Synthesis of Mercury-linked Ruthenium Clusters: The X-Ray Structure of the New Cluster Dianion $[\{Ru_6C(CO)_{16}\}_2Hg]^{2-}$ and the Cluster $[\{Ru_5C(CO)_{14}(\mu\text{-}Cl)\}_2Hg_2Cl_2]$†

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Reaction of the hexaruthenium dianion $[Ru_6C(CO)_{16}]^{2-}$ **1** as its $[N(PPh_3)_2]^+$ salt in CH_2Cl_2 with an equimolar quantity of $Hg(CF_3CO_2)_2$ leads to an uncharacterised black polymer of probable formula $[Ru_6C(CO)_{16}Hg]_n$. However, treatment of 2 equivalents of **1** in CH_2Cl_2 with 1 equivalent of $Hg(CF_3CO_2)_2$ or 2 equivalents of $HgCl_2$ in the same solvent has yielded the new dodecaruthenium dianion $[\{Ru_6C(CO)_{16}\}_2Hg]^{2-}$ **2**. This red dianion has been characterised as its $[N(PPh_3)_2]^+$ salt by single-crystal X-ray diffraction analysis and shown to contain two octahedral Ru_6C units linked through a mercury atom. It is probably produced from the uncharacterised intermediate monoanion $[Ru_6C(CO)_{16}(HgX)]^-$ **3a** (X = Cl or CF_3CO_2). In agreement with this suggestion, treatment of **1** with the compound $Hg(CF_3)(CF_3CO_2)$ yields the monoanion $[Ru_6C(CO)_{16}(HgCF_3)]^-$ **3b** which has been fully characterised on the basis of its spectroscopic data. We have also observed that the neutral pentaruthenium cluster $[Ru_5C(CO)_{15}]$ **4** reacts with $HgCl_2$ in CH_2Cl_2 to produce the dark red decaruthenium species $[\{Ru_5C(CO)_{14}(\mu\text{-}Cl)\}_2Hg_2Cl_2]$ **5**. On the basis of single-crystal X-ray diffraction analysis this cluster has been shown to consist of two distorted bridged-butterfly $Ru_5C(CO)_{14}(\mu\text{-}Cl)$ units linked by a $Hg_2(\mu\text{-}Cl)_2$ unit. In solution, it appears that the dimeric cluster **5** undergoes dissociation to a monomer believed to be $[Ru_5C(CO)_{14}(\mu\text{-}Cl)(HgCl)]$ **6**. The mass spectrum of cluster **5** is not totally consistent with this unit and in the fast atom bombardment mass spectrum, the ion corresponding to $[Ru_5C(CO)_{13}(\mu\text{-}Cl)(HgCl)]$ **7** is observed.

Condensation reactions between anionic carbonyl clusters and mercury(II) salts have been shown to be an important route for the formation of high-nuclearity clusters. A number of clusters with a core geometry M_nHg_m have been synthesised by the reactions of M_n anions with HgX_2 or $Hg(CF_3CO_2)_2$.[1] A variety of metal-core geometries have been found for these clusters, including those in which Hg atoms are directly bound to one another to form Hg_2 or Hg_3 units.[2] We now report the new anionic compound $[\{Ru_6C(CO)_{16}\}_2Hg]^{2-}$ in which two Ru_6C units are linked through a Hg atom and $[\{Ru_5C(CO)_{14}(\mu\text{-}Cl)\}_2Hg_2Cl_2]$ in which two Ru_5C units are linked through an $Hg_2(\mu\text{-}Cl)_2$ unit. In solution it would appear that the latter dimeric cluster undergoes dissociation to the monomer $[Ru_5C(CO)_{14}(\mu\text{-}Cl)(HgCl)]$.

Results and Discussion

The reaction of the dianion $[Ru_6C(CO)_{16}]^{2-}$ **1** with mercury salts depends on the nature of the mercury salt, $HgCl_2$, $Hg(CF_3CO_2)_2$, or $Hg(CF_3)(CF_3CO_2)$, and on the stoichiometry of the reactants. When the reaction of **1** was carried out with $Hg(CF_3CO_2)_2$ in the ratio 1:1 a black insoluble polymer, which could not be fully characterised, was produced. There is good reason to suppose that this polymeric compound has the formula $[Ru_6C(CO)_{16}Hg]_n$. Certainly the analytical data are in moderate agreement and in the IR spectrum (CsI) three bands are observed at 2034 (sh), 2019s and 1836 cm^{-1} similar to what is observed for other clusters containing the $Ru_6C(CO)_{16}$ unit.[3] In contrast, when 1 mol of the dianion $[Ru_6C(CO)_{16}]^{2-}$ **1** as its $[N(PPh_3)_2]^+$ salt was allowed to react with 1 mol of $HgCl_2$ or 0.5 mol of $Hg(CF_3CO_2)_2$ in CH_2Cl_2 for approximately 15 min the new dodecaruthenium dianion $[\{Ru_6C(CO)_{16}\}_2Hg]^{2-}$ **2** was produced. After crystallisation from CH_2Cl_2–hexane this red dianion was characterised as its $[N(PPh_3)_2]^+$ salt on the basis of its IR spectrum ν_{CO} 2048m and 2021vs cm^{-1} and fast-atom bombardment (FAB) mass spectrum which gave a parent molecular-ion peak. Dark red crystals good enough for single-crystal X-ray diffraction analysis were grown from CH_2Cl_2–hexane.

