A Face-bonded Cycloheptatrienyl Ligand: *X*-Ray Crystal Structure of $[Ru_3(CO)_6(\mu_3\text{-}SBu^t)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$

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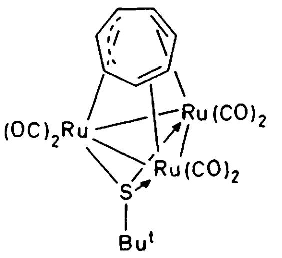
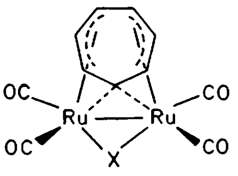
Summary The sulphur–ruthenium cluster $[Ru_3H(CO)_9(\mu_3\text{-}SBu^t)]$ reacts with cycloheptatriene to form the complex $[Ru_3(CO)_6(\mu_3\text{-}SBu^t)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$, shown by *X*-ray diffraction to contain the first example of a face-bonded cycloheptatrienyl ligand.

THE cycloheptatrienyl (C_7H_7) ligand occurs in many complexes bound to a single transition metal, but is also capable of acting as a bridge between two metal atoms, as in $[FeRh(CO)_5\{\mu_2\text{-}(\eta^7\text{-}C_7H_7)\}]$[1] and $[Ru_3(CO)_6\{\mu_2\text{-}(\eta^7\text{-}C_7H_7)\}(C_7H_9)]$.[2] The same is true for cyclo-octatetraene. However, while cyclo-octatetraene has been found to be bonded to the face of a metal triangle in two cases, namely in $[Co_3(CO)_6(\mu_3\text{-}CPh)\{\mu_3\text{-}(\eta^6\text{-}C_8H_8)\}]$[3] and $[Ni_3(CO)_3(CF_3C_2CF_3)\{\mu_3\text{-}(\eta^8\text{-}C_8H_8)\}]$,[4] no corresponding cycloheptatrienyl complex has been reported. We now describe the first such species.



(1)



(2)

a; X = SBu^t
b; X = Cl, Br, or I

Reaction of the sulphur–ruthenium cluster $[Ru_3H(CO)_9(\mu_3\text{-}SBu^t)]$ with cycloheptatriene in boiling heptane for 18 h provides (12%) yellow crystalline $[Ru_3(CO)_6(\mu_3\text{-}SBu^t)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$ (**1**) [m.p. 105 °C, τ ($CDCl_3$) 6·24 (s, 7H) and 7·70 (s, 9H)], together with a small amount of $[Ru_2(CO)_4(\mu_2\text{-}SBu^t)\{\mu_2\text{-}(\eta^7\text{-}C_7H_7)\}]$ (**2a**) [m.p. 124 °C; τ ($CDCl_3$) 6·22 (s, 7H) and 8·21 (s, 9H)] whose halide analogues (**2b**) are known.[2] Several features of the spectra of (**1**) indicated the presence of $\mu_3\text{-}C_7H_7$ rather than $\mu_2\text{-}C_7H_7$, notably the evident symmetry of the molecule [ν(CO) (hexane) 2 026w, 1 999vs, and 1 953s cm^{-1}] and the unusually high field ^{13}C n.m.r. shift (38·7 p.p.m. downfield of $SiMe_4$) of the C_7H_7 ligand. In contrast, ^{13}C shifts for $\mu_2\text{-}C_7H_7$ in (**2a**), $[FeRh(CO)_5\{\mu_2\text{-}(\eta^7\text{-}C_7H_7)\}]$, and $[Ru_3(CO)_6\{\mu_2\text{-}(\eta^7\text{-}C_7H_7)\}(C_7H_9)]$ occur at 61·0, 64·9, and 66·6 p.p.m., respectively. An *X*-ray diffraction study of (**1**) was therefore undertaken.

