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Synthesis of Novel Mixed-metal Clusters of Mercury and Osmium; Crystal and Molecular Structures of *cis*-$[\mathrm{Os(CO)_4\{(\mu\text{-}Hg)Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}CH{=}CHPh)\}_2}]$ and $[\mathrm{\{Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}CH{=}CHPh)\}_2(\mu_4\text{-}Hg)}]$

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Reaction of $[\mathrm{Os_3H_2(CO)_{10}}]$ with $\mathrm{Hg(C{\equiv}CPh)_2}$ afforded the novel mixed-metal clusters *cis*-$[\mathrm{Os(CO)_4\{(\mu\text{-}Hg)Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}CH{=}CHPh)\}_2}]$ **1** and $[\mathrm{\{Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}CH{=}CHPh)\}_2(\mu_4\text{-}Hg)}]$ **2** in moderate yield, the crystal structures of which have been determined; **1** converts into **2** *via* Hg–Os bond cleavage under ambient conditions.

Organomercury fragments which readily attach to a variety of transition metals have been used as building blocks in heterometallic clusters as well as in the synthesis of high-nuclearity clusters.[1–6] Recently, with the help of the ^{13}C NMR technique, the fluxional behaviour of mercury-containing clusters in solution has been investigated extensively. One remarkable conclusion drawn from these studies is that a μ-Hg moiety has about the same mobility in these clusters as has a μ-hydride ligand.[7] Furthermore, the photochemical reactivity of some high-nuclearity clusters has also revealed that it is possible to open up new synthetic routes to chemical species and metal-framework structures which are inaccessible under thermal conditions.[8,9] Herein, we report some preliminary work on triosmium–mercury metal clusters containing a new mixed-metal framework.

We have found that treatment of the highly reactive cluster $[\mathrm{Os_3H_2(CO)_{10}}]$ with 1 equivalent of the organomercury species $\mathrm{Hg(C{\equiv}CPh)_2}$ at room temperature for 3 h afforded two new osmium–mercury clusters: red-orange *cis*-$[\mathrm{Os(CO)_4\{(\mu\text{-}Hg)Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}CH{=}CHPh)\}_2}]$ **1** and reddish violet $[\mathrm{\{Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}CH{=}CHPh)\}_2(\mu_4\text{-}Hg)}]$ **2** in 30 and 20% yield respectively. A small amount of the known non-mercury cluster $[\mathrm{Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^2\text{-}C{\equiv}CPh)}]$[10] (5%) and metallic mercury have also been isolated (confirmed by IR and ^{1}H NMR spectroscopy). Both clusters **1** and **2** were isolated as air-stable solids[†] resulting from Hg–C bond cleavage in $\mathrm{Hg(C{\equiv}CPh)_2}$. Compound **1** undergoes Hg–Os bond cleavage and is converted into **2** with extrusion of a $\mathrm{HgOs(CO)_4}$ fragment under ambient conditions over a period of 3 d (Scheme 1). However, the conversion rate can be much reduced by lowering the temperature to −20 °C. As shown by IR and ^{1}H NMR spectroscopy, both of the C≡C bonds of the ligand moieties have been partially hydrogenated to become C=C bonds by rearrangement of the two bridging hydrides of $[\mathrm{Os_3H_2(CO)_{10}}]$. To establish the geometries of **1** and **2**, their crystal structures have been determined.[‡]

The molecular structure of compound **1** is depicted in Fig. 1. The molecule possesses a C_2 idealized symmetry and comprises a central $\mathrm{Os(CO)_4}$ fragment with two *cis*-co-ordinated $\mathrm{(\mu\text{-}Hg)Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}CH{=}CHPh)}$ units. The central Hg(1)–Os(1) and Hg(1*)–Os(1) bond distances [2.683(1) Å] are significantly shorter than the two asymmetric mercury–osmium bonds, Hg(1)–Os(2) 2.856(1) Å and Hg(1)–Os(3) 2.803(1) Å. The Hg(1)–Os(1)–Hg(1*) angle [87.09(6)°] and the intramolecular Hg ··· Hg distance (3.70 Å) both indicate very weak interaction between the two *cis*-$\mathrm{(\mu\text{-}Hg)Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}CH{=}CHPh)}$ fragments. A similar observation was made in *cis*-$[\mathrm{Ru(CO)_4\{(\mu\text{-}Hg)Ru_3(CO)_9(\mu_3\text{-}C{\equiv}CCMe_3)\}_2}]$[12] (Hg–Ru–Hg 84°, Hg ··· Hg 3.55 Å). The geometry around the Hg(1) or Hg(1*) atoms is triangular, involving three osmium atoms. Atoms Os(1), Hg(1), Os(2) and Os(3) are almost coplanar (maximum deviation of 0.004 Å from their least-squares plane). Within the osmium triangle, the variation in metal–metal bond distances is significant: Os(2)–Os(3) 2.901(1), Os(2)–Os(4) 2.842(1) and Os(3)–Os(4) 2.927(1) Å. Also, the unsupported Os(3)–Os(4) bonding edge is substantially elongated being even longer than the mercury-bridged Os(2)–Os(3) edge. This elongation can be explained in terms of electronic effects since electron counting at each osmium atoms suggests that Os(3) is the most electron rich.

