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Synthesis, characterisation and molecular structure of $[Ru_5C(CO)_{15}(HgCF_3)(CF_3CO_2)]$

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Abstract

Treatment of $[Ru_5C(CO)_{15}]$ with one equivalent of $[Hg(CF_3)(CF_3CO_2)]$, in CH_2Cl_2, at room temperature affords the new cluster $[Ru_5C(CO)_{15}(HgCF_3)(CF_3CO_2)]$ (1) in quantitative yield. A single crystal X-ray structural study of **1** shows that it contains a bridged-butterfly Ru_5 metal core with the $HgCF_3$ fragment bridging at the hinge position and the trifluoroacetate coordinated to the bridging ruthenium atom through one oxygen atom.

The chemistry of heterometallic ruthenium and osmium carbonyl clusters containing mercury atoms is of current interest [1]. It has been shown that by a suitable choice of the mercury reagent and of reaction conditions the cluster $[Os_{10}C(CO)_{24}]^{2-}$ gives a range of Hg-containing clusters with various metal frameworks [2]. In an investigation of the reactivity of Hg-electrophiles towards ruthenium clusters, we recently reported the syntheses of $[\{Ru_5C(CO)_{14}(\mu\text{-}Cl)\}_2Hg_2Cl_2]$ and $[\{Ru_6C(CO)_{16}\}_2Hg]^{2-}$ from the reactions of $[Ru_5C(CO)_{15}]$ and $[Ru_6C(CO)_{16}]^{2-}$ with $HgCl_2$, respectively. We now report the preparation of a new pentaruthenium carbido cluster $[Ru_5C(CO)_{15}(HgCF_3)(CF_3CO_2)]$ (1) from the reaction of $[Ru_5C(CO)_{15}]$ with $[Hg(CF_3)(CF_3CO_2)]$.

Treatment of a dichloromethane solution of $[Ru_5C(CO)_{15}]$ with one molar equivalent of $[Hg(CF_3)(CF_3CO_2)]$ at ambient temperature for 1 h gives **1** in quantitative yield after chromatographic separation on silica. The compound **1** has been characterised by both spectroscopic [IR(ν(CO), cm^{-1}, CH_2Cl_2): 2118m, 2091s, 2076vs,br, 2058m, 2039m, 2031m, 2021w, 1992w; FAB MS: $m/z = 1205$ (^{101}Ru) corresponds to $[M - CF_3CO_2]^+$] and crystallographic techniques. Orange-yellow crystals of **1** suitable for an X-ray diffraction study were obtained by slow evaporation of a dichloromethane-hexane solution at −20°C during 2 days. The

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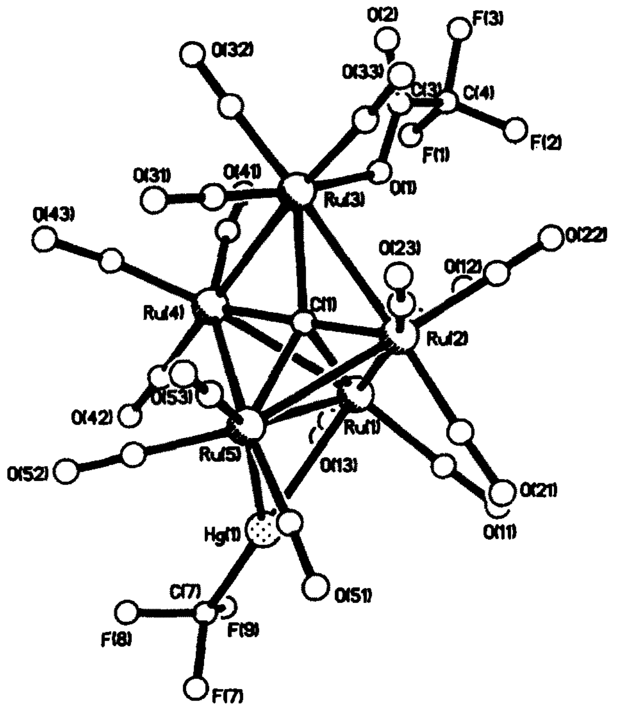

Fig. 1. The molecular structure of [Ru$_5$C(CO)$_{15}$(HgCF$_3$)(CF$_3$CO$_2$)] (**1**). Bond lengths (Å) and angles (°) (parameters for second molecule are in square brackets). Ru(1)–Ru(2), 2.862(3) [2.873(3)]; Ru(1)–Ru(4), 2.870(3) [2.867(3)]; Ru(1)–Ru(5), 2.889(4) [2.883(4)]; Ru(2)–Ru(3), 2.918(3) [2.922(3)]; Ru(2)–Ru(5), 2.855(3) [2.840(3)]; Ru(3)–Ru(4), 2.893(3) [2.873(3)]; Ru(4)–Ru(5), 2.884(3) [2.908(3)]; Ru(1)–Hg(1), 2.790(2) [2.805(2)]; Ru(5)–Hg(1), 2.774(3) [2.759(3)]; Ru(3)–O(1), 2.153(16) [2.131(17)], C(3)–O(1), 1.230(30) [1.316(26)]; C(3)–O(2), 1.231(33) [1.230(28)]; Ru(1)–Hg(1)–Ru(5), 62.6(1) [62.4(1)]; Ru(3)–O(1)–C(3), 119(1) [120(2)]; O(1)–C(3)–O(2), 128(3) [125(2)]; O(1)–C(3)–C(4), 112(2) [115(2)], O(2)–C(3)–C(4), 120(2) [120(2)].

molecular structure of **1** is shown in Fig. 1, together with some important bond parameters. * The five ruthenium atoms define a bridged butterfly geometry where the hinge of the butterfly is bridged by the Hg atom of the HgCF$_3$ group.

