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Synthesis, characterization and molecular structure of two Ru_4 clusters with β-alkylstyrene ligands

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The ruthenium clusters $[Ru_4(CO)_{10}(C_9H_{10})]$ **1** and $[Ru_4(CO)_{10}(C_{10}H_{12})]$ **2** have been obtained together with other products from the reaction of $[Ru_3(CO)_{12}]$ with allylbenzene or 4-phenylbut-1-ene respectively in octane under reflux. Their molecular structures have been elucidated by single-crystal X-ray crystallography. That of **1** exhibits two co-ordination isomers in the solid state for the facial bonded ligand. Force–field calculations on each isomer revealed a small energy difference between them.

A variety of modes of bonding of arene ligands to metal cluster surfaces have been observed.[1] All are dominated by two main interactions, *viz.* the η^6 and μ_3-$\eta^2:\eta^2:\eta^2$ modes. Since the first μ_3-$\eta^2:\eta^2:\eta^2$-bonded arene cluster was established in 1985,[2] a considerable number of other clusters with a range of different nuclearities and metal type, mainly of Ru, Os, Co and Rh, with this facial bonding interaction have been characterised.[3] All such clusters bear the same structural relationship with the carbocycle placed over the metal triangle and twisted by 30° such that three C=C bonds lie above the metal atoms. The most striking feature is the alternation of long and short bonds within the C_6 ring, which resembles that of the hypothetical cyclohexa-1,3,5-triene molecule (structure **A**). This deviation from the ideal D_{6h} symmetry of 'free' benzene to a 'Kekulé-type' structure mimics that observed for benzene chemisorbed at surface metal atoms in low-Miller-index planes of close-packed arrays of a metallic lattice.[4] Even with unsaturated side chains like isopropenyl this conformation is maintained with an additional cluster link to the exocyclic double bond.[5] Recently, we reported the molecular structure of $[Ru_5C(CO)_{11}(\mu_3$-$PhCHCHMe)]$ in which a different arene bonding mode over a metal triangle [6] was observed, and exhibited the first example of a $\eta^2:\eta^3:\eta^3$ co-ordination of the ligand to the metal framework. This is similar to that previously postulated as the hypothetical transition state in the formation of $[Co_3(\eta$-$C_5H_5)_3(\mu_3$-arene$)]$.[7]

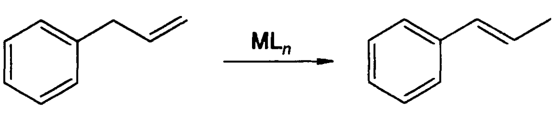
We now report two new tetranuclear compounds, which bear the same arene ligand but bonded in two different bonding modes, *viz.* $\eta^2:\eta^2:\eta^4$ and $\eta^2:\eta^3:\eta^3$.

Results and Discussion

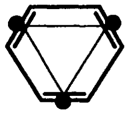
From the thermolysis of triruthenium dodecacarbonyl, $[Ru_3(CO)_{12}]$, in octane in the presence of an excess of either allylbenzene or 4-phenylbut-1-ene the compounds $[Ru_4(CO)_{10}(C_9H_{10})]$ **1** or $[Ru_4(CO)_{10}(C_{10}H_{12})]$ **2** respectively may be obtained together with several other minor products which will not be discussed further.

Table 1 Assignment of the ^1H NMR spectra for compounds **1** and **2**

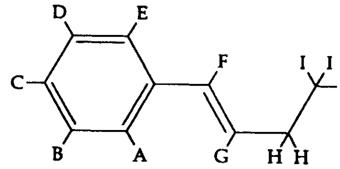
Signal	1	2
A	−0.17	−0.19
B	5.21	5.20
C	4.26	4.27
D	4.74	4.75
E	4.26	4.27
F	4.19	4.20
G	2.16	2.12
H	1.61	1.97/1.66
I	—	0.99



Scheme 1 Isomerisation of the double bond in the presence of transition-metal compounds



