Benzene in a New Face-capping Bonding Mode: Molecular Structures of $[Ru_6C(CO)_{11}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)]$ and $[Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$

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A new co-ordination mode for benzene ligands in cluster complexes, in which the ring is symmetrically placed above a metal triangle has been crystallographically established in the carbonyl complexes $[Ru_6C(CO)_{11}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)]$ and $[Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$.

Despite the continuing interest in the chemistry of arene ligands attached to mononuclear transition metals,[1] there has been relatively little attention paid to the interaction between arenes and transition metal cluster complexes. This is perhaps surprising since such interactions might be expected to mimic the interactions of arenes with metal surfaces, a subject about which there is considerable speculation.[2] In the few previous reports of arenes bonded to clusters the organic ring has been found to co-ordinate in either a conventional η^6-mode to one metal centre, as in $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me)]$[3] and $[Ru_4(CO)_9(\eta^6\text{-}C_6H_6)(C_6H_8)]$,[4] or as a benzyne ligand, bonding to three metals *via* two σ- and one π-bond, as in $[Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}C_6H_4)(\mu\text{-}X)]$ (X = H,[5] SMe,[6] AsMe$_2$[7]).

In this communication we report two synthetic approaches which lead to the formation of clusters that contain a benzene ligand bonded as a triene in a novel 'face-capping' mode.

The first synthetic approach involves the introduction of the benzene ligand into the cluster unit *via* a preformed mononuclear complex. The transition from η^6-terminal to $\mu_3\text{-}\eta^2:\eta^2:\eta^2$-face-capping ligation occurs during the course of the reaction. The reaction of $[N(PPh_3)_2]_2[Ru_5C(CO)_{14}]$[8] with $[Ru(\eta^6\text{-}C_6H_6)(PhCN)_3][ClO_4]$[9] in CH_2Cl_2, under reflux, affords the cluster $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)]$ in high yield. This

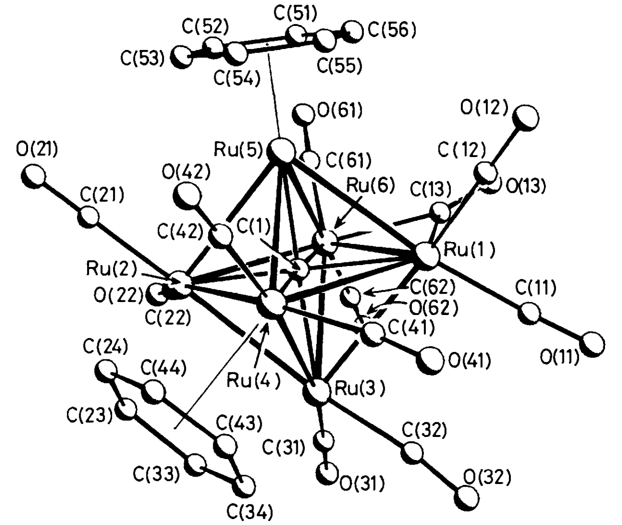

Figure 1. The molecular structure of $[Ru_6C(CO)_{11}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)]$ showing the atom labelling scheme. Important bond lengths (Å): Ru(1)–Ru(3), 2.908(1); Ru(1)–Ru(4), 3.006(1); Ru(1)–Ru(5), 2.864(1); Ru(1)–Ru(6), 2.819(1); Ru(2)–Ru(3), 2.864(1); Ru(2)–Ru(4), 2.919(1); Ru(2)–Ru(5), 2.879(1); Ru(2)–Ru(6), 2.907(1); Ru(2)–Ru(4), 2.846(1); Ru(3)–Ru(6), 2.926(1); Ru(4)–Ru(5) 2.848(1); Ru(5)–Ru(6) 2.880(1); mean Ru–C(carbido), 2.043; Ru(2)–C(23), 2.21(1); Ru(2)–C(24), 2.35(1); Ru(3)–C(33), 2.31(1); Ru(3)–C(34) 2.24(1); Ru(4)–C(43), 2.26(1); Ru(4)–C(44), 2.25(1); C(23)–C(24), 1.42(2); C(23)–C(33), 1.46(2); C(33)–C(34), 1.39(2); C(34)–C(43), 1.50(2); C(43)–C(44), 1.37(2); C(44)–C(24), 1.48(2).

complex has been obtained previously, in low yield, when $[Ru_3(CO)_{12}]$ is heated in benzene.[10]

