Organosulphur–Transition-metal Chemistry. Part 5.[1] Face Bonding of Cycloheptatrienyl and Cyclo-octatetraene Ligands in Sulphur–Ruthenium Clusters: Crystal and Molecular Structure of $[Ru_3(CO)_6(\mu_3\text{-}SBu^t)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$ †

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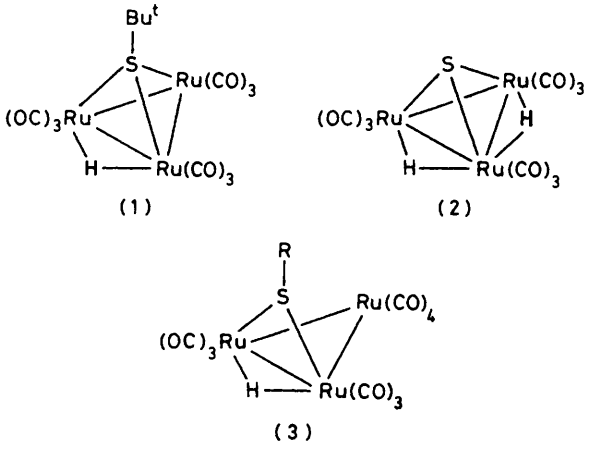
The sulphur–ruthenium cluster complex $[Ru_3H(CO)_9(\mu_3\text{-}SBu^t)]$ reacts with cycloheptatriene in boiling heptane to give $[Ru_3(CO)_6(\mu_3\text{-}SBu^t)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$ and $[Ru_2(CO)_4(\mu\text{-}SBu^t)\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}]$. The former contains a face-bridging cycloheptatrienyl ligand, established through an *X*-ray diffraction study. Crystals are monoclinic, space group *C*2/*c*, with eight molecules in a unit cell of dimensions $a = 14.875(6)$, $b = 8.902(6)$, $c = 30.977(2)$ Å, and $\beta = 94.785(4)°$. The structure has been solved by conventional techniques, revealing the ruthenium atoms to be present in isosceles triangular units disordered in *ca.* 2 : 1 ratio *via* a 60° rotation in the ruthenium plane. Refinement was by least squares for 3 860 data to *R* 0.041. The ruthenium triangle is bridged on one side by a $\mu_3\text{-}SBu^t$ ligand and on the other by a face-bonded C_7H_7 ring which is planar and lies parallel to the face at a distance of 2.07 Å. The hydrogens of the C_7H_7 ligand are inclined away from the metal triangle as a result of π-orbital reorientation. The ruthenium–carbon (ring) distances are compatible with bonding of the C_7H_7 ligand in η^2,η^2,η^3 fashion to the metal triangle, each atom of which bears two terminal carbonyl groups, but n.m.r. spectra show that the ring rotates freely relative to the face in solution. The high-field ^{13}C n.m.r. shift (38.7 p.p.m.) for the $\mu_3\text{-}(\eta^7\text{-}C_7H_7)$ ligand is characteristic, comparing with 61.0 p.p.m. for similarly fluxional $\mu\text{-}(\eta^7\text{-}C_7H_7)$ in $[Ru_2(CO)_4(\mu\text{-}SBu^t)\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}]$. Treating $[Ru_3(CO)_6(\mu_3\text{-}SBu^t)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$ with CO results in cluster fragmentation to yield $[Ru_2(CO)_4(\mu\text{-}SBu^t)\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}]$, a reaction attributed to the ability of both SBu^t and C_7H_7 ligands to vary their mode of co-ordination. Reactions of $[Ru_3H(CO)_9(\mu_3\text{-}SBu^t)]$ with cyclo-octatetraene, cyclo-octatriene, and cyclopentadiene also effect cluster breakdown, forming $[Ru_2(CO)_4(\mu\text{-}SBu^t)\{\mu\text{-}(\eta^7\text{-}C_8H_9)\}]$ or $[Ru_2(\mu\text{-}H)(CO)_2(\mu\text{-}SBu^t)(\eta\text{-}C_5H_5)_2]$.

The sulphur–ruthenium cluster in $[Ru_3H_2(CO)_9(\mu_3\text{-}S)]$ is less easily destroyed. The reaction with cyclo-octatetraene provides $[Ru_3(CO)_6(\mu_3\text{-}S)\{\mu_3\text{-}(\eta^8\text{-}C_8H_8)\}]$, containing rare face-bonded fluxional C_8H_8, while with cycloheptatriene the complexes $[Ru_3(CO)_4(\mu_3\text{-}S)(\eta^5\text{-}C_7H_9)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$, $[Ru_4(CO)_6(\mu_3\text{-}S)(\eta^5\text{-}C_7H_9)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$, and $[Ru_4(CO)_8(\mu_4\text{-}S)\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}_2]$ are obtained, partly characterised using the ^{13}C n.m.r. criterion of the C_7H_7 bonding mode.

