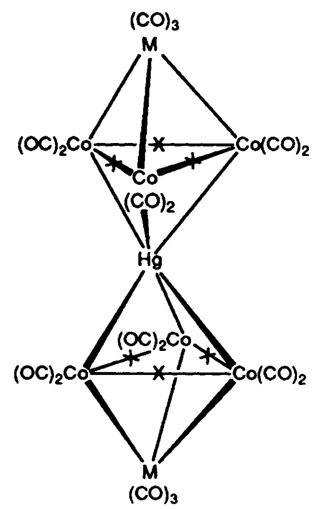
$$\underset{\mathbf{2b}}{2[RuCo_3(CO)_{12}\{\mu_3\text{-}HgBr\}]} \longrightarrow \underset{\mathbf{7b}}{[\mu_6\text{-}Hg\{RuCo_3(CO)_{12}\}_2]} + HgBr_2 \quad (5)$$

edge-bridging metal fragments have been observed in a number of complexes containing Hg–M metal–metal bonds.[37] The iron analogue **7a** was formed in the redistribution reaction (4). A rational synthesis for **7b** was then developed, involving the

[$MCo_3(CO)_{12}(HgBr)$] + K[$MCo_3(CO)_{12}$] ⟶

2a M = Fe

2b M = Ru

 (6)

7a M = Fe

7b M = Ru

reaction of **2b** with 1 equivalent of K[$RuCo_3(CO)_{12}$] [equation (6)]. Its detailed molecular structure was further established by X-ray diffraction (Fig. 4).[30] The iron analogue [μ_6-$Hg\{FeCo_3(\mu$-$CO)_3(CO)_9\}_2$] **7a** was similarly prepared by reaction (6). Both **7a** and **7b** have a very limited solubility in usual solvents, such as acetone, and tend to decompose upon solubilization. We found that **7a** and **7b** were obtained in higher yield by the direct reaction of 2 equivalents of **1a** or **1b** with $Hg(O_2CMe)_2$ in water, which instantaneously afforded a blue-green or green precipitate of the sandwich cluster, respectively [equation (7)].

$$2K[MCo_3(CO)_{12}] + Hg(O_2CMe)_2 \xrightarrow{H_2O} [\mu_6\text{-}Hg\{MCo_3(CO)_{12}\}_2] \quad (7)$$

7a M = Fe
7b M = Ru

Clusters **7a** and **7b** are best characterized by their UV/VIS spectra, which contain a band at 616 and 548 nm, respectively. Their IR spectra in the ν(CO) region, which show typical absorptions for terminal and bridging carbonyls, are closely related to those of **2a** and **2b**, reflecting the high symmetry of the molecule.

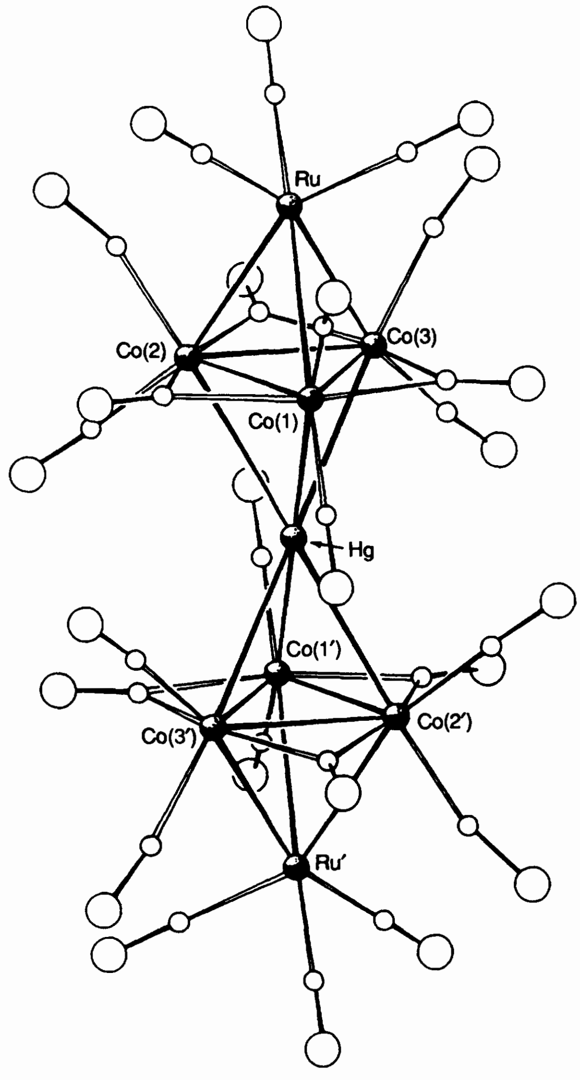


Fig. 4 View of the molecular structure of cluster **7b** [30]

The X-ray study has revealed that the complex is centrosymmetric with the Hg atom lying on the centre of symmetry.[30] The distorted-octahedral environment of the Hg atom is related to that found in [μ_6-Hg{Pt_3(2,6-$Me_2C_6H_3NC)_6$}$_2$][16a] or in [$Os_{18}HgH_x(C)_2(CO)_{42}$]$^{3-}$.[23a] Preliminary reactivity studies indicate that heating **7a** in toluene leads to metal–metal bond cleavage with formation, among other things, of metallic Hg and [$Co_4(CO)_9(\eta^6$-$C_6H_5Me)$].[38] The reaction of **7a** with [NEt_4]Cl in dichloromethane led to extrusion of Hg^{2+} since it afforded [NEt_4][$FeCo_3(CO)_{12}$] and $HgCl_2$.