The molecular structure of compound **2** is shown in Fig. 1 while some selected bond lengths and bond angles are presented in Table 1. The bimetallic cluster comprises of two distorted $Ru_6C(CO)_{16}$ octahedra linked by two edge-related ruthenium atoms to a central mercury atom. Each of these two octahedra contains an interstitial carbon atom and is clearly related to the parent hexaruthenium carbido-cluster $[Ru_6C(CO)_{16}]^{2-}$. Of the sixteen carbonyl groups about each Ru_6 unit twelve are terminally bonded and four form asymmetric bridges in a configuration similar to that observed in the $[AsPh_4]^+$ salt of the parent dianion $[Ru_6C(CO)_{16}]^{2-}$.[3] In the central Ru_4Hg section of the molecule the two Ru(1)–Hg and Ru(2)–Hg bond lengths of 2.839(2) and 2.826(2) Å are similar whereas the two other bond lengths Ru(7)–Hg and Ru(8)–Hg of 2.902(1) and 2.787(2) Å are substantially different. These same four ruthenium atoms Ru(1), Ru(2), Ru(7) and Ru(8) form a distorted-tetrahedral arrangement around the central Hg atom as has been observed previously in the linked cluster $[\{Ru_3(CO)_9(C_2Bu^t)\}_2Hg]$.[1a] The Ru–Ru bonds bridged by the Hg atom are longer than any other Ru–Ru bonds within the cluster but are similar to that 3.10(2) Å found in the related thallium-bridged mixed-metal cluster $[\{Ru_6C(CO)_{16}\}_2Tl][AsPh_4]$[4] and that of 3.072(11) Å in the copper-bridged derivative $[\{Ru_6C(CO)_{16}\}Cu(MeCN)_2]$.[5] The remaining Ru–Ru distances (mean 2.87 Å) and the Ru–C (carbide) distances (mean 2.05 Å) do not differ significantly from the values of 2.89 and 2.05 Å, respectively, found in the parent dianion.[3]

The ^1H NMR spectrum of compound **2** shows no resonances

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

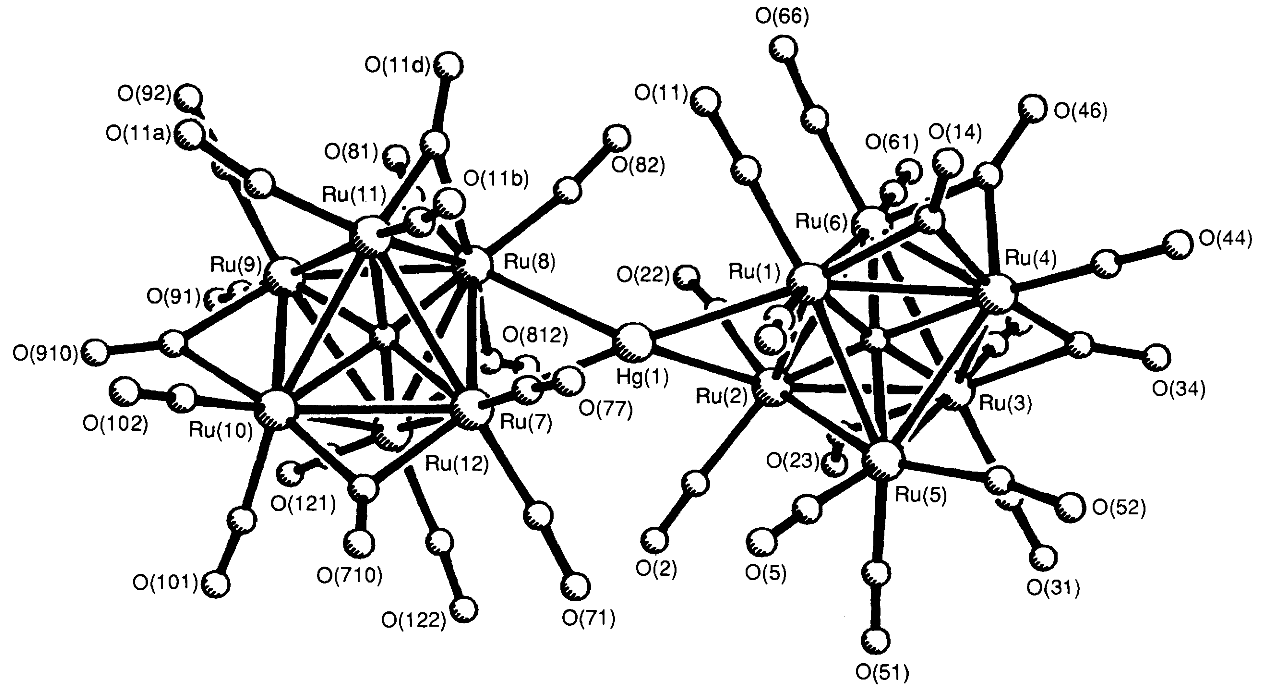

Fig. 1 The molecular structure of $[N(PPh_3)_2]_2[\{Ru_6C(CO)_{16}\}_2Hg]$ **2**

Table 1 Selected bond lengths (Å) and angles (°) for $[N(PPh_3)_2]_2[\{Ru_6C(CO)_{16}\}_2Hg]$ **2**

