The Synthesis and Characterisation of the Octaruthenium–benzene Cluster $[Ru_8H_4(CO)_{18}(\eta^6\text{-}C_6H_6)]$

Brian F. G. Johnson,*[a] Caroline M. Martin,[a] Dario Braga,[b] Fabrizia Grepioni*[b] and Emilio Parisini[b]

[a] *Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ*
[b] *Dipartimento di Chimica G. Ciamician, Università de Bologna, Via Selmi 2, 40126 Bologna, Italy*

The reaction of cyclohexene, C_6H_{10}, with $Ru_3(CO)_{12}$ yields the new octaruthenium–benzene cluster $[Ru_8H_4(CO)_{18}(\eta^6\text{-}C_6H_6)]$ which has been fully characterised in solution by conventional spectroscopic methods and in the solid state by a single crystal X-ray diffraction analysis.

Research into cluster compounds containing a coordinated benzene ligand has been stimulated largely by their potential to serve as models for the interaction of benzene on a metal (111) surface.[1] Although the benzene clusters seen to date have served as reasonable models, until now studies on ruthenium clusters bearing only carbonyls and hydrides in addition to the benzene ligand have been limited to nuclearities between three and six.[2] There is a need to explore in greater detail the interactions of benzene and other arenes with clusters of higher nuclearities, which might be more reasonably considered to approach the bulk metallic regime. In other work we have established that the Kekulé distortions in the benzene molecule bonded to a trimetallic cluster face increase with cluster size.[3] We report here the synthesis of the first example of an octaruthenium–benzene cluster which also exhibits properties consistent with a change in the nature of the benzene as the number of the metal atoms increases.

On heating a solution of $Ru_3(CO)_{12}$ in octane containing C_6H_8, or reaction directly in benzene, has been shown to yield benzene-containing tetraruthenium butterfly and hexaruthenium octahedral carbido clusters, respectively.[4,5] We now report that in a similar reaction using C_6H_{10}, three major products are formed. Two are the same as those reported previously, *viz.* $[Ru_4(CO)_{12}(C_6H_8)]$ and $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)]$, but the third is the new octaruthenium cluster $[Ru_8H_4(CO)_{18}(\eta^6\text{-}C_6H_6)]$ **1**. This novel compound has been characterised by spectroscopy† and its structure determined by single crystal X-ray diffraction.

The solid state molecular structure of **1**‡ is shown in Fig. 1, together with some relevant structural parameters. The ruthenium cluster consists of an octahedron capped by two additional metal atoms on two triangular faces sharing a common vertex. The metal core geometry can also be formally derived from the tetracapped octahedral metal framework shared by $[Ru_{10}HC(CO)_{24}]^-$ (ref. 6*a*,*b*) or $[Ru_{10}C(CO)_{24}]^{2-}$ (ref. 6*a*,*c*) and is also observed in a number of osmium derivatives,[7] by removal of two capping metals. The metal atom arrangement of compound **1** has been previously observed only for the osmium cluster anion $[Os_8(CO)_{22}]^{2-}$,[8] and for the mixed neutral cluster $[Os_6Pt_2(CO)_{17}(C_8H_{12})_2]$.[9] Interestingly, these compounds and complex **1** all share the same number of valence shell electrons, *i.e.* 110 electrons. The Ru–Ru bond distances range from 2.770(1) to 3.057(1) Å. The benzene ligand is η^6-bound to the only octahedron vertex not belonging to the capped triangular faces. Two symmetrically bridging CO ligands span two opposite Ru edges connecting the capped triangles, while the remaining 16 COs are terminally bound, three on each Ru cap and two on all the Ru atoms not involved in the arene substitution. Only two of the four hydride atoms could be experimentally observed triply bridging the Ru triangular faces adjacent to those capped; their position was verified using the program XHYDEX,[10] which also gave indication of a third hydride bridging one of the longest Ru–Ru edges [Ru(1)–Ru(7)]. The position of this hydride could also be inferred by the presence of a large niche in the ligand envelope accompanied by a pronounced distortion of the CO ligands, which are bent away from the metal–metal bond. The location of the fourth hydride is more critical, due to the absence of preferential cavities in the ligand coverage and of a clear-cut potential energy minimum on the cluster surface; this atom is probably disordered over different cluster sites or is placed inside the octahedral cavity. A similarly complicated distribution of the hydrides has been observed in a recent neutron diffraction study at 20 K on the dianion $[Os_{10}H_4(CO)_{24}]^{2-}$,[7b] where the hydrido ligands were located on the cluster surface, two in μ_3 and two in μ_2 sites. In spite of the size and complexity of compound **1**, the molecules arrange themselves in pairs throughout the crystal, with the benzene ligands facing each other in a graphitic fashion (distance between the ring planes 3.32 Å), as observed in a number of arene transition metal clusters.[11]