We have also treated 2 equivalents of compound **1a** with Hg_2X_2 (X = Cl or I) in an attempt to synthesise a molecule in which the Hg_2 moiety would be sandwiched between two $FeCo_3(CO)_{12}$ cluster units, a situation reminiscent of that observed in [Hg_2{$Pt_3(\mu$-CO$)_3$(PPhPr$^i_2$)$_3$}$_2$].[17] However, no reaction occurred at ambient temperature. Heating of the reaction mixture led to fragmentation.

The reaction of **2a** with another tetrahedral cluster anion [$NiOs_3(\mu$-H$)_2(CO)_9$(cp)]$^-$ [39] also afforded **7a** together with known [$NiOs_3(\mu$-H$)_2(CO)_9$(cp)(μ-HgBr)] [39] [equation (8)].

[$FeCo_3(CO)_{12}(\mu_3$-HgBr)] + Na[$NiOs_3(\mu$-H$)_2(CO)_9$(cp)] ⟶
2a
[μ_6-Hg{$FeCo_3(CO)_{12}$}$_2$] +
7a
[$NiOs_3(\mu$-H$)_2(CO)_9$(cp)(μ-HgBr)] + NaBr + ··· (8)

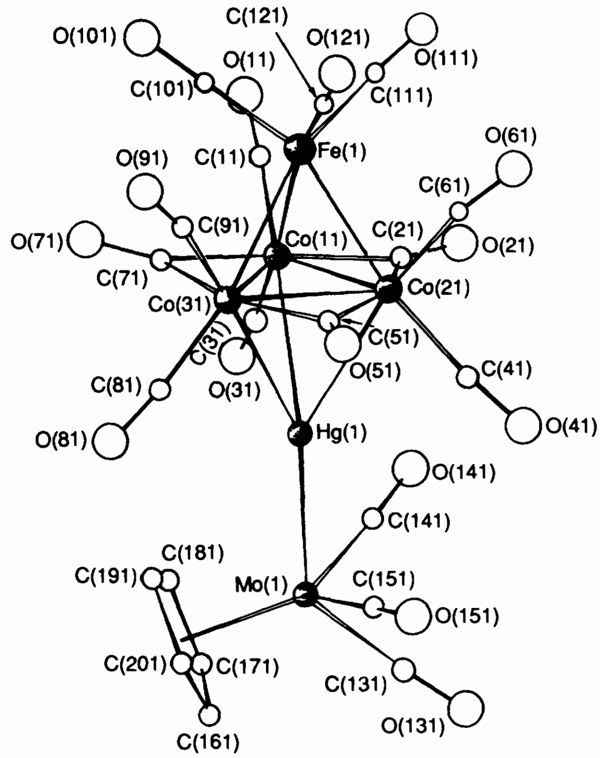


Fig. 5 View of the molecular structure of one molecule of compound **6a** showing the numbering scheme used

The desired cluster [$FeCo_3(CO)_{12}(\mu_5$-Hg)$NiOs_3(\mu$-H$)_2(CO)_9$-cp] was not observed. The first step of this reaction probably consists of a redistribution according to equation (5), followed by the reaction of [$NiOs_3(\mu$-H$)_2(CO)_9$(cp)]$^-$ with $HgBr_2$. However, the nonanuclear cluster [μ_6-Hg{$NiOs_3(\mu$-H$)_2(CO)_9$-(cp)}$_2$], which would be analogous to clusters **7**, was not observed. It should be noted that electrophilic metal reagents have previously been observed to react with [$NiOs_3(\mu$-H$)_2$-$(CO)_9$(cp)]$^-$ to form edge-bridged tetrahedral clusters, consistent with the negative charge of the precursor being mostly localized between two osmium centres. This contrasts with the situation in clusters **1** which have their negative charge distributed between the three cobalt centres.

(*d*) *Crystal Structure of* [$FeCo_3(\mu$-CO$)_3(CO)_9${μ_3-HgMo-$(CO)_3$(cp)}] **6a**.—Two crystallographically independent, but very similar, molecules are present in the asymmetric unit. A view of one is shown in Fig. 5 together with the numbering scheme used. Selected bond distances and angles in the two independent molecules are given in Table 1. The differences in the values found for the two molecules may be due either to their rather low accuracy (evidenced by the rather high estimated standard deviations) or to packing forces. The structure consists of a $FeCo_3$ tetrahedron with the Co_3 face capped by a HgMo(CO)$_3$(cp) fragment in a slightly asymmetric manner, reminiscent of the bonding of the HgMe fragment in [N($PPh_3)_2$][$Fe_4(CO)_{13}(\mu$-HgMe)].[12] Each Co–Co edge is bridged by an almost symmetric carbonyl ligand. Three terminal carbonyls are bonded to the Fe atom, and two to each Co atom. The Hg atom is in strongly distorted-tetrahedral arrangement involving the three Co atoms and the Mo atom. The $FeCo_3$Hg metal core forms a trigonal bipyramid with the Fe and Hg atoms at the apices, at respectively 2.130(5) [2.128(5)] Å above and 2.409(3) [2.395(2)] Å below the plane of the Co atoms (hereafter the values in square brackets refer to the second molecule). This arrangement is quite similar to that in the MCo_3M' cores (M = Fe or Ru; M′ = Cu, Ag or Au) where the M′(PPh_3) fragment triply bridges the Co_3 triangle