Hg–Ru(1)	2.839(2)	Hg–Ru(2)	2.826(2)
Hg–Ru(7)	2.787(2)	Hg–Ru(8)	2.902(1)
Ru(1)–Ru(2)	3.138(2)	Ru(1)–Ru(4)	2.809(2)
Ru(1)–Ru(5)	2.883(2)	Ru(1)–Ru(6)	2.909(2)
Ru(2)–Ru(3)	2.823(2)	Ru(2)–Ru(5)	2.861(1)
Ru(2)–Ru(6)	2.947(2)	Ru(3)–Ru(4)	2.804(2)
Ru(3)–Ru(5)	2.867(2)	Ru(3)–Ru(6)	2.909(2)
Ru(4)–Ru(5)	2.975(2)	Ru(4)–Ru(6)	2.814(2)
Ru(7)–Ru(8)	3.114(2)	Ru(7)–Ru(10)	2.818(2)
Ru(7)–Ru(11)	2.893(2)	Ru(7)–Ru(12)	2.890(2)
Ru(8)–Ru(9)	2.838(2)	Ru(8)–Ru(11)	2.892(2)
Ru(8)–Ru(12)	2.862(2)	Ru(9)–Ru(10)	2.814(2)
Ru(9)–Ru(11)	2.868(2)	Ru(9)–Ru(12)	2.896(2)
Ru(10)–Ru(12)	2.871(2)	Ru(1)–C(1)	2.036(13)
Ru(2)–C(1)	2.029(14)	Ru(3)–C(1)	2.054(13)
Ru(4)–C(1)	2.079(14)	Ru(5)–C(1)	2.069(14)
Ru(6)–C(1)	2.027(14)	Ru(7)–C(2)	2.052(10)
Ru(8)–C(2)	2.002(17)	Ru(9)–C(2)	2.059(10)
Ru(10)–C(2)	2.092(17)	Ru(11)–C(2)	2.032(14)
Ru(12)–C(2)	2.027(14)	Ru(10)–Ru(11)	2.901(3)
Ru(1)–Hg–Ru(2)	67.3(1)	Ru(1)–Hg–Ru(7)	134.1(1)
Ru(2)–Hg–Ru(7)	143.4(1)	Ru(1)–Hg–Ru(8)	138.2(1)
Ru(2)–Hg–Ru(8)	121.3(1)	Ru(7)–Hg–Ru(8)	66.3(1)
Ru(1)–C(1)–Ru(2)	101.0(6)	Ru(1)–C(1)–Ru(3)	171.0(7)
Ru(2)–C(1)–Ru(3)	87.5(5)	Ru(3)–C(1)–Ru(4)	85.4(8)
Ru(1)–C(1)–Ru(5)	89.2(6)	Ru(1)–C(1)–Ru(4)	86.1(5)
Ru(2)–C(1)–Ru(4)	172.9(7)	Ru(2)–C(1)–Ru(5)	88.5(6)
Ru(3)–C(1)–Ru(5)	88.1(4)	Ru(4)–C(1)–Ru(5)	91.6(4)
Ru(1)–C(1)–Ru(6)	91.5(5)	Ru(2)–C(1)–Ru(6)	93.2(4)
Ru(3)–C(1)–Ru(6)	90.9(6)	Ru(4)–C(1)–Ru(6)	86.5(6)
Ru(5)–C(1)–Ru(6)	178.0(7)	Ru(7)–C(2)–Ru(8)	100.3(6)
Ru(7)–C(2)–Ru(9)	171.0(9)	Ru(8)–C(2)–Ru(9)	88.7(5)
Ru(7)–C(2)–Ru(10)	85.7(5)	Ru(8)–C(2)–Ru(10)	173.9(5)
Ru(9)–C(2)–Ru(10)	85.4(5)	Ru(7)–C(2)–Ru(11)	90.2(5)
Ru(8)–C(2)–Ru(11)	91.6(7)	Ru(9)–C(2)–Ru(11)	89.0(4)
Ru(10)–C(2)–Ru(11)	89.4(6)	Ru(7)–C(2)–Ru(12)	90.2(5)
Ru(8)–C(2)–Ru(12)	90.5(6)	Ru(9)–C(2)–Ru(12)	90.2(5)
Ru(10)–C(2)–Ru(12)	88.4(6)	Ru(11)–C(2)–Ru(12)	177.7(9)

other than those due to the $[N(PPh_3)_2]^+$ counter ion. The ^{13}C NMR spectrum at 290 K indicates that there is a total carbonyl fluxionality on the NMR time scale since only a single, sharp resonance is observed at δ 209.78 in the terminal carbonyl region of the spectrum. On lowering the temperature to 200 K the peak only broadens out very slightly. The carbido-resonance is observed at δ 413.86. The solid-state infrared spectrum of the $[NEt_4]^+$ salt of **2** was recorded in CsI at 113 K in the region 600–800 cm^{-1}. The strong bands at 756, 743, 726 and 685 cm^{-1} may be assigned to a carbide ligand inside an octahedral Ru_6 cluster.[6]

Treatment of compound **1** with an equimolar quantity of $Hg(CF_3)(CF_3CO_2)$ in CH_2Cl_2 yields after separation by TLC the monoanion $[Ru_6C(CO)_{16}(HgCF_3)]^-$ **3b** which has been characterised on the basis of its spectroscopic data. The molecular weight was established from negative-ion mass spectroscopy (FAB) and the IR spectrum for a sample in CH_2Cl_2 showed four ν_{CO} bands at 2066w, 2043 (sh), 2018vs and 1829w(br) cm^{-1}. The formation of this cluster leads us to speculate that the reaction of **1** with HgX_2 proceeds *via* the intermediacy of the monoanion $[Ru_6C(CO)_{16}(HgX)]^-$ **3a** (X = Cl or CF_3CO_2). When the above reaction was carried out with **1** and $Hg(CF_3CO_2)_2$ in the ratio 1:1 a black insoluble polymer, which could not be fully characterised, was produced. The material was also produced on reaction of the new dodecaruthenium dianion $[\{Ru_6C(CO)_{16}\}_2Hg]^{2-}$ **2** with an additional 0.5 mol of $Hg(CF_3CO_2)_2$. This latter observation leads us to conclude that the polymeric material probably corresponds to an infinite structure of general formula $[Ru_6C(CO)_{16}Hg]_n$.

The reaction of $[Ru_5C(CO)_{15}]$ **4** with $HgCl_2$ in CH_2Cl_2 yields a dark red crystalline solid which exhibits IR stretching frequencies at 2113m, 2085m, 2071s, 2041m and 2021m cm^{-1}. In order to establish the precise nature of this compound a single-crystal X-ray diffraction analysis was undertaken. On the basis of this analysis the cluster has been formulated as $[\{Ru_5C(CO)_{14}(\mu\text{-}Cl)\}_2Hg_2Cl_2]$ **5**. In the crystal structure the asymmetric unit contains two independent, but structurally similar, half molecules. Each of these units lies close to a centre of symmetry and the dimeric structure is generated by this symmetry operation. The molecular structure of one molecule of **5** is shown in Fig. 2, and selected bond parameters from both molecules are listed in Table 2. Two pentanuclear Ru_5C units are linked through a Hg_2Cl_2 bridge in a manner similar to that observed in $[\{Ru_3(CO)_9(C_6H_9)(HgBr)\}_2]$.[7] The two chloride

