Synthesis and Molecular Structure of Tetraruthenium Clusters carrying Facial Arene Ligands

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The reaction of $Ru_3(CO)_{12}$ with 1,3-diisopropenylbenzene (C_6H_4-$\{CMeCH_2\}_2$-1,3) and isopropenylbenzene (C_6H_5-$\{CMeCH_2\}$) in refluxing octane affords the novel species $Ru_4(CO)_9(\mu_3$-η^2:η^2:η^2-$C_6H_4\{\eta^2$-$CMeCH_2\}_2$-1,3) and $Ru_4(CO)_{10}(\mu_3$-η^2:η^2:η^2-$C_6H_5\{\eta^2$-$CMeCH_2\})$ in which the unsaturated systems fully interact with the cluster unit formally supplying 10 and 8 electrons, respectively.

The μ_3-η^2:η^2:η^2 bonding mode for benzene has been of great interest since it was first discovered in 1985.[1] The challenge to synthesise clusters of differing nuclearity containing arenes in the so-called face-capping mode has been well met, with a number of synthetic methods designed to target such compounds.[2] Face-capping arene units have been introduced into clusters (or clusters assembled on the arene) in species with nuclearities of three (Ru,[3a] Os,[3b] Co,[3c] Rh[3d]), five (Ru[3]) and six (Ru,[3f] Os[3g]). For some time it has been our goal to produce a tetranuclear cluster bearing a facial ring. Several tetrahedral cobalt and osmium clusters with η^6-terminal arene ligands are documented in the literature,[2b,4] produced by controlled chemical methods. We have finally realised out goal using arenes with isopropenyl groups.

The reaction of $Ru_3(CO)_{12}$ with 1,3-diisopropenylbenzene and isopropenylbenzene in octane at reflux for 1.5 h affords a variety of compounds including two tetranuclear products formed in moderate yield which can be isolated by chromatography on silica.† These compounds have been characterized as $Ru_4(CO)_9(\mu_3$-η^2:η^2:η^2-$C_6H_4\{\eta^2$-$CMeCH_2\}_2$-1,3) **1** and $Ru_4(CO)_{10}(\mu_3$-η^2:η^2:η^2-$C_6H_5\{\eta^2$-$CMeCH_2\})$ **2**. Spectroscopic data‡ for these compounds are in complete agreement with the molecular structures observed in the solid state,§ and it would appear that the η^2-interaction(s) between the isopropenyl unit and the metal anchor the ring in place, prohibiting rotation of the ring.

The solid state molecular structures of **1** and **2** are closely related (see Fig. 1). These complexes represent the first examples of face-capping six-membered rings on a tetranuclear cluster. Due to the unusual nature of the interaction of the ring with the cluster framework, a plan view of **1** is also shown (Fig. 2). Relevant bond lengths are reported in the caption of Fig. 1 for both complexes. The four ruthenium atoms adopt a tetrahedral arrangement in which all the bond lengths are in the range 2.662(2)–2.882(2) Å for **1** and 2.6829(12)–2.9082(12) Å for **2**. In both complexes two Ru–Ru bonds are spanned by briding COs. Clearly the most important feature of the molecules is the interaction of the ring systems and of the unsaturated side-arms with the cluster face. The five η^2-interactions of the diisopropenylbenzene ligand and the four η^2-interactions of the isopropenylbenzene ligand formally contribute 10 and 8 electrons, respectively to the clusters. This electron contribution yields a total electron count of 60 which is customary for a tetrahedral cluster. It can be seen from Fig. 2 that the ring in **1** is slightly off-centre with respect to eclipsing of the mid-points of the C=C double bonds over the metal atoms. In **1**, two of the C atoms above these metals are connected to the side-arms and bend towards the cluster in order