Crystal data: $C_{17}H_{16}O_6Ru_3S$, $M = 651{\cdot}6$, monoclinic, space group $C2/c$, $a = 14{\cdot}875(6)$, $b = 8{\cdot}902(6)$, $c = 30{\cdot}977(2)$ Å, $\beta = 94{\cdot}785(4)°$, $U = 4087(4)$ Å^3, $Z = 8$, $D_m = 2{\cdot}096$, $D_c = 2{\cdot}12$ g cm^{-3}, $F(000) = 2512$, Mo-K_α radiation ($\lambda = 0{\cdot}71069$ Å), μ(Mo-K_α) = 22·6 cm^{-1}. The metal atoms were located by direct methods, with ring hydrogen atoms and all other non-hydrogen atoms being found from successive electron density difference syntheses. Current R is 0·041 for 4005 data [−70 °C, Syntex $P2_1$ four-circle diffractometer, $2\theta < 60°$, $I \geqslant 2\sigma(I)$].†

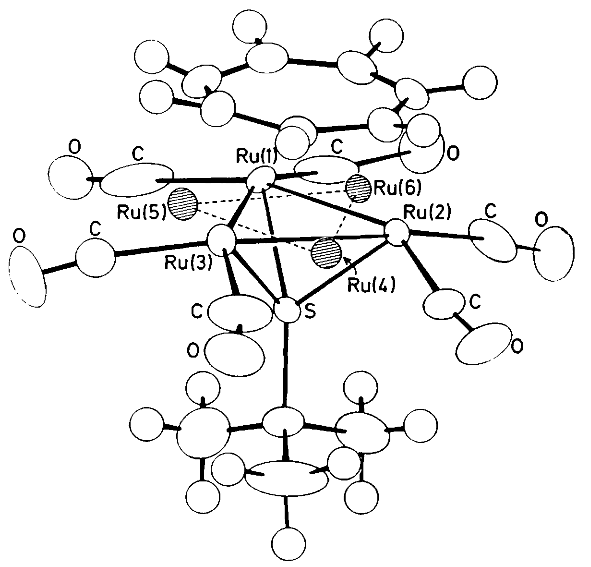


FIGURE 1. Molecular structure of $[Ru_3(CO)_6(\mu_3\text{-}SBu^t)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$ (**1**).

The molecular geometry is shown in Figure 1, with Figure 2 providing a view normal to the Ru_3 plane. The ruthenium atoms form approximately isosceles triangles which are positionally disordered in the ratio 2 : 1, the less-populated orientation being shown shaded in the Figures. This disorder does not extend to any other part of the molecule, a striking consequence of which is that each of the terminal carbonyl groups is effectively 'shared' by two possible metal atom sites. The two carbonyl groups on each ruthenium atom are inclined out of the Ru_3 plane by *ca.* 14° towards an SBu^t group which caps the triangle symmetrically. Bonded to the opposite face is a cycloheptatrienyl ligand which is planar to within 0·04 Å and lying parallel to the face (angle between C_7 and Ru_3 planes is 0·85°) at a distance of 2·06 Å.

The hydrogen atoms of the C_7H_7 ring lie out of the C_7 plane away from the metal atoms, at an elevation angle of *ca.* 14°. Recently it has been predicted[5] and observed[6] that when C_7H_7 is complexed with a single transition metal atom re-orientation of ring π-orbitals will occur in order to maximise overlap with hybridised metal *d*-orbitals, causing the hydrogen atoms to lie out of the C_7 plane towards the

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† 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.

metal atom. Clearly, the co-ordination of C_7H_7 to a metal triangle makes an opposite demand on the orientation of the ring π-orbitals, as might be expected.

The Ru–C(ring) distances (Figure 2) are consistent with η^3-bonding of the apical ruthenium Ru(1) to an allylic C(73)—C(75) unit, with the basal atoms Ru(2) and Ru(3) η^2-bonded to C(76)–C(77) and C(71)–C(72), respectively. However, the planarity and similarity of C–C distances [1·400—1·435(8) Å] within the C_7H_7 system are indicative of aromaticity, *i.e.* co-ordination of $C_7H_7^+$. This implies a corresponding formal one-electron reduction of the $Ru_3(CO)_6(SBu^t)$ fragment, in turn allowing a common +2 oxidation state for the ruthenium atoms, which is apparently reflected in the identical Ru–S distances.