The molecular structure of compound **2** is depicted in Fig. 2. The complex consists of a C_2 axis passing through the central Hg atom with two butterfly osmium–mercury clusters sharing a common wingtip. In the butterflies the dihedral angles between the wings are 125.8 and 124.2° which are slightly larger than

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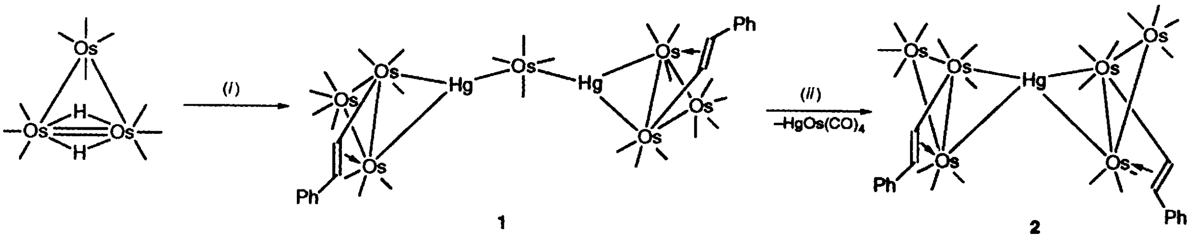
[†] Spectroscopic data: **1**, IR ν(CO) ($\mathrm{CH_2Cl_2}$) 2095s, 2072m, 2047vs, 2011s, 1997s, 1980m and 1950w cm^{-1}; ^{1}H NMR [$\mathrm{(CD_3)_2CO}$] δ 8.40 (d, 2 H, *J* = 14, vinyl H), 7.46 (m, 10 H, phenyl H) and 5.68 (d, 2 H, *J* = 14 Hz, vinyl H); FAB mass *m*/*z* 2612 (calc. 2612); **2**, IR ν(CO) 2104m, 2091s, 2050vs, 2008s and 1974m cm^{-1}; ^{1}H NMR δ 8.33 (d, *J* = 14, 2 H, vinyl H), 7.47 (m, 10 H, phenyl H) and 5.85 (d, 2 H, *J* = 14 Hz, vinyl H); FAB mass *m*/*z* 2108 (calc. 2108).

[‡] Crystal data: **1**, $\mathrm{C_{40}H_{14}Hg_2O_{24}Os_7{\cdot}2H_2O}$, M = 2647.14, monoclinic, space group $C2/c$ (no. 15), a = 13.612(1), b = 13.766(1), c = 29.734(3) Å, β = 93.25(2)°, U = 5562.9(7) Å^3, Z = 4, D_c = 3.162 g cm^{-3}, F(000) = 4632, Mo-Kα radiation (λ = 0.710 73 Å), μ(Mo-Kα) = 215.19 cm^{-1}, dimensions 0.24 × 0.42 × 0.44 mm, 2493 observed diffractometer data [$I > 3\sigma(I)$], ψ scan absorption correction, structure solved by direct methods (SIR 88)[11] and Fourier-difference techniques, refined by full-matrix least-squares analysis (Os and Hg anisotropic) to R = 0.041, R' = 0.051, $w = 4F_o^2/\sigma^2(F_o^2)$; **2**, $\mathrm{C_{36}H_{14}O_{20}Os_6Hg}$, M = 2108.28, triclinic space group $P\bar{1}$ (no. 2), a = 13.988(2), b = 16.864(7), c = 9.735(1) Å, α = 96.56(2), β = 105.93(1), γ = 92.21(2)°, U = 2188(1) Å^3, Z = 2, D_c = 3.201 g cm^{-3}, F(000) = 1852, Mo-Kα radiation (λ = 0.710 73 Å), μ(Mo-Kα) = 209.48 cm^{-1}, dimensions 0.28 × 0.33 × 0.41 mm, 4262 observed diffractometer data [$I > 3\sigma(I)$], ψ scan absorption correction, structure solved and refined as for **1** to R = 0.034, R' = 0.039. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