A



B

The spectroscopic data for both compounds are consistent with the view that they possess a similar structure. Thus, the ^1H NMR spectra (recorded in $CDCl_3$, Table 1) indicate that during the reaction isomerisation of the exocyclic double bond conjugated to the arene occurs as is shown in Scheme 1. In a separate experiment we have observed that in the presence of $[Ru_3(CO)_{12}]$ both allylbenzene and 4-phenylbut-1-ene are completely isomerised to β-alkylstyrene within a matter of minutes. A similar observation had been recorded earlier by Wadepohl *et al.*[8] in the thermolysis of $[Co(\eta^5$-$C_5H_5)(C_2H_4)_2]$ with the same organo-species. Tentative assignments of the two spectra were confirmed by the usual decoupling techniques. The ^1H NMR spectrum of **1** in $CDCl_3$ shows eight signals labelled for convenience A–H. On irradiation at signal A the coupling of *ca.* 6 Hz was removed from signal B and the coupling of *ca.* 0.5 Hz from the signal C/E. Irradiation at signal B was found to affect both A and C/E with in each case a loss of coupling of *ca.* 6 Hz. Further irradiation experiments allowed us to confirm that the signals A–E arise from the aromatic ring protons as is demonstrated in **B**. The remaining signals F–H may be reasonably assigned to the protons of the alkene and methyl group. Signal G is coupled to F (10.4 Hz) and also to H (6 Hz). Hence, on this basis, the exocyclic double bond would appear to be present in the *trans* conformation.

The ^1H NMR spectrum of compound **2** is very similar to that of **1** except that the two protons on C(9) are now stereoisotropic and appear separately (see Table 1).

Molecular structures of compounds 1 and 2

Good, well shaped, orange-red crystals of compounds **1** and **2** were grown reproducibly from a CH_2Cl_2–hexane solvent mixture. Compound **1** crystallises with three different molecules