THE triangular metal cluster complex $[Ru_3(CO)_{12}]$ reacts with cyclic polyolefins to provide an array of products.[2] These often arise from cluster fragmentation and can involve substantial rearrangement of the hydrocarbons. New and unusual modes of co-ordination have been recognised and fluxional behaviour is widespread. We sought to extend this area by investigating the reactivity of clusters in which the Ru_3 triangle is capped by a sulphur ligand as in, for example, $[Ru_3H(CO)_9(\mu_3\text{-}SBu^t)]$ (1) and $[Ru_3H_2(CO)_9(\mu_3\text{-}S)]$ (2).[3-6] Interest centred on whether (*a*) the ability of bridging sulphur ligands to vary their mode of co-ordination would be significant, (*b*) cluster fragmentation would be suppressed, (*c*) hydrogen transfer from metal to hydrocarbon would occur, and (*d*) new modes of hydrocarbon co-ordination would arise. A preliminary account of this work has appeared.[7]



RESULTS AND DISCUSSION

Reactions of $[Ru_3H(CO)_9(\mu_3\text{-}SBu^t)]$ (1).—The nature of the product formed from the reaction of a thiol RSH and $[Ru_3(CO)_{12}]$ is dependent upon the sulphur substituent. When R is a primary alkyl group such as Et or Bu^n a decacarbonyl complex $[Ru_3H(CO)_{10}(\mu\text{-}SR)]$ (3) is produced in which the SR ligand bridges an edge of the Ru_3 triangle,[3] but we have found that when R is Bu^t the SBu^t ligand caps the triangle in $[Ru_3H(CO)_9(\mu_3\text{-}SBu^t)]$ (1). Similar behaviour has been observed for the analogous iron system and was attributed to steric effects,[8] but the variation in basicity of sulphur brought about by R cannot be insignificant. The complex (1) is obtained in good yield from $[Ru_3(CO)_{12}]$ and Bu^tSH, and under pressure (15 atm ‡) of CO it is converted into $[Ru_3H(CO)_{10}(\mu\text{-}SBu^t)]$ (3). Decarbonylation to give (1) is effected by either melting (97 °C) the solid complex or heating briefly in boiling hexane. This capacity for

† 1,1,2,2,3,3-Hexacarbonyl-μ_3-1′—3′ : 4′—5′ : 6′—7′-η-cycloheptatrienyl-μ_3-t-butylthio-*triangulo*-triruthenium.

‡ Throughout this paper: 1 atm = 101 325 Pa.

TABLE 1

Data for new compounds

Compound	M.p. (θ_c/°C)	Analysis (%) [a] C	H	S	M [a,b]
(4) $[Ru_2(CO)_4(SBu^t)(C_7H_7)]$	124 [c]	36.3 (36.4)	3.4 (3.2)	6.6 (6.5)	495 (495)
(8) $[Ru_2(CO)_4(SBu^t)(C_8H_9)]$	134 [c]	37.9 (37.8)	3.7 (3.5)	6.4 (6.3)	509 (509)
(11) $[Ru_2(CO)_2(H)(SBu^t)(C_5H_5)_2]$	151	39.8 (40.0)	4.3 (4.2)	8.4 (6.7)	479 (479)
(5) $[Ru_3(CO)_6(SBu^t)(C_7H_7)]$	105—107	31.8 (31.4)	2.7 (2.5)	5.0 (6.6)	651 (651)
(10) $[Ru_3(CO)_6S(C_8H_8)]$	154 [c]	27.4 (27.5)	1.4 (1.4)	5.8 (5.2)	609 (609)
(12) $[Ru_3(CO)_4S(C_7H_9)(C_7H_7)]$	162 [c]	34.1 (34.1)	2.9 (2.5)	4.8 (5.0)	633 (633)
(13) $[Ru_4(CO)_6S(C_7H_9)(C_7H_7)]$	200	30.0 (30.0)	1.9 (2.0)	5.0 (4.1)	91 [d] (790)
(14) $[Ru_4(CO)_8S(C_7H_7)_2]$	148 [c]	31.0 (31.2)	1.8 (1.8)	4.1 (3.8)	844 (844)

[a] Calculated values are given in parentheses. [b] Mass spectrometry. [c] Melts with decomposition. [d] Heaviest ion ($C_7H_7^+$).