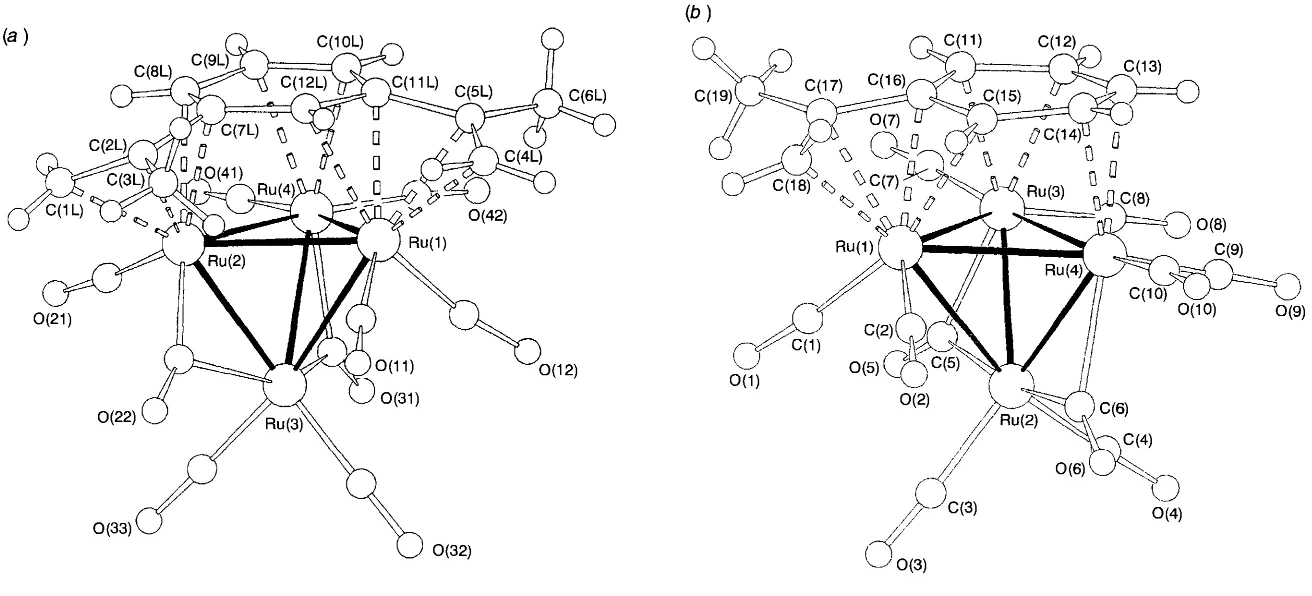

Fig. 1 Solid state molecular structures of (*a*) **1** and (*b*) **2** showing the atomic labelling schemes, the C atoms of the CO ligands carry the same numbering as the corresponding O atom. Relevant structural parameters are for **1**: Ru(1)–Ru(2) 2.882(2), Ru(1)–Ru(3) 2.860(2), Ru(1)–Ru(4) 2.823(2), Ru(2)–Ru(3) 2.662(2), Ru(2)–Ru(4) 2.830(2), Ru(3)–Ru(4) 2.837(2), Ru(1)–C(11L) 2.156(12), Ru(1)–C(12L) 2.278(11), Ru(2)–C(7L) 2.159(11), Ru(2)–C(8L) 2.264(11), Ru(4)–C(9L) 2.365(12), Ru(4)–C(10L) 2.344(11), Ru(2)–C(1L) 2.281(12), Ru(2)–C(2L) 2.212(12), Ru(1)–C(4L) 2.271(12), Ru(1)–C(5L) 2.214(12) Å; for **2**: Ru(1)–Ru(2) 2.8647(12), Ru(1)–Ru(3) 2.8517(11), Ru(1)–Ru(4) 2.8795(12), Ru(2)–Ru(3) 2.6933(12), Ru(2)–Ru(4) 2.6829(12), Ru(3)–Ru(4) 2.9082(12), Ru(3)–C(11) 2.257(11), Ru(3)–C(12) 2.283(11), Ru(4)–C(13) 2.400(12), Ru(4)–C(14) 2.201(11), Ru(1)–C(15) 2.318(10), Ru(1)–C(16) 2.180(9), Ru(1)–C(17) 2.190(10), Ru(1)–C(18) 2.236(10) Å.

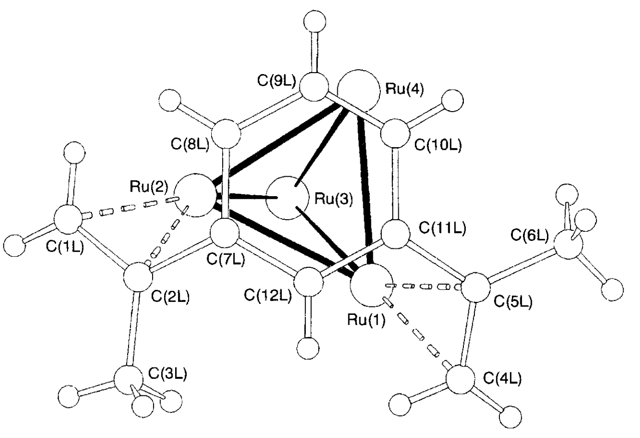

Fig. 2 Plan view of **1**; the COs have been omitted for clarity

to form a favourable bonding interaction with the cluster unit. A similar arrangement is observed in **2**, except that the missing side-arm has been replaced by a CO ligand.