Table 1 Selected bond distances (Å) and angles (°) in $[FeCo_3(\mu\text{-}CO)_3(CO)_9\{\mu_3\text{-}HgMo(CO)_3(cp)\}]$ **6a** *

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Hg–Mo(1)	2.717(4)	2.719(4)	Fe–C(10)	1.78(3)	1.81(3)
Hg–Co(1)	2.872(5)	2.797(5)	Fe–C(11)	1.81(3)	1.86(3)
Hg–Co(2)	2.771(7)	2.820(7)	Fe–C(12)	1.81(4)	1.80(4)
Hg–Co(3)	2.807(6)	2.798(6)	Mo–C(13)	1.97(3)	2.05(3)
Fe–Co(1)	2.586(9)	2.575(9)	Mo–C(14)	1.94(3)	1.92(4)
Fe–Co(2)	2.581(7)	2.589(6)	Mo–C(15)	2.01(3)	2.07(3)
Fe–Co(3)	2.576(7)	2.577(7)	C(1)–O(1)	1.15(3)	1.21(3)
Co(1)–Co(2)	2.539(8)	2.525(8)	C(2)–O(2)	1.20(4)	1.18(4)
Co(1)–Co(3)	2.520(7)	2.533(7)	C(3)–O(3)	1.15(5)	1.14(5)
Co(2)–Co(3)	2.510(7)	2.524(6)	C(4)–O(4)	1.16(4)	1.20(3)
Co(1)–C(1)	1.77(3)	1.69(3)	C(5)–O(5)	1.15(4)	1.16(4)
Co(1)–C(2)	1.90(4)	1.99(3)	C(6)–O(6)	1.17(5)	1.14(4)
Co(1)–C(3)	1.78(4)	1.79(4)	C(7)–O(7)	1.20(4)	1.16(4)
Co(1)–C(7)	1.91(3)	1.90(3)	C(8)–O(8)	1.14(4)	1.12(4)
Co(2)–C(2)	1.97(3)	1.94(3)	C(9)–O(9)	1.18(4)	1.15(4)
Co(2)–C(4)	1.79(3)	1.74(3)	C(10)–O(10)	1.17(4)	1.13(4)
Co(2)–C(5)	1.94(3)	1.96(3)	C(11)–O(11)	1.10(4)	1.10(4)
Co(2)–C(6)	1.77(4)	1.77(3)	C(12)–O(12)	1.14(5)	1.14(5)
Co(3)–C(5)	1.93(3)	1.95(3)	C(13)–O(13)	1.16(4)	1.12(4)
Co(3)–C(7)	1.95(3)	2.02(3)	C(14)–O(14)	1.19(4)	1.22(5)
Co(3)–C(8)	1.76(3)	1.80(3)	C(15)–O(15)	1.13(4)	1.08(4)
Co(3)–C(9)	1.72(4)	1.77(3)			
Co(2)–Co(1)–Co(3)	59.5(2)	59.9(2)	Co(1)–C(2)–O(2)	142(3)	135(2)
Co(1)–Co(2)–Co(3)	59.9(2)	60.2(2)	Co(2)–C(2)–O(2)	136(3)	143(3)
Co(1)–Co(3)–Co(2)	60.6(2)	59.9(2)	Co(1)–C(2)–Co(2)	82(1)	80(1)
Co(1)–Fe–Co(2)	58.9(2)	58.6(2)	Co(1)–C(3)–O(3)	175(3)	169(3)
Co(1)–Fe–Co(3)	58.4(2)	58.9(2)	Co(2)–C(4)–O(4)	174(3)	177(3)
Co(2)–Fe–Co(3)	58.3(2)	58.5(2)	Co(2)–C(5)–O(5)	141(3)	139(2)
Co(1)–Hg–Co(2)	53.5(2)	53.4(2)	Co(3)–C(5)–O(5)	139(3)	141(2)
Co(1)–Hg–Co(3)	52.7(2)	53.8(2)	Co(2)–C(5)–Co(3)	81(1)	81(1)
Co(2)–Hg–Co(3)	53.5(2)	53.4(2)	Co(2)–C(6)–O(6)	170(3)	168(3)
Mo–Hg–Co(1)	139.0(2)	144.0(2)	Co(3)–C(7)–O(7)	136(2)	133(2)
Mo–Hg–Co(2)	149.0(2)	151.5(2)	Co(1)–C(7)–O(7)	142(2)	147(3)
Mo–Hg–Co(3)	155.9(2)	150.0(2)	Co(1)–C(7)–Co(3)	81(1)	80(1)
CE–Mo–Hg	109.8(9)	112.1(9)	Co(3)–C(8)–O(8)	172(3)	175(3)
CE–Mo–C(13)	118.2(14)	118.1(14)	Co(3)–C(9)–O(9)	169(3)	174(3)
CE–Mo–C(14)	127.9(16)	126.5(17)	Fe–C(10)–O(10)	179(3)	177(3)
CE–Mo–C(15)	124.4(13)	128.5(12)	Fe–C(11)–O(11)	177(3)	176(3)
Hg–Mo–C(14)	73.3(11)	71.7(12)	Fe–C(12)–O(12)	178(3)	175(3)
Hg–Mo–C(15)	75.1(10)	74.0(9)	Mo–C(13)–O(13)	175(3)	169(3)
C(13)–Mo–C(14)	76.9(14)	75.7(15)	Mo–C(14)–O(14)	178(3)	172(3)
C(13)–Mo–C(15)	78.8(14)	78.3(13)	Mo–C(15)–O(15)	177(3)	175(2)
Co(1)–C(1)–O(1)	174(3)	171(3)			

