Journal of Organometallic Chemistry, 420 (1991) 431–442
Elsevier Sequoia S.A., Lausanne
JOM 22157

Mercury–ruthenium mixed-metal carbonyl clusters containing 2-amido-6-methylpyridine (ampy) as a μ_3,η^2-ligand. Crystal structures of $[Ru_6(\mu_4\text{-}Hg)(\mu_3\text{-ampy})_2(CO)_{18}] \cdot 2C_4H_8O$ and $[Ru_3(\mu\text{-}HgBr)(\mu_3\text{-ampy})(CO)_9]$

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(Received June 3rd, 1991)

Abstract

The cluster $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_9]$ (1) (Hampy = 2-amino-6-methylpyridine) reacts with $HgPh_2$ to give $[Ru_6(\mu_4\text{-}Hg)(\mu_3\text{-ampy})_2(CO)_{18}]$ (2). An X-ray diffraction study of the solvate 2·2THF has shown it to contain two "$Ru_3(\mu_3\text{-ampy})(CO)_9$" moieties bridged by a mercury atom which is bonded to the two NH-bridged ruthenium atoms of each trinuclear moiety. Complex 2 reacts with mercury(II) halides to give $[Ru_3(\mu\text{-}HgX)(\mu_3\text{-ampy})(CO_9]$ (X = Cl(3), Br(4), I(5)). The crystal structure of cluster 4 shows it to contain a HgBr fragment spanning the same Ru–Ru edge as the amido group of the ampy ligand. Some reactions of the clusters 2 and 3 are also described.

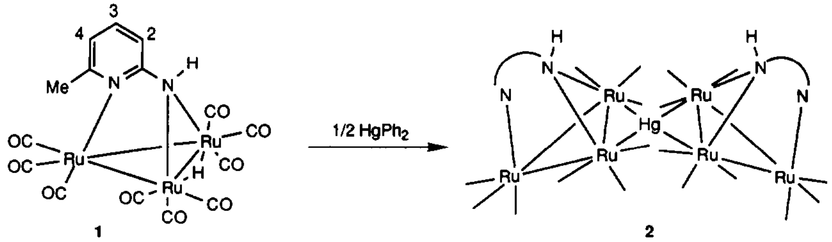
Introduction

In recent years, there has been considerable interest in mercury-containing transition metal clusters [1–10]. These studies have revealed isolobal relationships between Hg^{2+}, Ag^+ and Au^+ and between HgX^+ (X = halide), H^+, AgL^+ and AuL^+ (L = neutral ligand) [2]. In most cases the cluster complexes were prepared by reaction of the corresponding carbonylate anions with mercury(II) salts [1,2].

We have previously described the synthesis [11] and some reactivity [12] of the cluster $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_9]$ (1) (Hampy = 2-amino-6-methylpyridine), showing that the ampy ligand holds the metal atoms very firmly, preventing cluster degradation at high temperatures. We describe below the synthesis and reactions of mercury-containing ruthenium clusters derived from compound **1**.

Results and discussion

Spectroscopic (IR, NMR) and chromatographic (TLC) techniques showed that the reaction of $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_9]$ (**1**) with various amounts of $HgCl_2$ in



Scheme 1.

refluxing tetrahydrofuran (THF) gave complex mixtures of compounds (which could not be separated), and also that no reaction occurred at room temperature. In contrast, treatment of complex **1** with $HgPh_2$ in refluxing THF provided the heptanuclear cluster $[Ru_6(\mu_4\text{-}Hg)(\mu_3\text{-ampy})_2(CO)_{18}]$ (**2**) (Scheme 1) as the only detectable product, regardless of the ratio of reactants. Complex **2** was characterised by spectroscopic (Table 1) and crystallographic methods.

The molecular structure of the solvate **2** · 2THF and its most relevant bond distances and angles are shown in Fig. 1 and Table 2. The structure can be described as two "$HgRu_3(\mu_3\text{-ampy})(CO)_9$" units (esentially identical to that in compound **4**, which is discussed below) which share the Hg atom in such a way that the two Ru_2Hg planes form a dihedral angle of 35.8°. The Hg–Ru distances (Hg(1)–Ru(1) 2.839(1), Hg(1)–Ru(2) 2.859(1), Hg(1)–Ru(51) 2.841(1), Hg(1)–Ru(52) 2.842(1) Å) are approx. 0.1Å longer than those in compound **4**. The lengthening of the Hg–Ru distances may be caused by steric repulsions between the equatorial CO ligands attached to the Hg-bridged Ru–Ru edges, while the angle between the two Ru_2Hg planes is the one which minimises these repulsions [4–7].

