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Preliminary communication

The reaction of  $\text{Hg}(\text{O}_2\text{CCF}_3)_2$  with  $[\text{Os}_6(\text{CO})_{18}]$ ; synthesis and crystal structures of two new products:  
 $[\text{HOs}_5\text{Hg}_2(\text{CO})_{15}(\text{O}_2\text{CCF}_3)_3]$  and *cis*- $[\text{Os}_4(\text{CO})_{12}(\text{O}_2\text{CCF}_3)_2]$

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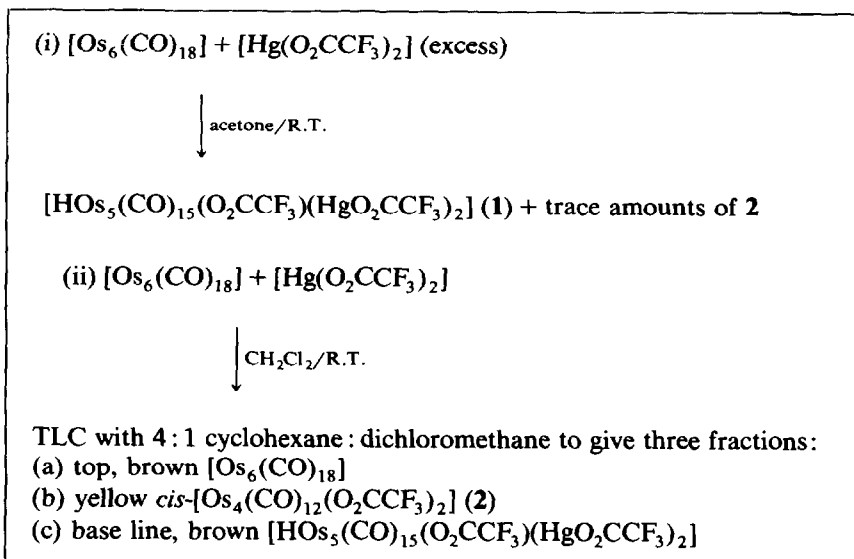
**Abstract**

Further studies of the reaction between mercury(II) trifluoroacetate and  $[\text{Os}_6(\text{CO})_{18}]$  have given the new heterometallic derivatives  $[\text{HOs}_5\text{Hg}_2(\text{CO})_{15}(\text{O}_2\text{CCF}_3)_3]$  (**1**) and *cis*- $[\text{Os}_4(\text{CO})_{12}(\text{O}_2\text{CCF}_3)_2]$  (**2**). Compound **2** differs from *trans*- $[\text{Os}_4(\text{CO})_{12}(\text{O}_2\text{CCF}_3)_2]$ , isolated earlier from this reaction, in having the two acetate ligands on the same side of the  $\text{Os}_4$  plane. Both compounds **1** and **2** have been fully characterised by single-crystal X-ray analysis.

Cluster compounds of the iron triad are of interest as models for a variety of metal-catalysed reactions of organic species; for example, the ruthenium and osmium carbonyl compounds containing carboxylate ligands,  $[\text{MH}(\text{O}_2\text{CCF}_3)(\text{CO})(\text{PPh}_3)_2]$  and  $[\text{M}(\text{O}_2\text{CCF}_3)(\text{CO})(\text{PPh}_3)_2]$  ( $\text{M} = \text{Ru}, \text{Os}$ ), have been used for the catalytic hydrogenation of diphenylacetylene [1]. Despite this, osmium clusters containing carboxylate ligands are rare. We recently reported the formation of the rhomboidal 'ladder' clusters  $[\text{Os}_6(\text{CO})_{18}(\text{O}_2\text{CCF}_3)_2]$  (**3**) and  $[\text{Os}_4(\text{CO})_{12}(\text{O}_2\text{CCF}_3)_2]$  (**4**) from the reaction of  $\text{Hg}(\text{O}_2\text{CCF}_3)_2$  with  $[\text{Os}_6(\text{CO})_{18}]$  [2].