TABLE 2

Infrared and n.m.r. data for new compounds

Compound	Carbonyl stretching bands (cm^{-1}) [a]	^1H N.m.r. (τ) [b]	^{13}C N.m.r. (p.p.m.) [c]
(4)	2 020m, 2 001s, 1 959s, 1 950m	6.20 (s, 7 H), 8.21 (s, 9 H); 6.84 (s, 7 H), 8.26 (s, 9 H) [c]	34.6, 48.1, 61.0, 196.8, 199.1
(8)	2 017m, 1 995s, 1 954s, 1 944m	4.74 (m, 1 H), 5.10 (m, 1 H), 6.66 (m, 2 H), 7.44 (m, 4 H), 8.28 (m, 1 H), 8.32 (s, 9 H)	−11.5, 24.0, 35.0, 47.6, 49.6, 50.1, 50.6, 52.7, 83.0, 97.3, 198.6, 199.2, 199.4, 200.0
(11)	1 952m, 1 929s	4.80 (s, 5 H), 4.91 (s, 5 H), 8.68 (s, 9 H), 24.19 (s, 1 H	
(5)	2 026w, 1 999vs, 1 953s	6.30 (s, 7 H), 7.72 (s, 9 H); 6.96 (s, 7 H), 7.96 (s, 9 H) [c]	33.4, 38.7, 55.6, 191.3
(10)	2 042m, 2 013s	6.08 (s); 7.06 (s) [c]	48.0, 190.9 [d]
(12)	2 013s, 1 983s, 1 941m, 1 929m [e]	4.22 (m, 1 H), 5.26 (m, 2 H), 6.18 (m, 2 H), 6.56 (s, 7 H), 7.06 (m, 2 H), 8.40 (m, 2 H)	33.6, 39.1, 67.5, 93.5, 105.2 [d,f]
(13)	1 985 (sh), 1 977s, 1 945 (sh), 1 809m [g]	4.33 (s, 1 H), 5.33 (m, 2 H), 6.61 (s, 7 H), 6.78 (m, 2 H), 7.06 (m, 2 H), 8.30 (m, 2 H)	
(14)	2 041s, 2 014vs, 2 006s, 1 969w, 1 957vs, 1 951m [e]	5.74 (s)	64.3 [d,f]

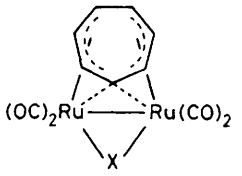
[a] In hexane solution unless otherwise stated. [b] In $CDCl_3$ solution unless otherwise stated. [c] In $C_6D_5CD_3$ solution. [d] In CD_2Cl_2 solution. [e] In cyclohexane solution. [f] CO not detected. [g] In CH_2Cl_2 solution.

interchange between μ and μ_3 modes of sulphur-ligand co-ordination has also been recognised for the isopropyl analogues of (1) and (3).[9] Even more interesting is the reaction of $[Os_3H(CO)_9(\mu_3\text{-}SR)]$ (R = Me or Et) with ethylene, when a change to μ-SR releases a co-ordination site for the olefin under mild conditions.[9]

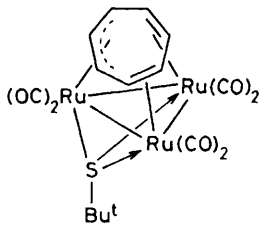
The cluster (1) reacts with cycloheptatriene in boiling heptane to give two new complexes as stable yellow crystalline materials. These were characterised as $[Ru_2(CO)_4(\mu\text{-}SBu^t)\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}]$ (4) and $[Ru_3(CO)_6(\mu_3\text{-}SBu^t)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$ (5) on the basis of elemental analyses and mass, i.r., ^1H, and ^{13}C n.m.r. spectra (Tables 1 and 2). A very low yield of known $[Ru_3(CO)_6(\eta^5\text{-}C_7H_9)\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}]$ [10] was also obtained.