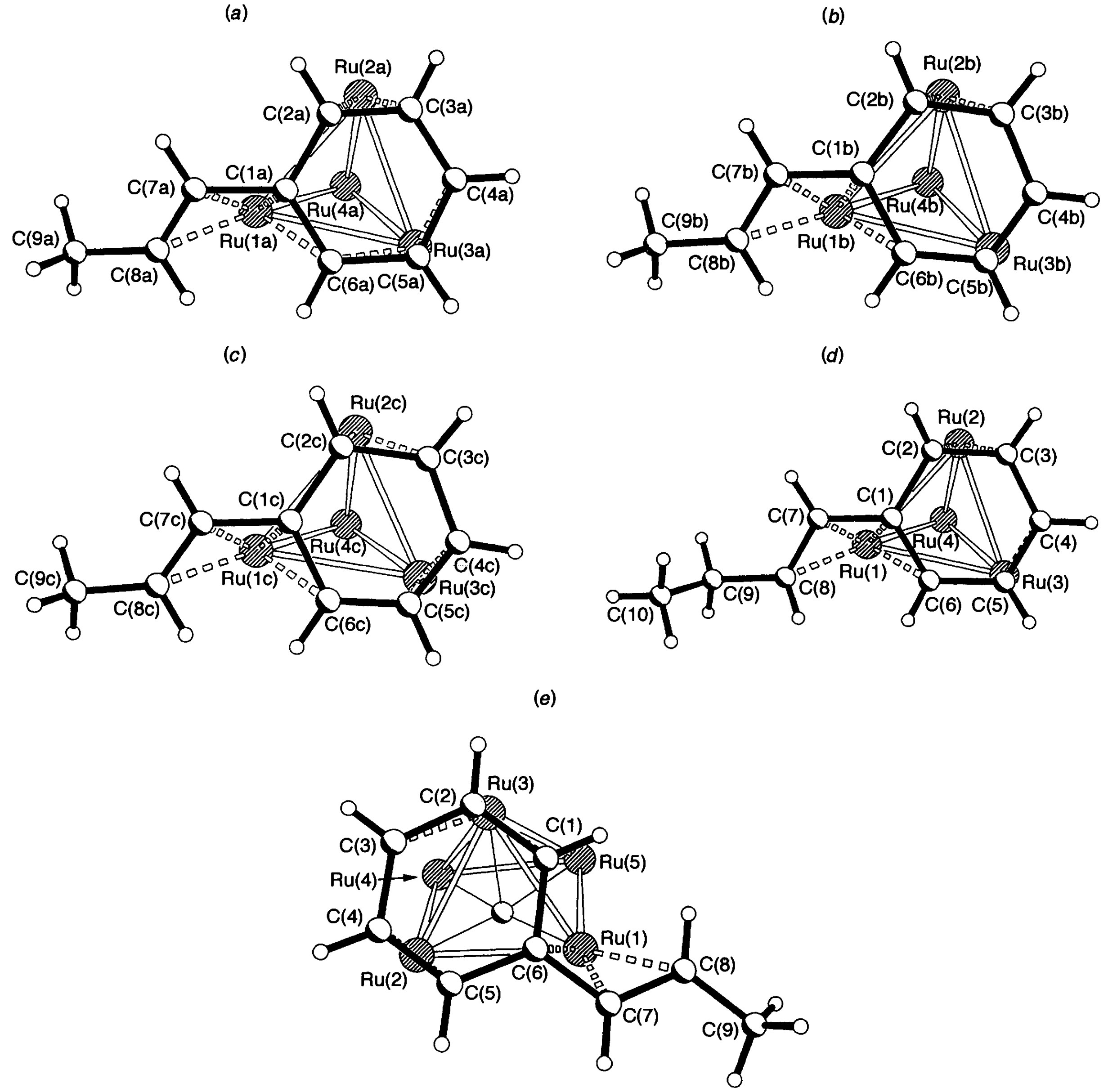


Fig. 1 Comparative projection of the ring co-ordination planes in compounds **1A** (*a*), **1B** (*b*), **1C** (*c*), **2** (*d*) and [$Ru_5C(CO)_{11}(\mu_3$-PhCHCHMe)] (*e*) showing the slight off-centre displacement of the ring with respect to the midpoint of the C=C double bonds over the metal atoms in all the structures, and the small rotation of the ligand about the co-ordination axis. The CO ligands have been omitted for clarity

in the unit cell. These differ not only in the measured bond lengths but also in their overall geometry. The arrangements of the ruthenium tetrahedra and the ten carbonyl ligands are nearly identical for all molecules **1A**–**1C** and **2**. In each case the structures are related by the same type of interaction of the ring system and the unsaturated side arms with the basal trimetallic face. The ligands formally contribute eight electrons to the metal cluster unit, six from the benzene ring and two from the exocyclic double bond. Thus, the total electron count for these tetrahedral species is 60, in keeping with the total number of valence electrons typically associated with such tetrahedral clusters. A slightly off-centre displacement of the ring with respect to the eclipsed configuration of the midpoints of the C=C double bonds with the metal atoms is observed in all structures. This probably arises from the π interaction of the side arm with Ru(1). A small degree of rotation of the ligand about the C_3 co-ordination axis through the apical ruthenium atom is also observed. This is shown in Fig. 1 where the off-centre displacements of the ring co-ordination planes in **1A**–**1C** and **2** are compared. The smallest degree of rotation is observed for cluster **2** (see also Fig. 2). The overall organo-co-ordination mode is thus best described as $\eta^2:\eta^2:\eta^4$. Within the ring there is also the now characteristic alternation of long and short C–C bonds and the ring is placed such that the midpoints of the three C=C bonds are placed more or less over the three basal ruthenium atoms.

As the rotation of the organo-ligand over the trimetal cluster surface is increased in going from compound **1C** to **1A** the bonding mode changes slowly from $\eta^2:\eta^2:\eta^4$ towards the alternative $\eta^2:\eta^3:\eta^3$ arrangement, as clearly demonstrated in the three molecules **1C**, **1B** and **1A** (Fig. 3). This change in the co-ordination mode is reflected in a change in Ru–C distances, and the alternation of long and short C–C bond lengths and the geometry of the ligand. For η^3 co-ordination within the ring the C–C bonds are almost the same length (Table 3). At the same time the difference between the Ru(3)–C(5) and Ru(3)–C(6) bond length on one side of the ring and Ru(3)–C(4) on the other increases. As a result the geometry of the organo-ligand undergoes some change; the η^3 co-ordination introduces torsion into the six-membered ring[9] and the central carbon of the η^3 unit moves out of the six-carbon ligand plane. The distance of C(5) to the best plane through C(1), C(2), C(3), C(4)