* CE is the centroid of the cyclopentadienyl ring C(16)–C(20).

through the M′ atom [31] and to the $RuCo_3Hg$ and $(RuCo_3)_2Hg$ cores found in **5b** (Fig. 3) [29] and in **7b** (Fig. 4).[30]

When considering the centroid of the cyclopentadienyl ring, CE, the carbonyl carbon atoms C(13), C(1′), C(1) and Hg, the co-ordination around Mo can be described as a four-legged piano stool, the angles between the Mo–CE vector and C(13), C(14), C(15) or Hg ranging from 109.8(9) [112.1(9)] to 127.9(16) [128.5(12)]°. These atoms are almost coplanar, the displacements out of the mean plane being −0.15(3) [−0.14(3)], 0.18(4) [0.19(4)], 0.12(3) [0.09(3)] and −0.001(3) [−0.001(3)] Å respectively, with the Mo atom out of the plane by −1.017(3) [−1.073(3)] Å. The angle ω between the Co-bound axial and equatorial CO ligands is almost identical in each case (see Table 2). The Fe–Co distances [range 2.575(9)–2.589(6) Å] should be compared with those found in *e.g.* $[FeCo_3H(CO)_{11}(PPh_2H)]$ [range 2.535(1)–2.561(1) Å],[36] $[FeCo_3H(CO)_9\{P(OMe)_3\}_3]$ [range 2.558(1)–2.562(1) Å][40] or $[FeCo_3(CO)_{12}\{\mu_3\text{-}Au\text{-}(PPh_3)\}]$ **4a** [range 2.515(9)–2.600(8) Å].[32a,41] The distance of the Fe cap to the Co_3 plane of 2.130(5) [2.128(5)] Å is slightly longer in **6a** than those in $[FeCo_3H(CO)_{11}(PPh_2H)]$ (2.097 [2.105] Å) [36] or in **4a** (2.103 Å).[41] The Hg atom is at a distance of 2.409(3) [2.395(2)] Å from the Co_3 plane, a value which is closer to that in **7b** [2.382(1) Å] than in **5b** [2.344(3) Å], while the Co–Co bond lengths are comparable in these clusters. The main structural features of **6a**, **5b** and **7b** are compared in Table 2. It is noteworthy that in the $FeCo_3Hg$ or $RuCo_3Hg$ cores the values of the Hg–Co distances spread over a rather large range (and also in the two independent molecules of **6a**), unlike the Fe–Co (or Ru–Co) and Co–Co distances, which are comparable. A comparison between **4a** and **4b** (Table 3) shows that, within the precision of the structural determinations, the Co–Co and Au–Co bond lengths are very similar in these isoelectronic clusters and that the capping fragment has no significant effect on the distance between the d^{10} ion and the Co_3 plane (2.293 and 2.296 Å, respectively). The longer distance observed in **6a** between Hg and the Co_3 plane cannot be assigned to the presence of a $Fe(CO)_3$ cap, in place of the $Ru(CO)_3$ cap in **5b** and **7b**. This lengthening must therefore have its origin in the nature of the substituent R at Hg: $Co(CO)_4$ in **5b** is more electronegative than $Mo(CO)_3(cp)$ in **6a** or $RuCo_3(CO)_{12}$ in **7b**, and the last two behave in a similar way. Rosenberg *et al.*[11c] have made similar observations in $[Os_3(\mu_3\text{-}\eta^2\text{-}C_2Bu^t)(CO)_9(\mu\text{-}HgR)]$ and found a shortening of the μ-Hg–Os bonds when replacing R = $Mo(CO)_3(cp)$ with $Co(CO)_4$. This was accompanied by a significant lengthening of the bridged Os–Os bond and it was also suggested to be due to the well known greater

Table 2 Comparison of the main structural features of compounds **6a**, **5b** and **7b**

