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Mercury-bridged transition-metal clusters. Synthesis of pentanuclear Ru_3HgM (M = Mo, W, or Co) clusters and X-ray structure of $[\{Ru_3(\mu_3,\eta^2\text{-ampy})(CO)_9\}(\mu_3\text{-Hg})Co(CO)_4]$ (Hampy = 2-amino-6-methylpyridine)

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Abstract

Redistribution reactions of the compound $[Ru_3(\mu\text{-HgCl})(\mu_3,\eta^2\text{-ampy})(CO)_9]$ (1) (Hampy = 2-amino-6-methylpyridine) with the metal–metal bonded transition-metal dimers $[M_2Cp_2(CO)_6]$ (M = Mo or W) and $[Co_2(CO)_8]$ give a separable mixture of the mixed-metal clusters $[\{Ru_3(\mu_3,\eta^2\text{-ampy})(CO)_9\}(\mu_3\text{-Hg})ML_n]$ ($ML_n = MoCp(CO)_3$ (2), $WCp(CO)_3$ (3), $Co(CO)_4$ (4)) and the corresponding chloro complexes $[MClL_n]$. The compounds **2–4** contain an $Hg\text{-}ML_n$ fragment spanning the same Ru–Ru edge as the amido moiety of the ampy ligand, as has been determined by ^{13}C NMR spectroscopy and, in the case of complex **4**, by an X-ray diffraction study. Crystal data for **4**: triclinic, space group $P\bar{1}$, $a = 9.598(3)$, $b = 11.817(3)$, $c = 12.835(6)$ Å, $\alpha = 76.40(3)$, $\beta = 75.34(4)$, $\gamma = 83.34(3)°$, $V = 1366(1)$ Å^3, $Z = 2$; $R = 0.0359$, $R_w = 0.0362$ for 3508 observed reflections and 372 variables.

Introduction

The number of compounds in which a mercury atom bridges two different metallic fragments has increased considerably in the last decade [1–10]. Three synthetic methods predominate in the preparations of this class of compound: (a) the reaction of a neutral complex containing a mercury halide moiety with an electron-rich anionic compound [1–8], as shown in eqs. 1 and 2, (b) the redistribu-

$$[Ru_3(\mu\text{-HgI})(\mu_3,\eta^2\text{-}C_2{}^tBu)(CO)_9] + [MoCp(CO)_3]^- \longrightarrow$$
$$[\{Ru_3(\mu_3,\eta^2\text{-}C_2{}^tBu)(CO)_9\}(\mu_3\text{-Hg})MoCp(CO)_3] + I^- \quad (1)$$

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$$[Fe_2(CO)_8]^{2-} + [Mo(HgCl)Cp(CO)_3] \longrightarrow$$
$$[\{Fe_2(CO)_8\}(\mu_3\text{-}Hg)MoCp(CO)_3]^- + Cl^- \quad (2)$$

tion reaction of two symmetric complexes containing bridging mercury atoms to give an asymmetric derivative [9] (eq. 3), and (c) the insertion of a metal fragment into the R–Hg bond of a transition-metal complex containing an R–Hg moiety [10] (eq. 4).

$$[\{Pt(C_6Cl_5)(PPh_3)_2\}_2(\mu\text{-}Hg)] + [\{FeCp(CO)_2\}_2(\mu\text{-}Hg)] \longrightarrow$$
$$2[(C_6Cl_5)(PPh_3)_2Pt(\mu\text{-}Hg)FeCp(CO)_2] \quad (3)$$

$$[R\text{-}HgMoCp(CO)_3] + [Pt(C_2H_4)(PPh_3)_2] \longrightarrow$$
$$[(Ph_3P)_2(R)Pt(\mu\text{-}Hg)MoCp(CO)_3] + C_2H_4 \quad (4)$$

It is generally assumed that most of the two-centre two-electron transition-metal mercury complexes redistribute to asymmetric species [9,11–13] (eq. 3), whereas complexes containing three-centre two-electron transition-metal mercury bonds redistribute to symmetric compounds, particularly at high temperatures [4,8,14–16] (eq. 5). These processes are believed to proceed through a bimolecular, four-centre, interchange mechanism [17].