It seemed likely that in solution each Ru_3 unit of compound **2** would have a low rotation barrier about the axis defined by the Hg atom and the mid-points of the bridged Ru–Ru edges (Scheme 2), as has been implied by NMR spectroscopy in the clusters $[Fe_4Co_2(\mu_4\text{-}Hg)(C_5H_5)_2(\mu_3\text{-}COMe)_2(CO)_{14}]$ [7] and $[Ru_7(\mu_3\text{-}Hg)_2(\mu_3\text{-}C_6H_9)_2(CO)_{22}]$ [8]. To check this view, a variable temperature ^{13}C NMR study was undertaken. The observed spectrum at −85 °C (Fig. 2), which is similar to those obtained at higher temperatures, shows only five CO resonances. In the solid state there is a two-fold axis (non-crystallographic) which relates the two Ru_3 units, but

Table 1

Selected NMR and IR spectroscopic data

Complex	$\delta(^1H)$[a]					$\nu(CO)$[b]
	H^3	H^4	H^5	NH	Me	
1	6.97(d)	7.53(t)	6.78(d)	7.25(s,br)	2.67(s)	2071w, 2054m, 2043vs, 2025sh, 1989sh, 1975s, 1970sh, 1954sh, 1918w
2	7.09(d)	7.64(t)	6.75(d)	6.50(s,br)	2.76(s)	2075w, 2043vs, 2027vs, 1996s, 1985sh, 1968sh
3	7.09(d)	7.63(t)	6.74(d)	6.52(s,br)	2.75(s)	2075w, 2043vs, 2027vs, 1996s, 1985sh, 1969sh
4	7.09(d)	7.60(t)	6.75(d)	6.58(s,br)	2.74(s)	2074w, 2042vs, 2027vs, 1995s, 1982sh, 1966sh

[a] Spectra recorded in acetone-d_6 (300 MHz, 25 °C); chemical shifts are referred to internal TMS; coupling constants for H^3, H^4 and H^5 are approx. 7 Hz. [b] Recorded in THF.

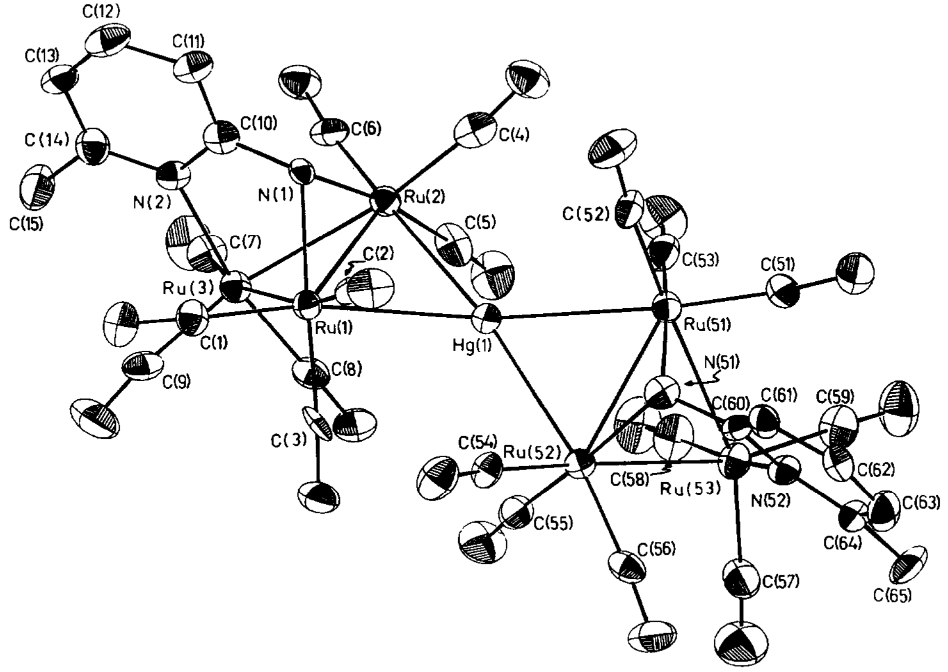


Fig. 1. Molecular structure of $[Ru_6(\mu_4\text{-}Hg)(\mu_3\text{-ampy})_2(CO)_{18}]$ (2).

there is no symmetry plane; thus the ^{13}C NMR spectrum of the static molecule should show nine CO resonances. The observed spectra are therefore consistent with a rapid rotation of each Ru_3 unit, with no CO scrambling, as shown in Scheme 2. However, a facile migration of the Hg atom around the edges of the Ru_3 triangles cannot be ruled out, since this type of dynamic process was observed previously in the complex $[Fe_4Rh_2(\mu_4\text{-}Hg)(C_5H_5)_2(\mu_3\text{-}COMe)_2(CO)_{14}]$ [7].

The reactions of complex **2** with triphenylphosphine, hydrogen, iodine and mercury(II) halides were investigated. Reactions of **2** with one or two equivalents of triphenylphosphine gave mixtures of compounds (which were not separated) that probably arise from replacement of CO on both Ru_3 units. Bubbling of hydrogen through a THF solution of complex **2** at reflux temperature caused deposition of metallic mercury; the IR spectrum of the resulting solution showed that it contained only complex **1**. The reaction of **2** with iodine under UV irradiation led to cluster break down, affording a mixture of $[Ru_3(\mu\text{-}HgI)(\mu_3\text{-ampy})(CO)_9]$ (**5**) and another product, probably $[Ru_3(\mu\text{-}I)(\mu_3\text{-ampy})(CO)_9]$, which could not be characterised owing to its high unstability. A similar reaction has been reported for the complex $[Ru_6(\mu_4\text{-}Hg)(\mu_3\text{-}C_6H_9)_2(CO)_{18}]$ [9].