	$FeCo_3HgMo$ **6a**[a]	$RuCo_3HgCo$ **5b**	$Hg(RuCo_3)_2$ **7b**
Co–Co distances (Å)	2.539(8) [2.525(8)]	2.509(6)	2.522(3)
	2.520(7) [2.533(7)]	2.519(7)	2.547(2)
	2.510(7) [2.524(6)]	2.499(7)	2.520(2)
Fe(Ru)–Co distances (Å)	2.586(9) [2.575(9)]	2.686(5)	2.687(3)
	2.581(7) [2.589(6)]	2.686(5)	2.681(3)
	2.576(7) [2.577(7)]	2.677(6)	2.689(4)
Hg–Co distances (Å)	2.872(5) [2.797(5)]	2.765(5)	2.816(2)
	2.771(7) [2.820(7)]	2.706(5)	2.791(3)
	2.807(6) [2.798(6)]	2.799(5)	2.777(2)
$d_{Fe(Ru)}$ from the Co_3 plane (Å)	2.130(5) [2.128(5)]	2.258(4)	2.254(3)
d_{Hg} from the Co_3 plane (Å)	2.409(3) [2.395(2)]	2.344(3)	2.382(1)
Cone angle,[b] θ/°	$\widehat{Fe}$ 68.7(2) [70.9(2)]	$\widehat{Ru}$ 65.4(2)	$\widehat{Ru}$ 65.9(1)
	$\widehat{Hg}$ 62.4(2) [65.9(2)]	$\widehat{Hg}$ 63.5(2)	$\widehat{Hg}$ 63.0(1)
Angle between carbonyls, ω/°	94(2) [92(2)]	95(2)	94.3(6)
	95(2) [97(1)]	96(2)	94.7(6)
	98(2) [94(1)]	93(2)	94.7(6)

[a] The values in square brackets refer to the other molecule in the asymmetric unit. [b] The cone angle at Fe(Ru) and Hg is related to the angles at the vertices. In the case of an irregular bipyramid we may define an averaged value for each vertex as $\theta = \frac{1}{3}\Sigma_i\theta_i$ where θ_i are the angles between the normal to the base and each edge.

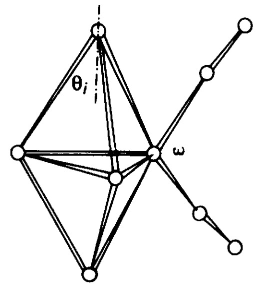


Table 3 Comparison between the main bond distances (Å) of compounds **4a** and **4b**

	$FeCo_3Au$ **4a**	$RuCo_3Au$ **4b**
Co–Co	2.537(8)	2.539(6)
	2.518(3)	2.497(5)
	2.506(8)	2.543(6)
Fe(Ru)–Co	2.561(3)	2.679(4)
	2.600(8)	2.664(4)
	2.515(9)	2.687(5)
Au–Co	2.720(5)	2.745(4)
	2.709(2)	2.679(4)
	2.716(7)	2.704(4)
$d_{Fe(Ru)}$ to the Co_3 plane	2.103	2.240(3)
d_{Au} to the Co_3 plane	2.293	2.296(2)

electronegativity of the $Co(CO)_4^-$ moiety compared with $Mo(CO)_3(cp)^-$. The pairs **4a**, **6a** and **4b**, **5b** allow further interesting comparisons. The Au atom is always closer to the Co_3 face than is Hg, by *ca.* 0.1 and 0.05 Å, respectively. This parallels the difference in metal atom radii of Au (1.442 Å) and Hg (1.503 Å),[42] although in closely related molecules the gold–element and mercury-element distances are almost identical, *e.g.* $AuCl_2^-$ [2.257(4) Å][43] and $HgCl_2$ (2.25 Å),[44] $Au[Co(CO)_4]_2^-$ (2.509 Å) and $Hg[Co(CO)_4]_2$ (2.500 and 2.498 Å).[45] The Hg–Mo distance in **6a** of 2.717(4) [2.719(4)] Å is intermediate between those found in $[Ru_3(\mu_3\text{-}\eta^2\text{-}C_2Bu^t)(CO)_9\{\mu\text{-}HgMo(CO)_3(cp)\}]$ [2.743(2) Å][7b] or in $[Hg\{Mo(CO)_3(cp)\}_2]$ [2.746(2) Å][46] and in $[Mo(CO)_3(cp)(HgCl)]$ [2.673(3) Å].[2e] An almost identical value [2.718(3) Å] has been recently reported for the Hg–Mo bond in an edge-bridged $Os_3(\mu\text{-}HgMo)$ cluster.[11c] In $[\{MoHgMo(CO)_3(cp)\}_4]$,[19] which has a metallocubane structure, the Hg atom is tetrahedrally co-ordinated to four Mo atoms, and the Hg–Mo distance of the $HgMo(CO)_3(cp)$ fragment of 2.692(3) Å is similar with that found in **6a** in which the Hg atom is also tetrahedrally co-ordinated.

The fragment $HgMo(CO)_3(cp)$ in compound **6a** behaves similarly to $HgCo(CO)_4$ in **5b** and both are isolobal with the $M'(PPh_3)$ (M′ = Cu, Ag or Au) groups. In this family of clusters the Cu, Ag, Au or Hg atoms may be considered as sp hybridized, one lobe pointing towards the centre of the Co_3 triangle. A similar bonding of the Hg atom can also be envisaged in **7b** where the mercury is placed in a sandwich between the staggered Co_3 planes, at 2.382(1) Å from each plane (the Hg atom lying on an inversion centre). Comparison within a family of the structurally related clusters allows a qualitative estimate of the influence of their constitutive fragments on the bonding.