$$2[\{Ru_3(\mu_3,\eta^2\text{-}C_2{}^tBu)(CO)_9\}(\mu_3\text{-}Hg)MoCp(CO)_3] \longrightarrow$$
$$[\{Ru_3(\mu_3,\eta^2\text{-}C_2{}^tBu)(CO)_9\}_2(\mu_4\text{-}Hg)] + [\{MoCp(CO)_3\}_2(\mu\text{-}Hg)] \quad (5)$$

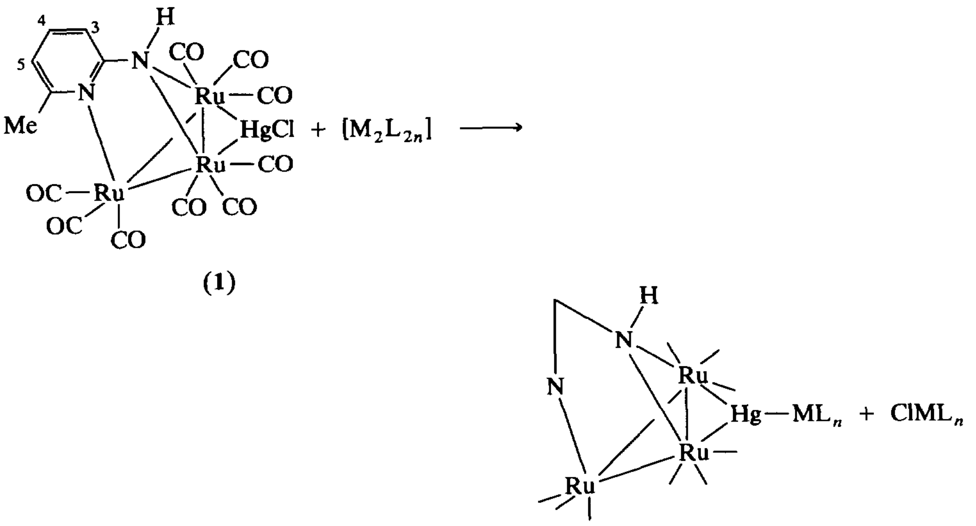
In previous papers we have described the addition of mercury electrophiles to bi- [18,19] and tri-nuclear [16] ruthenium carbonyl complexes containing metal–metal bonds. We now report the synthesis of some mixed-metal clusters, such as $[\{Ru_3(\mu_3,\eta^2\text{-ampy})(CO)_9\}(\mu_3\text{-Hg})ML_n]$ (ML_n = $MoCp(CO)_3$ (**2**), $WCp(CO)_3$ (**3**), or $Co(CO)_4$ (**4**); Hampy = 2-amino-6-methylpyridine), through redistribution reactions of a triruthenium carbonyl cluster containing an HgCl moiety, namely the compound $[Ru_3(\mu\text{-HgCl})(\mu_3,\eta^2\text{-ampy})(CO)_9]$ (**1**) [16], with metal–metal bonded transition-metal dimers, namely $[M_2Cp_2(CO)_6]$ (M = Mo or W) or $[Co_2(CO)_8]$. The chloro-complexes $[MClL_n]$ are the by-products of these reactions.