In order to make a meaningful comparison between benzene clusters of differing nuclearity, it is important that the compounds in question are compatible. Clearly this new cluster extends the sequence already observed for high nuclearity clusters since it is neutral, it contains only carbonyls and hydrides in addition to the benzene ligand, and the metal atom to which the benzene bonds has a connectivity of four. We have predicted that as the nuclearity of a cluster increased (and hence became more like a bulk metal) the chemical shift

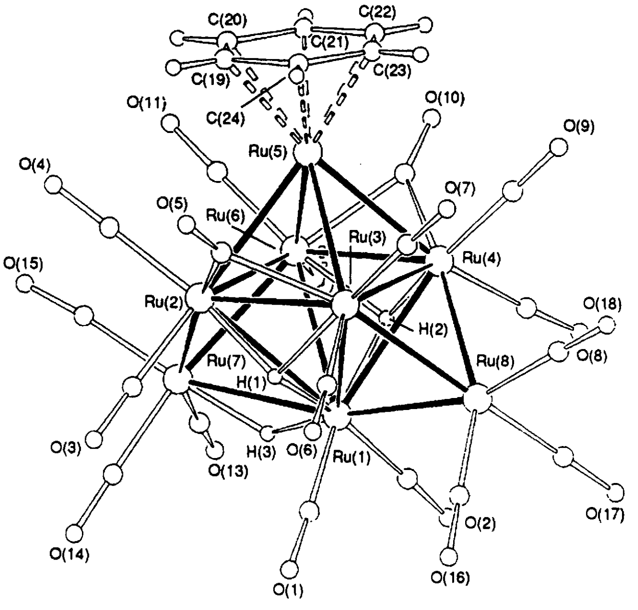

Fig. 1 Molecular structure of $[Ru_8H_4(CO)_{18}(\eta^6\text{-}C_6H_6)]$ **1**, showing the labelling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms. Relevant bond distances (Å) are: Ru(1)–Ru(2), 3.025(1); Ru(1)–Ru(3), 3.001(1); Ru(1)–Ru(4), 2.963(1); Ru(1)–Ru(6), 3.057(1); Ru(1)–Ru(7), 3.056(1); Ru(1)–Ru(8), 2.818(1); Ru(2)–Ru(3), 2.808(1); Ru(2)–Ru(5), 2.855(1); Ru(2)–Ru(6), 2.870(1); Ru(2)–Ru(7), 2.785(1); Ru(3)–Ru(4), 2.912(1); Ru(3)–Ru(5), 2.861(1); Ru(3)–Ru(8), 2.746(1); Ru(4)–Ru(5), 2.885(1); Ru(4)–Ru(6), 2.796(1); Ru(4)–Ru(8), 2.757(1); Ru(5)–Ru(6), 2.861(1); Ru(6)–Ru(7), 2.770(1); mean Ru–C($CO_{terminal}$), 1.882(5); mean Ru–C($CO_{bridging}$), 2.139(5); mean C–O, 1.136(6); mean Ru–C(benzene), 2.208(5); mean C–C, 1.40(1); mean H(μ_3)–Ru, 1.83(1); H(3)–Ru(1), 1.62(1); H(3)–Ru(7), 1.69(1).

in the ^{1}H NMR should decrease.[3] This is now confirmed by experiment. Thus [$Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$] exhibits a ^{1}H NMR resonance at δ 5.93,[2c] [$Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)$] at δ 5.56,[2e] and in **1** the resonance is observed at δ 5.40. It would appear from these preliminary experiments that the nature of the benzene–cluster interaction may be followed quite readily as a function of cluster size and may shed further light on the complexities of interactions on the bulk surface. We believe these differences in chemical shift arise from the π-accepting capability of the cluster unit and hope to delineate this phenomenon by preparing and characterising a range of higher nuclearity benzene clusters.

We thank the SERC and ICI (Wilton) (C. M. M.), and MURST (Italy) (D. B., F. G., E. P.) for financial support. D. B., F. G. and B. F. G. J. acknowledge NATO for a travel grant.

Received, 23rd February 1994; Com. 4/01118J

Footnotes

† *Spectroscopic data* for [$Ru_8H_4(CO)_{18}(\eta^6\text{-}C_6H_6)$]: IR ($CH_2Cl_2$) $\upsilon_{(CO)}$/cm^{-1}: 2091m, 2080m, 2066vs, 2031s, 2006w sh, 1966w, 1922w; ^{1}H NMR ($CDCl_3$): δ 5.40 (s, 6 H), −17.80 (s, 2 H), −19.26 (s br, 2 H); positive fast atom bombardment mass spectrum M$^+$ obs. 1394, calc. 1395.