Further investigation of the degradation reactions of  $[\text{Os}_6(\text{CO})_{18}]$  with  $\text{Hg}(\text{O}_2\text{CCF}_3)_2$  has led to the isolation of two new cluster compounds (Scheme 1). A small quantity of crystalline material was isolated and shown by X-ray crystallography \* to be  $[\text{HOs}_5\text{Hg}_2(\text{CO})_{15}(\text{O}_2\text{CCF}_3)_3]$  (Fig. 1). It has an  $\text{Os}_5$  core similar to the previously characterised dihydride monoanion  $[\text{H}_2\text{Os}_5(\text{CO})_{15}\text{I}]^-$  [3] with the two

\* Crystal data for  $1 \cdot 0.5(\text{CH}_2\text{Cl}_2)$ :  $\text{C}_{21}\text{HF}_3\text{Hg}_2\text{O}_{21}\text{Os}_5/0.5\text{CH}_2\text{Cl}_2$ ,  $M = 2154.86$ , triclinic, space group  $P\bar{1}$ ,  $a$  21.384(5),  $b$  9.732(2),  $c$  9.267(2) Å,  $\alpha$  101.23(2),  $\beta$  87.63 (1),  $\gamma$  101.61(2)°,  $U$  1852.91 Å<sup>3</sup>,  $F(000) = 1874$ ,  $\mu(\text{Mo-K}\alpha)$  254.60 cm<sup>-1</sup>,  $Z = 2$ ,  $D_c$  3.86 g cm<sup>-3</sup>. Data were collected in the  $\theta$ -range 3–25° with a scan width of 0.80°;  $R = 0.0626$  for 2805 reflections with  $I/\sigma(I) > 3.0$ . A table of atom coordinates and a complete list of bond lengths and angles has been deposited with the Cambridge Crystallographic Data Centre.