Treatment of complex **2** with one equivalent of HgX_2 (X = Cl, Br, I), in THF solution at room temperature, gave the clusters $[Ru_3(\mu\text{-}HgX)(\mu_3\text{-ampy})(CO)_9]$ (**3**–**5**) (Scheme 3) in quantitative yields. Their spectroscopic data (Table 1) are nearly identical, suggesting that they have similar structures; the structure of one of them was determined by crystallographic methods.

The tetranuclear cluster **4** consists of a triangle of Ru atoms (Ru(1)–Ru(2) 2.895(3), Ru(2)–Ru(3) 2.757(3), Ru(1)–Ru(3) 2.762(3) Å) bonded to nine CO

Table 2

Selected bond lengths (Å) and angles (°) in [Ru$_6$(μ_4-Hg)(μ_3-ampy)$_2$(CO)$_{18}$] (2·2THF)

Hg(1)–Ru(1)	2.839(1)	Hg(1)–Ru(51)	2.841(1)
Hg(1)–Ru(2)	2.859(1)	Hg(1)–Ru(52)	2.842(1)
Ru(1)–Ru(2)	2.834(2)	Ru(51)–Ru(52)	2.842(2)
Ru(1)–Ru(3)	2.770(2)	Ru(51)–Ru(53)	2.788(2)
Ru(1)–N(1)	2.13(1)	Ru(51)–N(51)	2.14(1)
Ru(2)–Ru(3)	2.775(2)	Ru(52)–Ru(53)	2.762(2)
Ru(2)–N(1)	2.12(1)	Ru(52)–N(51)	2.11(1)
Ru(3)–N(2)	2.22(1)	Ru(53)–N(52)	2.24(1)
Ru–C	1.89 [a]	C–O	1.15 [a]
Ru(2)–Hg(1)–Ru(1)	59.66(4)	Ru(52)–Hg(1)–Ru(51)	60.01(4)
Ru(51)–Hg(1)–Ru(1)	160.22(4)	Ru(51)–Hg(1)–Ru(2)	125.62(4)
Ru(52)–Hg(1)–Ru(1)	120.91(4)	Ru(52)–Hg(1)–Ru(2)	164.28(4)
Ru(2)–Ru(1)–Hg(1)	60.52(4)	Ru(52)–Ru(51)–Hg(1)	60.00(4)
Ru(3)–Ru(1)–Hg(1)	105.41(5)	Ru(53)–Ru(51)–Hg(1)	105.73(5)
Ru(3)–Ru(1)–Ru(2)	59.34(4)	Ru(53)–Ru(51)–Ru(52)	58.74(5)
Ru(1)–Ru(2)–Hg(1)	59.82(4)	Ru(51)–Ru(52)–Hg(1)	59.99(4)
Ru(3)–Ru(2)–Hg(1)	104.76(5)	Ru(53)–Ru(52)–Hg(1)	106.45(5)
Ru(3)–Ru(2)–Ru(1)	59.18(4)	Ru(53)–Ru(52)–Ru(51)	59.66(5)
Ru(2)–Ru(3)–Ru(1)	61.48(4)	Ru(52)–Ru(53)–Ru(51)	61.60(5)
N(1)–Ru(1)–Hg(1)	94.9(3)	N(51)–Ru(51)–Hg(1)	92.8(4)
N(1)–Ru(1)–Ru(2)	48.2(3)	N(51)–Ru(51)–Ru(52)	47.5(3)
N(1)–Ru(1)–Ru(3)	74.6(3)	N(51)–Ru(51)–Ru(53)	74.1(3)
N(1)–Ru(2)–Hg(1)	94.4(3)	N(51)–Ru(52)–Hg(1)	93.4(4)
N(1)–Ru(2)–Ru(1)	48.3(3)	N(51)–Ru(52)–Ru(51)	48.4(3)
N(1)–Ru(2)–Ru(3)	74.5(3)	N(51)–Ru(52)–Ru(53)	75.1(4)
N(2)–Ru(3)–Ru(1)	82.6(3)	N(52)–Ru(53)–Ru(51)	83.2(3)
N(2)–Ru(3)–Ru(2)	84.3(3)	N(52)–Ru(53)–Ru(52)	81.4(3)
Ru(2)–N(1)–Ru(1)	83.6(4)	Ru(52)–N(51)–Ru(51)	84.1(4)

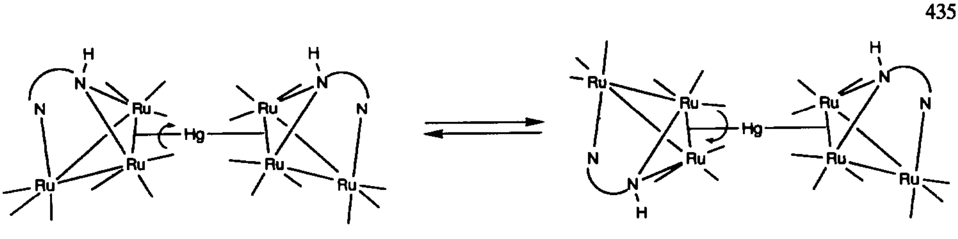
[a] Averaged values.