The diruthenium complex (4) was readily identified by its i.r. spectrum, which has four carbonyl-stretching bands in a pattern very similar to that of the halide complexes $[Ru_2(CO)_4(\mu\text{-}X)\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}]$ (6).[10] The latter have been shown, through an X-ray diffraction study on $[Ru_2(CO)_4(\mu\text{-}I)\{\mu\text{-}(\eta^7\text{-}C_7H_6Ph)\}]$,[11] to contain a cycloheptatrienyl ligand co-ordinated to two ruthenium atoms as illustrated, while n.m.r. spectra indicate that the ring is undergoing rapid fluxional rotation in solution. A similar mode of co-ordination appears likely for (4), whose C_7H_7 ligand is also fluxional: at room temperature the ^1H and ^{13}C n.m.r. spectra each have a single sharp signal for the C_7H_7 ring. The proton signal is quite solvent dependent, being at τ 6.84 in $[^2H_8]$toluene and τ 6.20 in $CDCl_3$. In contrast to the complexes (6), whose spectra are unchanged on cooling to −100 °C, the spectra of (4) show substantial broadening of the C_7H_7 and SBu^t group signals at this temperature. This clear evidence of slower fluxional motion for (4) is discussed in more detail, and in connection with the similar behaviour of (7), in Part 6 of this series, which describes the synthesis of both complexes from the reactions of $[Ru_3(CO)_{12}]$ and C_7H_7SR-7.[12]

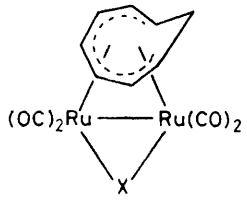
The major product of the reaction of (1) with cycloheptatriene is (5), which retains the Ru_3S framework of the cluster. The i.r. spectrum has only two strong



(4; X = SBu^t)
(6; X = Cl, Br or I)
(7; X = SMe)



(5)



(8; X = SBu^t)
(9; X = I)

carbonyl-stretching bands, indicating a high symmetry for the molecule. This suggested that the cycloheptatrienyl ligand bridges a face of the Ru_3 triangle rather than being localised on an edge, a feature which is also demanded by electron counting. In addition, the ^{13}C n.m.r. spectrum of (5) displays an unusual high-field shift for the carbons of the C_7H_7 ring (which are equivalent as a consequence of fluxional rotation of the ring). The shift is 38.7 p.p.m., in marked contrast to those for the μ-(η^7-C_7H_7) rings in (4), [$FeRh(CO)_5${μ-(η^7-C_7H_7)}],[13] and [$Ru_3(CO)_6${μ-(η^7-C_7H_7)}(C_7H_9)] [10] of 61.0, 64.9, and 66.6 p.p.m. respectively. No previous example of a face-bridged cycloheptatrienyl ligand had been reported and an *X*-ray diffraction study of (5) was therefore undertaken.

The *X*-ray analysis (Tables 3—6) establishes that the molecule consists of an isosceles triangle of ruthenium atoms, with an SBu^t group capping one side of the triangle and a C_7H_7 ligand bonded to the other, and with two terminal carbonyls attached to each ruthenium. The molecular geometry is shown in Figure 1, with Figure 2 providing a view perpendicular to the Ru_3 plane. The contents of the unit cell are reproduced in Figure 3.

The ruthenium atoms form approximately isosceles triangles which are positionally disordered in the ratio 2 : 1; the less populated orientation is shown shaded in the Figures. As a direct consequence of this disorder the carbonyl ligands also show some positional disorder, and the larger than normal thermal parameters of the carbonyl-carbon atoms reflect the fact that these represent two overlapping carbonyl positions. Although the oxygen atoms also show signs of disorder, the ring-carbon atoms C(71)—C(77), the sulphur atom, and the tertiary carbon C(100) do not. By reference to Table 4 it can be seen that the metal–metal bonding distances