Scheme 1

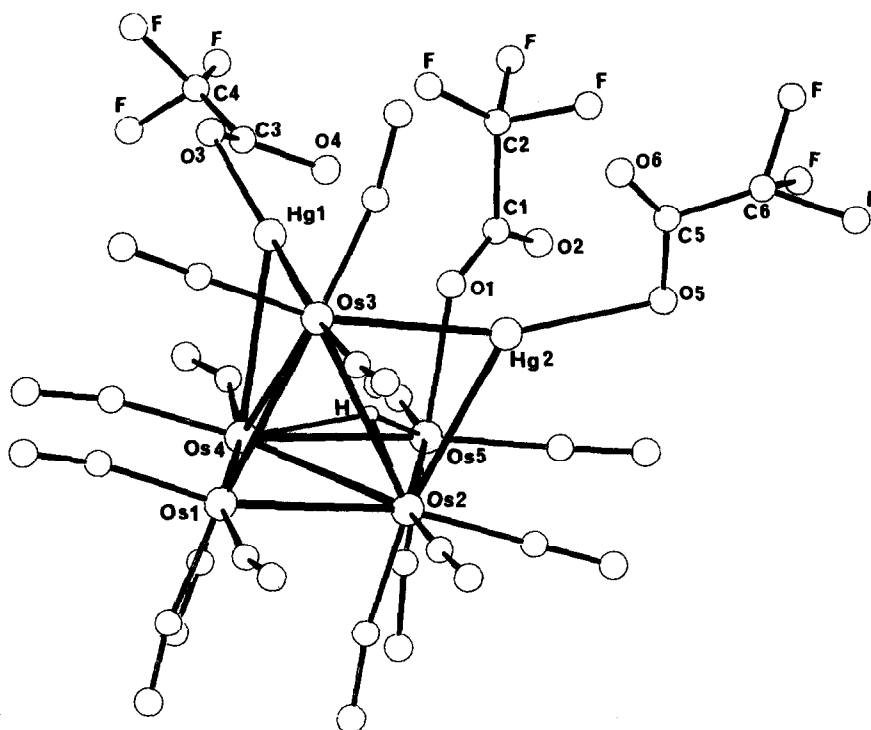


Fig. 1. Molecular structure of  $[\text{HOs}_5\text{Hg}_2(\text{CO})_{15}(\text{O}_2\text{CCF}_3)_3]$  (1); principal bond lengths ( $\text{\AA}$ ): Os(1)–Os(2) 2.859(3), Os(1)–Os(3) 2.851(3), Os(1)–Os(4) 2.800(2), Os(2)–Os(3) 3.086(3), Os(2)–Os(4) 2.814(3), Os(2)–Os(5) 2.935(2), Os(3)–Os(4) 3.122(3), Os(4)–Os(5) 2.891(3), Os(2)–Hg(2) 2.748(3), Os(3)–Hg(1) 2.696(2), Os(3)–Hg(2) 2.712(3), Os(4)–Hg(1) 2.783(3), Os(5)–O(1) 2.16(3), Hg(1)–O(3) 2.21(3), Hg(2)–O(5) 2.28(4), Os–C (carbonyl) range 1.78(6)–1.93(5), C–O (carbonyl) range 1.12(7)–1.26(8).

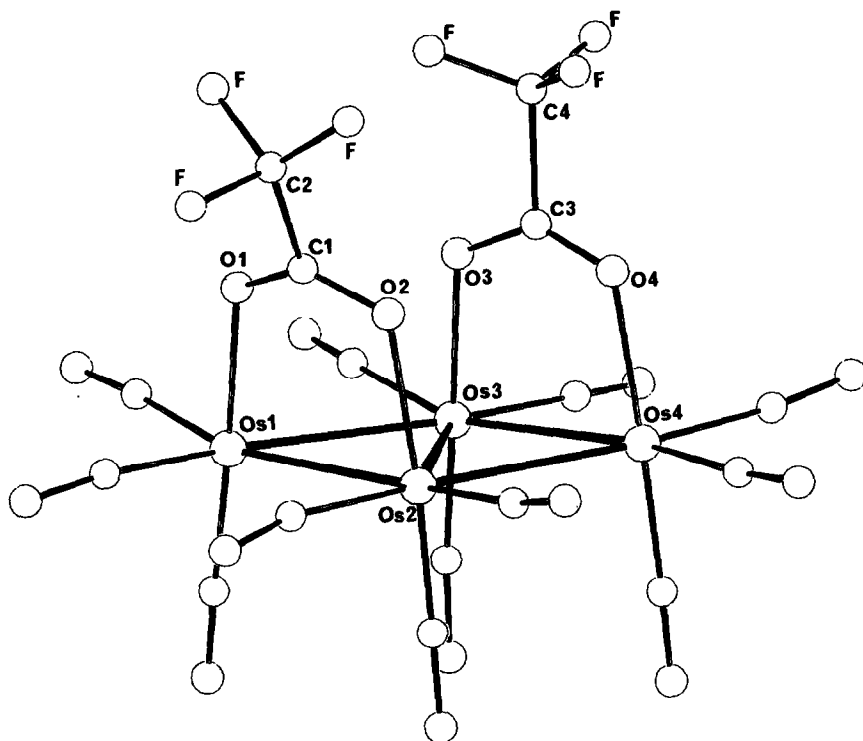


Fig. 2. The molecular structure of *cis*-[Os<sub>4</sub>(CO)<sub>12</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>] (2). Principal bond lengths (Å): Os(1)–Os(2) 2.808(2), Os(1)–Os(3) 2.908(3), Os(2)–Os(3) 2.831(2), Os(2)–Os(4) 2.924(2), Os(3)–Os(4) 2.782(2), Os(1)–O(1) 2.12(3), Os(2)–O(2) 2.18(2), Os(3)–O(3) 2.14(2), Os(4)–O(4) 2.15(2); Os–C (carbonyl) range 1.77(4)–1.96(4), C–O (carbonyl) range 1.14(4)–1.24(5).

hydride ligands replaced by the formally isolobal mercury(II) ligands. The bridged tetrahedral Os<sub>4</sub> core is an alternate to the square pyramid for a 74-electron cluster and the presence of a hydrido ligand in **1** is required to give this electron count. The structure is consistent with it being in a μ<sub>3</sub>-site inside the butterfly fragment as illustrated in Fig. 1. There was no evidence for it in its <sup>1</sup>H NMR spectrum even on cooling the sample to 200 K, possibly indicating that the hydride is fluxional at these temperatures on NMR time scale.