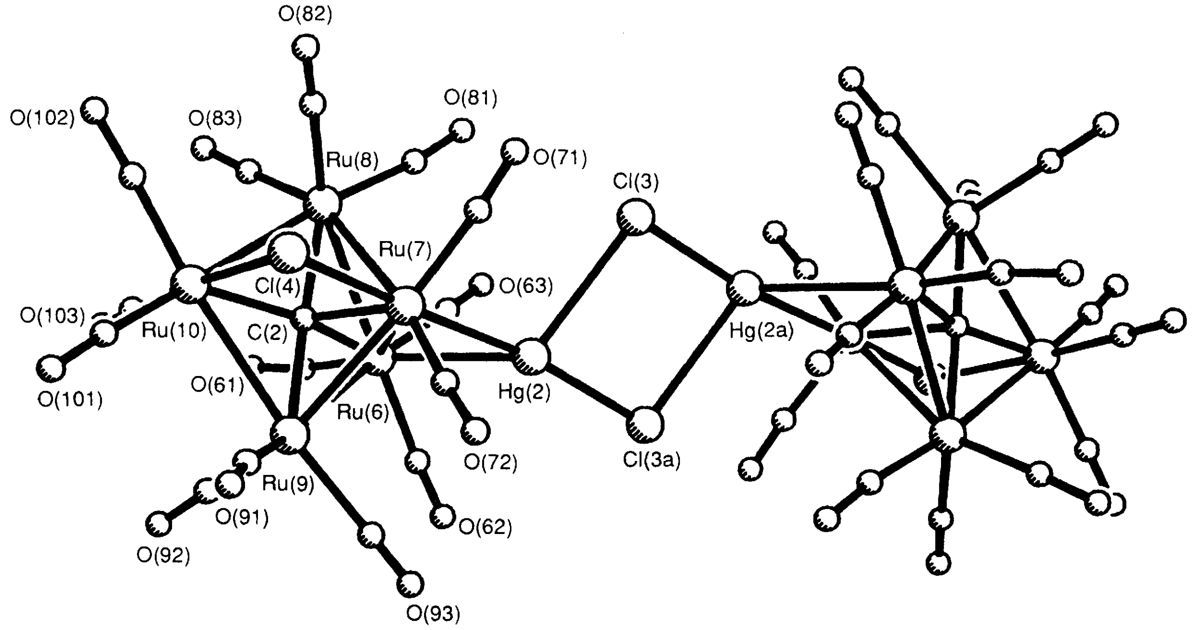

Fig. 2 The molecular structure of one molecule of $[\{Ru_5C(CO)_{14}(\mu\text{-}Cl)\}_2Hg_2Cl_2]$ **5**

Table 2 Selected bond lengths (Å) and angles (°) for $[\{Ru_5C(CO)_{14}(\mu\text{-}Cl)\}_2Hg_2Cl_2]\cdot0.5CHCl_3$ **5**

Hg(1)–Ru(1)	2.862(3)	Hg(1)–Ru(2)	2.612(3)
Hg(1)–Cl(1)	2.386(10)	Ru(1)–Ru(2)	3.024(3)
Ru(1)–Ru(3)	2.859(4)	Ru(1)–Ru(4)	2.861(3)
Ru(1)–C(1)	2.083(23)	Ru(2)–Ru(3)	2.831(3)
Ru(2)–Ru(4)	2.810(3)	Ru(2)–C(1)	2.040(25)
Ru(3)–Ru(5)	2.880(3)	Ru(3)–C(1)	1.976(23)
Ru(4)–Ru(5)	2.878(4)	Ru(4)–C(1)	1.992(23)
Ru(5)–Cl(2)	2.494(8)	Ru(5)–C(1)	2.050(23)
Hg(2)–Cl(3)	2.961(11)	Hg(2)–Ru(6a)	2.870(3)
Hg(2)–Ru(7a)	2.622(3)	Hg(2)–Cl(3a)	2.412(10)
Ru(6)–Ru(7)	2.998(3)	Ru(6)–Ru(8)	2.849(4)
Ru(6)–Ru(9)	2.854(3)	Ru(7)–Ru(8)	2.838(4)
Ru(7)–Ru(9)	2.838(3)	Ru(6)–C(2)	2.089(23)
Ru(7)–C(2)	2.045(26)	Ru(7)–Cl(4)	2.488(4)
Ru(8)–Ru(10)	2.879(3)	Ru(8)–C(2)	1.986(2)
Ru(9)–Ru(10)	2.884(4)	Ru(9)–C(2)	1.980(26)
Ru(10)–Cl(4)	2.485(8)	Ru(10)–C(2)	2.049(23)
Ru(1)–Hg(1)–Ru(2)	66.9(1)	Ru(1)–Hg(1)–Cl(1)	119.8(3)
Ru(2)–Hg(1)–Cl(1)	166.5(3)	Ru(2)–Cl(2)–Ru(5)	85.1(2)
Ru(1)–C(1)–Ru(2)	94.4(10)	Ru(1)–C(1)–Ru(3)	89.5(8)
Ru(2)–C(1)–Ru(3)	89.7(11)	Ru(3)–C(1)–Ru(4)	177.5(13)
Ru(1)–C(1)–Ru(5)	154.5(14)	Ru(2)–C(1)–Ru(5)	111.1(11)
Ru(3)–C(1)–Ru(5)	91.3(10)	Ru(4)–C(1)–Ru(5)	90.8(9)
Cl(3)–Hg(2)–Ru(6)	115.1(3)	Cl(3)–Hg(2)–Ru(7)	108.6(2)
Ru(6)–Hg(2)–Ru(7)	66.0(1)	Cl(3)–Hg(2)–Cl(3a)	80.3(4)
Ru(6a)–Hg(2)–Cl(3a)	121.1(3)	Ru(7a)–Hg(2)–Cl(3a)	165.8(3)
Hg(2)–Cl(3)–Hg(2a)	99.7(4)	Ru(7)–Cl(4)–Ru(10)	85.5(3)
Ru(6)–C(2)–Ru(7)	93.0(10)	Ru(6)–C(2)–Ru(8)	88.7(9)
Ru(7)–C(2)–Ru(8)	89.5(10)	Ru(6)–C(2)–Ru(9)	177.5(13)
Ru(7)–C(2)–Ru(9)	89.7(11)	Ru(8)–C(2)–Ru(9)	89.0(10)
Ru(6)–C(2)–Ru(10)	156.0(14)	Ru(7)–C(2)–Ru(10)	111.1(12)
Ru(8)–C(2)–Ru(10)	91.0(10)	Ru(9)–C(2)–Ru(10)	91.4(9)