Results and discussion

Synthetic aspects

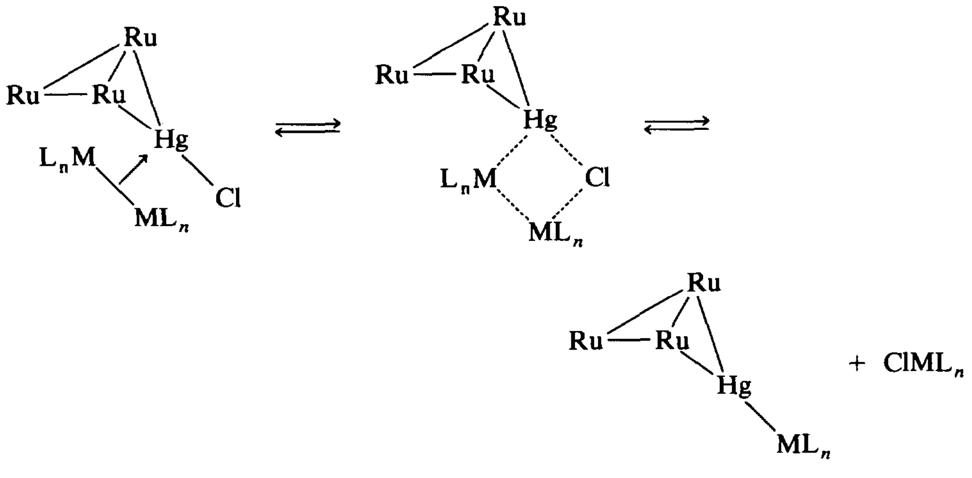
IR monitoring of the reaction of complex **1** with an equimolecular amount of $[Mo_2Cp_2(CO)_6]$ in refluxing THF indicated that when all of complex **1** had been consumed, some $[Mo_2Cp_2(CO)_6]$ still remained in solution. Chromatography of this solution gave four compounds, the known complexes $[Mo_2Cp_2(CO)_6]$ [20], $[\{Ru_3(\mu_3,\eta^2\text{-ampy})(CO)_9\}_2(\mu_4\text{-Hg})]$ [16] and $[MoClCp(CO)_3]$ [21], and the new species $[\{Ru_3(\mu_3,\eta^2\text{-ampy})(CO)_9\}(\mu_3\text{-Hg})MoCp(CO)_3]$ (**2**). No reaction was observed at room temperature.

These results can be explained assuming that two different processes are taking place at the same time. One process would be the symmetrization reaction of complex **1** to give $[\{Ru_3(\mu_3,\eta^2\text{-ampy})(CO)_9\}_2(\mu_4\text{-Hg})]$ and $HgCl_2$, as reported previously [16], while the other process would involve the redistribution reaction of



	ML_n
2	$MoCp(CO)_3$
3	$WCp(CO)_3$
4	$Co(CO)_4$

Scheme 1



Scheme 2.

complex **1** with [$Mo_2Cp_2(CO)_6$] to give a mixture of complex **2** and [$MoClCp(CO)_3$] (Scheme 1). All this would explain the presence of [{$Ru_3(\mu_3,\eta^2$-ampy)$(CO)_9\}_2(\mu_4$-Hg)] and unreacted [$Mo_2Cp_2(CO)_6$] in the reaction mixture. We subsequently proved that the last two compounds do not react with each other.

A mechanism which would account for the nature of the products of the reaction of complex **1** with [$Mo_2Cp_2(CO)_6$] is outlined in Scheme 2. The tricoordinated mercury atom of complex **1** does have empty orbitals able to accept electron density from the filled orbitals responsible for the metal–metal bond of $[Mo_2Cp_2(CO)_6]$. This interaction would enhance the electrophilic character of the molybdenum atoms, making them susceptible to interact with the chlorine atom of complex **1**. This would end, through a four-centre transition state, in the products **2** and $[MoClCp(CO)_3]$. This mechanism agrees with those proposed previously for other redistribution reactions involving mercury compounds [7,17].