Experimental

Schlenk-tube techniques were used throughout the experiments and all reactions were performed under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. The salts $Na[Co(CO)_4]$ and $Na[Mo(CO)_3(cp)]\cdot 2dme$ (dme = 1,2-dimethoxyethane)[47] and the clusters $K[MCo_3(CO)_{12}]$ (M = Fe **1a**[48] or Ru **1b**[32b]) were prepared as reported. Infrared spectra were recorded in the region 4000–400 cm^{-1} on a Perkin-Elmer 398 spectrophotometer. ^1H NMR spectra on a FT-Bruker SY 200 spectrometer ($CDCl_3$ solution), UV spectra on a Beckman Acta CIII spectrophotometer (CH_2Cl_2 solutions) and mass spectra on a Thompson THN 208 spectrometer.

Syntheses.—$[MCo_3(CO)_{12}(HgBr)]$ (M = Fe **2a** *or* Ru **2b**). A diethyl ether solution (20 cm^3) of compound **1a** or **1b** (0.51 mmol) was added to a suspension of $HgBr_2$ (0.185 g, 0.51 mmol) in diethyl ether (10 cm^3). The solution immediately became violet and a black precipitate was formed. After being stirred for 0.5 h at room temperature the solution was filtered. The black solid residue was washed with hot toluene and crystallized from dichloromethane, affording **2a** or **2b**, respectively. Compound

Table 4 Fractional coordinates ($\times 10^4$) with estimated standard deviations (e.s.d.s) in parentheses for the non-hydrogen atoms of compound **6a**

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Hg(1)	8 829(1)	4 816(2)	−1 092(1)	Hg(2)	3 820(1)	160(2)	2 079(1)
Mo(1)	8 778(1)	3 800(3)	−97(1)	Mo(2)	3 832(1)	252(3)	3 159(1)
Co(11)	8 151(2)	5 183(6)	−2 305(2)	Co(12)	3 188(2)	582(5)	893(2)
Co(21)	9 079(2)	4 196(6)	−2 022(2)	Co(22)	4 141(2)	1 318(5)	1 233(2)
Co(31)	8 916(2)	7 061(6)	−1 869(2)	Co(32)	3 879(2)	−1 575(5)	1 164(2)
Fe(1)	8 652(2)	6 038(6)	−2 914(2)	Fe(2)	3 647(2)	26(6)	219(2)
O(11)	7 255(9)	5 263(28)	−3 435(11)	O(12)	2 343(9)	1 133(27)	−238(10)
O(21)	8 247(9)	1 786(30)	−2 514(11)	O(22)	3 394(8)	4 021(26)	915(9)
O(31)	7 451(8)	4 356(25)	−1 759(10)	O(32)	2 471(8)	1 741(27)	1 373(10)
O(41)	9 687(9)	1 726(30)	−1 189(11)	O(42)	4 844(8)	2 878(25)	2 319(9)
O(51)	10 006(8)	6 215(26)	−1 495(9)	O(52)	4 996(8)	−980(23)	1 502(9)
O(61)	9 519(9)	3 031(28)	−2 813(11)	O(62)	4 662(8)	2 829(26)	595(9)
O(71)	7 879(8)	8 575(25)	−2 296(9)	O(72)	2 796(7)	−2 710(24)	759(9)
O(81)	9 162(9)	8 973(30)	−838(11)	O(82)	4 112(7)	−3 987(24)	2 070(8)
O(91)	9 201(9)	9 666(28)	−2 426(10)	O(92)	3 997(8)	−3 964(27)	395(10)
O(101)	7 955(9)	8 608(32)	−3 602(11)	O(102)	2 908(8)	−2 233(26)	−601(10)
O(111)	8 251(9)	3 637(30)	−3 824(11)	O(112)	3 328(8)	2 879(28)	−535(10)
O(121)	9 492(9)	6 941(28)	−3 268(10)	O(122)	4 499(8)	−908(25)	−101(9)
O(131)	9 059(12)	484(36)	523(13)	O(132)	4 328(10)	2 727(32)	4 180(12)
O(141)	8 132(9)	1 395(30)	−1 083(11)	O(142)	3 331(9)	3 493(32)	2 571(11)
O(151)	9 959(10)	3 354(32)	143(11)	O(152)	5 019(8)	391(22)	3 384(9)
C(11)	7 625(11)	5 212(35)	−3 005(13)	C(12)	2 725(12)	907(36)	215(14)
C(21)	8 397(13)	3 103(44)	−2 345(16)	C(22)	3 537(10)	2 696(35)	1 034(12)
C(31)	7 744(12)	4 648(36)	−1 952(13)	C(32)	2 753(11)	1 156(36)	1 213(13)
C(41)	9 440(11)	2 734(37)	−1 493(14)	C(42)	4 553(11)	2 218(35)	1 883(13)
C(51)	9 564(12)	5 956(37)	−1 706(14)	C(52)	4 566(11)	−522(32)	1 385(12)
C(61)	9 310(12)	3 573(40)	−2 540(15)	C(62)	4 431(10)	2 139(34)	795(12)
C(71)	8 162(10)	7 430(35)	−2 185(12)	C(72)	3 091(11)	−1 662(35)	876(12)
C(81)	9 058(12)	8 131(39)	−1 223(14)	C(82)	4 012(11)	−3 023(39)	1 734(14)
C(91)	9 067(11)	8 523(38)	−2 251(13)	C(92)	3 936(10)	−2 968(35)	671(13)
C(101)	8 229(13)	7 588(43)	−3 326(15)	C(102)	3 192(12)	−1 341(38)	−297(14)
C(111)	8 395(13)	4 572(40)	−3 489(15)	C(112)	3 462(11)	1 827(38)	−254(14)
C(121)	9 173(12)	6 579(39)	−3 123(14)	C(122)	4 183(12)	−549(34)	46(13)
C(131)	8 950(12)	1 741(40)	316(14)	C(132)	4 117(12)	1 969(39)	3 789(15)
C(141)	8 384(14)	2 285(43)	−700(17)	C(142)	3 523(14)	2 195(47)	2 761(17)
C(151)	9 535(12)	3 557(37)	51(14)	C(152)	4 607(11)	390(33)	3 284(12)
C(161)	8 746(12)	4 996(41)	723(14)	C(162)	3 675(13)	−1 256(42)	3 831(15)
C(171)	8 225(12)	4 652(38)	322(14)	C(172)	3 198(12)	−745(36)	3 441(14)
C(181)	8 082(12)	5 488(36)	−195(14)	C(182)	3 043(10)	−1 293(35)	2 854(12)
C(191)	8 510(11)	6 487(36)	−124(13)	C(192)	3 475(11)	−2 368(36)	2 885(13)
C(201)	8 934(12)	6 116(39)	447(14)	C(202)	3 848(13)	−2 412(44)	3 510(16)