The second new compound was identified as *cis*-[Os<sub>4</sub>(CO)<sub>12</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>] (**2**) by spectroscopy \*\* and X-ray structure analysis \*\*\* (Fig. 2). As in the previously reported *trans*-compound, the two trifluoroacetate ligands bridge opposite 'rungs' of the ladder framework in sites axial to the metal framework but in **2** they are both on

\*\* Selected spectroscopic data for **1**: IR ν(CO) (acetone), 2129m, 2044s, 1960m cm<sup>-1</sup>. For **2**: IR ν(CO) (CH<sub>2</sub>Cl<sub>2</sub>), 2139vw, 2114m, 2086s, 2051s, 2022m, 1968w cm<sup>-1</sup>. FAB (+ve) mass spectrum, *m/z* = 1324.0.

\*\*\* Crystal data for **2**: C<sub>14</sub>F<sub>6</sub>O<sub>14</sub>Os<sub>4</sub>, *M* = 1266.93, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* 11.622(2), *b* 24.036(5), *c* 8.939(1) Å, β 94.89(1)°, *U* 2487.99 Å<sup>3</sup>, *D*<sub>c</sub> 3.38 g cm<sup>-3</sup>, *F*(000) = 2216, *Z* = 4, μ(Mo-*K*<sub>α</sub>) = 204.7 cm<sup>-1</sup>. Data were collected in the θ-range 3–25° with a scan width of 0.80°; *R* = 0.0567 for 1786 reflections with *I*/σ(*I*) > 3.0. A table of atom coordinates and a complete list of bond lengths and angles has been deposited with the Cambridge Crystallographic Data Centre.

the same side of the cluster, giving the molecule virtual  $C_2$  symmetry. The osmium–osmium bond distances for **2** follow the same pattern as **4**, with the trifluoroacetate bridged edges [Os(1)–Os(2) 2.808(2), Os(3)–Os(4) 2.782(2) Å] being considerably shorter than those that are unbridged [Os(1)–Os(3) 2.908(3), Os(2)–Os(4) 2.924(2) Å], and the diagonal being of intermediate length [Os(2)–Os(3) 2.831(2) Å].

In  $\text{CH}_2\text{Cl}_2$  solutions, only the *cis*-isomer of  $[\text{Os}_4(\text{CO})_{12}(\text{O}_2\text{CCF}_3)_2]$  is detected by IR spectroscopy; however, on crystallisation with hexane as precipitant, rearrangement occurs and the *trans*-isomer is deposited first as the major product, followed by fine needles of *cis*- $[\text{Os}_4(\text{CO})_{12}(\text{O}_2\text{CCF}_3)_2]$ . Thus, it appears that isomerisation occurs in the solution with the equilibrium favouring the *cis*-product; the less soluble *trans*-isomer is removed from the mixture first until the hexane concentration in the dichloromethane solution is high enough to cause deposition of the *cis*-isomer.

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## References

- 1 A. Dobson, D.S. Moore, S.D. Robinson, M.B. Hursthouse and L. New, *J. Organomet. Chem.*, 177 (1979) C8.
- 2 M.P. Diebold, S.R. Drake, B.F.G. Johnson, J. Lewis, M. McPartlin and H.R. Powell, *J. Chem. Soc., Chem. Commun.*, (1988) 1358.
- 3 G.R. John, B.F.G. Johnson, J. Lewis, W.J. Nelson and M. McPartlin, *J. Organomet. Chem.*, 171 (1979) C14.