A tetranuclear cluster sandwiched between edge-bridging cycloheptatrienyl rings: the synthesis and characterisation of $[Ru_4(CO)_7(\mu\text{-}C_7H_7)_2]$

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The reaction of $[Ru_3(CO)_{12}]$ with cycloheptatriene affords $[Ru_4(CO)_7(\mu\text{-}C_7H_7)_2]$ an example of a new class of sandwich cluster which is characterised in the solid-state by single-crystal X-ray diffraction and shown to contain an unusual arrangement of two parallel edge-bridging organic rings.

The metallocenes and other related sandwich complexes have caught the imagination of chemists since their initial discovery and continue to play an important role in the development of the subject.[1] Over the years sandwich compounds have found applications in a number of areas of technological importance.[2] For some time we have been interested in incorporating clusters of metal atoms between decks of organic rings and have made a number of sandwich clusters in which an octahedral ruthenium unit is sandwiched between two arene rings which bond to single metal atoms of the octahedron.[3–6] A further goal has been to sandwich a cluster between two face-capping rings and while this is yet to be realised a number of clusters containing one face-capping and one terminally coordinated ring have been prepared. However, in these compounds the arenes are not parallel to one another.[7–11] Here, we report the synthesis and full characterisation of a highly unusual tetranuclear cluster, in which a Ru_4 tetrahedron is sandwiched between two parallel edge-bridging cycloheptatrienyl rings. As such this represents a new class of sandwich compound.

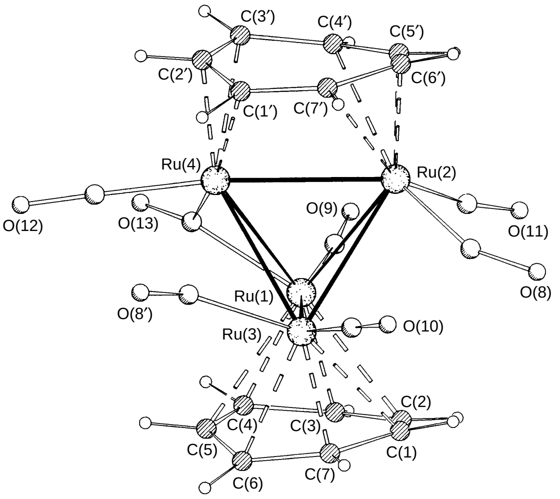

Fig. 1 The molecular structure of **1** in the solid state showing the atomic labelling scheme, the O atoms of the carbonyl ligands bear the same numbering as their corresponding C atoms. Relevant bond lengths (Å): Ru(1)–Ru(2) 2.853(2), Ru(1)–Ru(3) 2.728(2), Ru(1)–Ru(4) 2.745(1), Ru(2)–Ru(3) 2.868(2), Ru(2)–Ru(4) 2.731(2), Ru(3)–Ru(4) 2.810(2), Ru(1)–C(2) 2.468(9), Ru(1)–C(3) 2.007(8), Ru(1)–C(4) 1.950(8), Ru(1)–Ru(5) 2.663(8), Ru(3)–C(1) 2.384(7), Ru(3)–C(6) 2.247(7), Ru(3)–C(7) 1.926(10), Ru(2)–C(4′) 2.465(8), Ru(2)–C(5′) 1.915(11), Ru(2)–C(6′) 2.175(7), Ru(2)–Ru(7′) 2.639(7), Ru(4)–C(1′) 2.183(7), Ru(4)–C(2′) 1.900(9), Ru(4)–C(3′) 2.332(8), C(1)–C(2) 1.411(1), C(1)–C(7) 1.372(11), C(2)–C(3) 1.330(11), C(3)–C(4) 1.442(11), C(4)–C(5) 1.325(11), C(5)–C(6) 1.426(11), C(6)–C(7) 1.368(11), Ru(2)–C(8) 1.849(8), Ru(3)–C(8′) 1.993(10), Ru(1)–C(9) 1.86(2), Ru(3)–Ru(10) 1.88(2), Ru(2)–C(11) 1.86(2), Ru(4)–C(12) 1.84(2), Ru(1)–C(13) 2.012(13), Ru(4)–C(13) 2.193(13), C(8)–O(8) 1.143(10), C(8′)–O(8′) 1.143(10), C(9)–O(9) 1.14(2), C(10)–O(10) 1.14(2), C(11)–O(11) 1.13(2), C(12)–O(12) 1.13(2), C(13)–O(13) 1.15(2).

The ligand-exchange reaction between $[Ru_3(CO)_{12}]$ and $[Mo(CO)_3(\eta^6\text{-}C_7H_8)]$ produced a number of products including green $[Ru_4(CO)_7(\mu\text{-}C_7H_7)_2]$ **1** in 10% yield which has been fully characterised by spectroscopy† and single-crystal X-ray crystallography.‡ Higher yields were subsequently obtained from the direct reaction of $[Ru_3(CO)_{12}]$ and cycloheptatriene.§

The structure of **1** is shown in Fig. 1 and constitutes an unprecedented example of a sandwich compound in which a tetranuclear Ru_4 cluster is encapsulated between two cycloheptatrienyl ligands. The ligands edge-bridge two non-contiguous Ru–Ru bonds on the tetrahedron. The Ru–C distances are in the range 1.900(9)–2.663(8) Å; the shortest bonds being with atoms C(3) and C(4) and C(2′) and C(5′) which lie just above the two pairs of Ru atoms. The almost flat rings (maximum elevation from the mean plane 0.14 Å) formally donate seven electrons to the cluster, and the bonding may be described formally as $\mu\text{-}\eta^4:\eta^3$. The ^1H NMR spectrum in $CDCl_3$ exhibits one signal at δ 4.18 which may be taken to indicate that all the protons are equivalent on the NMR timescale suggesting the rings rotate freely in solution.