The thermal reaction of complex **1** with $[W_2Cp_2(CO)_6]$ gave a result completely analogous to that described above for the molybdenum derivative. However, treatment of complex **1** with an equimolecular amount of $[Co_2(CO)_8]$ in refluxing THF gave, within a few minutes, the compound $[\{Ru_3(\mu_3,\eta^2\text{-ampy})(CO)_9\}(\mu_3\text{-Hg})Co(CO)_4]$ (**4**) and an off-white, insoluble material; no $[\{Ru_3(\mu_3,\eta^2\text{-ampy})(CO)_9\}_2(\mu_4\text{-Hg})]$ was detected by thin layer chromatography. We think that the reaction with $[Co_2(CO)_8]$ follows the same mechanism as that described above for the molybdenum derivative and that, as no $[\{Ru_3(\mu_3,\eta^2\text{-ampy})(CO)_9\}_2(\mu_4\text{-Hg})]$ was observed, the reaction of **1** with $[Co_2(CO)_8]$ must be much faster than the symmetrization reaction of complex **1** to give $[\{Ru_3(\mu_3,\eta^2\text{-ampy})(CO)_9\}_2(\mu_4\text{-Hg})]$ and $HgCl_2$. The off-white solid was very insoluble in all solvents and therefore it could not be completely characterized; since its IR spectrum confirmed the presence of CO and the absence of the ampy, we think that this material is polymeric, probably corresponding to the formula $[\{CoCl(CO)_x\}_n]$ ($x \leq 3$); in fact, the compound $[CoCl(CO)_4]$, which is the expected reaction product, has never been isolated owing to its high instability [22].

It is known that the symmetrization reaction of complex **1** to give $[\{Ru_3(\mu_3,\eta^2\text{-ampy})(CO)_9\}_2(\mu_4\text{-Hg})]$ and $HgCl_2$ is much slower under photochemical than under thermal conditions [16]. Accordingly, higher yields of compounds **2** and **3** were obtained by treating the compounds $[M_2Cp_2(CO)_6]$ ($M = Mo$ or W) with an equimolecular amount of complex **1** at 10°C under UV irradiation. However, although these reactions should follow a different mechanism from that proposed in Scheme 2 (it is known that the molybdenum and tungsten dimers form radicals under UV irradiation [23]), the results, apart from the yields, were similar to those obtained by the thermal method. These facts suggest that radical processes in the thermal reactions cannot be completely ruled out.

Attempts to extend the observations discussed so far to reactions of complex **1** with other metal–metal bonded carbonyl compounds were also carried out. However, both the thermal and the photochemical reactions of complex **1** with equimolecular amounts of $[Fe_2Cp_2(CO)_4]$, $[Fe_2(CO)_9]$ or $[Mn_2(CO)_{10}]$ proved to be extremely slow, the compound $[\{Ru_3(\mu_3,\eta^2\text{-ampy})(CO)_9\}_2(\mu_4\text{-Hg})]$ being the major product of these reactions.

The only previous description of a reaction of a metal cluster containing an HgX (X = halogen) moiety with a neutral carbonyl compound having metal–metal bonds is the reaction of $[Ru_3(\mu\text{-HgI})(\mu_3,\eta^2\text{-}C_2{}^tBu)(CO)_9]$ with $[Ru_3(CO)_{12}]$, which gives $[\{Ru_3(\mu_3,\eta^2\text{-}C_2{}^tBu)(CO)_9\}_2(\mu_3\text{-Hg})_2Ru(CO)_4]$ as the major product [8].

Structural characterization of compounds 2–4.

The incorporation of the ML_n fragments into the clusters was confirmed by IR and NMR spectroscopies. Their ^1H NMR spectra (Table 1) are closely related, suggesting analogous structures. Their $^{13}C\{^1H\}$ NMR spectra were most useful in

Table 1

^{1}H NMR and IR spectroscopic data

Compound	$\delta(^1H)$ [a]						$\nu(CO)$ [b]
	H^3	H^4	H^5	NH	Me	Cp	
2	7.01 (d)	7.58 (t)	6.76 (d)	2.87 (s,br)	2.69 (s)	5.53 (s)	2065w, 2033vs, 2017s, 1981s, 1970sh, 1998w, 1975m
3	7.01 (d)	7.58 (t)	6.76 (d)	2.81 (s,br)	2.69 (s)	5.64 (s)	2065w, 2033vs, 2017s, 1982m, 1962m, 1891w, 1870m
4	6.84 (d)	7.41 (t)	6.43 (d)	4.57 (s,br)	2.69 (s)		2077w, 2058m, 2040vs, 2024s, 1994s, 1985sh, 1969sh

[a] Spectra recorded in acetone-d_6 (**2** and **3**) or $CDCl_3$ (**4**) (300 MHz, 25°C); chemical shifts are refered to internal tetramethylsilane; coupling constants for H^3, H^4 and H^5 are approx. 7.4 Hz. [b] Recorded in THF.