This hexanuclear cluster may then be reduced with Na_2CO_3–MeOH to produce the new dianion $[Ru_6C(CO)_{12}(C_6H_6)]^{2-}$ which on treatment with a further aliquot of $[Ru(C_6H_6)(PhCN)_3]^{2+}$ gives as the major product the dark-red cluster, $[Ru_6C(CO)_{11}(C_6H_6)_2]$.† A single crystal *X*-ray analysis‡ shows that one of the C_6H_6 rings adopts the conventional η^6-terminal mode but the other takes up the $\mu_3\text{-}\eta^2:\eta^2:\eta^2$-face-capping mode (Figure 1) which has not previously been observed in a cluster system. However, this is exactly the mode of co-ordination found in a LEED study of benzene attached to a rhodium surface.[11] The analogy is strengthened by an examination of the face of the cluster which is capped by the benzene. The two carbonyls on each Ru atom are almost co-planar with the metal triangle and the plane of the benzene ring makes an angle of 0.5° with the metal triangle. An unusual feature of the structure is the apparent alternation of bond lengths around the benzene ring. The lengths of the C–C bonds which span the Ru atoms average 1.39(2) Å while the unattached C–C bond lengths average 1.48(2) Å. This type of alternation is hinted at in the LEED study.[11] Distortion of bond lengths around aromatic rings has been noted previously when, for example, a metal is co-ordinated to just two of the carbon atoms in the ring.[12]

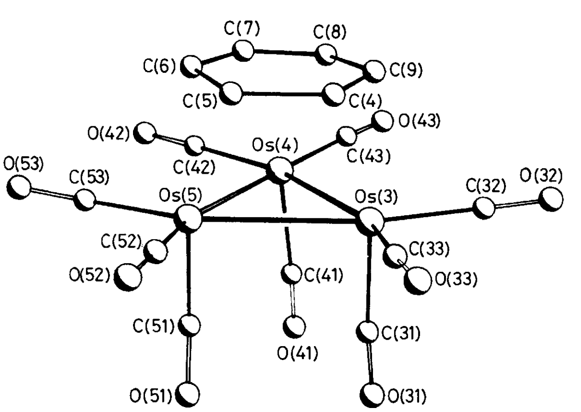

Figure 2. The molecular structure of $[Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ showing the atom labelling scheme. Important bond lengths (Å): Os(3)–Os(4), 2.878(1); Os(4)–Os(5), 2.856(1); Os(3)–Os(5), 2.862(1); Os(3)–C(4), 2.27(2); Os(3)–C(9), 2.39(2); Os(4)–C(7), 2.28(2); Os(4)–C(8), 2.27(2); Os(5)–C(5), 2.32(3); Os(5)–C(6), 2.42(3); C(4)–C(5), 1.56(4); C(5)–C(6), 1.45(4); C(6)–C(7), 1.52(4); C(7)–C(8), 1.37(3); C(8)–C(9), 1.45(3); C(4)–C(9), 1.40(3).

In the second synthetic approach a cyclohexadiene complex is dehydrogenated to give the face-capping benzene ligand. The reaction of $[Os_3H_2(CO)_{10}]$ with cyclohexadiene affords $[Os_3H(CO)_9(C_6H_7)]$ as the major product.[13] This cluster, in turn, has been reported to react with $[CPh_3][BF_4]$ to give a complex formulated as $[Os_3H(CO)_9(C_6H_6)][BF_4]$ on the basis of ^1H n.m.r. spectra. If $[Os_3H(CO)_9(C_6H_7)]$ is treated successively with $[CPh_3][BF_4]$ and then DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) the new cluster $[Os_3(CO)_9(C_6H_6)]$ is isolated in high yield.§ The ^1H n.m.r. spectrum of this complex displays a singlet resonance at δ 4.46, similar to that observed for the $\mu_3\text{-}\eta^2:\eta^2:\eta^2$-benzene ligand in $[Ru_6C(CO)_{11}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$. An *X*-ray analysis¶ of $[Os_3(CO)_9(C_6H_6)]$ (Figure 2) shows that the benzene adopts

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† *Spectroscopic data* for $[Ru_6C(CO)_{11}(C_6H_6)_2]$: i.r. ($CH_2Cl_2$ solution) ν_{CO} 2039m, 2002s, 1995sh, 1990sh, 1950w, 1897w cm^{-1}; ^1H n.m.r. (CD_2Cl_2 solution) δ 4.14, 5.54.