2a (0.260 g, 58%) (Found: C, 17.0. Calc. for $C_{12}BrCo_3FeHgO_{12}$: C, 16.95%): IR (CH_2Cl_2) ν(CO)/cm^{-1} 2090w, 2048s, 2020m and 1883m; UV (CH_2Cl_2) λ_{max}/nm 340, 395(sh) and 564. Compound **2b** (0.250 g, 54%) (Found: C, 15.8. Calc. for $C_{12}BrCo_3HgO_{12}Ru$: C, 16.10%): IR (CH_2Cl_2) ν(CO)/cm^{-1} 2101m, 2058(sh), 2045s and 1884m; UV (CH_2Cl_2) λ_{max}/nm 325, 355(sh), 390(sh) and 498.

The filtered solution was evaporated under reduced pressure. Extraction of the solid residue with toluene gave compound **5a** or **5b**, respectively, in very low yield. When the reaction time was increased **2** was obtained in lower yield owing to decomposition favouring formation of **5**.

[$MCo_3(CO)_{12}\{\mu_3$-$HgCo(CO)_4\}$] (M = Fe **5a** *or* Ru **5b**). A suspension of Na[$Co(CO)_4$] (0.13 mmol) in dichloromethane (10 cm^3) was added to a suspension of compound **2a** or **2b** (0.13 mmol) in dichloromethane (15 cm^3). After being stirred for 0.25 h at room temperature the violet solution was filtered and evaporated under reduced pressure. Extraction of the solid residue with hexane gave compound **5a** or **5b**, respectively. In the case of the reaction with **2b** the filtered hexane solution was placed at −15 °C, and gave after 2 d black-violet needles of form A of **5b** (yield 56%) and after 4 d dark red microcrystals of form B of **5b** (yield 12%). Compound **5a** (0.060 g, 49%) (Found: C, 20.1. Calc. for $C_{16}Co_4FeHgO_{16}$: C, 20.45%); IR (hexane) ν(CO)/cm^{-1} 2075s, 2041vs, 2006m and 1883m; UV (CH_2Cl_2) λ_{max}/nm 326, 400(sh) and 573. Compound **5b** (0.071 g, 56%) (Found: C, 19.0. Calc. for $C_{16}Co_4HgO_{16}Ru$: C, 19.5%): IR (hexane) ν(CO)/cm^{-1} 2081s, 2040vs, 2002m and 1884s; UV (CH_2Cl_2) λ_{max}/nm 325, 395(sh) and 506; *m/z* 988 (M^+ using ^{102}Ru and ^{202}Hg).

[$MCo_3(CO)_{12}\{\mu_3$-$HgMo(CO)_3(cp)\}$] (M = Fe **6a** *or* Ru **6b**). A suspension of Na[$Mo(CO)_3(cp)$]·2dme (0.089 g, 0.20 mmol) in dichloromethane (10 cm^3) was added to a suspension of compound **2a** or **2b** (0.20 mmol) in dichloromethane (20 cm^3). After being stirred for 0.25 h at room temperature the deep red solution was filtered and evaporated under reduced pressure. Extraction of the solid residue with hot hexane gave **6a** or **6b** together with a small amount of yellow crystals of Hg[$Mo(CO)_3(cp)$]$_2$. Compound **6a** (0.046 g, 22%) (Found: C, 23.2; H, 0.7. Calc. for $C_{20}H_5Co_3FeHgMoO_{15}$: C, 23.70; H, 0.50%): IR (hexane) ν(CO)/cm^{-1} 2079w, 2038s, 2005s, 1940w, 1919s, 1879w and 1872m; UV (CH_2Cl_2) λ_{max}/nm 336, 400(sh) and 572; *m/z* 1015 (M^+ using ^{56}Fe, ^{202}Hg and ^{96}Mo). Compound **6b** (0.089 g, 42%) (Found: C, 22.4; H, 0.5. Calc. for $C_{20}H_5Co_3HgMoO_{15}Ru$: C, 22.65; H, 0.50%): IR (hexane) ν(CO)/cm^{-1} 2092m, 2045s, 2032s, 2017w, 2004m, 1939m, 1919m, 1878m and 1871m; UV (CH_2Cl_2) λ_{max}/nm 333, 390(sh) and 505; ^{1}H NMR ($CDCl_3$) δ 5.27 (C_5H_5); *m/z* 1060 (M^+ using ^{200}Hg, ^{96}Mo and ^{102}Ru).