Table 2

$^{13}C\{^1H\}$ NMR data [a]

Compound	Ru–*C*O	M–*C*O	ampy	Cp
2	202.2, 201.7, 197.0, 189.7, 177.4	228.4, 203.2	160.0, 138.3, 128.9, 119.9, 108.2, 29.7	87.7
3	203.6, 203.3, 198.2, 190.8, 178.6	218.4, 204.6	161.2, 139.4, 130.0, 121.1, 109.3, 29.8	87.5
4	201.4, 200.2, 199.3, 197.3, 190.0	207.5 (br)	177.8, 160.9, 139.2, 121.0, 108.9, 29.6	

[a] Spectra recorded in CD_2Cl_2 (**2** and **3**) or $CDCl_3$ (**4**) (75 MHz, 25°C), all resonances are singlets, chemical shifts (δ, ppm) are refered to internal tetramethylsilane.

assigning a structure to these compounds, since they show only five resonances for the ruthenium-bonded carbonyls, indicating that the complexes have C_s symmetry, with the mirror plane containing the ampy ligand; therefore, the $HgML_n$ fragments should span the amido-bridged Ru–Ru edge (Table 2).

The structures proposed on the basis of NMR data (Scheme 1) were confirmed by an X-ray diffraction structure determination of complex 4 (Fig. 1). The atomic coordinates and a selection of bond distances and angles are given in Tables 3 and 4. The cluster consists of an isosceles triangle of ruthenium atoms with the longest edge spanned by a mercury atom which is also bonded to a $Co(CO)_4$ moiety. The μ_3,η^2-ampy ligand occupies three axial coordination sites, linked to the Ru(3) atom through the pyridine nitrogen N(2) and to the other two Ru atoms through the exocyclic nitrogen N(1). The plane containing Ru(1)–N(1)–Ru(2) and that of the pyridine ring is nearly perpendicular to the Ru_3 plane (dihedral angles (98.5(2) and 89.6(2)°, respectively). The mercury atom displays an approximately triangular coordination, surrounded by the Ru(1), Ru(2) and the cobalt atoms. The plane Ru(1)–Ru(2)–Hg(1) and that of the Ru_3 triangle form a dihedral angle of 121.22(7)°. The valence shell of the Ru_3 cluster is completed by nine carbonyl ligands, three in axial positions (*trans* to the nitrogen atoms of the ampy ligand) and six in equatorial positions (four *trans* to ruthenium atoms and two *trans* to the mercury atom). The coordination around the cobalt atom is approximately trigonal bipyramidal with one axial site occupied by the mercury atom and the other four sites occupied by carbonyl ligands. Overall, this structure has many aspects in common with those of the clusters $[Ru_3(\mu\text{-}HgBr)(\mu_3,\eta^2\text{-ampy})(CO)_9]$ [16] and $[\{Os_3(\mu_3,\eta^2\text{-}C_2{}^tBu)(CO)_9\}(\mu_3\text{-}Hg)Co(CO)_4]$ [6].