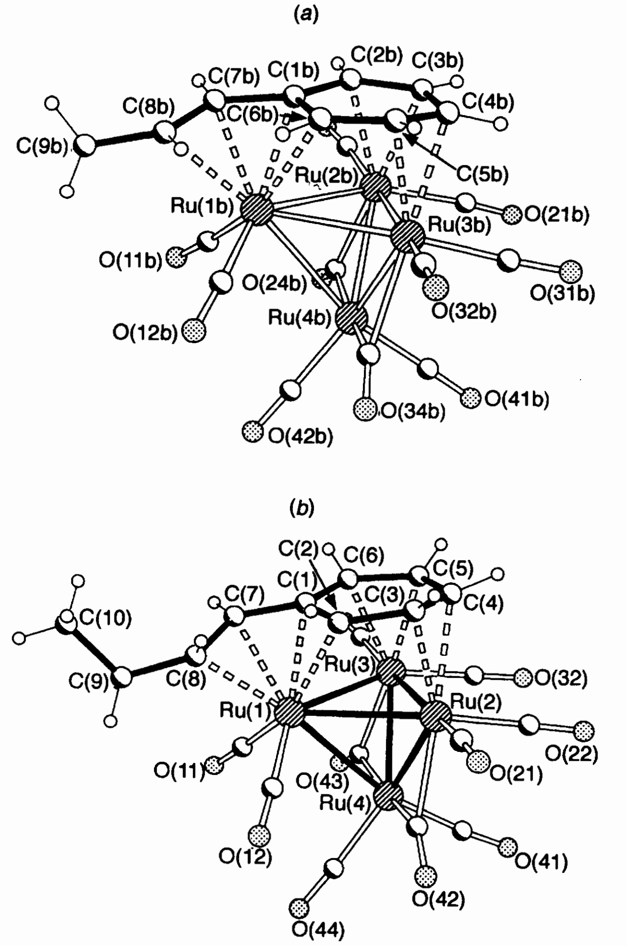


Fig. 2 Molecular structures of (*a*) $[Ru_4(CO)_{10}(C_9H_{10})]$ **1B**, and (*b*) $[Ru_4(CO)_{10}(C_{10}H_{12})]$ **2**; carbon atoms of the CO groups bear the same numbering as that of the corresponding O atoms

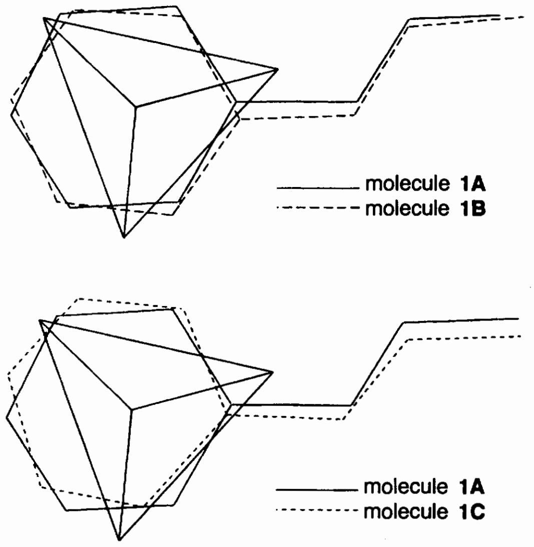


Fig. 3 Superpositions of (*a*) molecules **1A** and **1B**, (*b*) **1A** and **1C**

and C(6) increases from 0.130 Å for **1C** and **2** to 0.136 Å for **1B** and 0.166 Å for **1A** and may be compared to the 0.184 Å observed with $[Ru_5C(CO)_{11}(\mu_3\text{-PhCHCHMe})]$ in going from $\eta^2:\eta^2:\eta^4$ to $\eta^2:\eta^3:\eta^3$ co-ordination in that pentanuclear cluster. A further important aspect in deciding between the bonding types $\eta^2:\eta^2:\eta^4$ and $\eta^2:\eta^3:\eta^3$ is the co-ordination sphere about atom C(6) which belongs to either the η^4 or to the η^3 mode. We suggest that the almost identical, relatively long C(6)–Ru(1) and C(6)–Ru(3) bond lengths in **1A** should be considered to correspond to a two-electron three-centre bond, and hence **1A** may be viewed as a transition state between the two extreme co-ordination modes. Thus, the molecules **1A**–**1C** present three different stages in the transition from the $\eta^2:\eta^3:\eta^3$- to the $\eta^2:\eta^2:\eta^4$-bonding arrangement. The simultaneous presence of these co-ordination modes in the crystal suggests that there is a small energy difference between them.

Force-field calculations* on both molecules **1A** and **1C** indicate a small energy difference between the two isomers. Isomer **1C** with the $\eta^2:\eta^2:\eta^4$ co-ordination is the most stable conformation. The calculation for isomer **1A**, with and without a Ru(1a)–C(6a) bond, gives a slightly lower energy for the compound without this bond. However, the calculated structure indicates a longer distance between these atoms than is actually observed in the crystal. Therefore we presume that there is a weak bonding interaction between these atoms, and the molecular structure of **1A** is best regarded as a transition state between the two extreme $\eta^2:\eta^2:\eta^4$- and $\eta^2:\eta^3:\eta^3$-bonding modes.