TABLE 3

Fractional atomic co-ordinates of the bonded atoms of (5) with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	0.302 2(1)	−0.180 7(1)	0.427 5(1)
Ru(2)	0.367 8(1)	0.051 7(1)	0.374 3(1)
Ru(3)	0.450 3(1)	−0.231 8(1)	0.376 0(1)
Ru(4)	0.440 1(1)	−0.059 6(1)	0.359 7(1)
Ru(5)	0.383 0(1)	−0.303 0(1)	0.409 8(0)
Ru(6)	0.295 1(1)	−0.013 6(1)	0.411 2(0)
S	0.304 9(1)	−0.172 9(1)	0.354 2(1)
C(100)	0.226 6(3)	−0.224 5(5)	0.306 5(1)
C(101)	0.153 4(5)	−0.109 7(9)	0.302 7(3)
C(102)	0.280 3(5)	−0.225 3(11)	0.267 9(2)
C(103)	0.187 8(6)	−0.372 6(8)	0.315 3(2)
C(71)	0.545 9(3)	−0.053 8(6)	0.411 3(2)
C(72)	0.532 3(3)	−0.185 3(6)	0.434 5(2)
C(73)	0.461 5(4)	−0.218 2(6)	0.461 4(2)
C(74)	0.397 7(4)	−0.118 6(7)	0.477 2(2)
C(75)	0.379 9(4)	0.031 2(6)	0.464 8(2)
C(76)	0.427 7(3)	0.126 1(5)	0.437 8(2)
C(77)	0.500 8(3)	0.088 0(5)	0.413 4(2)
C(11)	0.284 5(5)	−0.393 7(10)	0.442 0(2)
C(12)	0.189 4(4)	−0.090 6(9)	0.441 6(2)
C(21)	0.418 0(4)	0.123 5(7)	0.323 4(2)
C(22)	0.269 5(5)	0.191 0(8)	0.375 7(2)
C(31)	0.454 8(5)	−0.449 1(7)	0.379 4(2)
C(32)	0.514 3(4)	−0.205 8(9)	0.325 4(2)
O(11)	0.265 8(3)	−0.508 1(5)	0.453 2(1)
O(12)	0.122 8(3)	−0.064 9(5)	0.453 2(1)
O(21)	0.435 3(3)	0.185 9(6)	0.295 1(1)
O(22)	0.223 0(3)	0.281 6(5)	0.369 4(2)
O(31)	0.470 7(4)	−0.565 3(5)	0.374 2(2)
O(32)	0.554 4(3)	−0.218 5(6)	0.297 5(1)
H(11)	0.181 3(5)	−0.000 6(9)	0.296 3(3)
H(12)	0.120 8(5)	−0.105 8(9)	0.332 5(3)
H(13)	0.104 7(5)	−0.140 3(9)	0.276 3(3)
H(21)	0.333 3(5)	−0.308 5(11)	0.271 7(2)
H(22)	0.309 8(5)	−0.115 4(11)	0.264 8(2)
H(23)	0.236 4(5)	−0.250 1(11)	0.239 3(2)
H(31)	0.241 4(6)	−0.454 8(8)	0.318 1(2)
H(32)	0.139 1(6)	−0.403 4(8)	0.289 0(2)
H(33)	0.155 2(6)	−0.368 9(8)	0.345 2(2)
H(71)	0.602 4(33)	−0.050 9(53)	0.397 7(15)
H(72) *	0.575 9	−0.258 3	0.495 2
H(73)	0.470 0(40)	−0.296 2(68)	0.477 3(19)
H(74)	0.371 0(42)	−0.144 7(71)	0.499 2(20)
H(75)	0.345 1(38)	0.082 5(65)	0.483 7(18)
H(76)	0.414 1(33)	0.242 5(57)	0.438 7(16)
H(77)	0.533 1(33)	0.159 5(55)	0.400 9(16)

* Positional parameter not refined during last cycles of refinement.

are not identical for the two sets of disordered positions and neither are the other interatomic distances. For simplicity, the following discussion will refer to the Ru_3 triangle which has occupational parameters of $\frac{2}{3}$ and is represented by Ru(1), Ru(2), and Ru(3). The Ru–Ru distances lie in the range 2.80—2.87 Å and are not, therefore, significantly different from that in [Ru_3-$(CO)_{12}$] (2.85 Å).[14] In [$Ru_3H_2(CO)_9(\mu_3$-S)] (2) there is also an isosceles triangle of metal atoms, with Ru–Ru distances of *ca.* 2.73 and 2.88 Å; [6] the two equal long edges of the triangle are presumably bridged by hydrogen, so comparison with (1) is not valid.

One consequence of the disorder in the carbonyl-carbon and metal-atom positions is the apparent deviation from

TABLE 4

Interatomic distances (Å) between bonded atoms of (5)* with estimated standard deviations in parentheses