bridges in the Hg_2Cl_2 unit are asymmetric, Hg(2)–Cl(3) and Hg(2)–Cl(3a) being 2.961(11) and 2.412(10) Å respectively, in the molecule shown in Fig. 2. The five ruthenium atoms in the two Ru_5 units form a distorted bridged-butterfly arrangement in each case. For each half of the molecule the Hg atom asymmetrically bridges the 'hinge' bond of the bridged butterfly. Along one open edge of this capped butterfly is a bridging halogen atom similar to that observed in the related cluster $[Ru_5C(CO)_{14}(\mu\text{-}AuPPh_3)(\mu\text{-}Br)]$.[8] The presence of the mercury metal atom causes a lengthening of this Ru–Ru edge, and the Ru(1)–Ru(2) and Ru(6)–Ru(7) bond lengths are the largest bonded Ru–Ru distances in the structure. The average bond length of 2.88 Å for the other Ru–Ru bonds is within the range normally recorded (2.70–2.90 Å) in other Ru_5 clusters. The average Ru–C (carbide) distance of 2.03 Å is similar to that in $[Ru_5C(CO)_{14}(\mu\text{-}AuPPh_3)(\mu\text{-}Br)]$.[8] The fourteen carbonyls in each molecule are essentially linear and occupy terminal bonding sites. The solid-state IR spectrum of compound **5** was recorded as a KBr disc at 123 K. It shows two very well resolved and almost symmetrical bands at 776 and 729 cm^{-1} which may be assigned to the carbide ligand in a square-pyramidal structure.[9]

There is good evidence to suggest that in the gas phase the dimer **5** undergoes dissociation into two monomeric units **6** by cleavage of the Hg–Cl donor bond [equations (1) and (2)].

$$\underset{\mathbf{5}}{[\{Ru_5C(CO)_{14}(\mu\text{-}Cl)\}_2Hg_2Cl_2]} \rightleftharpoons \underset{\mathbf{6}}{2[Ru_5C(CO)_{14}(\mu\text{-}Cl)(HgCl)]} \quad (1)$$

$$\underset{\mathbf{6}}{2[Ru_5C(CO)_{14}(\mu\text{-}Cl)\}(HgCl)]} \xrightleftharpoons{-CO} \underset{\mathbf{7}}{2[Ru_5C(CO)_{13}(\mu\text{-}Cl)(HgCl)]} \quad (2)$$

Thus, the FAB mass spectrum exhibits an intense peak at an *m/z* value of 1154 which corresponds to the monomeric formulation **7**. No evidence was found for peaks in the region expected for the dimer **5** and the monomer **6**.

Experimental

General.—Although many of the reaction products are air stable, all the reactions were performed under an atmosphere of dry, oxygen-free, nitrogen. Technical grade solvents were purified by standard procedures before use. The dianions $[Ru_6C(CO)_{16}]^{2-}$,[3] $[Ru_5C(CO)_{15}]$,[10] $Hg(CF_3CO_2)_2$[11] and $Hg(CF_3)(CF_3CO_2)$[12] were prepared by the reported procedures.

