

Synthesis and Characterisation of $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)]$

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The cluster benzene complex $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)]$ which contains a benzene ligand in a face-capping co-ordination mode has been prepared, and its molecular structure investigated by a single crystal X-ray analysis which provides unambiguous evidence for C–C length alternation.

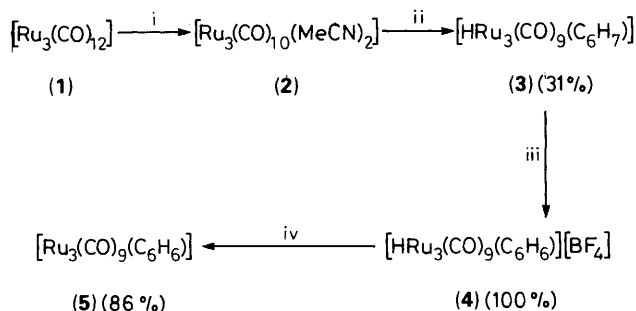
We have recently established¹ a new face-capping bonding mode for benzene in the triosmium cluster $[\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)]$ that bears a striking resemblance to the Kekulé-type distortion found for benzene adsorbed on Rh(111)² and Os(001)³ single crystal surfaces. We now report the preparation of the corresponding ruthenium derivative and its full characterisation by single crystal X-ray analysis which provides clear evidence for C–C bond length alternation within the C_6H_6 and out-of-plane C–H bonding.

The reaction of the activated cluster $[\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2]$ (2) with cyclohexa-1,3-diene in benzene under reflux affords $[\text{HRu}_3(\text{CO})_9(\text{C}_6\text{H}_7)]$ (3) as the major product. This cluster, in turn, reacts with $[\text{CPh}_3][\text{BF}_4]$ in CH_2Cl_2 to give the benzene complex cation $[\text{HRu}_3(\text{CO})_9(\text{C}_6\text{H}_6)][\text{BF}_4]$ (4). Treatment of (4) with DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) in CH_2Cl_2 yields the new benzene cluster $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$ (5) in moderate yield. Apart from the use of (2) as the active Ru_3 -cluster precursor this route parallels that previ-

Table 1. Spectroscopic data for the new Ru_3 cluster complexes.

	¹ H NMR, $\delta(\text{CDCl}_3)$	IR(CH_2Cl_2), $\nu_{\text{CO}}/\text{cm}^{-1}$
$[\text{HRu}_3(\text{CO})_9(\text{C}_6\text{H}_7)]$ (3)	4.93 (1 H, m), 4.04 (2 H, m), 3.68 (1 H, m), 2.95 (2 H, m), 2.17 (1 H, m), –21.16 (1 H, d)	2083m, 2055s, 2032vs, 2008m, br, 1958m
$[\text{HRu}_3(\text{CO})_9(\text{C}_6\text{H}_6)]\text{BF}_4$ (4)	6.10 (6 H, s), –20.11 (5) ^a	2115w, 2091s, 2068vs, 2049 m ^b
$[\text{Ru}_3(\text{CO})_9(\text{C}_6\text{H}_6)]$ (5)	4.56 (6 H, s)	2.071m, 2027vs, 1996s, 1976s, sh

^a ¹H NMR in $(\text{CD}_3)_2\text{CO}$. ^b IR in MeNO.



Scheme 1. The synthesis of $[\text{Ru}_3(\text{CO})_9(\mu_3\eta^2:\eta^2:\eta^2\text{-C}_6\text{H}_6)]$ from $\text{Ru}_3(\text{CO})_{12}$. *Reagents and conditions:* i, $\text{Me}_3\text{NO}/\text{CH}_2\text{Cl}_2$ solution added dropwise in the reaction solution of $\text{CH}_2\text{Cl}_2/\text{MeCN}$ at -78°C ; ii, refluxing benzene in the presence of cyclohexa-1,3-diene; iii, $[\text{CPh}_3][\text{BF}_4]$ in CH_2Cl_2 ; iv, DBU in CH_2Cl_2 .

ously reported¹ for the analogous osmium derivative. Complexes (3), (4), and (5) have been fully characterised on the basis of their spectroscopic data (see Table 1), which compare favourably with those found for the corresponding osmium derivatives, and in the case of (3) and (5) by a single crystal X-ray analysis.[†]