Ru(1)–Ru(2)	2.866(1)	Ru(4)–Ru(5)	2.836(1)
Ru(2)–Ru(3)	2.805(1)	Ru(5)–Ru(6)	2.891(1)
Ru(3)–Ru(1)	2.863(1)	Ru(6)–Ru(4)	2.817(1)
Ru(1)–S	2.274(1)	Ru(4)–S	2.243(1)
Ru(2)–S	2.273(1)	Ru(5)–S	2.307(1)
Ru(3)–S	2.273(1)	Ru(6)–S	2.278(1)
Ru(1)–C(11)	1.971(8)	Ru(4)–C(21)	1.993(6)
Ru(1)–C(12)	1.943(6)	Ru(4)–C(32)	2.058(6)
Ru(2)–C(21)	1.911(5)	Ru(5)–C(11)	2.009(7)
Ru(2)–C(22)	1.921(6)	Ru(5)–C(31)	1.970(6)
Ru(3)–C(31)	1.938(6)	Ru(6)–C(12)	2.019(6)
Ru(3)–C(32)	1.912(6)	Ru(6)–C(22)	2.146(8)
Ru(1)–C(73)	2.533(5)	Ru(4)–C(71)	2.148(5)
Ru(1)–C(74)	2.082(5)	Ru(4)–C(77)	2.249(5)
Ru(1)–C(75)	2.451(5)	Ru(5)–C(72)	2.517(5)
Ru(2)–C(76)	2.192(5)	Ru(5)–C(73)	2.043(5)
Ru(2)–C(77)	2.254(5)	Ru(6)–C(74)	2.620(6)
Ru(3)–C(71)	2.339(5)	Ru(6)–C(75)	2.039(5)
Ru(3)–C(72)	2.141(5)	Ru(6)–C(76)	2.417(5)
C(11)–O(11)	1.120(8)	S–C(100)	1.862(4)
C(12)–O(12)	1.105(7)	C(100)–C(101)	1.491(8)
C(21)–O(21)	1.087(6)	C(100)–C(102)	1.491(7)
C(22)–O(22)	1.070(7)	C(100)–C(103)	1.474(8)
C(31)–O(31)	1.077(7)		
C(32)–O(32)	1.096(6)		
C(71)–C(72)	1.398(7)	C(71)–H(71)	0.971(48)
C(72)–C(73)	1.425(8)	C(72)–H(72)	0.917(5)
C(73)–C(74)	1.416(8)	C(73)–H(73)	0.855(59)
C(74)–C(75)	1.407(8)	C(74)–H(74)	0.849(61)
C(75)–C(76)	1.420(8)	C(75)–H(75)	0.932(57)
C(76)–C(77)	1.417(7)	C(76)–H(76)	1.057(50)
C(77)–C(71)	1.434(7)	C(77)–H(77)	0.904(49)

* C–H distances fixed at 1.08 Å: C(101)–H(11), C(102)–H(21), C(103)–H(31), C(101)–H(12), C(102)–H(22), C(103)–H(32), C(101)–H(13), C(102)–H(23), C(103)–H(33).

TABLE 5

Important internuclear bond angles (°) of (5) with estimated standard deviations in parentheses

Ru(1)–Ru(2)–Ru(3)	60.6(1)	Ru(4)–Ru(5)–Ru(6)	58.9(1)
Ru(2)–Ru(3)–Ru(1)	60.7(1)	Ru(5)–Ru(6)–Ru(4)	59.6(1)
Ru(3)–Ru(1)–Ru(2)	58.6(1)	Ru(6)–Ru(4)–Ru(5)	61.5(1)
Ru(3)–Ru(1)–C(11)	95.6(3)	Ru(6)–Ru(4)–C(21)	95.9(2)
Ru(2)–Ru(1)–C(12)	100.0(2)	Ru(5)–Ru(4)–C(32)	89.8(2)
Ru(3)–Ru(2)–C(21)	96.7(2)	Ru(6)–Ru(5)–C(11)	90.1(3)
Ru(1)–Ru(2)–C(22)	99.0(3)	Ru(4)–Ru(5)–C(31)	92.6(2)
Ru(1)–Ru(3)–C(31)	98.7(2)	Ru(5)–Ru(6)–C(12)	94.3(2)
Ru(2)–Ru(3)–C(32)	97.0(2)	Ru(4)–Ru(6)–C(22)	86.8(2)
C(12)–Ru(1)–C(11)	102.2(4)	C(32)–Ru(4)–C(21)	107.2(3)
C(22)–Ru(2)–C(21)	98.8(3)	C(31)–Ru(5)–C(11)	114.7(4)
C(31)–Ru(3)–C(32)	98.6(3)	C(22)–Ru(6)–C(12)	114.5(3)
Ru(1)–C(11)–O(11)	171.0(8)	Ru(5)–C(11)–O(11)	137.0(8)
Ru(1)–C(12)–O(12)	166.6(7)	Ru(6)–C(12)–O(12)	146.7(7)
Ru(2)–C(21)–O(21)	166.5(6)	Ru(4)–C(21)–O(21)	146.5(6)
Ru(2)–C(22)–O(22)	164.7(9)	Ru(6)–C(22)–O(22)	144.9(8)
Ru(3)–C(31)–O(31)	163.2(7)	Ru(5)–C(31)–O(31)	147.3(7)
Ru(3)–C(32)–O(32)	166.7(7)	Ru(4)–C(32)–O(32)	145.4(7)
Ru(1)–S–Ru(2)	78.2(1)	Ru(4)–S–Ru(5)	77.1(1)
Ru(2)–S–Ru(3)	76.2(1)	Ru(5)–S–Ru(6)	78.2(1)
Ru(1)–S–Ru(3)	78.0(1)	Ru(4)–S–Ru(6)	77.1(1)
Ru(2)–S–C(100)	130.6(2)	Ru(5)–S–C(100)	135.3(2)
Ru(1)–S–C(100)	136.3(1)	Ru(4)–S–C(100)	132.0(1)
Ru(3)–S–C(100)	134.0(2)	Ru(6)–S–C(100)	133.9(2)
S–C(100)–C(101)	107.3(4)	C(102)–C(100)–C(101)	112.1(6)
S–C(100)–C(102)	107.2(4)	C(103)–C(100)–C(101)	109.5(6)
S–C(100)–C(103)	107.6(4)	C(103)–C(100)–C(102)	112.8(6)
C(77)–C(71)–C(72)	128.7(4)		
C(71)–C(72)–C(73)	128.2(5)		
C(72)–C(73)–C(74)	128.5(5)		
C(73)–C(74)–C(75)	127.9(5)		
C(74)–C(75)–C(76)	129.3(5)		
C(75)–C(76)–C(77)	128.0(5)		
C(76)–C(77)–C(71)	128.2(5)		