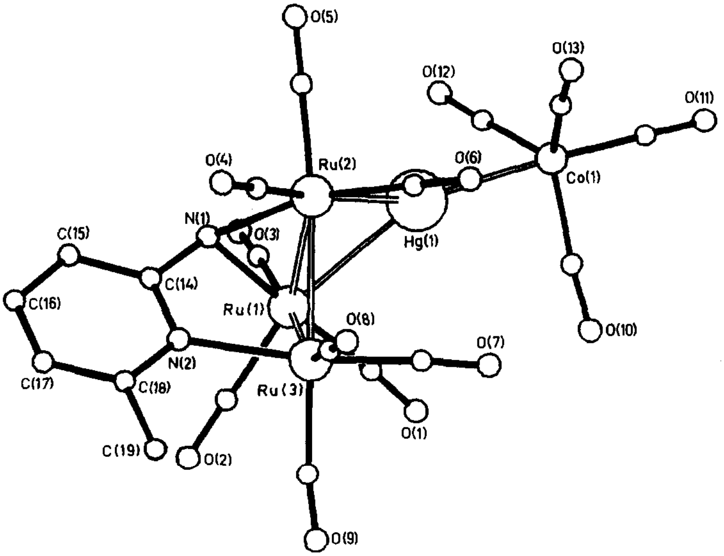


Fig. 1. Molecular structure of complex 4. The numbers of the carbonyl carbon atoms have been omitted for clarity, but are the same as those of the corresponding oxygen atoms.

Table 3

Fractional atomic coordinates for compound 4

Atom	*x*	*y*	*z*
Hg1	0.23332(4)	0.07316(3)	0.19282(3)
Ru1	0.32444(7)	0.29804(6)	0.12403(5)
Ru2	0.39469(7)	0.13985(6)	0.31600(6)
Ru3	0.24340(7)	0.35108(6)	0.33027(6)
Co1	0.0697(1)	−0.0748(1)	0.1738(1)
N1	0.5135(7)	0.2649(6)	0.1863(5)
N2	0.4608(7)	0.4161(6)	0.2846(6)
C1	0.143(1)	0.3218(8)	0.0879(7)
O1	0.0353(7)	0.3433(7)	0.0635(7)
C2	0.3318(9)	0.4600(8)	0.0916(8)
O2	0.3343(8)	0.5620(6)	0.0660(6)
C3	0.419(1)	0.2542(8)	−0.0151(8)
O3	0.4720(9)	0.2362(8)	−0.1007(6)
C4	0.485(1)	0.1685(8)	0.4206(8)
O4	0.5429(9)	0.1861(8)	0.4825(7)
C5	0.517(1)	0.0025(9)	0.2818(8)
O5	0.5893(9)	−0.0792(7)	0.2712(8)
C6	0.252(1)	0.0558(8)	0.4301(8)
O6	0.1730(9)	0.0090(7)	0.5029(6)
C7	0.075(1)	0.2742(8)	0.3484(7)
O7	−0.0307(7)	0.2325(7)	0.3582(6)
C8	0.224(1)	0.325(1)	0.4879(9)
O8	0.2062(9)	0.3026(9)	0.5807(6)
C9	0.138(1)	0.4997(9)	0.303(1)
O9	0.063(1)	0.5794(8)	0.290(1)
C10	−0.060(1)	0.0465(9)	0.186(1)
O10	−0.1508(9)	0.1165(8)	0.1994(9)
C11	−0.049(1)	−0.1703(9)	0.1525(9)
O11	−0.124(1)	−0.2309(8)	0.1410(8)
C12	0.210(1)	−0.0762(9)	0.0531(9)
O12	0.300(1)	−0.0822(9)	−0.0233(7)
C13	0.108(1)	−0.1515(8)	0.3010(9)
O13	0.125(1)	−0.2034(7)	0.3844(7)
C14	0.5615(8)	0.3578(7)	0.2182(7)
C15	0.7059(9)	0.3867(8)	0.1797(8)
C16	0.746(1)	0.480(1)	0.210(1)
C17	0.645(1)	0.5396(9)	0.2782(9)
C18	0.503(1)	0.5070(8)	0.3143(8)
C19	0.392(1)	0.573(1)	0.387(1)

Experimental

Solvents were dried and distilled under dinitrogen prior to use. All manipulations, except thin layer chromatography (TLC), were carried out under dinitrogen, using standard Schlenk-vacuum line techniques. The compounds **1** [16], $[Mo_2Cp_2(CO)_6]$ [20] and $[W_2Cp_2(CO)_6]$ [20] were prepared as described previously; all other reagents were obtained from Aldrich and used as received. Chromatographies were performed using silica-gel on PET polyester plates (purchased from Aldrich). ^1H and ^{13}C NMR spectra were run on a Bruker AC-300 instrument. IR spectra were recorded on a Perkin–Elmer FT 1720-X spectrophotometer. The X-ray diffraction analysis was carried out on an Enraf–Nonius CAD4 single crystal diffractometer; all calculations were made on a MicroVAX 3400 computer at the Scientific Computer Centre of the University of Oviedo.