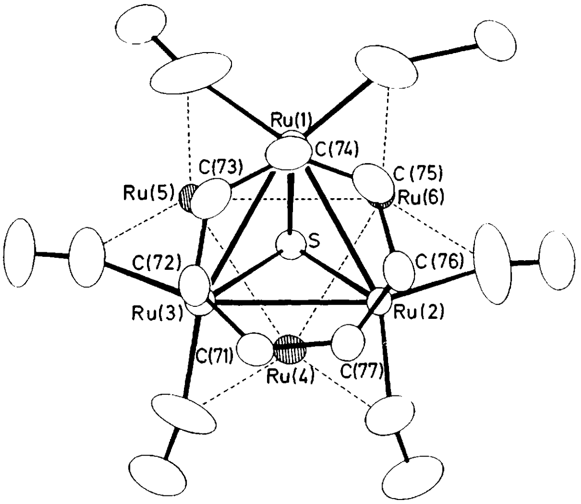

FIGURE 2. View of $[Ru_3(CO)_6(\mu_3\text{-SBu}^t)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$ (**1**) normal to the Ru_3 plane; Bu^t group and ring hydrogen atoms are omitted. Bond lengths are: Ru(1)–Ru(2), 2·866(1); Ru(1)–Ru(3), 2·863(1); Ru(2)–Ru(3), 2·805(1); Ru(4)–Ru(5), 2·835(2); Ru(5)–Ru(6), 2·891(2); Ru(4)–Ru(6), 2·891(2); Ru(1)–S, 2·274(1); Ru(2)–S, 2·272(1); Ru(3)–S, 2·273(1); Ru(1)–C(73), 2·533(6); Ru(1)–C(74), 2·084(6); Ru(1)–C(75), 2·453(5); Ru(2)–C(76), 2·189(5); Ru(2)–C(77), 2·254(5); Ru(3)–C(71) 2·399(5); Ru(3)–C(72), 2·141(5); mean Ru(1—3)–CO, 1·933(7); and mean Ru(4—6)–CO, 2·033(7) Å.

The versatility of the C_7H_7 ligand is shown by its conversion from a μ_3- to a μ_2-mode upon treatment of (**1**) with carbon monoxide (15 atm at 25 °C, acetone solution), when (**2a**) is formed quantitatively. It is likely that a change[7] from μ_3- to μ_2-SBu^t is instrumental in allowing CO attack on (**1**), with subsequent ejection of $Ru(CO)_4$; $[Ru_3(CO)_{12}]$ is observed as a co-product of (**2a**).

A reaction analogous to that of $[Ru_3H(CO)_9(\mu_3\text{-SBu}^t)]$ with cycloheptatriene occurs between $[Ru_3H_2(CO)_9(\mu_3\text{-S})]$ and cyclo-octatetraene under the same conditions. Here three carbonyl groups and two hydrides are replaced by an 8π-electron ring in forming the complex $[Ru_3(CO)_6(\mu_3\text{-S})\{\mu_3\text{-}(\eta^8\text{-}C_8H_8)\}]$, containing rare face-bonded cyclo-octatetraene. The μ_3-C_8H_8 ligand, like μ_3-C_7H_7 in (**1**), has a high field ^{13}C n.m.r. shift (48·0 p.p.m.), and clearly both undergo fluxional rotation relative to the Ru_3 face.

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[1] M. J. Bennett, J. L. Pratt, K. A. Simpson, L. K. K. LiShingMan, and J. Takats, *J. Amer. Chem. Soc.*, 1976, **98**, 4810.
[2] J. C. Burt, S. A. R. Knox, and F. G. A. Stone, *J.C.S. Dalton*, 1975, 731.
[3] B. H. Robinson and J. L. Spencer, *J. Organometallic Chem.*, 1971, **33**, 97.
[4] J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J.C.S. Dalton*, 1979, 506.
[5] M. Elian, M. M. L. Chen, D. M. P. Mingos, and R. Hoffmann, *Inorg. Chem.*, 1976, **15**, 1148.
[6] M. Green, H. P. Kirsch, F. G. A. Stone, and A. J. Welch, *Inorg. Chim. Acta*, 1978, **29**, 101.
[7] B. F. G. Johnson, J. Lewis, D. Pippard, and P. R. Raithby, *J.C.S. Chem. Comm.*, 1978, 551.