# Synthesis and Crystallographic Characterisation of $[Ru_7C(CO)_{16}(C_9H_8)]$ and $[Ru_7C(CO)_{16}(C_{12}H_{12})]$: Facial $\pi$ Bonding and $\sigma$ Bonding from the same Ring System

**Alexander J. Blake,[a] Paul J. Dyson,[a] Petra E. Gaede,[a] Brian F. G. Johnson,*,[a] Dario Braga[b] and Emilio Parisini[b]**
[a] *Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK*
[b] *Dipartimento di Chimica, Universita di Bologna, Via Selmi 2, 40126 Bologna, Italy*

---

The heptanuclear clusters $[Ru_7C(CO)_{16}(C_9H_8)]$ and $[Ru_7C(CO)_{16}(C_{12}H_{12})]$ have been isolated from the reaction between $[Ru_3(CO)_{12}]$ and isopropenyl- or 1,3-diisopropenyl-benzene and their crystal structures determined: the $Ru_7$ cores represent rare examples of spiked octahedra; the organo-ligands are bound through all four $\pi$ bonds to a metal face and through two $\sigma$ bonds to the ruthenium spike, donating a total of ten electrons.

---

There is considerable interest in the different co-ordination modes that small organic molecules can adopt. For example, over twenty different bonding modes have been identified for acetylenic ligands in which $\sigma$ and $\pi$ bonding (or a combination of both) takes place.[1] With unsaturated organic rings two main distinctions may be used to classify the bonding type. First, $\pi$-bonded systems in which the ring bonds to one, two or three metal centres solely through the $\pi$ electrons,[2] and secondly $\sigma$ systems in which one or more C–H bonds undergo cleavage with the formation of metal–carbon $\sigma$ bonds.[3] These latter systems are often in association with $\pi$ bonds but not generally through the entire $\pi$ system. The synthesis of compounds of both types is important in furthering our understanding of the chemisorption of molecules to metal surfaces,[4] and also understanding the effect such bonding modes have on the reactivity of the organic molecule. (Examples of organic syntheses from organometallic compounds may be found in most organometallic textbooks; the reactivity of ligands participating in multicentre bonding modes has been less well developed although some examples are cited in ref. 2.)

In the course of our studies on arene clusters we have focused our attention on the synthesis of clusters with facially bonded six-membered carbocycles. Here we report the synthesis and structural characterisation of two highly unusual heptanuclear clusters showing a spiked-octahedral metal core and carrying an isopropenylbenzene ($C_9H_{10}$) or 1,3-diisopropenylbenzene ($C_{12}H_{14}$) ligand formally donating ten electrons to the cluster unit, six from the arene ring, two from the $\pi$ bond of the isopropenyl group, and two from a pair of Ru–C $\sigma$ bonds.

The thermolysis of $[Ru_3(CO)_{12}]$ with either $C_9H_{10}$ or $C_{12}H_{14}$ in octane results in the formation of a number of products which may be isolated by thin-layer chromatography.[†] The two main products from these reactions consist of tri- and tetra-nuclear clusters in which the organic ligands bond facially to three ruthenium atoms using all of the $\pi$ electrons available.[5] Several other compounds are also produced, albeit in much lower yields, with metal nuclearities ranging from two to seven. One from each reaction has a nuclearity of seven; they have been characterised as $[Ru_7C(CO)_{16}(C_9H_8)]$ **1** and $[Ru_7C(CO)_{16}(C_{12}H_{12})]$ **2** from a combination of spectroscopy and single-crystal X-ray diffraction studies.[‡]

The solid-state molecular structures of compounds **1** and **2** are shown in Fig. 1(*a*) and 1(*b*). The metal cores comprise a $Ru_6$ octahedron encapsulating a carbide atom. A seventh Ru atom protrudes from a vertex of the octahedron. This type of spiked-