We are currently examining the other products isolated from these reactions and developing more controlled synthetic methods for their introduction into cluster systems.

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Footnotes

† Thermolysis of $Ru_3(CO)_{12}$ (150 mg) in octane (15 ml) containing either diisopropenylbenzene or isopropenylbenzene (1 ml) for 1.5 h results in the formation of a deep red–brown solution. Removal of the solvent *in vacuo*, followed by thin layer chromatography on silica using dichloromethane–hexane (1 : 4, v/v) as eluent results in the isolation of several products. In both cases the red–brown band with the lowest elution rate is extracted into dichloromethane. These bands have been characterised as $Ru_4(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_4\{\eta^2\text{-}CMeCH_2\}_2\text{-}1,3)$ **1** (27%) and $Ru_4(CO)_{10}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_5\{\eta^2\text{-}CMeCH_2\})$ **2** (12%) for the diisopropenylbenzene and isopropenylbenzene reactions, respectively. The remaining products isolated from these reactions are currently being characterised.

‡ *Spectroscopic data* for **1**: IR ν_{CO}/cm^{-1} (CH_2Cl_2): 2050 (m), 2001 (vs), 1968 (w, br), 1924 (w, br), 1794 (w, vbr). Positive FAB–MS *m*/*z*: 815 (calc. 815). ^1H NMR ($CDCl_3$): δ 5.47 (m, 1H), 5.22 (m, 1H), 3.33 (m, 1H), 2.94 (m, 1H), 1.87 (m, 1H), 1.72 (m, 1H), 1.49 (s, 3H), 1.37 (s, 3H), 0.55 (m, 1H), 0.28 (m, 1H).

For **2**: IR ν_{CO}/cm^{-1} (CH_2Cl_2): 2089 (w), 2060 (m), 2029 (vs), 1967 (w), 1834 (w, br). Positive FAB–MS *m*/*z*: 802 (calc. 803). ^1H NMR ($CDCl_3$): δ 5.23 (m, 1H), 4.76 (m, 1H), 4.74 (m, 1H), 4.36 (m, 1H), 3.05 (m, 1H), 1.56 (m, 1H), 1.15 (s, 3H), 0.85 (m, 1H).

§ *Crystal data* for **1**: $Ru_4O_9C_{21}H_{14}$, M = 814.60, triclinic, space group $P\bar{1}$ (no. 2), a = 8.835(4), b = 8.899 (4), c = 15.422(8) Å, α = 96.04(3), β = 92.14(3), γ = 111.36(3)°, U = 1119.2(9) Å^3, Z = 2, ρ_{cacl} = 2.417 g cm^{-3}, $F(000)$ = 776, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) 2.699 mm^{-1}. Absorption correction: minimum and maximum correction 0.879 and 1.097.[5a] Refinement on $(F_o)^2$ for 2913 data and 157 parameters (Ru anisotropic), $wR2$ = 0.2120 (all data), conventional R = 0.0474 (2381 data with $F_o > 4\sigma F_o$).

For **2**: $Ru_4O_{10}C_{19}H_{10}$, M = 802.55, monoclinic, space group $P2_1/n$ (no. 14), a = 9.057(4), b = 15.14(1), c = 15.846(6) Å, β = 93.36(4)°, U = 2169.1(9) Å^3, Z = 4, ρ_{calc} = 2.458 g cm^{-3}, $F(000)$ = 1520, λ(Mo-Kα) = 0.71069 Å, μ(Mo-Kα) 2.786 mm^{-1}. Absorption correction: minimum and maximum correction 0.885 and 1.092. Refinement on $(F_o)^2$ for 3787 data and 298 parameters (all non-H atoms anisotropic), $wR2$ = 0.1648 (all data), conventional R = 0.0472 (2709 data with $F_o > 4\sigma F_o$). The computer program SHELX93[5b] was used for structure solution and refinement.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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