Table 3

Selected bond lenghts (Å) and angles (°) in [Ru$_3$(μ-HgBr)(μ_3-ampy)(CO)$_9$] (4)

Hg(1)–Br(1)	2.512(3)	Hg(1)–Ru(1)	2.735(2)
Hg(1)–Ru(2)	2.744(2)	Ru(1)–Ru(2)	2.895(3)
Ru(1)–Ru(3)	2.762(3)	Ru(2)–Ru(3)	2.757(3)
Ru(1)–N(1)	2.09(2)	Ru(2)–N(1)	2.12(2)
Ru(3)–N(2)	2.19(2)	Ru–C	1.89 [a]
C–O	1.14 [a]		
Ru(1)–Hg(1)–Br(1)	147.0(1)	Ru(2)–Hg(1)–Br(1)	149.1(1)
Ru(2)–Hg(1)–Ru(1)	63.79(6)	Ru(2)–Ru(1)–Hg(1)	58.26(6)
Ru(1)–Ru(2)–Hg(1)	57.95(6)	Ru(3)–Ru(2)–Hg(1)	102.52(9)
Ru(3)–Ru(1)–Hg(1)	102.62(8)	Ru(3)–Ru(2)–Ru(1)	58.46(7)
Ru(2)–Ru(3)–Ru(1)	63.27(8)	Ru(3)–Ru(1)–Ru(2)	58.28(7)
N(1)–Ru(1)–Hg(1)	91.7(6)	N(1)–Ru(2)–Hg(1)	90.9(6)
N(1)–Ru(1)–Ru(3)	74.2(5)	N(1)–Ru(2)–Ru(1)	46.2(6)
N(1)–Ru(2)–Ru(3)	74.0(6)	N(1)–Ru(1)–Ru(2)	46.9(6)
N(2)–Ru(3)–Ru(1)	83.1(5)	N(2)–Ru(3)–Ru(2)	81.9(5)
Ru(2)–N(1)–Ru(1)	86.9(9)		

[a] Averaged values.



Scheme 2.

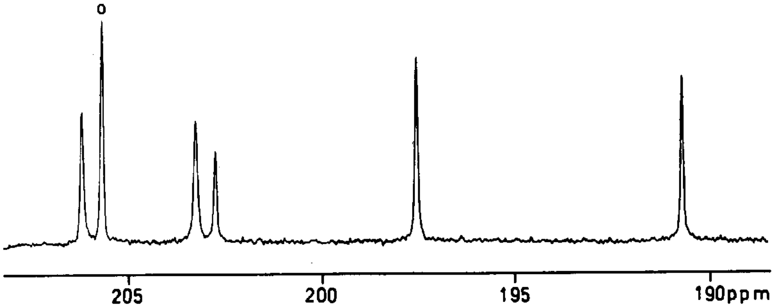
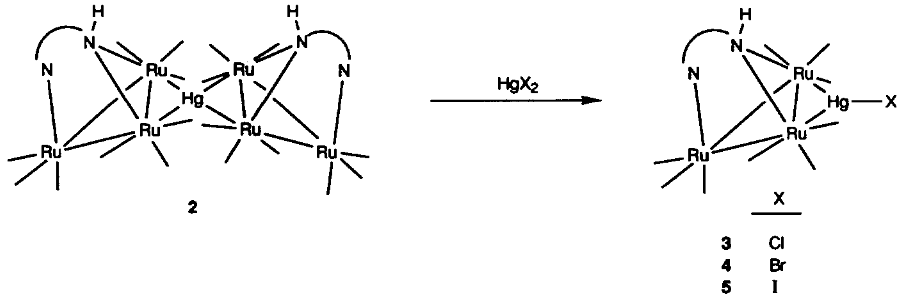


Fig. 2. $^{13}C\{^1H\}$ NMR spectrum (acetone-d_6, 75.5 MHz, −85 °C) of a ^{13}CO-enriched sample of $[Ru_6(\mu_4\text{-Hg})(\mu_3\text{-ampy})_2(CO)_{18}]$ (**2**). The peak marked with a circle comes from the solvent.



Scheme 3.

groups (three to each Ru atom), to the two N atoms of an ampy ligand, and to the Hg atom of a HgBr fragment. The ampy ligand is bonded to the Ru(3) atom through the pyridine nitrogen N(2) (Ru(3)–N(2) 2.19(2) Å), while the exocyclic nitrogen N(1) bridges the other two Ru atoms (Ru(1)–N(1) 2.09(2), Ru(2)–N(1) 2.12(2) Å), the plane Ru(1)–N(1)–Ru(2) being nearly perpendicular to the Ru_3 plane (dihedral angle 81.9 °). The pyridine ring is roughly planar and almost perpendicular to the Ru_3 plane (dihedral angle 87.1 °). The coordination of the Hg atom is triangular, being bonded to the longest Ru–Ru edge (Hg(1)–Ru(1) 2.735(2), Hg(1)–Ru(2) 2.744(2) Å) and to a Br atom (Hg(1)–Br(1) 2.512(3) Å). The plane Ru(1)–Hg(1)–Ru(2) forms a dihedral angle of 48.2 ° with the Ru_3 plane. The three axial CO ligands are approximately *trans* to the N–Ru bonds, while two of the six equatorial CO ligands are *trans* to the Hg atom and the remaining four are nearly *trans* to Ru–Ru bonds. Overall this structure is analogous to that of each $HgRu_3$ unit of complex **2**, and is reminiscent of that of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}anpy)(CO)_9]$ (Hanpy = 2-anilinopyridine) [11], in which the hydride has been replaced by a HgBr fragment, causing a lengthening of the bridged Ru–Ru edge from 2.753(1) to 2.895(3) Å. This structure is also reminiscent of the cluster $[Ru_3(\mu\text{-}HgBr)(\mu_3\text{-}C_6H_9)(CO_9]$, though the latter is a dimer in the solid state, in which two Br atoms bridge two "$HgRu_3(\mu_3\text{-}C_6H_9)(CO)_9$" moieties [10].