[$Hg\{FeCo_3(CO)_{12}\}_2$] **7a**. A solution of $Hg(O_2CMe)_2$ (0.146 g, 0.45 mmol) in water (20 cm^3) was added to a solution of [$Co(Me_2CO)_6$][$FeCo_3(CO)_{12}$]$_2$ (0.700 g, 0.45 mmol) dissolved in water (50 cm^3). A deep blue solid precipitated immediately. After stirring for 0.25 h at room temperature, complex **7a** was isolated by filtration as an almost insoluble deep blue powder, which was first washed with water (2 × 20 cm^3), then with diethyl ether (20 cm^3) and dried under vacuum (0.420 g, 69%) (Found: C, 21.1. Calc. for $C_{24}Co_6Fe_2HgO_{24}$: C, 21.55%); IR (KBr) ν(CO)/cm^{-1} 2071s, 2025vs, 1980(sh), 1920w and 1870s; UV (CH_2Cl_2) λ_{max}/nm 330 and 616.

[Hg{$RuCo_3(CO)_{12}$}$_2$] **7b**. A solution of Na[$RuCo_3(CO)_{12}$]·thf (0.039 g, 0.06 mmol) (thf = tetrahydrofuran) in dichloromethane (10 cm^3) was added to a suspension of compound **2b** (0.055 g, 0.06 mmol) in dichloromethane (5 cm^3). After stirring for 0.25 h at room temperature, complex **7b** was isolated by filtration as almost insoluble violet microcrystals, which were washed with diethyl ether (10 cm^3) and dried under vacuum (0.042 g, 47%) (Found: C, 19.8. Calc. for $C_{24}Co_6HgO_{24}Ru_2$: C, 20.20%); IR (KBr) ν(CO)/cm^{-1} 2083s, 2033vs, 1972m, 1912w and 1879s; UV [CH_2Cl_2–thf (10:1)] λ_{max}/nm 326, 365(sh) and 548.

X-Ray Data Collection, Structure Solution and Refinement of Compound **6a**.—The crystals of compound **6a** were very small and a dark violet crystal of approximate dimensions 0.04 × 0.10 × 0.35 mm was used for the X-ray analysis. Unit-cell parameters were obtained by least-squares refinement of the θ values of 29 carefully centred reflections (θ 20–32°).

Crystal data. $C_{20}H_5Co_3FeHgMoO_{15}$, M = 1014.43, monoclinic, space group $P2_1/c$, a = 28.123(9), b = 8.400(5), c = 25.290(8) Å, β = 114.72(2)°, U = 5 427(4) $Å^3$, Z = 8, D_c = 2.483 g cm^{-3}, $F(000)$ = 3792, μ(Cu-Kα) = 340.41 cm^{-1}.

Data were collected at room temperature on a Siemens AED diffractometer using nickel-filtered radiation (λ = 1.541 78 Å) and the θ–2θ scan technique, the individual profiles having been analysed according to Lehmann and Larsen.[49] All the reflections with θ in the range 3–60° were measured. Of 7882 independent reflections, 3016 having $I > 2\sigma(I)$ were considered observed and used in the analysis. The intensity of one standard reflection was measured after 50 reflections as a general check on crystal and instrument stability. No significant change in the measured intensities was observed during the data collection. A semiempirical correction for the absorption effects was applied[50] using the program ABSORB[51] (maximum and minimum correction factors 1.531 and 0.755).

The structure was solved by direct and Fourier methods and refined by block-matrix least squares first with isotropic and then with anisotropic thermal parameters for the Hg, Mo, Fe and Co atoms only. No attempt was made to locate the hydrogen atoms of the cyclopentadienyl rings. The SHELX package of crystallographic programs was used for the computations.[52] The weighting scheme used in the last cycles of refinement was $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ where K and g were 0.696 and 0.005 at convergence. Final R and R' values were 0.0596 and 0.0713. The analytical scattering factors, corrected for the real and imaginary parts of the anomalous dispersions, were taken from ref. 53. The final atomic coordinates for the non-hydrogen atoms are given in Table 4.

All calculations were performed on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico dell'Italia Nord-Orientale, Bologna, and on the GOULD-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles for compound **6a**. The crystallographic material pertaining to the structures of **5b**[29] and **7a**[30] is available from the same source or from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, Germany.

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