$[\{Ru_3(\mu_3,\eta^2\text{-}ampy)(CO)_9\}(\mu_3\text{-}Hg)MoCp(CO)_3]$ (2)

A solution of complex **1** (80 mg, 0.089 mmol) and $[Mo_2Cp_2(CO)_6]$ (43.7 mg, 0.089 mmol) in THF (10 ml) was heated at reflux temperature for 30 min. The solution was concentrated to approx. 1 ml and chromatographed on TLC plates. Elution with toluene/dichloromethane (1:1) gave four bands. Bands 1 (red), 3 (pink) and 4 (orange) were identified as $[Mo_2Cp_2(CO)_6]$, $[\{Ru_3(\mu_3,\eta^2\text{-}ampy)(CO)_9\}_2(\mu_4\text{-}Hg)]$ and $[MoClCp(CO)_3]$, respectively, by comparison of their R_f values with those of authentic samples. Band 2 (deep-orange) was extracted with THF, the solution evaporated to dryness, and the residue washed with hexane to give complex **2** as a red-orange solid (32 mg, 33%). When the initial solution, instead of being heated under reflux, was irradiated with UV light (mercury lamp) at 10°C for 20 min, the same four compounds were separated by TLC, with complex **2** isolated in 49% yield.

$[\{Ru_3(\mu_3,\eta^2\text{-}ampy)(CO)_9\}(\mu_3\text{-}Hg)WCp(CO)_3]$ (3)

A solution of complex **1** (80 mg, 0.089 mmol) and $[W_2Cp_2(CO)_6]$ (59.4 mg, 0.089 mmol) in THF (10 ml) was heated at reflux temperature for 30 min. The solution was concentrated to approx. 1 ml and chromatographed on TLC plates. Elution with toluene/dichloromethane (2:1) gave four bands. Bands 1 (red-violet), 3 (pink) and 4 (orange) were identified as $[W_2Cp_2(CO)_6]$, $[\{Ru_3(\mu_3,\eta^2\text{-}ampy)(CO)_9\}_2(\mu_4\text{-}Hg)]$ and $[WClCp(CO)_3]$, respectively, by comparison of their R_f values with those of authentic samples. Band 2 (orange) was extracted with THF, the solution evaporated to dryness, and the residue washed with hexane to give complex **3** as an orange solid (31 mg, 29%). When the initial solution, instead of being heated under reflux, was irradiated with UV light (mercury lamp) at 10°C for 20 min, the same four compounds were separated by TLC, with complex **3** isolated in 51% yield.

Table 4

Selected bond distances (Å) and angles (°) in complex **4**

Bond distances			
Hg(1)–Ru(1)	2.766(1)	Hg(1)–Ru(2)	2.762(1)
Hg(1)–Co(1)	2.571(1)	Ru(1)–Ru(2)	2.899(1)
Ru(1)–Ru(3)	2.762(1)	Ru(2)–Ru(3)	2.759(1)
Ru(1)–N(1)	2.123(7)	Ru(2)–N(1)	2.128(6)
Ru(3)–N(2)	2.197(6)		
Bond angles			
Ru(2)–Hg(1)–Ru(1)	63.30(1)	Co(1)–Hg(1)–Ru(1)	146.90(1)
Co(1)–Hg(1)–Ru(2)	148.80(1)	Ru(2)–Ru(1)–Hg(1)	58.30(1)
Ru(3)–Ru(1)–Hg(1)	95.70(1)	Ru(3)–Ru(2)–Hg(1)	95.80(1)
Ru(1)–Ru(2)–Hg(1)	58.40(1)	Ru(3)–Ru(1)–Ru(2)	58.30(1)
Ru(3)–Ru(2)–Ru(1)	58.40(1)	Ru(2)–Ru(3)–Ru(1)	63.30(1)
Ru(1)–N(1)–Ru(2)	86.0(2)		