It is of interest that if the rotation of the organo-ligand is continued in the same direction of the basal Ru_3 triangle then a system is derived in which a direct agostic interaction of an adjacent ring proton with a Ru atom occurs. Eventually, following C–H bond cleavage from both the ring and the exocyclic methylene group, this would lead to a metallacycle of type $[Ru_4(CO)_{10}(C_9H_8)]$ **3**. It would appear that, by good fortune, the possible reaction sequence for the conversion of **1C** into **3** finds strong support from the crystallographic data. The relevance of these studies to corresponding work on metal surfaces is clear; the ability of β-allylstyrenes and other related organic systems to undergo a change in bonding mode by rotation is of importance especially since it would appear to be a deciding factor in C–H bond-cleavage reactions.

Conclusion

In this work we have demonstrated that there is a simple mechanistic relationship between the $\eta^2:\eta^2:\eta^4$- and the $\eta^2:\eta^3:\eta^3$-bonding modes observed for compounds of simple cluster units, in this case Ru_4, and substituted arenes containing a conjugated exocyclic bond. In such a substituted arene plane over an appropriate trimetallic face in the $\eta^2:\eta^2:\eta^4$ mode simple rotation more or less through the pseudo-three-fold axis of the arene ring leads first to the $\eta^2:\eta^3:\eta^3$-bonding arrangement, then to the probable reaction intermediate for C–H bond cleavage and finally to a proposed metallacycle product of the type previously observed. It is of further interest that the three molecular arrangements observed here for the cluster $[Ru_4(CO)_{10}(C_9H_{10})]$ appear to correspond to the proposed reaction sequence $\eta^2:\eta^2:\eta^4 \longrightarrow \eta^2:\eta^3:\eta^3 \longrightarrow [Ru_4(CO)_{10}(C_9H_8)]$.

Experimental

General procedures and materials

All reactions were carried out using octane (Aldrich Chemicals) under a nitrogen atmosphere. The work-up of the products was carried out using standard laboratory-grade solvents. Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier-transform spectrometer, mass spectra by positive fast atom bombardment on a Kratos MS50TC, calibrated with CsI, and ^1H NMR spectra using a Bruker AM200 spectrometer referenced to internal $SiMe_4$. The cluster $[Ru_3(CO)_{12}]$ was prepared according to the literature method. Allylbenzene and 4-phenylbut-1-ene (Aldrich) were used without any further purification.

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* Based on molecular mechanics (version MM+) program HYPERCHEM 3.0 with the Polar–Rubiere algorithm.[10]

Table 2 Selected bond lengths (Å) for $[Ru_4(CO)_{10}(C_9H_{10})]$ **1A**–**1C** and $[Ru_4(CO)_{10}(C_{10}H_{12})]$ **2**

	1A	**1B**	**1C**	**2**
Ru(1)–C(1)	2.17(2)	2.20(2)	2.20(2)	2.183(8)
Ru(1)–C(6)	2.46(2)	2.40(2)	2.42(2)	2.400(9)
Ru(1)–C(7)	2.19(2)	2.16(2)	2.14(2)	2.189(9)
Ru(1)–C(8)	2.29(2)	2.26(2)	2.31(2)	2.281(9)
Ru(2)–C(2)	2.30(2)	2.25(2)	2.21(2)	2.270(9)
Ru(2)–C(3)	2.27(2)	2.32(2)	2.45(2)	2.267(8)
Ru(3)–C(4)	2.47(2)	2.37(2)	2.24(2)	2.410(9)
Ru(3)–C(5)	2.17(2)	2.19(2)	2.20(2)	2.162(9)
Ru(3)–C(6)	2.55(2)	2.62(2)*	2.63(2)*	2.617(9)*
C(1)–C(2)	1.44(3)	1.47(3)	1.48(3)	1.508(12)
C(1)–C(6)	1.40(3)	1.47(3)	1.44(3)	1.407(13)
C(1)–C(7)	1.50(3)	1.43(2)	1.45(3)	1.419(13)
C(2)–C(3)	1.31(3)	1.40(2)	1.41(3)	1.418(13)
C(3)–C(4)	1.36(3)	1.40(2)	1.45(2)	1.440(12)
C(4)–C(5)	1.42(3)	1.36(3)	1.29(3)	1.358(13)
C(5)–C(6)	1.43(3)	1.32(3)	1.30(3)	1.425(14)
C(7)–C(8)	1.29(3)	1.34(2)	1.33(3)	1.395(13)
C(8)–C(9)	1.48(2)	1.47(2)	1.44(2)	1.497(14)
C(9)–C(10)				1.491(14)

* Not in the range of a bonding interaction.