TABLE 6

Equations of significant least-squares planes. Deviations of relevant atoms from these planes are given in square brackets; displacements (Å), and angular deviations (°)

Plane (1): Ru(1)–Ru(2)–Ru(3)

$$0.6376x + 0.2949y + 0.7117z = 11.5392$$

[Ru(4), 0.0061; Ru(5), −0.0185; Ru(6), 0.0192] C(11), 11.43; C(12), 12.47; C(21), 15.30; C(22), 13.42; C(31), 13.62; C(32), 15.10; av., 13.56

Plane (2): Ru(4)–Ru(5)–Ru(6)

$$0.6422x + 0.2825y + 0.712\,62z = 11.5915$$

[Ru(1), 0.0002; Ru(2), −0.0227; Ru(3), 0.0141] C(11), 10.76; C(12), 12.98; C(21), 15.49; C(22), 14.09; C(31), 12.87; C(32), 15.10; av., 13.55

Plane (3): C(71)–C(77)

$$0.6316x + 0.2847y + 0.7212z = 13.7018$$

[C(71), −0.0264; C(72), 0.0446; C(73), −0.0397; C(74), 0.0268; C(75), −0.0221; C(76), 0.0196; C(77), −0.0027] H(71), 10.82; H(72), 12.50; H(73), 15.63; H(74), 13.57; H(75), 16.04; H(76), 10.98; H(77), 15; av., 12.87

Angles (°) between planes:

1–3	0.88
2–3	0.79

linearity of the carbonyl ligands. The Ru–C–O angles range over 163—171°, to be compared with 177—178° in the related complex $[Fe_3H(CO)_9(\mu_3\text{-}SPr^i)]$ [14] and 178—180° for the equatorial carbonyls in $[Ru_3(CO)_{12}]$.[13] The axial carbonyls of $[Ru_3(CO)_{12}]$ depart by *ca.* 7° from linearity, attributed to van der Waals repulsion between oxygen atoms, but there are no such repulsions of any significance in (5).

The co-ordination about each ruthenium is approximately octahedral if the C_7H_7 ring is considered to occupy one site. The opening of the OC–Ru–CO angle to *ca.* 98—102° from an idealised 90° is general for equatorial $M(CO)_2$ groups which are symmetrically bonded in a triangular array to two other metal atoms. For example, the complexes $[Ru_3(CO)_{12}]$,[14] $[FeCo_2(CO)_9(\mu_3\text{-}S)]$,[15] $[Fe_3H(CO)_9(\mu_3\text{-}SPr^i)]$,[16] and $[Os_3(CO)_{12}]$,[17] have, on average, M–M–M and OC–M–CO angles of 60 and 104, 60 and 97, 60 and 95, and 60 and 103° respectively. Further distortion is caused by the presence of a capping ligand, which leads to a tilt of the carbonyls away from the cap. In (5) the carbon [C(11)—C(32)]–Ru bonds are bent away from the plane of the metal triangle by *ca.* 13°, while in $[FeCo_2(CO)_9(\mu_3\text{-}S)]$ and $[Co_3(CO)_9(\mu_3\text{-}S)]$ this angle is *ca.* 16°.[16]