All attempts to prepare complex **3** by reaction of the hydride **1** with ClHgPh or with $HgCl_2$ and KOH were unsuccessful, mixtures were obtained that could not be separated. However, the clusters $[Ru_3(\mu\text{-}HgX)(\mu_3\text{-}C_6H_9)(CO)_9]$ (X = Br, I) have been made by use of such procedures [4].

Although stable at room temperature, complex **3** decomposed in refluxing THF or under UV irradiation to give a mixture of products. Chromatography (TLC) of the solutions gave three bands; the first band was identified as complex **2**, the second one was unreacted complex **3**, while the slowest moving band was shown (by ^1H NMR) to be a mixture of several compounds. A similar mixture (but without complex **2**) was obtained when complex **3** was treated with various amounts of $HgCl_2$. These results suggest that when heated, or when irradiated with UV light, complex **3** decomposes partially into **2** and $HgCl_2$, and that the remaining complex **3** reacts with the formed $HgCl_2$ to give a mixture of products. The nature of these products is uncertain, although it is known that the Lewis acid character of $HgCl_2$ is high enough to allow formation of stable adducts with complexes containing metal–metal bonds [13,14] or with complexes containing halogen ligands (giving halogen-bridged derivatives) [14].

Complex **3** was treated with hydrogen (1 atm) in refluxing THF to give the hydride **1** and some other products, as shown by TLC and IR spectroscopy. These other products probably arise from the reaction of **1** with mercury(I) chloride. No metallic mercury was observed. However, no reaction took place at room temperature and so we are not sure whether complex **3** reacts with hydrogen directly or, as suggested above, decomposes in refluxing THF before reacting with hydrogen. When a THF solution of complex **3** was refluxed for 30 min and then treated with hydrogen, the results were the same as when hydrogen was introduced at the beginning of the reaction.

Experimental

Solvents were dried and distilled under nitrogen prior to use. All reactions were carried out under nitrogen, by Schlenk techniques. The compound $[Ru_3(\mu\text{-}H)(\mu_3\text{-}ampy)(CO)_9]$ (**1**) was prepared from $[Ru_3(CO)_{12}]$ as described previously [11]. The ^{13}C NMR spectra were recorded with ^{13}CO-enriched compounds which were made from ^{13}CO-enriched (approx. 30%) $[Ru_3(CO)_{12}]$ [15]. All other reagents were purchased from Aldrich and used as received. Separations by thin layer chromatography (TLC) were carried out on plates (20 × 20cm) coated with silica-gel (Aldrich). Instrumentation was as follows: Perkin Elmer FT 1720-X (IR), Bruker AC-300 (NMR) and Philips PW-1100 (X-ray diffraction).

Preparation of $[Ru_6(\mu_4\text{-}Hg)(\mu_3\text{-}ampy)_2(CO)_{18}]$ *(2)*

A solution of complex **1** (700 mg, 1.055 mmol) and $HgPh_2$ (190 mg, 0.547 mmol) in THF (10 ml) was heated at the reflux temperature for 1 h. The solution was evaporated to dryness and the residue washed with hexane (5 ml) to give the solvate **2** · 2THF as dark red crystals (715 mg, 81%). $^{13}C\{^1H\}$ NMR (acetone-d_6, 75.5 MHz, 22 ° C), $\delta(CO)$: 207.3 (s, 2C), 204.6 (s, 2C), 203.9 (s, 1C), 199.0 (s, 2C), 192.5 (s, 2C) ppm.

Reaction of complex 2 with triphenylphosphine

A solution of complex **2** · 2THF (40 mg, 0.024 mmol) and triphenylphosphine (14 mg, 0.052 mmol) in refluxing THF (5 ml) was stirred for 3 h. The solvent was removed under reduced pressure and the residue shown to be a mixture of compounds by $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz, 22 ° C): 37.3 (s), 35.6 (s), 34.4 (s), 31.3 (s), 29.6 (s), 16.3 (s), 15.0 (s), 13.6 (s) ppm, the highest peak being that at 31.3 ppm.

Reaction of complex 2 with hydrogen

Hydrogen was bubbled through a solution of complex **2** · 2THF (40 mg, 0.024 mmol) in THF (10 ml) at reflux temperature for 1 h. Deposition of metallic mercury was observed. The IR spectrum of the solution indicated that it contained only complex **1**.