---

[†] The cluster $[Ru_3(CO)_{12}]$ (250 mg) was heated to reflux in octane (20 $cm^3$) for 4 h in the presence of $C_9H_{10}$ or $C_{12}H_{14}$ (1 $cm^3$). The solvent was removed *in vacuo* and the products separated by TLC using 30% dichloromethane–hexane as eluent. In each case the bottom red-brown band was extracted into dichloromethane and characterised as $[Ru_7C(CO)_{16}(C_9H_8)]$ **1** or $[Ru_7C(CO)_{16}(C_{12}H_{12})]$ **2**. Spectroscopic data: **1**, IR($CH_2Cl_2$) $\tilde{\nu}_{CO}$ 2088m, 2060s, 2032vs, 2010m, 1988w, 1970w, 1934w (sh), 1833w (br) and 1810w (br) $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta$ 6.98 (s, $H^8$), 5.31 (m, $H^1$), 5.07 (m, 2 H, $H^{2/3}$), 4.90 (m, $H^4$) and 0.99 (s, 3 H, $H^9$); mass spectrum, $m/z$ = 1284 ($M^+$, calc. 1283) [Found (Calc.): C, 23.70 (24.35); H, 0.60 (0.60)%]; **2**, IR ($CH_2Cl_2$) $\tilde{\nu}_{CO}$ 2087m, 2060s, 2033vs, 2024vs, 2004s, 1977m (sh), 1969w (sh), 1932w (br) and 1836w (br) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.01 (s, $H^8$), 5.41 (m, $H^{11b}$), 5.39 (m, $H^{11a}$), 5.33 (m, $H^3$), 5.26 (s, br, $H^1$), 5.14 (m, $H^4$), 2.29 (s, 3 H, $H^{12}$) and 1.05 (s, 3 H, $H^9$); mass spectrum, $m/z$ 1326 ($M^+$, calc. 1323).

[‡] Crystal data: **1**, $C_{26}H_8O_{16}Ru_7{\cdot}0.5CH_2Cl_2$, $M = 1301.54$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.837(5)$, $b = 10.023(4)$, $c = 17.159(9)$ Å, $\alpha = 77.32(3)$, $\beta = 84.75(3)$, $\gamma = 77.22(3)°$, $U = 1608.0(13)$ Å$^3$, $Z = 2$, 150(2) K, $D_c = 2.688$ g $cm^{-3}$, $F(000) = 1217$, crystal dimensions $0.04 \times 0.31 \times 0.39$ mm, $2\theta_{max} = 45°$, $\lambda$(Mo-K$\alpha$) = 0.710 73 Å, $\mu$(Mo-K$\alpha$) = 3.314 $mm^{-1}$; minimum and maximum absorption correction 0.905 and 1.078;[6] refinement on $(F_o)^2$ for 3864 data and 303 parameters (Ru and most O atoms anisotropic), $wR2 = 0.1964$ (all data), conventional $R = 0.0610$ [3306 data with $F_o > 4\sigma(F_o)$, weighting scheme $w^{-1} = \sigma^2(F) + 0.0004\ F^2$]; **2**, $C_{29}H_{12}O_{16}Ru_7$, $M = 1323.88$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 16.179(6)$, $b = 20.080(10)$, $c = 10.518(4)$ Å, $U = 3417(3)$ Å$^3$, $Z = 4$, 293(2) K, $D_c = 2.573$ g $cm^{-3}$, $F(000) = 2488$, crystal dimensions $0.15 \times 0.12 \times 0.20$ mm, $2\theta_{max} = 50°$, $\lambda$(Mo-K$\alpha$) = 0.710 73 Å, $\mu$(Mo-K$\alpha$) = 3.083 $mm^{-1}$; minimum and maximum absorption correction 0.791 and 1.134;[6] refinement on $(F_o)^2$ for 3371 data and 469 parameters (all non-H atoms anisotropic), $wR2 = 0.1226$ (all data), conventional $R = 0.0454$ [2686 data with $F_o > 4\sigma(F_o)$, weighting scheme: $w^{-1} = \sigma^2(F) + 0.0004F^2$]. H atoms were placed in geometrically calculated positions. The program SHELX 93[7] was used for the structure solution and refinement. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