In the few previous reports of arenes bonded to ruthenium clusters the organic ring has been found to co-ordinate in either a conventional η^6 -mode as in $[\text{Ru}_6\text{C}(\text{CO})_{14}(\mu_3\text{C}_6\text{H}_3\text{Me}_3)]$,⁴ $[\text{Ru}_6\text{C}(\text{CO})_{11}(\text{C}_6\text{H}_6)_2]$,¹ or $[\text{Ru}_4(\text{CO})_9(\eta^6\text{-C}_6\text{H}_6)(\text{C}_6\text{H}_8)]$,⁵ or as a benzyne ligand as in $[\text{Ru}_5(\text{CO})_{13}(\mu_4\text{-PPh})(\mu_5\text{-C}_6\text{H}_4)]$.⁶ Complex (5) provides another example of C_6H_6 bonded in the $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ mode. The molecular structures of (5) and (3), as determined by X-ray diffraction, as shown in Figures 1 and 2, respectively, together with the most relevant structural parameters. It is to be emphasized that data of very good quality could be obtained for both species, thus allowing, *inter alia*, unambiguous description of the bonding between the unsaturated ligands and the metal frames, and direct location of all H atoms including the H (hydride) ligand of (3). In (5), 'long' and 'short' C–C bonds [mean 1.45(1), and 1.40(2) Å] alternate within the C_6H_6 ligand, the latter bonds being involved in the co-ordination to the metal atoms. Ru–C distances are also not equivalent ['long' 2.360(5), 'short' 2.301(5) Å] owing to the twist of the benzene moiety with

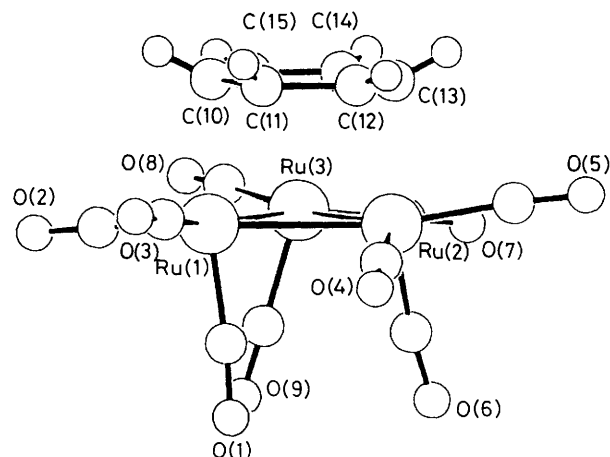


Figure 1. The molecular structure of $[\text{Ru}_3(\text{CO})_9(\text{C}_6\text{H}_6)]$ showing the atom labelling. The C atoms of the CO groups bear the same numbering as the corresponding O atoms. Relevant bond distances (Å) and angles ($^\circ$) include: Ru(1)–Ru(2) 2.829(1), Ru(1)–Ru(3) 2.855(1), Ru(2)–Ru(3) 2.827(1), Ru(1)–C(10) 2.348(5), Ru(1)–C(11) 2.287(5), Ru(2)–C(12) 2.377(5), Ru(2)–C(13) 2.306(5), Ru(2)–C(14) 2.356(4), Ru(3)–C(15) 2.310(5), mean Ru–C(CO) radial 1.92(1), C(CO)–O(CO) radial 1.12(1), Ru–C(CO) axial 1.88(1), C(CO)–O(CO) axial 1.15(1), C(10)–C(11) 1.41(1), C(11)–C(12) 1.45(1), C(12)–C(13) 1.37(1), C(13)–C(14) 1.45(1), C(14)–C(15) 1.41(1), C(10)–C(15) 1.44(1); C(10)–C(11)–C(12) 118.2(4), C(11)–C(12)–C(13) 121.7(4), C(12)–C(13)–C(14) 119.5(4), C(13)–C(14)–C(15) 120.2(4), C(14)–C(15)–C(10) 119.3(4), C(15)–C(10)–C(11) 121.0(4).