‡ *Crystal data* for **1**, $C_{24}H_{10}O_{18}Ru_8$: M = 1394.89, monoclinic, space group $P2_1/n$, a = 15.930(7), b = 12.909(5), c = 16.43(2) Å, β = 95.51(6)°, U = 3363.1 Å^3, Z = 4, D_c = 2.78 g cm^{-1}, $F(000)$ = 2600, μ(Mo-Kα) = 32.81 cm^{-1}, $3.0 < \theta < 25°$, final wR_2 (on F^2, all data) = 0.0658, final R_1 [on F, for 4687 unique reflections with $I > 2\sigma(I)$] = 0.0222, 6401 collected reflections, 5869 unique reflections used in the refinement, G.o.F. (on F^2) = 1.04. All non-H atoms allowed to vibrate anisotropically. The H(benzene) atoms were added in calculated positions (C–H, 0.93 Å) and refined riding on the respective C atoms. H(benzene) atoms were refined isotropically, while thermal parameters for the three refined H(hydride) atoms were fixed to 0.05 Å^2. All calculations were performed using the crystallographic programs SHELX86[12a] and SHELXL93.[12b] Atomic coordinates, anisotropic thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors.

References

1 M. A. Van Hove, R. F. Lin and G. A. Somorjai, *J. Am. Chem. Soc.*, 1986, **108**, 2532; R. F. Lin, G. S. Blackman, M. A. Van Hove and G. A. Somorjai, *Acta Crystallogr., Sect. B*, 1987, **43**, 368 and references therein.

2 (*a*) B. F. G. Johnson, J. Lewis, M. Martinelli, A. H. Wright, D. Braga and F. Grepioni, *J. Chem. Soc., Chem. Commun.*, 1990, 364; (*b*) D. Braga, F. Grepioni, B. F. G. Johnson, J. Lewis, C. E. Housecroft and M. Martinelli, *Organometallics*, 1991, **10**, 1260; (*c*) D. Braga, F. Grepioni, P. Sabatino, P. J. Dyson, B. F. G. Johnson, J. Lewis, P. J. Bailey, P. R. Raithby and D. Stalke, *J. Chem. Soc., Dalton Trans.*, 1993, 985; (*d*) M. P. Gomez-Sal, B. F. G. Johnson, J. Lewis, P. R. Raithby and A. H. Wright, *J. Chem. Soc., Chem. Commun.*, 1985, 1682; (*e*) P. J. Dyson, B. F. G. Johnson, J. Lewis, M. Martinelli, D. Braga and F. Grepioni, *J. Am. Chem. Soc.*, 1993, **115**, 9062.

3 B. F. G. Johnson, *J. Organomet. Chem.*, special issue to be published June 1994.

4 S. Aime, L. Milone, D. Osella, G. A. Vaglio, M. Valle, A. Tiripicchio and M. Tiripiccho Camellini, *Inorg. Chim. Acta*, 1979, **34**, 49.

5 C. R. Eady, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1975, 2606.

6 (*a*) P. J. Bailey, B. F. G. Johnson, J. Lewis, M. McPartlin and H. R. Powell, *J. Organomet. Chem.*, 1989, **377**, C17; (*b*) M. P. Cifuentes and M. G. Humphrey, *Organometallics*, 1993, **12**, 4272; (*c*) T. Chihara, R. Komoto, K. Kobayashi, H. Yamazaki and Y. Matsuura, *Inorg. Chem.*, 1989, **28**, 964.

7 (*a*) D. Braga and F. Grepioni, *Organometallics*, 1992, **11**, 1256, and references therein; (*b*) A. Bashall, L. H. Gade, J. Lewis, B. F. G. Johnson, G. McIntyre and M. McPartlin, *Angew. Chem. Int. Ed. Engl.*, 1991, **30**, 1164.

8 P. F. Jackson, B. F. G. Johnson, J. Lewis and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1980, 60.

9 C. Couture, D. H. Farrar and R. J. Goudsmit, *Inorg. Chim. Acta*, 1984, **89**, L29.

10 A. G. Orpen, XHYDEX, A Program for Locating Hydrides, Bristol University, 1980; see also A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1980, 2509.

11 D. Braga and F. Grepioni, *Acc. Chem. Res.*, 1994, **27**, 51.

12 (*a*) G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467; (*b*) G. M. Sheldrick, SHELXL93, University of Gottingen, Germany, 1993.