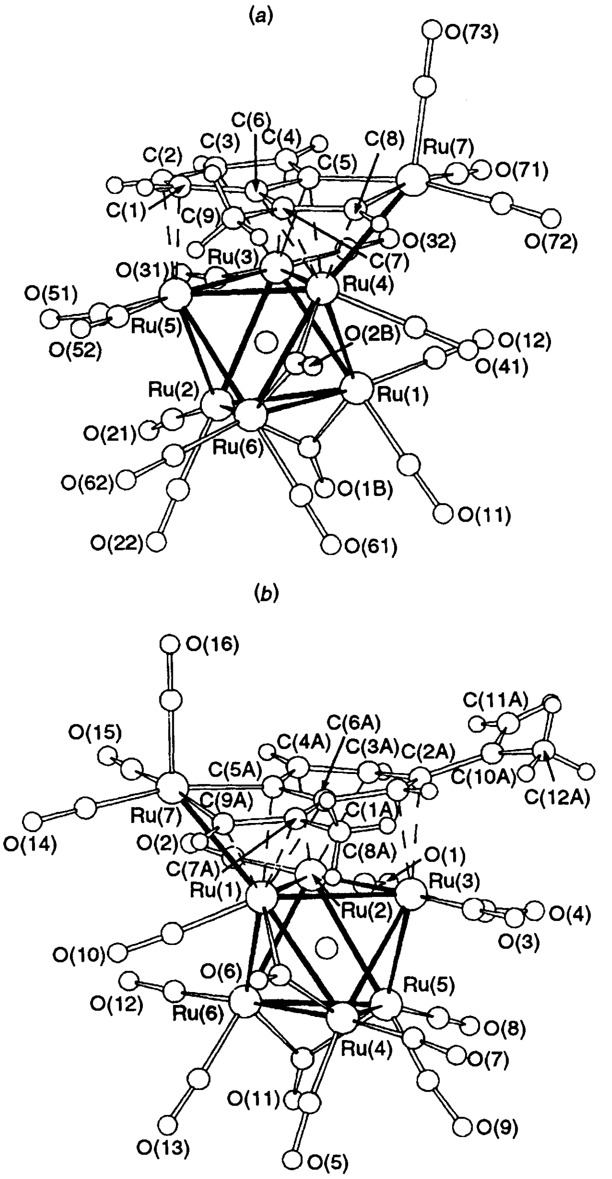

**Fig. 1** Molecular structures of clusters **1** (*a*) and **2** (*b*) in the solid state showing the atomic labelling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atom. Selected bond lengths (Å): for **1**, Ru(1)–Ru(2) 2.772(2), Ru(1)–Ru(3) 2.904(2), Ru(1)–Ru(4) 2.910(2), Ru(1)–Ru(6) 2.969(2), Ru(2)–Ru(3) 2.906(2), Ru(2)–Ru(5) 3.011(2), Ru(2)–Ru(6) 2.897(2), Ru(3)–Ru(4) 2.980(2), Ru(3)–Ru(5) 2.818(2), Ru(4)–Ru(5) 2.911(2), Ru(4)–Ru(6) 2.823(2), Ru(4)–Ru(7) 2.733(2), Ru(5)–Ru(6) 2.879(2), Ru(3)–C(3) 2.29(2), Ru(3)–C(4) 2.206(14), Ru(4)–C(5) 2.30(2), Ru(4)–C(6) 2.29(2), Ru(4)–C(7) 2.328(14), Ru(4)–C(8) 2.29(2), Ru(5)–C(1) 2.23(2), Ru(5)–C(2) 2.32(2), Ru(7)–C(5) 2.08(2), Ru(7)–C(8) 2.04(2); for **2**, Ru(1)–Ru(2) 2.918(2), Ru(1)–Ru(3) 2.978(2), Ru(1)–Ru(4) 2.845(2), Ru(1)–Ru(6) 2.942(2), Ru(1)–Ru(7) 2.769(2), Ru(2)–Ru(3) 2.813(2), Ru(2)–Ru(5) 2.932(2), Ru(2)–Ru(6) 2.880(2), Ru(3)–Ru(4) 2.912(2), Ru(3)–Ru(5) 2.912(2), Ru(4)–Ru(5) 2.905(2), Ru(4)–Ru(6) 2.963(2), Ru(5)–Ru(6) 2.780(2), Ru(3)–C(1A) 2.20(2), Ru(3)–C(2A) 2.36(2), Ru(2)–C(3A) 2.34(2), Ru(2)–C(4A) 2.245(14), Ru(1)–C(5A) 2.283(14), Ru(7)–C(5A) 2.056(14), Ru(1)–C(6A) 2.30(2), Ru(1)–C(7A) 2.32(2), Ru(1)–C(9A) 2.30(2), Ru(7)–C(9A) 2.04(2)