Scheme 1 (*i*) $Hg(C{\equiv}CPh)_2$, CH_2Cl_2, room temperature, 3 h; (*ii*) acetone, room temperature, 3 d

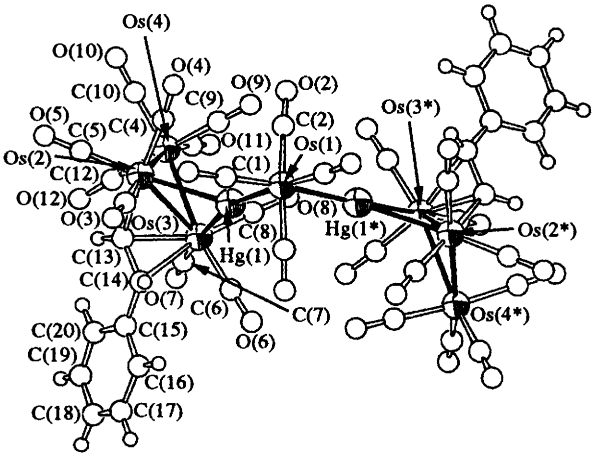


Fig. 1 Molecular structure of compound **1** showing the atomic numbering scheme. Selected bond distances (Å) and angles (°): Hg(1)–Os(1) 2.683(1), Hg(1)–Os(2) 2.856(1), Hg(1)–Os(3) 2.803(1), Os(2)–Os(3) 2.901(1), Os(2)–Os(4) 2.842(1), Os(3)–Os(4) 2.927(1), Os(2)–C(13) 2.09(2), Os(3)–C(13) 2.29(2), Os(3)–C(14) 2.41(2) and C(13)–C(14) 1.43(3); Hg(1)–Os(1)–Hg(1*) 87.09(6), Os(1)–Hg(1)–Os(2) 134.09(4), Os(1)–Hg(1)–Os(3) 164.23(5), Os(2)–Hg(1)–Os(3) 61.63(3), Os(2)–Os(3)–Os(4) 58.38(3), Os(2)–Os(4)–Os(3) 60.37(3), Os(3)–Os(2)–Os(4) 61.25(3), Hg(1)–Os(2)–Os(3) 58.27(30), Hg(1)–Os(3)–Os(2) 60.05(3), Os(3)–C(13)–C(14) 76(1) and Os(3)–C(14)–C(13) 67(1)

the average value in $[\{Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}S)\}_2(\mu_4\text{-}Hg)]$ (114°)[7] and similar to that in $[\{Ru_3(CO)_9(\mu_3\text{-}C{\equiv}CCMe_3)\}(\mu_4\text{-}Hg)]$ (125°).[13] The geometry around the central mercury atom is tetrahedrally distorted with a dihedral angle of 52.3° between the Hg–Os(2)–Os(3) and Hg–Os(4)–Os(5) planes. As in **1**, the unsupported Os(1)–Os(3) 2.922(1) Å and Os(4)–Os(6) 2.915(1) Å edges are substantially elongated.

The organic moieties CH=CHPh in compounds **1** and **2** are co-ordinated to the trinuclear framework in the usual μ-η^2 bonding mode. This is also reflected in the rather large differences in the chemical shifts (2.72 ppm) of the two *trans*-vinyl protons in their ^1H NMR spectra.[10] The *trans* configuration of the two vinyl protons is reflected in their coupling constants, ≈ 14 Hz. All the bond distances and angles in the ligand moieties in **1** and **2** are similar to those in $[Os_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}CH{=}CHEt)]$.[14] The formation of **1** is not well understood. The origin of the central $Os(CO)_4$ fragment most probably results from degradation of the $Os_3(CO)_{10}$ metal core of the starting cluster, $[Os_3H_2(CO)_{10}]$. The formation of **2** from **1**, which involves Hg–Os bond cleavage, extrusion of a $HgOs(CO)_4$ fragment and rotation of each Os_3 unit, is also not clear. Nevertheless, **1** represents a previously unobserved mercury–osmium mixed-metal framework. Further investigations concerning the above questions, the fluxional behaviour of **1** and **2** and the fate of the extruded $HgOs(CO)_4$ fragment are in progress.