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* Crystal data for [Ru$_5$C(CO)$_{15}$(HgCF$_3$)(CF$_3$CO$_2$)]: C$_{19}$F$_6$O$_{17}$Ru$_5$Hg, $M = 1320.1$, orthorhombic, space group $Pca2_1$ (no. 29), $a = 20.530(5)$, $b = 9.721(4)$, $c = 30.635(8)$ Å, $V = 6114(3)$ Å^3, $D_c = 2.868$ g cm^{-3}, $Z = 8$, $F(000) = 4832$, $\lambda(\text{Mo}-K_\alpha) = 0.71069$ Å, $\mu(\text{Mo}-K_\alpha) = 74.76$ cm^{-1}. Orange block, crystal dimensions: 0.25 × 0.35 × 0.40 mm. 9029 reflections measured on a Nicolet R3m/V four circle diffractometer ($5.0° \leq 2\theta \leq 45.0°$), corrected for absorption (Ψ-scan method), 7756 unique reflections and 6559 observed with $F > 3\sigma(F)$, structure solved by a combination of direct methods and difference Fourier techniques and refined by full-matrix least-squares analysis, with Hg and Ru atoms assigned anisotropic displacement parameters. The asymmetric unit contains two crystallographic independent but structurally similar molecules of **1**; the CF$_3$ groups on HgCF$_3$ fragments of both molecules are disordered. The weighting scheme employed was $w = [\sigma^2(F) + 0.0012F^2]^{-1}$. The final residuals were $R = 0.054$ and $R_w = 0.052$. The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. Any request should be accompanied by a full literature citation for this communication.

The trifluoroacetate group is coordinated to the wingtip-bridging ruthenium atom through one oxygen atom. A similar coordination mode of $CF_3CO_2^-$ ligand in cluster compounds was observed in $[Os_3H(CO)_9(PPh_2)(CF_3CO_2)]$ [4]. Each ruthenium atom is attached to three terminally-bonded carbonyl groups, as in the case of the parent cluster $[Ru_5C(CO)_{15}]$. There is a change in geometry from that of the parent cluster which is a 74 electron square-based pyramid to the 76 electron bridged butterfly in **1** upon oxidative addition of $[Hg(CF_3)(CF_3CO_2)]$. It has been reported that the compounds $[Ru_5YC(CO)_{15}X]$ are obtained by oxidative addition of YX (Y = H, $AuPPh_3$; X = Cl, Br, I)] [5]. In the case of the gold derivative the molecule contains a bridged-butterfly ruthenium metal core with the gold fragment bridging the hinge and the halide terminally coordinated to the ruthenium atom that spans the wingtips of the butterfly; *i.e.* a similar arrangement to that in **1**. On subsequent heating the complexes $[Ru_5YC(CO)_{15}X]$ lose a CO molecule to give $[Ru_5YC(CO)_{14}(\mu-X)]$, in which the halogen bridges the two ruthenium atoms and acts as a three electron donor [5]. In contrast, the compound **1** is relatively stable and does not lose CO in refluxing $CHCl_3$ during 15 h. Although the $CF_3CO_2^-$ group is capable of acting as three electron donor, there is no evidence for the formation of $[Ru_5C(CO)_{14}(HgCF_3)(CF_3CO_2)]$.

Reaction of $[Ru_5C(CO)_{14}]^{2-}$ with an equimolar quantity of $[Hg(CF_3)(CF_3CO_2)]$ in CH_2Cl_2 gives, after separation by TLC on silica, the monoanion $[Ru_5C(CO)_{14}(HgCF_3)]^-$ **2** in good yield (90%). The compound has been characterised on the basis of spectroscopic data. The molecular formula was established from negative-ion FAB mass spectroscopy (m/z = 1178, calculated 1179) and the IR spectrum in CH_2Cl_2 showed ν(CO) bands at 2065w, 2020s, 2009s. Unfortunately all attempts to grow single crystals of **2** suitable for X-ray work were unsuccessful. We assume that the $HgCF_3$ group coordinates in an edge-bridging or face-capping bonding mode; the edge-bridging mode is more common in penta- and hexa-ruthenium carbonyl complexes.

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References

1 M.P. Diebold, B.F.G. Johnson, J. Lewis, V.P. Saharan, M. McPartlin and H.R. Powell, J. Organomet. Chem., 405 (1991) C25; P.J. Bailey, B.F.G. Johnson, J. Lewis, M. McPartlin and H.R. Powell, J. Chem. Soc., Chem. Commun., (1989) 513; E. Rosenberg, K.I. Hardcastle, M.W. Day, R. Gobetto, S. Hajela and R. Muftikian, Organometallics, 10 (1991) 203.

2 L.H. Gade, B.F.G. Johnson, J. Lewis, M. McPartlin and H.R. Powell, J. Chem. Soc., Chem. Commun., (1990) 110; E. Charalambous, L.H. Gade, B.F.G. Johnson, T. Kotch, A.J. Lees, J. Lewis and M. McPartlin, Angew. Chem., Int. Ed. Engl., 29 (1990) 1332.

3 B.F.G. Johnson, W.L. Kwik, J. Lewis, P.R. Raithby and V.P. Saharan, J. Chem. Soc., Dalton Trans., (1991) 1037.

4 S.B. Colbran, P.T. Irele, B.F.G. Johnson, P.T. Kaye, J. Lewis and P.R. Raithby, J. Chem. Soc., Dalton Trans., (1989) 2033.

5 A.G. Cowie, B.F.G. Johnson, J. Lewis, J.N. Nicholls, P.R. Raithby and M.J. Rosales, J. Chem. Soc., Dalton Trans., (1983) 2311.