‡ *Crystal data:* $[Ru_6C(CO)_{11}(C_6H_6)_2]$, M = 1082.76, triclinic, space group $P\bar{1}$ (No. 2), a = 9.351(3), b = 9.676(3), c = 15.601(3) Å, α = 92.65(2), β = 92.42(3), γ = 106.42(3)°, U = 1350.3 Å^3, Z = 2, D_c = 2.66 g cm^{-3}, F(000) = 1016, μ(Mo-K_α) = 7.22 cm^{-1}. Intensity data ($2\theta_{max.}$ = 50.0°) were recorded on a Stoe–Siemens four-circle diffractometer using graphite monochromated Mo-K_α radiation and an ω–θ scan technique. The data were corrected for absorption and averaged to give 2629 unique observed reflections [$F > 4\sigma(F)$]. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by blocked full matrix least squares to R = 0.039. The positional parameters of the hydrogen atoms of the $\mu_6\text{-}\eta^2$-benzene ligand were allowed to refine freely but were assigned a common isotropic temperature factor. The η^6-benzene was positionally disordered over two sites, and was refined as two interlocking hexagons (C–C 1.395 Å) with a common isotropic temperature factor and occupancies k and $1-k$; k refined to 0.85(1).

§ *Spectroscopic data* for $[Os_3(CO)_9(C_6H_6)]$: i.r. (cyclohexane solution) ν_{CO} 2081m, 2035s, 1986m, 1970w cm^{-1}; ^1H n.m.r. (CD_2Cl_2 solution) δ 4.46.

¶ *Crystal data:* $[Os_3(CO)_9(C_6H_6)]$, M = 900.8, monoclinic, space group *Im* (non-standard setting of *Cm*; No. 8), a = 8.412(1), b = 35.449(4), c = 8.877(1) Å, β = 92.44(1)°, U = 2644.7 Å^3, Z = 6, D_c = 3.39 g cm^{-3}, F(000) = 2376, μ(Mo-K_α) = 216.07 cm^{-1}. Intensity data ($2\theta_{max.}$ = 50.0°) were recorded on a Stoe–Siemens four-circle diffractometer using graphite-monochromated Mo-K_α radiation and an ω–θ scan technique. The data were corrected for absorption and averaged to give 2465 unique, observed reflections [$F > 4\sigma(F)$]. The structure was solved by a combination of direct methods and Fourier difference techniques and refined by full matrix least squares (Os and O anisotropic) to R = 0.032. The asymmetric unit contains 1.5 molecules with a crystallographic mirror plane passing through one molecule.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

the same face-capping mode as in the hexaruthenium cluster. The benzene-capped triosmium cluster has approximate C_{3v} symmetry, and the plane of the benzene ring lies only 1.1° out of the plane defined by the Os atoms and equatorial carbonyl groups. The high estimated standard deviations associated with aromatic C–C distances preclude an accurate assessment of the bonding within the ring, but the overall trend of alternating 'long' and 'short' bonds is similar to that in the μ_3-η^2:η^2:η^2-C_6H_6 ring of the Ru_6 cluster.

The molecule $[Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ may be compared with $[Os_3H_2(CO)_9(C_6H_4)]$. The latter cluster is prepared[5] by the reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with benzene. The fact that no interconversion between the two isomers has been observed indicates that the preparative route is crucial to the mode of co-ordination of ligands such as benzene.

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References

1 R. G. Gastinger and K. J. Klabunde, *Transition Met. Chem.*, 1979, **4**, 1.
2 E. L. Muetterties, *Pure Appl. Chem.*, 1982, **54**, 83.
3 R. Mason and W. R. Robinson, *J. Chem. Soc., Chem. Commun.*, 1968, 468.
4 S. Aime, L. Milone, D. Osella, G. A. Vaglio, M. Valle, A. Tiripicchio, and M. Tiripicchio Camellini, *Inorg. Chim. Acta*, 1979, **34**, 49.
5 R. J. Goudsmit, B. F. G. Johnson, J. Lewis, P. R. Raithby, and M. J. Rosales, *J. Chem. Soc., Dalton Trans.*, 1983, 2257.
6 R. D. Adams, D. A. Katahira, and L.-W. Yang, *Organometallics*, 1982, **1**, 235.
7 A. J. Deeming, I. P. Rothwell, M. B. Hursthouse, and J. D. J. Backer-Dirks, *J. Chem. Soc., Dalton Trans.*, 1981, 1879.
8 B. F. G. Johnson, J. Lewis, W. J. H. Nelson, J. N. Nicholls, J. Puga, P. R. Raithby, M. J. Rosales, M. Schröder, and M. D. Vargas, *J. Chem. Soc., Dalton Trans.*, 1983, 2447.
9 M. A. Bennett and A. K. Smith, *J. Chem. Soc., Dalton Trans.*, 1974, 233.
10 C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1975, 2606.
11 M. A. van Hove, Rangfu Lin, and G. A. Somarjai, *Phys. Rev. Lett.*, 1983, **51**, 778.
12 J. Browning, M. Green, B. R. Penfold, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1973, 31.
13 E. G. Bryan, B. F. G. Johnson, J. W. Kelland, and M. McPartlin, *J. Chem. Soc., Chem. Commun.*, 1976, 254.