Table 3 Atomic coordinates (× 10^4) for compound **2**

Atom	*x*	*y*	*z*
Hg	7 463(1)	2 562(2)	2 500(1)
Ru(1)	9 205(1)	2 962(1)	2 683(1)
Ru(2)	8 368(1)	1 822(1)	3 531(1)
Ru(3)	10 041(1)	1 815(1)	4 312(1)
Ru(4)	10 766(1)	2 783(1)	3 513(1)
Ru(5)	9 804(1)	3 308(1)	4 227(1)
Ru(6)	9 293(1)	1 386(1)	2 748(1)
Ru(7)	6 355(1)	3 399(1)	2 242(1)
Ru(8)	5 728(1)	1 667(1)	1 397(1)
Ru(9)	4 066(1)	1 755(1)	718(1)
Ru(10)	4 636(1)	3 307(1)	1 508(1)
Ru(11)	5 537(1)	2 978(1)	684(1)
Ru(12)	4 945(1)	2 073(1)	2 275(1)
C(1)	9 523(8)	2 333(8)	3 473(6)
C(2)	5 258(8)	2 514(8)	1 484(6)
C(11A)	4 857(16)	3 287(17)	−99(10)
O(11A)	4 359(12)	3 285(14)	−663(7)
C(11D)	5 866(20)	2 292(17)	337(15)
O(11D)	5 919(16)	1 934(14)	−120(13)
C(11B)	6 414(14)	3 880(11)	699(17)
O(11B)	6 940(13)	4 419(10)	645(13)
O(122)	5 568(8)	2 572(8)	3 875(6)
O(14)	10 685(7)	3 659(8)	2 240(6)
C(14)	10 401(10)	3 334(10)	2 614(8)
O(23)	8 514(8)	794(8)	4 648(7)
O(46)	10 910(9)	1 637(9)	2 477(7)
O(91)	2 593(8)	328(8)	711(7)
O(82)	6 855(8)	878(9)	1 109(7)
O(31)	10 868(9)	2 266(11)	5 932(7)
C(23)	8 745(10)	1 220(11)	4 317(8)
O(121)	3 324(8)	974(8)	2 334(6)
O(81)	4 421(7)	119(7)	389(7)
O(34)	12 040(8)	2 325(8)	4 745(6)
O(22)	7 077(9)	217(8)	2 551(9)
O(71)	7 202(9)	3 839(9)	3 863(7)
O(11)	8 345(10)	2 556(9)	1 061(7)
C(21)	7 632(10)	2 037(11)	3 937(9)
C(34)	11 355(10)	2 328(10)	4 332(8)
O(5)	9 181(12)	4 696(9)	4 033(9)
O(2)	7 207(9)	2 101(8)	4 210(7)
C(46)	10 506(11)	1 796(12)	2 766(8)
O(12)	9 451(9)	4 702(8)	2 642(8)
C(101)	4 328(12)	4 081(11)	1 004(10)
C(12A)	3 944(11)	1 372(10)	2 306(8)
C(12B)	5 366(11)	2 393(10)	3 274(9)
O(101)	4 190(11)	4 580(9)	712(9)
C(11)	8 669(11)	2 699(10)	1 672(9)
C(91)	3 140(10)	860(10)	723(8)
C(92)	3 593(11)	1 501(11)	−298(9)
C(71)	6 884(10)	3 631(10)	3 230(11)
O(710)	5 978(10)	4 873(9)	2 530(10)
C(710)	5 753(13)	4 236(12)	2 270(12)
C(12)	9 296(11)	4 036(11)	2 650(9)
O(92)	3 246(10)	1 278(10)	−903(7)
C(82)	6 473(10)	1 185(10)	1 266(8)
C(81)	4 796(10)	713(10)	713(8)
O(61)	9 165(14)	−328(9)	2 728(11)
C(31)	10 551(12)	2 100(13)	5 330(10)
O(51)	9 572(14)	3 322(10)	5 610(9)
C(51)	9 635(14)	3 298(11)	5 075(11)
C(22)	7 569(13)	821(12)	2 866(11)
O(812)	5 588(8)	629(8)	2 533(7)
O(52)	11 691(8)	4 454(8)	4 988(8)
O(66)	8 485(9)	891(10)	1 133(7)
O(910)	2 686(8)	2 467(9)	471(7)
O(33)	10 273(11)	210(10)	4 371(9)
O(102)	3 798(11)	3 291(11)	2 547(8)
O(44)	12 565(9)	3 718(11)	3 643(9)
C(910)	3 384(13)	2 472(10)	709(9)
C(66)	8 778(10)	1 100(11)	1 758(10)
C(102)	4 120(14)	3 253(16)	2 179(11)
C(55)	9 394(13)	4 162(11)	4 092(10)
C(52)	10 982(13)	3 972(13)	4 652(12)
C(812)	5 495(11)	1 150(12)	2 258(9)
N(1)	5 119(8)	2 546(7)	5 919(6)
P(1)	5 661(2)	3 408(2)	6 396(2)
C(112)	7 450(7)	4 239(6)	6 926(4)
C(113)	8 236	4 469	6 863
C(114)	8 255	4 218	6 215
C(115)	7 488	3 736	5 631
C(116)	6 702	3 505	5 695
C(111)	6 683	3 756	6 343
C(122)	4 223(7)	3 807(5)	5 776(6)
C(123)	3 802	4 339	5 566
C(124)	4 286	5 147	5 652
C(125)	5 189	5 423	5 948
C(126)	5 610	4 891	6 158
C(121)	5 127	4 083	6 072
C(132)	5 393(6)	3 752(6)	7 605(6)
C(133)	5 503	3 727	8 314
C(134)	6 072	3 394	8 741
C(135)	6 531	3 087	8 459
C(136)	6 420	3 113	7 749
C(131)	5 851	3 445	7 322
P(2)	4 431(2)	1 706(2)	5 837(2)
C(212)	4 383(5)	1 554(5)	7 155(5)
C(213)	4 041	1 579	7 661
C(214)	3 265	1 704	7 471
C(215)	2 830	1 803	6 775
C(216)	3 172	1 777	6 269
C(211)	3 948	1 653	6 459
C(222)	2 861(7)	738(5)	4 730(5)
C(223)	2 235	514	4 019
C(224)	2 335	996	3 525
C(225)	3 062	1 703	3 741
C(226)	3 688	1 927	4 452
C(221)	3 587	1 444	4 946
C(232)	4 470(5)	214(6)	6 012(5)
C(233)	4 825	−372	6 046
C(234)	5 625	−195	6 013
C(235)	6 069	569	5 946
C(236)	5 714	1 115	5 911
C(221)	4 914	978	5 945
N(2)	9 765(7)	2 442(7)	9 133(6)
P(3)	10 525(2)	3 253(2)	9 253(2)
C(312)	11 811(7)	3 060(6)	8 933(5)
C(313)	12 203	2 994	8 472
C(314)	11 877	3 152	7 782
C(315)	11 160	3 377	7 552
C(316)	10 768	3 443	8 013
C(311)	11 094	3 284	8 703
C(322)	10 614(5)	4 783(6)	9 058(5)
C(323)	10 293	5 395	8 989
C(324)	9 470	5 254	8 964
C(325)	8 969	4 501	9 008
C(326)	9 291	3 889	9 077
C(321)	10 113	4 029	9 103
C(332)	11 088(6)	2 950(5)	10 630(5)
C(333)	11 620	3 150	11 368
C(334)	12 342	3 864	11 657
C(335)	12 533	4 379	11 208
C(336)	12 001	4 180	10 471
C(331)	11 279	3 465	10 182
P(4)	9 115(2)	1 648(2)	8 571(2)
C(412)	10 341(6)	985(5)	9 164(5)
C(413)	10 608	348	9 329
C(414)	9 995	−429	9 134
C(415)	9 114	−570	8 774
C(416)	8 846	68	8 610
C(411)	9 460	845	8 805
C(422)	7 304(6)	1 013(5)	7 972(4)
C(423)	6 504	819	8 008
C(424)	6 470	1 026	8 659
C(425)	7 236	1 426	9 275
C(426)	8 036	1 620	9 240
C(421)	8 070	1 413	8 588
C(432)	9 389(7)	1 360(6)	7 359(6)
C(433)	9 316	1 436	6 665

Table 3 (*continued*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C(33)	10 183(11)	811(13)	4 321(9)	C(434)	8 840	1 868	6 281
C(77)	7 244(13)	4 246(12)	2 189(11)	C(435)	8 437	2 223	6 591
C(44)	11 872(11)	3 348(14)	3 596(9)	C(436)	8 510	2 147	7 285
C(67)	9 916(16)	338(14)	2 735(11)	C(431)	8 986	1 715	7 669
O(77)	7 826(10)	4 771(9)	2 196(10)				