Reaction of complex 2 with iodine

A solution of complex **2** · 2THF (50 mg, 0.030 mmol) and iodine (17 mg, 0.067 mmol) in THF (7 ml) was irradiated with UV light (Pyrex filtered) for 1 h. Qualitative TLC analysis (dichlorometane/hexane, 1 : 1 as eluant) of the solution revealed the presence of two products. The solution was evaporated to dryness and the residue extracted with dichloromethane (5 ml). The IR spectrum of this extract showed that it contained only $[Ru_3(\mu\text{-HgI})(\mu_3\text{-ampy})(CO)_9]$ (**5**) (see below). The fraction insoluble in dichloromethane could not be identified.

Preparation of $[Ru_3(\mu\text{-HgX})(\mu_3\text{-ampy})(CO)_9]$ (X = Cl, 3; Br, 4; I, 5)

A solution of complex **2** · 2THF (400 mg, 0.240 mmol) and $HgCl_2$ (68 mg, 0.250 mmol) in THF (10 ml) was stirred at room temperature for 1.5 h. The colour changed from deep red to orange. The solution was evaporated to dryness and the residue washed with diethyl ether (two portions of 5 ml) to give complex **3** as an orange solid (380 mg, 88%). $^{13}C\{^1H\}$ NMR (acetone-d_6, 75.5 MHz, 22 ° C), $\delta(CO)$: 202.8 (s, 1C), 202.0 (s, 2C), 200.3 (s, 2C), 199.2 (s, 2C), 191.7 (s, 2C) ppm. The complexes **4** (83%) and **5** (87%) were prepared similarly from the appropriate mercury(II) halides.

Thermolysis of complex 3

A solution of complex **3** (100 mg, 0.111 mmol) was refluxed in THF (10 ml) for 30 min. The solution was concentrated and chromatographed on preparative TLC plates. Dichloromethane eluted two bands; the first one (red) contained the compound **2**, and the second one (orange) contained unreacted starting material **3**. The base line was eluted further with dichloromethane/methanol (10 : 1) to give a violet band, which was worked up and shown by ^1H NMR to be a mixture of at least three products.

Table 4

Crystallographic data for compounds **2**·2THF and **4**

	2·2THF	**4**
Formula	$C_{38}H_{30}HgN_4O_{20}Ru_6$	$C_{15}H_7BrHgN_2O_9Ru_3$
M	1669.7	942.9
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, P-1
a (Å)	24.327(14)	8.351(7)
b (Å)	17.757(1)	8.937(7)
c (Å)	11.792(3)	15.915(10)
α (°)	90	88.33(7)
β (°)	100.72(1)	79.39(7)
γ (°)	90	78.21(7)
V (Å^3)	5005(4)	1143(4)
Z	4	2
D_c (g cm^{-3})	2.22	2.74
F(000)	3160	860
Crystal size (mm)	0.65×0.50×0.35	0.60×0.45×0.30
μ (cm^{-1})	48.6	103.8
T (°C)	18	18
Radiation, λ (Å)	Mo-K_α, 0.71069	Mo-K_α, 0.71069
Monochromator	Graphite	Graphite
Scan type	ω-2θ	ω-2θ
Scan width	$0.9+0.34\tan\theta$	$1.1+0.34\tan\theta$
θ range (°)	1–25	1–25
Standard reflections	2 every 2 h	2 every 2 h
Measured reflections	8700	3955
Observed reflections $I \geq 3\sigma(I)$	4225	1949
Refined parameters	624	282
Weighting scheme	Chebyshev [a]	Chebyshev [a]
$R = \Sigma\lvert\Delta F\rvert/\Sigma F_o$	0.049	0.069
$R' = [\Sigma w(\Delta F)^2/\Sigma wF_o^{\,2}]^{1/2}$	0.050	0.080

[a] $w = w'[1-((F_o-F_c)/6\sigma(F_o))^2]^2$, where $w' = 1/\Sigma_r = 1,\ldots,3 A_r T_r(X)$ with coefficients 1.08, 0.305 and 0.548 (for **2**·2THF) and 0.72, 0.36 and 0.31 (for **4**) for the Chebyshev polynomial $T_r(X)$ with $X = F_c/F_c(\text{max})$.

Reaction of complex 3 with hydrogen

Hydrogen was bubbled through a solution of complex **3** (40 mg, 0.045 mmol) in THF (40 ml) at reflux temperature. After 1 h the IR spectrum of the solution showed the presence of the hydride **1** as the major product. After 5.5 h the solution was evaporated to dryness. The ^{1}H NMR spectrum of the residue showed the presence of several products.

X-Ray crystal structure determinations of clusters 2 · 2THF and 4

Details of data collection and crystallographic analysis are given in Table 4. Cell constants were obtained by least-squares refinements of 25 reflections with θ in the range 15–16° (for **2** · 2THF) and 10–11° (for **4**). The structures were solved by direct methods and subsequent Fourier maps. Absorption corrections were applied using the program DIFABS [16] from CRYSTALS [17]; max, min transmission factors 1.21, 0.25 (**2** · 2THF) and 1.65, 0.71 (**4**). Non-hydrogen atoms were refined anisotropically by least-squares methods in six (**2** · 2THF) or four (**4**) blocks.