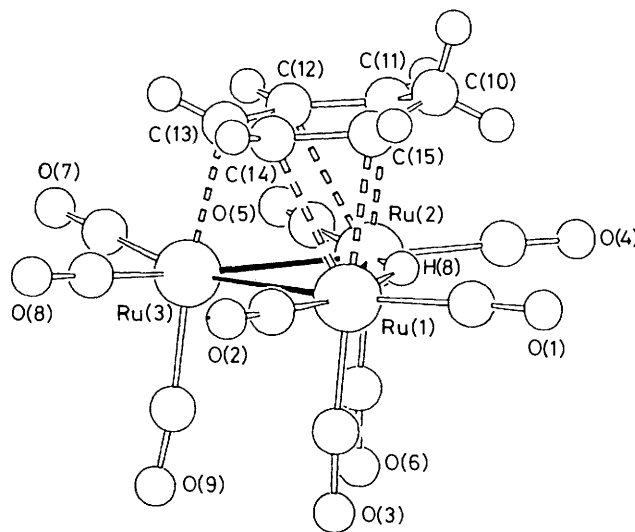


Figure 2. The molecular structure of $[\text{HRu}_3(\text{CO})_9(\text{C}_6\text{H}_7)]$ showing the atom labelling. C atoms of the CO groups bear the same numbering as the corresponding O atoms. Relevant bond distances (Å) and angles ($^\circ$) include: Ru(1)–Ru(2) 3.052(1), Ru(1)–Ru(3) 2.837(1), Ru(2)–Ru(3) 2.837(1), Ru(1)–H(8) 1.65(2), Ru(2)–H(8) 1.64(2), Ru(1)–C(14) 2.441(4), Ru(1)–C(15) 2.307(4), Ru(2)–C(11) 2.278(4), Ru(2)–C(12) 2.431(3), Ru(3)–C(13) 2.177(4), mean Ru–C(CO) radial 1.904(4), C(CO)–O(CO) radial 1.13(1); Ru(1)–C(3) 1.904(4), Ru(2)–C(6) 1.898(4), Ru(3)–C(9) 1.941(4), C(10)–C(11) 1.51(1), C(11)–C(12) 1.38(1), C(12)–C(13) 1.45(1), C(13)–C(14) 1.45(1), C(14)–C(15) 1.39(1), C(10)–C(15) 1.50(1); C(10)–C(11)–C(12) 119.5(4), C(11)–C(12)–C(13) 124.3(4), C(12)–C(13)–C(14) 114.9(4), C(13)–C(14)–C(15) 123.3(4), C(14)–C(15)–C(10) 120.7(4), C(15)–C(10)–C(11) 112.3(4), Ru(1)–H(8)–Ru(2) 137(2).

[†] *Crystal data* for (5): $\text{C}_{15}\text{H}_6\text{O}_9\text{Ru}_3$, $M = 633.4$, monoclinic, space group $P2_1$, $a = 9.027(1)$, $b = 12.665(2)$, $c = 9.049(3)$ Å, $\beta = 118.15(2)^\circ$, $U = 912.2$ Å³, $Z = 2$, $D_c = 2.31$ g cm⁻³, $F(000) = 600$, $\mu(\text{Mo-K}\alpha) = 22.6$ cm⁻¹, θ range $2.5\text{--}35^\circ$, final R value 0.026, $R_w = 0.031$ for 3469 out of 3807 independent reflections [$I_o > 2\sigma(I_o)$]. For (3): $\text{C}_{15}\text{H}_8\text{O}_9\text{Ru}_3$, $M = 637.3$, monoclinic, space group $P2_1$, $a = 8.487(6)$, $b = 12.031(3)$, $c = 9.073(2)$ Å, $\beta = 92.43(4)^\circ$, $U = 925.6$ Å³, $Z = 2$, $D_c = 2.29$ g cm⁻³, $F(000) = 604$, $\mu(\text{Mo-K}\alpha) = 22.3$ cm⁻¹, θ range $2.5\text{--}28^\circ$, final R value 0.017, $R_w = 0.019$ for 2228 out of 2414 independent reflections [$I_o > 2\sigma(I_o)$]. Common to both species: absorption correction was applied by the Walker and Stuart method [correction ranges 0.90–1.21 and 0.87–1.10 for (5) and (3), respectively].⁷ Intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer by the ω - 2θ scan method. H atoms, including the H(hydride) in (3) were directly located from the final difference Fourier maps. Average values of the C–H distances were refined in both (5) and (3) [0.92(2) and 0.95(2) Å, respectively]. Equivalence of the two Ru–H distances in (3) was also imposed [1.64(2) Å] according to the molecular symmetry. All non-hydrogen atoms were treated anisotropically; single isotropic thermal parameters were refined for chemically equivalent H atoms in (5) and (3) [H(benzene) in (5) 0.07; for (3): H(CH) 0.06, H(CH₂) 0.07, H(hydride) 0.08 Å²].⁸ Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

respect to the underlying Ru₃ triangle which causes deviation from exact staggering of the two fragments and torsion of the Ru(CO)₃ groups. Altogether the idealized symmetry is C₃. H atoms of the C₆H₆ ring bend away from the metal frame (average elevation from the C₆-plane 0.33 Å). The C₆H₇ ligand in (3) adopts a different rotameric configuration with respect to the metal frame, being almost eclipsed, although the entire ligand is 'shifted' slightly in order to optimize the σ-bonding between the atom opposite to the CH₂ [C(13)] group and the underlying Ru atom. The ligand contributes a total of five electrons *via* one σ-bond and two π-interactions.

The C–C bonds show a pattern in agreement with a 1,4 localization of the double bonds. As in (5) the H atoms are above the ligand plane. The H-(hydride) position is unusual, being almost coplanar with the Ru₃ triangle and close to the Ru–Ru bond. The positioning of this atom is supported by space-filling diagrams and by the usual arguments on CO ligand displacement. Finally, it is worth noting that Ru–C(CO) radial distances in (5) are longer than the axial ones [mean values 1.92(1) and 1.88(1) Å, respectively]. In contrast in (3) radial and axial Ru–C(CO) bond lengths are almost equivalent with the exception of the one 'trans' to the σ-interaction discussed above which shows the longest value

[Ru(3)–C(9) 1.941(4) Å] in agreement with a diminished π-back donation from the electron-poorer Ru(3) atom.

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