Synthesis and Characterization of the Bis-arene Sandwich Cluster $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)_2]$

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The bis-arene cluster complex $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)_2]$ **1** has been synthesised and characterized by single-crystal X-ray diffraction; it possesses a unique structure in which the octahedral cluster core is sandwiched between the two arenes.

Several years ago we reported the synthesis and structural characterization of the bis-benzene cluster $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$[1] which proved to be the first example of a cluster containing a benzene ligand bonded as a triene in a face-capping mode. This molecule is unusual also because the two benzenes are bonded differently with the second benzene co-ordinating in the more common terminal η^6 mode. More recently, we have discovered cluster compounds in which the reversible interchange between face-capping and terminally bonded arenes occurs readily.[2] We now report the synthesis and structural characterization of the novel species $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)_2]$ **1** which contains two η^6-bonded arenes occupying *trans* positions about a Ru_6 octahedron. This cluster constitutes the first example of a bis-arene complex in which a whole cluster is 'sandwiched' between two arene ligands.

Treatment of $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)]$[3] (50 mg in 50 cm^3 CH_2Cl_2) with 3 equivalents of Me_3NO (11 mg) in the presence of dihydromesitylene (1,3,5-trimethylcyclohexa-1,3-diene) (1 cm^3) gives $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)_2]$ **1** in moderate yield (8 mg, *ca.* 16%).† In contrast to the other reported hexaruthenium bis-arene species, $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$,[1] the ^1H NMR spectrum of **1** shows that the two arene ligands are equivalent, and the chemical shift of the methine protons indicates that they are η^6-co-ordinated. The molecular structure of **1** in the solid state has been characterized by X-ray diffraction‡ and is shown in Fig. 1 together with some relevant structural parameters.

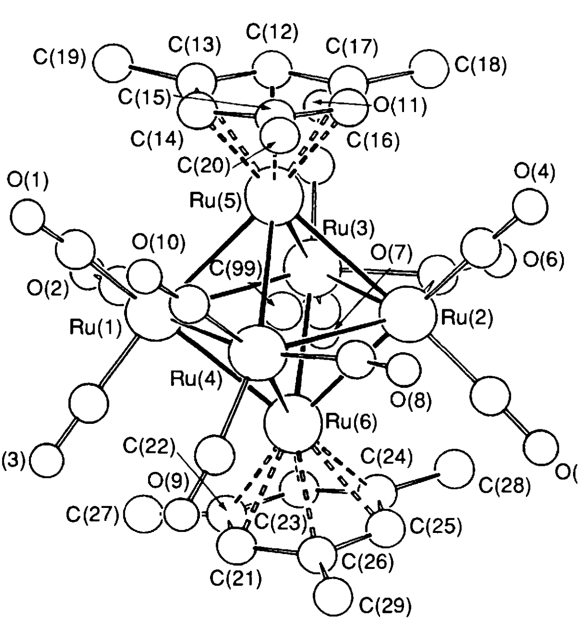

Fig. 1 Molecular structure of **1**, showing the labelling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms; H atoms of the mesitylene groups are omitted for clarity. Relevant bond distances (Å) and angles (°) include: Ru(1)–Ru(3) 3.089(1), Ru(1)–Ru(4) 2.796(1), Ru(1)–Ru(5) 2.865(1), Ru(1)–Ru(6) 2.865(1), Ru(2)–Ru(3) 2.871(1), Ru(2)–Ru(4) 2.917(1), Ru(2)–Ru(5) 2.848(1), Ru(2)–Ru(6) 2.853(1), Ru(3)–Ru(5) 2.838(1), Ru(3)–Ru(6) 2.842(1), Ru(4)–Ru(5) 2.857(1), Ru(4)–Ru(6) 2.876(1); mean Ru–C 1.89(1), mean C–O 1.13(1); Ru(2)–C(6) 2.06(1), Ru(3)–C(6) 2.08(1), C(6)–O(6) 1.17(1), Ru(3)–C(6)–Ru(2) 87.9(4); mean Ru–C_{ring} 2.26(1); mean C–C 1.41(1), mean C–C_{Me} 1.50(1)

The Ru–Ru bond distances range from 2.796(1) to 3.089(1) Å [mean 2.876(1) Å]. The mesitylene ligands are η^6-bound to two opposite ruthenium atoms of the octahedral framework [mean Ru–C distance 2.26(1) Å]. The two aromatic rings form angles of 5.6 [C(21)–C(26)] and 4.4° [C(12)–C(17)] with respect to the molecular equatorial plane. The Ru–C(carbide) distances involving the two substituted ruthenium atoms [Ru(5) and Ru(6)] are appreciably shorter than those involving the equatorial ruthenium atoms [1.97(1) *versus* 2.08(1) Å] so that the octahedral framework is squeezed along the arene co-ordination axis. A similar effect had been previously observed in the mono-arene species $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)]$[3] and $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)]$.[4] The CO-ligand distribution on the equatorial atoms recalls that observed in $[Ru_6C(CO)_{17}]$,[5] *i.e.*

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† IR (CH_2Cl_2) ν_{CO}: 2035m, 1995vs, 1972s, 1934m and 1793w (br) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 5.29 (s, 1 H) and 2.17 (s, 3 H). Electron impact mass spectrum: *m/z* 1167 (M^+).

‡ Crystal data for **1**, $C_{30}H_{24}O_{11}Ru_6$: $M = 1166.7$, monoclinic, space group $P2_1/c$, $a = 10.084(1)$, $b = 16.984(3)$, $c = 19.425(5)$ Å, $\beta = 88.94(1)$, $U = 3326.4$ $Å^3$, $Z = 4$, $D_c = 2.33$ g cm^{-3}, $F(000) = 2224$, $\mu(Mo\text{-}K\alpha) = 24.63$ cm^{-1}, $2.5 < \theta < 25°$, final R value 0.032, $R' = 0.035$ for 4437 out of 6231 independent reflections $[I_o > 2\sigma(I_o)]$ collected by the ω–2θ scan method. All non-H atoms allowed to vibrate anisotropically. The H atoms were added in calculated positions (C–H 1.08 Å) and refined riding on their respective C atoms; one isotropic thermal parameter was refined for the H(Me) atoms ($U_{iso} = 0.13$ $Å^2$). 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.*, 1992, Issue 1, pp. xx–xxv.

one bridging ligand, and two semi-bridging carbonyls lie in the equatorial plane, while eight terminal ligands are distributed above and below the plane.

Interestingly, the arene fragments establish intermolecular graphitic-like interactions in the crystal lattice (distance between arene planes *ca.* 3.6 Å) of the kind previously observed in the bis-benzene derivative $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)]$.[3]

The reason for the adoption of the bis-η^6 conformation when the arene is mesitylene, while two benzene ligands co-ordinated to the same cluster core adopt $\eta^6/\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ co-ordination modes, is not clear. However, both steric and electronic factors* may be envisaged and work is currently in progress to delineate these by synthesis of other Ru_6C bis-arene systems.

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* Models indicate that the η^6 bonding of mesitylene minimizes intramolecular interactions with CO groups. Work on related Ru_5 arene derivatives clearly indicates that the metal atom supporting the η^6-arene undergoes preferential nucleophilic attack by CO.