Table 5

Fractional atomic coordinates for compound **2**·2THF

Atom	*x*	*y*	*z*
Hg(1)	0.39319(3)	0.22059(4)	0.06741(5)
Ru(1)	0.41967(5)	0.36697(7)	−0.0030(1)
Ru(2)	0.40827(5)	0.24689(7)	−0.1640(1)
Ru(3)	0.35756(5)	0.38494(7)	−0.2233(1)
Ru(51)	0.40449(5)	0.07934(7)	0.1826(1)
Ru(52)	0.34689(5)	0.19929(7)	0.2693(1)
Ru(53)	0.30334(6)	0.05524(8)	0.2559(1)
0(1)	0.4376(5)	0.5324(7)	−0.040(1)
0(2)	0.5087(5)	0.3501(8)	0.214(1)
0(3)	0.3271(5)	0.4114(8)	0.124(1)
0(4)	0.4860(6)	0.1104(8)	−0.110(1)
0(5)	0.3031(6)	0.1508(8)	−0.216(1)
0(6)	0.4097(5)	0.2545(7)	−0.419(1)
0(7)	0.2953(7)	0.3701(9)	−0.472(1)
0(8)	0.2611(5)	0.3147(8)	−0.134(1)
0(9)	0.3078(7)	0.5394(9)	−0.193(2)
0(51)	0.4200(6)	−0.0795(8)	0.275(1)
0(52)	0.5264(6)	0.0990(9)	0.156(1)
0(53)	0.3675(7)	0.0203(8)	−0.062(1)
0(54)	0.4067(6)	0.3457(8)	0.349(1)
0(55)	0.2452(5)	0.2664(9)	0.112(1)
0(56)	0.2849(6)	0.2012(8)	0.471(1)
0(57)	0.1907(6)	0.090(1)	0.317(2)
0(58)	0.2504(7)	0.088(1)	0.010(1)
0(59)	0.2808(7)	−0.1122(8)	0.212(1)
N(1)	0.4722(5)	0.3285(6)	−0.1164(9)
N(2)	0.4402(5)	0.4168(7)	−0.263(1)
N(51)	0.4135(5)	0.1305(8)	0.349(1)
N(52)	0.3586(5)	0.0469(7)	0.430(1)
C(1)	0.4303(7)	0.470(1)	−0.025(1)
C(2)	0.4765(7)	0.3507(9)	0.133(1)
C(3)	0.3623(7)	0.3922(8)	0.077(1)
C(4)	0.4553(7)	0.162(1)	−0.123(1)
C(5)	0.3447(7)	0.185(1)	−0.196(2)
C(6)	0.4072(7)	0.255(1)	−0.321(1)
C(7)	0.3213(7)	0.374(1)	−0.383(1)
C(8)	0.2993(7)	0.3407(9)	−0.162(1)
C(9)	0.3286(7)	0.485(1)	−0.209(1)
C(10)	0.4843(7)	0.3801(9)	−0.199(1)
C(11)	0.5396(7)	0.394(1)	−0.208(1)
C(12)	0.5495(7)	0.451(1)	−0.282(2)
C(13)	0.5048(8)	0.487(1)	−0.348(1)
C(14)	0.4514(8)	0.470(1)	−0.336(1)
C(15)	0.4040(9)	0.512(1)	−0.409(2)
C(51)	0.4114(7)	−0.018(1)	0.241(1)
C(52)	0.4794(8)	0.0944(9)	0.163(1)
C(53)	0.3829(7)	0.044(1)	0.033(2)
C(54)	0.3839(6)	0.2929(9)	0.311(1)
C(55)	0.2839(8)	0.244(1)	0.169(1)
C(56)	0.3094(7)	0.1972(9)	0.391(2)
C(57)	0.2320(8)	0.076(1)	0.301(2)
C(58)	0.2721(9)	0.077(1)	0.105(2)

Table 5 (continued)

Atom	*x*	*y*	*z*
C(59)	0.2909(8)	−0.051(1)	0.231(2)
C(60)	0.4065(6)	0.0849(8)	0.440(1)
C(61)	0.4468(7)	0.0797(9)	0.540(1)
C(62)	0.4365(8)	0.0381(9)	0.633(1)
C(63)	0.3845(9)	0.002(1)	0.624(1)
C(64)	0.3448(8)	0.0087(9)	0.522(2)
C(65)	0.2906(9)	−0.035(1)	0.514(2)
O(10)	0.4163(7)	−0.264(1)	1.001(1)
C(16)	0.389(2)	−0.204(2)	1.047(4)
C(17)	0.342(2)	−0.187(2)	0.971(6)
C(18)	0.336(1)	−0.244(4)	0.884(3)
C(19)	0.380(1)	−0.290(2)	0.910(3)
O(11)	0.4758(7)	−0.2167(9)	0.557(2)
C(20)	0.429(1)	−0.197(2)	0.596(3)
C(21)	0.383(1)	−0.235(3)	0.534(4)
C(22)	0.400(1)	−0.272(2)	0.445(3)
C(23)	0.462(1)	−0.270(2)	0.473(4)