Table 4 Atomic coordinates (× 10^4) for compound **5**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Hg(1)	6 170(1)	1 615(1)	7 320(1)	Ru(7)	2 054(1)	−4 135(2)	5 883(1)
Ru(1)	7 390(1)	3 714(3)	7 207(1)	Ru(8)	1 223(1)	−1 973(2)	6 215(1)
Ru(2)	6 791(1)	1 263(2)	6 730(1)	Ru(9)	3 243(1)	−2 095(3)	5 724(1)
Ru(3)	8 527(1)	1 742(2)	6 960(1)	Ru(10)	3 005(1)	−1 710(3)	6 452(1)
Ru(4)	6 634(1)	4 067(2)	6 489(1)	Cl(3)	571(6)	−4 706(14)	4 650(3)
Ru(5)	8 134(1)	2 924(3)	6 262(1)	Cl(4)	2 952(5)	−4 332(8)	6 467(2)
Cl(1)	5 728(6)	1 386(15)	7 888(2)	C(2)	2 251(15)	−2 028(28)	5 979(7)
Cl(2)	7 247(5)	763(8)	6 146(2)	C(61)	1 594(19)	439(33)	5 551(8)
C(1)	7 601(14)	2 920(29)	6 719(6)	O(61)	1 603(16)	1 745(26)	5 613(8)
C(11)	7 758(20)	3 212(34)	7 712(10)	C(62)	1 820(18)	−1 368(30)	5 043(8)
O(11)	7 948(16)	2 849(33)	7 987(6)	O(62)	1 905(14)	−1 242(29)	4 759(6)
C(12)	8 178(20)	5 247(34)	7 207(9)	C(63)	301(21)	−1 285(34)	5 336(9)
O(12)	8 657(18)	6 112(32)	7 239(8)	O(63)	−379(14)	−1 116(27)	5 241(7)
C(13)	6 526(24)	4 994(42)	7 334(10)	C(71)	1 233(19)	−5 395(33)	6 017(8)
O(13)	6 088(20)	5 727(36)	7 463(10)	O(71)	787(17)	−6 111(27)	6 119(8)
C(21)	6 943(18)	−570(33)	6 905(8)	C(72)	2 741(21)	−5 353(37)	5 689(9)
O(21)	7 103(17)	−1 746(25)	7 004(7)	O(72)	3 183(17)	−6 262(24)	5 582(9)
C(22)	5 681(20)	1 089(31)	6 508(9)	C(81)	87(18)	−2 367(29)	6 027(8)
O(22)	5 002(13)	923(28)	6 366(7)	O(81)	−615(15)	−2 552(25)	5 948(7)
C(31)	8 686(19)	663(33)	7 404(9)	C(82)	1 133(19)	−3 082(34)	6 639(9)
O(31)	8 807(16)	84(32)	7 653(7)	O(82)	1 082(18)	−3 647(28)	6 871(7)
C(32)	9 604(22)	2 649(35)	7 063(9)	C(83)	982(17)	−195(30)	6 399(8)
O(32)	10 202(14)	3 347(31)	7 094(8)	O(83)	859(15)	839(27)	6 534(7)
C(33)	8 906(19)	94(33)	6 725(8)	C(91)	4 219(21)	−3 050(35)	5 928(9)
O(33)	9 129(15)	−913(27)	6 623(7)	O(91)	4 797(17)	−3 814(31)	6 025(9)
C(41)	5 587(18)	4 527(29)	6 664(8)	C(92)	3 756(20)	−335(37)	5 677(9)
O(41)	4 972(14)	4 646(34)	6 758(8)	O(92)	4 058(17)	740(28)	5 645(7)
C(42)	6 003(19)	3 586(31)	6 031(9)	C(93)	3 425(22)	−2 803(38)	5 240(11)
O(42)	5 639(15)	3 297(28)	5 789(7)	O(93)	3 538(18)	−3 186(37)	5 003(7)
C(43)	6 859(23)	5 933(40)	6 373(10)	C(101)	4 172(23)	−1 789(37)	6 628(10)
O(43)	6 956(22)	7 098(25)	6 279(7)	O(101)	4 910(15)	−1 894(29)	6 720(8)
C(51)	8 832(20)	4 491(37)	6 406(9)	C(102)	2 780(18)	−1 569(31)	6 925(8)
O(51)	9 208(18)	5 373(28)	6 494(7)	O(102)	2 697(21)	−1 544(36)	7 223(8)
C(52)	7 705(20)	3 804(33)	5 809(10)	C(103)	2 990(20)	223(37)	6 393(9)
O(52)	7 487(15)	4 364(31)	5 557(6)	O(103)	2 936(13)	1 446(24)	6 342(6)
C(53)	9 010(19)	1 930(31)	6 063(8)	Cl(5)	5 820(12)	3 495(25)	284(7)
O(53)	9 484(15)	1 314(31)	5 947(7)	Cl(6)	7 390(10)	2 208(20)	279(7)
Hg(2)	−1 130(1)	−5 743(1)	4 740(1)	Cl(7)	5 987(13)	446(24)	299(6)
Ru(6)	1 508(1)	−1 436(2)	5 508(1)	C(100)	6 300(53)	2 368(90)	167(23)

Mass spectral analyses were performed using a Kratos model MS902 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrophotometer, ^{1}H NMR spectra on a Bruker WH250 spectrometer, and ^{13}C NMR spectra on a Bruker WH 400 instrument. Elemental analyses were performed by the microanalytical services of this department.

Reactions of the Dianion **1** *with Mercury Salts.*—(*a*) Compound **1** (100 mg, 0.047 mmol) as its $[N(PPh_3)_2]^+$ salt was dissolved in dichloromethane (5 cm^3) and a solution of $Hg(CF_3CO_2)_2$ (20 mg, 0.047 mmol) in the same solvent (2 cm^3) added with stirring. The colour of the initial solution changed immediately from orange-red, typical of **1**, to red-brown and a black solid precipitated. After stirring for 1 h the solution was filtered and the black product washed with dichloromethane, acetone, and finally diethyl ether, yield 44 mg. It was found to be insoluble in all common organic solvents.

(*b*) Compound **1** (200 mg, 0.0931 mmol) as its $[N(PPh_3)_2]^+$ salt was dissolved in dichloromethane (20 cm^3) and a solution of $HgCl_2$ (25.2 mg, 0.093 mmol) in the same solvent (20 cm^3) added with stirring. The colour of the initial solution changed immediately from orange-red to dark red. After stirring for 15 min the solvent was removed and the solid residue was redissolved in dichloromethane (3 cm^3). TLC of the solution using acetone–hexane (3:2) as eluent gave a very intense dark red band of $[N(PPh_3)_2]_2[\{Ru_6C(CO)_{16}\}_2Hg]$ which was crystallised from CH_2Cl_2–hexane by slow evaporation at −20 °C. Yield = 130 mg, 82% (Found: C, 36.70; H, 1.7; N, 1.15; P, 3.60. Calc.: C, 36.40: H, 1.6; N, 0.65; P, 3.60%).

(*c*) The cluster $[N(PPh_3)_2]_2[Ru_6C(CO)_{16}]$ (150 mg, 0.07 mmol) was stirred with $Hg(CF_3)(CF_3CO_2)$ (26.78 mg, 0.07 mmol) in CH_2Cl_2 at room temperature for 0.5 h. The solvent was removed and the resulting solid was redissolved in dichloromethane (2 cm^3). The product was purified by TLC using acetone–hexane (3:2) as eluent. The only dark orange band collected, in quantitative yield, was identified as $[N(PPh_3)_2][Ru_6C(CO)_{16}(HgCF_3)]$ by spectroscopic analysis.