The structure is disordered in the solid state with a crystallographic twofold axis relating the two cycloheptatrienyl rings and generating two interpenetrating images of the cluster core. This disorder is reminiscent of that present in $[Co_4(CO)_{12}]$[12,13] and $[Fe_3(CO)_{12}]$.[14–16] As with these cases, the

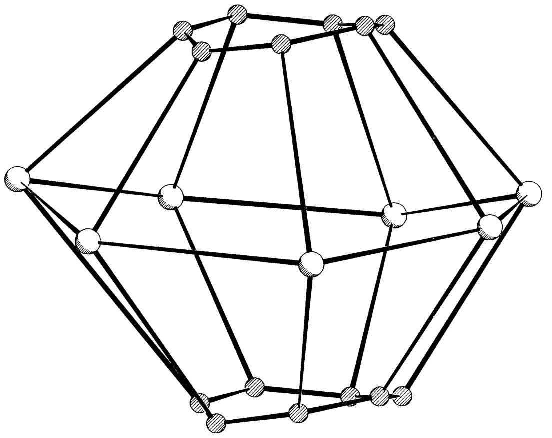

Fig. 2 The ligand polyhedron formed by the two opposite cycloheptatrienyl ligands and by the seven O atoms of the CO ligands

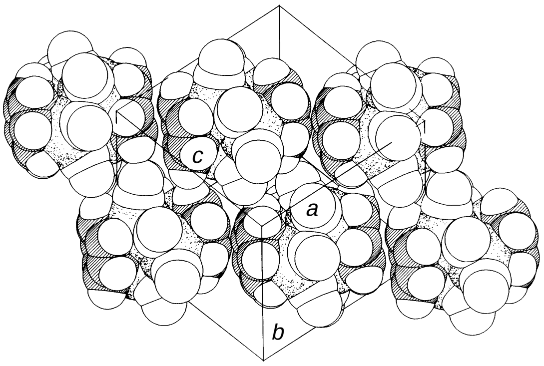

Fig. 3 Space-filling representation of the molecular piles in the crystal structure of **1**

disorder arises from the invariance of the outer ligand polyhedron with respect to the orientation of the inner cluster unit. The ligand polyhedron is novel and Fig. 2 shows that it corresponds to a hexadecahedron formed by the two opposite cycloheptatrienyl ligands and the 'belt' of seven CO groups. Diffraction data were of sufficient quality to allow resolution of all separate images of the ligand atoms excluding C(8)O(8).

A further point of interest resides in the molecular arrangement in the solid state. Molecules pile along the 101 diagonal of the cell with direct interactions between the rings (mean distance between the ring planes 3.46 Å). This packing arrangement is illustrated in Fig. 3. Similar packing arrangements have been observed for other cluster–arene systems.[17]

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Footnotes

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† *Spectroscopic data* for **1**: IR ν_{CO} (CH_2Cl_2) 1961vs, 1813m cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.18 (s).

‡ *Structural data* for **1**: $C_{21}H_{14}O_7Ru_4$, M = 782.60, monoclinic, space group = $C2/c$, a = 13.083(4), b = 12.692(4), c = 12.945(3) Å, β = 93.22(2)°, U = 2146.1(11) Å^3, Z = 4, D_c = 2.422 g cm^{-3}, $F(000)$ = 1488, crystal dimensions 0.18 × 0.16 × 0.16 mm, $2\theta_{max}$ = 50°, λ(Mo-Kα) = 0.710 69 Å, μ(Mo-Kα) = 2.803 mm^{-1}, refinement on $(F_0)^2$ for 1886 data and 208 parameters, wR_2 = 0.1456 (all data), conventional R = 0.0434. H-atoms were placed in geometrically calculated positions. The program SHELX 93 was used for the structure solution and refinement.[18] On decreasing the temperature to 223 K the orientation matrix is lost and the crystal diffracts poorly. This may indicate the occurrence of a phase transition, possibly associated with metal-frame reorientation, as observed in other carbonyl clusters.[19] Work is in progress to fully assess the phenomenon. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/479.

§ *Synthesis* of **1**: $Ru_3(CO)_{12}$ (0.1 g) and cycloheptatriene (0.5 ml) were dissolved in dry octane (30 ml) and heated to reflux for 5 h and the reaction mixture turned dark brown. The solvent was removed under reduced pressure and the residue dissolved in a minimum amount of CH_2Cl_2 and the products purified by TLC on silica plates using CH_2Cl_2–hexane (1 : 4, v/v) as the eluent. The dark green band was removed and the product extracted into CH_2Cl_2 and characterised as **1** (50%).

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