Table 5

Crystallographic and refinement data for complex 4

Formula	$C_{19}H_7CoHgN_2O_{13}Ru_3$	FW	1034.00
Crystal system	Triclinic	Space group	$P\bar{1}$
a (Å)	9.598(3)	b (Å)	11.817(3)
c (Å)	12.835(6)	α (deg)	76.40(3)
β (deg)	75.34(4)	γ (deg)	83.34(3)
V (Å^3)	1366(1)	Z	2
$D_{\text{calc.}}$ (g/cm^3)	2.51	Crystal size (mm)	0.3×0.3×0.1
Radiation (λ, Å)	Mo-K_α (0.71073)	Monochromator	Graphite
Temperature (K)	293	μ(Mo-K_α) (cm^{-1})	78.45
F(000)	956	Scan method	$\omega-2\theta$
h; k; l range	±11; ±13; −12, 15	θ limits (deg)	0–25
Measured reflections	7726	Unique reflections	4758
R_{int}	0.034	Reflections with $I \geq 3\sigma(I)$	3508
No. of variables	372	R [a]	0.0359
R_w [b]	0.0362	Δ/σ	0.001
ρ, max, min (e/Å^3)	1.23, −1.05		

[a] $R = \Sigma \| F_o | - F_c \| / \Sigma | F_o |$. [b] $R_w = \Sigma w^{1/2} \| F_o | - F_c \| / \Sigma w^{1/2} | F_o |$, $w = 1/[\sigma^2(F_o) + 0.0004 F_o^2]$, $\sigma(F_o)$ from counting statistics.

$[\{Ru_3(\mu_3,\eta^2\text{-ampy})(CO)_9\}(\mu_3\text{-Hg})Co(CO)_4]$ (4)

A solution of complex 1 (80 mg, 0.089 mmol) and $[Co_2(CO)_8]$ (30.5 mg, 0.089 mmol) in THF (15 ml) was heated at reflux temperature for 10 min. The solvent was removed under reduced pressure and the residue extracted with diethyl ether to give an off-white solid and an orange solution. The solution was evaporated to dryness, affording complex **4** as orange crystals (83 mg, 90%).

Crystal structure determination of compound 4

A red crystal of compound **4**, grown at −20°C in the interface of a layer of n-pentane on a solution of the complex in diethyl ether, was used for the X-ray analysis. Selected crystallographic and refinement data are collected in Table 5. Unit cell dimensions were determined from the angular settings of 25 reflections with $15 < \theta < 18°$. The space group was determined from structure determination. The intensity was checked by monitoring three standard reflections every 60 min. Profile analysis was performed on all reflections [24]. Lorentz and polarization corrections were applied and data reduced to $|F_o|$ values. The structure was solved by Patterson interpretation using SHELX86 [25]. Isotropic least-squares refinement, using a version [26a] of SHELX [26b], made by one of the authors, which is able to handle any number of atoms and parameters, converged to $R = 0.14$. An empirical absorption correction [27] (max and min correction factors 1.51 and 0.70) lowered this parameter to $R = 0.06$. Anisotropic refinements followed by a difference Fourier synthesis allowed the location of all the hydrogen atoms. Positional and anisotropic thermal parameters of the non-hydrogen atoms were refined. All the hydrogen atoms were isotropically refined, riding at distances of 1.08 Å on their parent atoms. Atomic scattering factors were taken from the *International Tables for X-Ray Crystallography* [28]. Geometrical calculations were made with PARST [29]. Tables of hydrogen atom coordinates, full lists of bond lengths and angles, and structure factors are available from the authors.

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