Reaction of Cluster **4** *with Mercury Salts.*—To a solution of the cluster **4** (25 mg, 0.027 mmol) in dichloromethane (20 cm^3) was added a solution of $HgCl_2$ (7.74 mg, 0.027 mmol) in the same solvent (20 cm^3) and the solution stirred for *ca.* 20 h. After removal of solvent the solid residue was dissolved in chloroform and crystallised by slow evaporation with hexane. The product **5** was obtained in 45–50% yield. (Found: C, 15.10. Calc. for $C_{30}Cl_4Hg_2O_{28}Ru_{10}$: C, 15.25%).

Crystal Structure Determination of $[N(PPh_3)_2]_2[\{Ru_6C(CO)_{16}\}_2Hg]$ **2**.—Suitable crystals were grown from CH_2Cl_2–hexane and mounted in 0.5 mm glass capillaries in the presence of mother-liquor.

Crystal data. $C_{106}H_{60}HgN_2O_{32}P_4Ru_{12}$, $M = 3410.07$, triclinic, space group $P\bar{1}$ (no. 2), $a = 17.960(3)$, $b = 18.058(4)$, $c = 20.471(4)$ Å, $\alpha = 93.03(2)$, $\beta = 112.29(1)$, $\gamma = 108.97(2)°$, $U = 5690(2)$ Å^3 (accurate cell from 40 reflections in range $20 < 2\theta < 25°$, $\lambda = 0.710\,69$ Å), $Z = 2$, $D_c = 1.990$ g cm^{-3}, $F(000) = 3268$. Dark red blocks. Crystal dimensions: $0.12 \times 0.30 \times 0.38$ mm. μ(Mo-Kα) = 22.3 cm^{-1}, $\mu R = 0.30$.

Data collection and processing. Nicolet R3mV diffractometer, 96-step ω–2θ scan mode, with scan width of 1.4° plus Kα splitting, scan speed 3.0–29.3° min^{-1}, graphite-monochromated Mo-Kα radiation. 15 943 Reflections measured ($5.0 \leqslant 2\theta \leqslant 45.0$, $\pm h \pm k, -l$), 14 784 unique [merging $R = 0.012$ after empirical absorption based on an ellipsoid fit of 298 azimuthal scan data (maximum, minimum transmission factors = 0.73, 0.25)] giving 10 598 with $F > 4\sigma(F)$. Three standard reflections showed no significant variation in intensity during data collection.

Structure analysis and refinement. Direct methods (Hg and Ru atoms) followed by Fourier difference techniques. Blocked full-matrix least squares with Hg, Ru, N, O, P and C atoms (in the anion) anisotropic. The phenyl rings were refined as rigid groups (C–C, 1.395 Å, C–C–C 120.0°), and phenyl H atoms were placed in idealised positions (C–H 0.98 Å) and allowed to ride on relevant C; H atoms assigned a common isotropic thermal parameter. The carbonyl ligands showed slight positional disorder and additional constraints were placed on these atoms [Ru–C 1.850(1), C–O 1.160(1) Å]. The weighting scheme $w = [\sigma^2(F) + 0.001F^2]^{-1}$ with $\sigma(F)$ from counting statistics gave satisfactory agreement analyses. The final converged residuals, R and R', for 679 parameters, were 0.061 and 0.064, respectively. A final difference map showed residual peaks of *ca.* 1.8 e Å^{-3} close to the Hg atom position but no other region of significant density. Final atomic coordinates are presented in Table 3.

Crystal Structure Determination of $[\{Ru_5C(CO)_{14}(\mu\text{-}Cl)\}_2Hg_2Cl_2]\cdot 0.5CHCl_3$ **5**.—Suitable single crystals were obtained by slow evaporation of $CHCl_3$–hexane and mounted in 0.5 mm glass capillaries in the presence of mother-liquor.

Crystal data. $C_{30}Cl_4Hg_2O_{28}Ru_{10}\cdot 0.5CHCl_3$, $M = 2421.66$, monoclinic, space group $P2/c$ (no. 13), $a = 16.013(4)$, $b = 9.468(2)$, $c = 38.227(9)$ Å, $\beta = 98.12(2)°$, $U = 5738$ Å^3 (accurate cell from 50 reflections in range $20 < 2\theta < 25°$, $\lambda = 0.710\,69$ Å), $Z = 4$, $D_c = 2.802$ g cm^{-3}, $F(000) = 4404$. Orange blocks. Crystal dimensions: $0.304 \times 0.380 \times 0.470$ mm. μ(Mo-Kα) = 81.7 cm^{-1}, $\mu R = 1.57$.

Data collection and processing. Stoe four-circle diffractometer, 30-step ω-scan mode, with step width 0.05° and step time in range 0.5–2.0 scan per step, graphite monochromated Mo-Kα radiation. 8369 Reflections measured ($5.0 \leqslant 2\theta \leqslant 45.0°$, $+h, -k, \pm l$), 6889 unique [merging $R = 0.060$ after empirical absorption corrections based on an ellipsoid fit of 11 sets of ψ scans (maximum, minimum transmission factors = 0.55, 0.16)] giving 5161 with $F > 4\sigma(F)$. Three standard reflections showed no significant variations in intensity.

Structure analysis and refinement. Direct methods (Hg and Ru atoms) followed by Fourier difference techniques. Full-matrix least squares with Hg, Ru, Cl, O and carbido–C atoms anisotropic. The atoms in the $CHCl_3$ solvent molecule were refined with occupancy fixed at 0.5. The weighting scheme $w = [\sigma^2(F) + 0.003F^2]^{-1}$ with $\sigma(F)$ from counting statistics gave reasonable analyses. Final converged residuals, R and R', were both 0.083 for 558 parameters. A final difference map showed residual peaks of *ca.* 3.3 e Å^{-3} close to the positions of the Hg atoms but no other region of significant electron density. Final atomic coordinates are presented in Table 4.

Both structures were solved and refined using the SHELXTL PLUS package installed in a MicroVaxe II computer.[13] Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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