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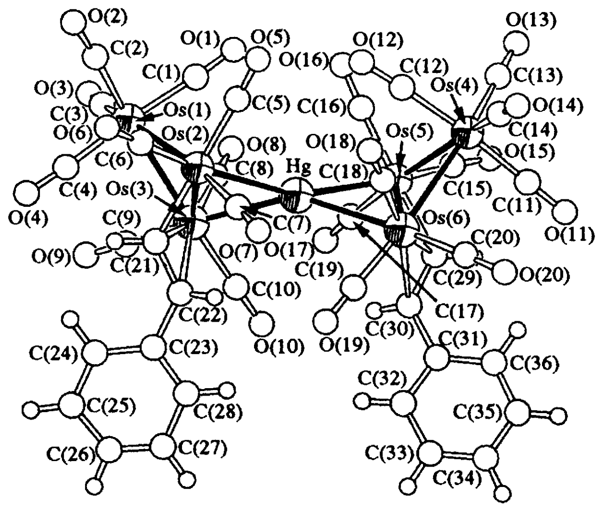

Fig. 2 Molecular structure of compound **2** showing the atomic numbering scheme. Selected bond distances (Å) and angles (°): Hg–Os(2) 2.895(1), Hg–Os(3) 2.823(1), Hg–Os(5) 2.887(1), Hg–Os(6) 2.824(1), Os(2)–Os(3) 2.888(1), Os(5)–Os(6) 2.89(1), Os(1)–Os(2) 2.866(1), Os(1)–Os(3) 2.922(1), Os(4)–Os(5) 2.860(1), Os(4)–Os(6) 2.915(1), Os(2)–C(21) 2.10(2), Os(3)–C(21) 2.28(2), Os(3)–C(22) 2.48(2), Os(5)–C(29) 2.10(2), Os(6)–C(29) 2.24(2) and Os(6)–C(30) 2.48(2); Os(2)–Hg–Os(3) 60.66(3), Os(5)–Hg–Os(6) 60.81(3), Hg–Os(2)–Os(3) 58.43(2), Hg–Os(3)–Os(2) 60.91(3), Hg–Os(5)–Os(6) 58.51(3), Hg–Os(6)–Os(5) 60.68(3), Os(1)–Os(2)–Os(3) 61.04(3), Os(1)–Os(3)–Os(2) 59.11(3), Os(2)–Os(1)–Os(3) 59.86(3), Os(4)–Os(5)–Os(6) 60.90(3), Os(4)–Os(6)–Os(5) 59.02(3) and Os(5)–Os(4)–Os(6) 60.08(3)

References

1 L. H. Gade, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 24.
2 Y. Yamamoto and H. Yamazaki, *Inorg. Chim. Acta*, 1994, **217**, 121.
3 B. F. G. Johnson, W. L. Kwik, J. Lewis, P. R. Raithby, V. P. Saharan and H. R. Powell, *J. Chem. Soc., Dalton Trans.*, 1991, 1037.
4 S. R. Drake, K. Henrick, B. F. G. Johnson, J. Lewis, M. McPartlin and J. Morris, *J. Chem. Soc., Chem. Commun.*, 1986, 928.
5 P. J. Bailey, B. F. G. Johnson, J. Lewis, M. McPartlin and H. R. Powell, *J. Chem. Soc., Chem. Commun.*, 1989, 1513.
6 L. H. Gade, B. F. G. Johnson, J. Lewis, M. McPartlin and H. R. Powell, *J. Chem. Soc., Chem. Commun.*, 1990, 110.
7 E. Rosenberg, K. I. Hardcastle, M. W. Day, R. Gobetto, S. Hajela and R. Muftikian, *Organometallics*, 1991, **10**, 203.
8 E. Charalambous, L. H. Gade, B. F. G. Johnson, T. Kotch, A. J. Lees, J. Lewis and M. McPartlin, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1137.
9 L. H. Gade, B. F. G. Johnson, J. Lewis, M. McPartlin, T. Kotch and A. J. Lees, *J. Am. Chem. Soc.*, 1991, **113**, 8698.
10 A. J. Deeming, S. Hasso and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1975, 1614.
11 M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna and D. Viterbo, *J. Appl. Crystallogr.*, 1989, **22**, 389.
12 E. Rosenberg, D. Ryckman, I.-N. Hsu and R. W. Gellert, *Inorg. Chem.*, 1986, **25**, 194.
13 S. Ermer, K. King, K. I. Hardcastle, E. Rosenberg, A. M. M. Lanfredi, A. Tiripicchio and M. T. Camellini, *Inorg. Chem.*, 1983, **22**, 1339.
14 J. J. Guy, B. E. Reichert and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1976, **32**, 3319.

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