octahedral metal core is very rare and has only been observed on one previous occasion,[8] where, as in the case of **1** and **2**, the ruthenium spike participates in the co-ordination of the ligand *via* two Ru–C σ bonds.

The $C_6$ rings co-ordinate to a trimetal face in a $\mu_3$-$\eta^2$:$\eta^2$:$\eta^2$ mode. In addition to the π interaction thus formed, a further π bond occurs from the unsaturated fragment of the side arm in compound **1** and from one of the two equivalent substituents in **2** to one of the underlying metal atoms. The β-carbon of the methylenic group together with an *o*-carbon of the ring both form σ bonds with the ruthenium spike. For both structures, the organo-moiety can be considered as a type of indene ring in which the $CH_2$ unit has been replaced by a $Ru(CO)_3$ fragment.

Although compounds **1** and **2** were initially isolated together with several other products from the thermolysis of $[Ru_3(CO)_{12}]$ with $C_9H_{10}$ and $C_{12}H_{14}$, we have since observed that they may also be produced by heating $[Ru_4(CO)_{10}(C_9H_{10})]$ or $[Ru_4(CO)_{10}(C_{12}H_{14})]$ with $[Ru_3(CO)_{12}]$ in toluene. The isopropenyl- and 1,3-diisopropenyl-benzene ligands are known to co-ordinate facially in the tetranuclear clusters,[5a] and appear to function as a template for the generation of higher-nuclearity clusters. In keeping with this suggestion we have established that the trinuclear cluster $[Ru_3(CO)_8(C_9H_{10})]$ also reacts with $[Ru_3(CO)_{12}]$ to give higher-nuclearity clusters.

## Acknowledgements

We thank the EPSRC for the provision of a four-circle diffractometer.

## References

1 E. Sappa, A. Tiripicchio and P. Braunstein, *Chem. Rev.*, 1983, **83**, 203; P. R. Raithby and M. J. Rosales, *Adv. Inorg. Chem. Radiochem.*, 1985, **29**, 169.
2 D. Braga, P. J. Dyson, F. Grepioni and B. F. G. Johnson, *Chem. Rev.*, 1994, **94**, 1585.
3 A. J. Deeming, in *Transition Metal Clusters*, ed. B. F. G. Johnson, Wiley, New York, 1980.
4 G. A. Somerjai, in *Catalyst Design—Progress and Perspectives*, ed. L. L. Hegedus, Wiley, New York, 1980.
5 (*a*) D. Braga, F. Grepioni, E. Parasini, P. J. Dyson, S. L. Ingham, B. F. G. Johnson and A. J. Blake, *J. Chem. Soc., Chem. Commun.*, 1995, 537; (*b*) D. Braga, J. J. Byrne, F. Grepioni, E. Parasini, P. J. Dyson, P. E. Gaede, B. F. G. Johnson and D. Reed, *Organometallics*, in the press.
6 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1993, **39**, 158.
7 G. M. Sheldrick, SHELX 93, Program for Crystal Structure Determination, University of Göttingen, 1993.
8 B. F. G. Johnson and D. S. Shephard, University of Edinburgh, unpublished work.

*Received* 20*th July* 1995; *Communication* 5/04789G