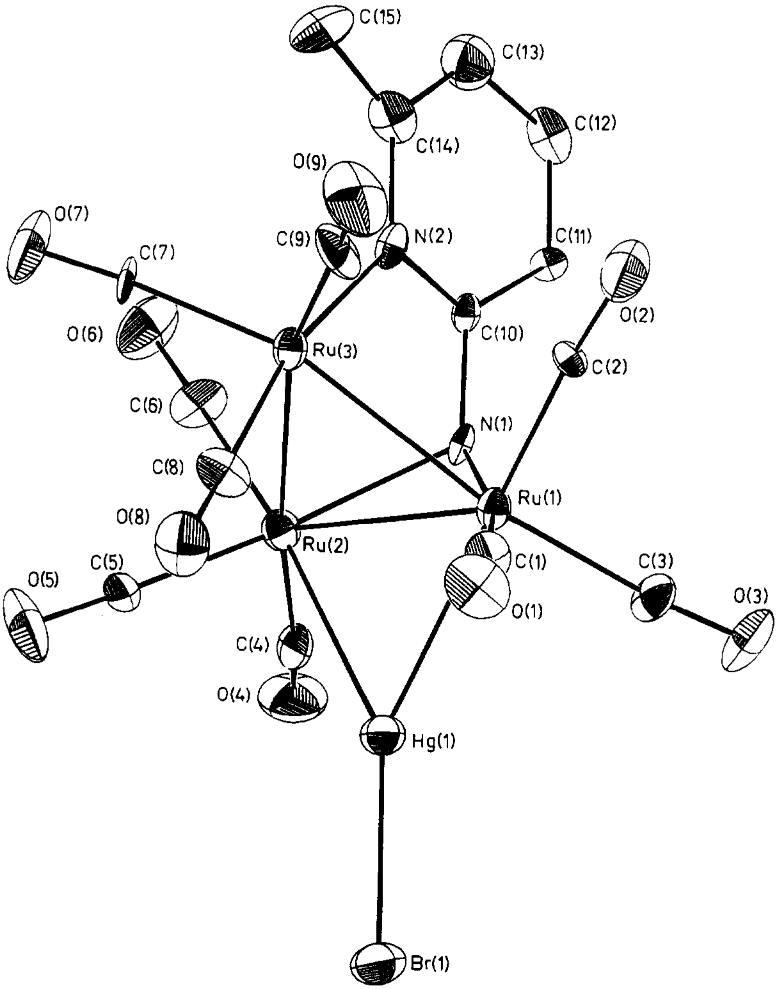


Fig. 3. Molecular structure of [$Ru_3(\mu\text{-HgBr})(\mu_3\text{-ampy})(CO)_9$] (**4**).

Table 6

Fractional atomic coordinates for compound **4**

Atom	x	y	z
Hg(1)	0.1137(2)	0.9818(1)	0.61483(8)
Br(1)	0.2965(5)	0.7613(4)	0.5271(2)
Ru(1)	0.0610(3)	1.2848(2)	0.6566(1)
Ru(2)	−0.1612(3)	1.0909(2)	0.7365(1)
Ru(3)	−0.0463(3)	1.2855(2)	0.8315(1)
N(1)	−0.197(3)	1.305(2)	0.675(1)
N(2)	−0.262(3)	1.447(2)	0.801(1)
O(1)	0.425(3)	1.222(3)	0.672(2)
O(2)	0.046(3)	1.616(3)	0.698(2)
O(3)	0.133(3)	1.348(3)	0.464(1)
O(4)	−0.339(4)	0.921(3)	0.629(2)
O(5)	−0.038(4)	0.818(3)	0.845(2)
O(6)	−0.463(3)	1.171(3)	0.871(2)
O(7)	−0.191(4)	1.184(4)	1.006(2)
O(8)	0.251(3)	1.034(3)	0.832(2)
O(9)	0.152(5)	1.497(3)	0.891(2)
C(1)	0.290(4)	1.249(3)	0.664(2)
C(2)	0.046(3)	1.488(2)	0.685(1)
C(3)	0.108(4)	1.318(4)	0.534(2)
C(4)	−0.255(6)	0.979(4)	0.662(2)
C(5)	−0.086(5)	0.918(3)	0.803(2)
C(6)	−0.349(3)	1.141(4)	0.820(2)
C(7)	−0149(4)	1.226(3)	0.942(2)
C(8)	0.132(4)	1.126(3)	0.830(2)
C(9)	0.071(4)	1.426(3)	0.866(2)
C(10)	−0.299(3)	1.433(2)	0.724(1)
C(11)	−0.425(2)	1.532(2)	0.687(1)
C(12)	−0.517(4)	1.654(3)	0.738(2)
C(13)	−0.485(5)	1.670(4)	0.821(3)
C(14)	−0.358(4)	1.569(3)	0.851(2)
C(15)	−0.324(5)	1.606(4)	0.935(2)

Hydrogen atoms were geometrically positioned on their parent atoms and were given an overall isotropic thermal parameter. No secondary extinction corrections were necessary. Scattering factors were corrected for anomalous dispersion. The weighting schemes were of the Chebyshev type [18]. The highest peaks in the last difference maps were in the vicinity of the Hg atoms. All calculations were carried out using the CRYSTALS package [17]. ORTEP diagrams (30% electron density vibration ellipsoids) of both compounds are depicted in Figs. 1 and 3. Atomic coordinates for the non-hydrogen atoms are given in Tables 5 and 6. Tables of H-atom coordinates, thermal parameters, a complete list of bond lengths and angles, and a list of structure factors are available from the authors.

Acknowledgments

We thank the CICYT (Spain) and the CNRS (France) for financial support and the FICYT (Spain) for a fellowship (to A.L.).

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