Thermolyses of $[Ru_3(CO)_{12}]$

With allylbenzene. Triruthenium dodecacarbonyl (350 mg) was heated in octane in the presence of an excess of allylbenzene (0.5 cm^3) for 3 h. The reaction was monitored by IR spectroscopy and spot TLC. On completion the solvent was removed *in vacuo* and the reaction mixture chromatographed. The products were separated using preparative TLC with hexane–dichloromethane (7:3). The bottom red-orange band contained the required product **1** (12 mg, 3.6%). ^1H NMR ($CDCl_3$): δ −0.17 (d, *J* 6, H^1), 1.62 (d, 3 H, *J* 6, H^9), 2.17 (dd, *J* 6, 10.4, H^8), 4.19 (d, *J* 10.4, H^7), 4.26 (m, H^{3,5}), 4.74 (m, H^4) and 5.21 (t, *J* 6 Hz, H^2). Mass spectrum (FAB): *m*/*z* 804 (M^+); calc. 805. IR (CH_2Cl_2): $\tilde{\nu}$/cm^{-1} 2060s, 2022vs, 2008s, 1984m, 1968m, 1854w and 1804w.

With 4-phenylbut-1-ene. Triruthenium dodecacarbonyl (450 mg) was heated in octane in the presence of an excess of 4-phenylbut-1-ene (0.5 cm^3) for 2 h. The reaction mixture was monitored and treated as above. The bottom red-orange band contained the required product **2** (31 mg, 5%). ^1H NMR ($CDCl_3$): δ −0.19 (d, *J* 6, H^1), 0.99 (t, 3 H, *J* 7, H^{10}), 1.61 (qnt, 2 H, *J* 7, H^9), 2.12 (m, H^8), 4.20 (d, *J* 10, H^7), 4.26 (t, *J* 6, H^5), 4.28 (t, *J* 6, H^3), 4.75 (t, *J* 6, H^4) and 5.19 (t, *J* 6 Hz, H^2). Mass spectrum (FAB): *m*/*z* 817 (M^+); calc. 819. IR (CH_2Cl_2): $\tilde{\nu}$/cm^{-1} 2060s, 2022vs, 2005s, 1985m, 1967m, 1854w and 1805w.

Crystallography

Crystal data for compound 1. $C_{19}H_{10}O_{10}Ru_4$, M = 802.55, triclinic, space group $P\bar{1}$ (no. 2), a = 9.045(3), b = 15.618(7), c = 23.034(8) Å, α = 81.99(4), β = 87.44(2), γ = 86.41(2)°, U = 3214(2) Å^3, Z = 6, 150(2) K, D_c = 2.488 g cm^{-3}, $F(000)$ = 2280, crystal dimensions 0.16 × 0.08 × 0.05 mm, $2\theta_{max}$ = 53°, λ(Mo-Kα) = 0.710 73 Å, μ(Mo-Kα) = 2.821 mm^{-1}, minimum and maximum absorption correction 0.397 and 0.558.

Refinement on $(F_o)^2$ for 13 341 data and 896 parameters (all non-H atoms anisotropic), $wR2$ = 0.2060 (all data), conventional R = 0.0634 [13 258 data with $F_o > 4\sigma(F_o)$, weighting scheme $w^{-1} = 0.0756\sigma^2(F) + 11.78F^2$]. Hydrogen atoms were placed in geometrically calculated positions. The program SHELXL 93[11] was used for the structure solution and refinement.

Crystal data for compound 2. $C_{20}H_{12}O_{10}Ru_4{\cdot}CH_2Cl_2$, M = 901.49, triclinic, space group $P\bar{1}$ (no. 2), a = 9.217(2), b = 11.258(2), c = 12.827(3) Å, α = 103.30(2), β = 91.42(2), γ = 92.38(2)°, U = 3214(2) Å^3, Z = 2, 150(2) K, D_c = 2.310 g cm^{-3}, $F(000)$ = 856, crystal dimensions 0.49 × 0.23 × 0.16 mm, $2\theta_{max}$ = 50°, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 2.550 mm^{-1}, minimum and maximum absorption correction 0.322 and 0.597.

Refinement on $(F_o)^2$ for 4558 data and 343 parameters (all non-H atoms anisotropic), $wR2$ = 0.1484 (all data), conventional R = 0.0533 [4554 data with $F_o > 4\sigma(F_o)$, $w^{-1} = 0.1051\sigma^2(F) + 3.33F^2$]. Other details as for compound **1**.

Atomic co-ordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/242.

Acknowledgements

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