The sulphur atom sits at a distance of 1.57 Å from the Ru_3 plane and is symmetrically placed, with a mean Ru–S distance of 2.27 Å. This may be compared with the M_3S pseudo-tetrahedral cores of $[Fe_3H(CO)_9(\mu_3\text{-}SPr^i)]$ [16] and $[Os_3H_2(CO)_9(\mu_3\text{-}S)]$,[18] where sulphur is 1.50 and 1.72 Å above the Fe_3 and Os_3 planes respectively,

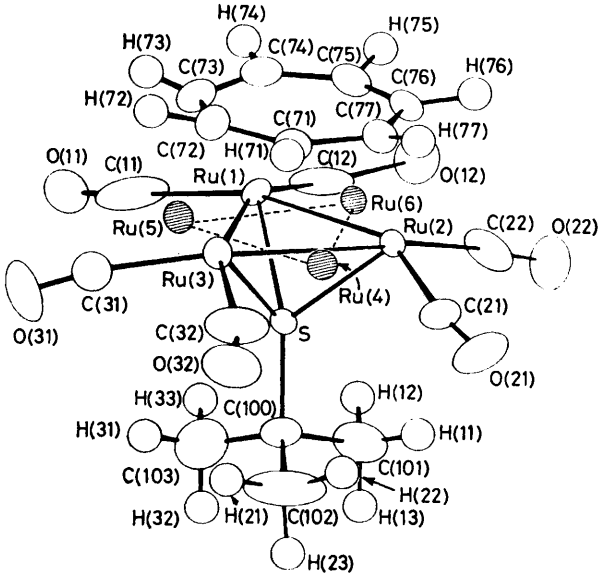


FIGURE 1 Perspective view of (5), with atomic numbering scheme. Thermal ellipsoids are constructed at the 50% probability level

with mean Fe–S and Os–S distances of 2.14 and 2.39 Å. The Bu^t group leans towards Ru(2) and slightly away from Ru(3), as seen by the angle of 176.6° which the S–C(100) bond makes with the normal to the Ru_3 plane and by the variation in the Ru–S–C(100) angles.

The most important feature of the structure of (5) is the presence of the face-bridging C_7H_7 ligand. The small ranges of the C–C distances around the ring (1.40—1.43; mean 1.42 Å) and of the internal ring angles (127.9—129.3°) allow it to be described as a regular heptagon, planar to within ±0.04 Å. The ring lies parallel to the face of the triangle, the angle between the C_7 and Ru_3 planes (Table 6) being 0.9°, and at an average distance of 2.07 Å. It is interesting that the hydrogen atoms of the C_7H_7 ring lie out of the C_7 plane at an elevation of *ca.* 13° on the side *away* from the metals. It has been predicted [19] and observed [20] that when C_7H_7 is bonded to a single transition-metal atom the hydrogen atoms lie

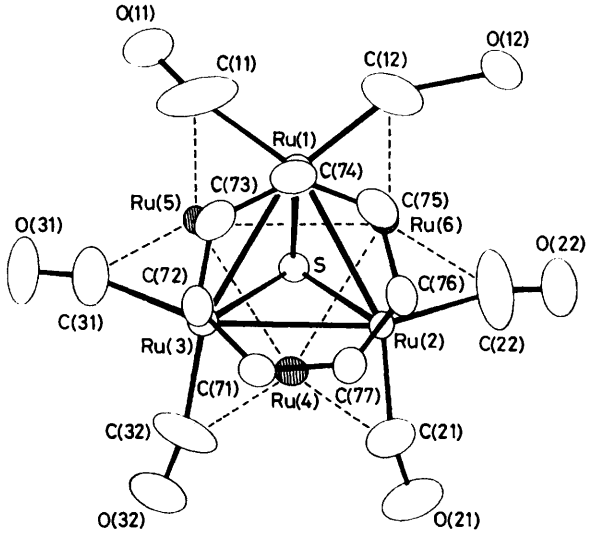


FIGURE 2 View of (5) normal to the ruthenium plane; ring-hydrogen atoms and the Bu^t group are omitted for clarity

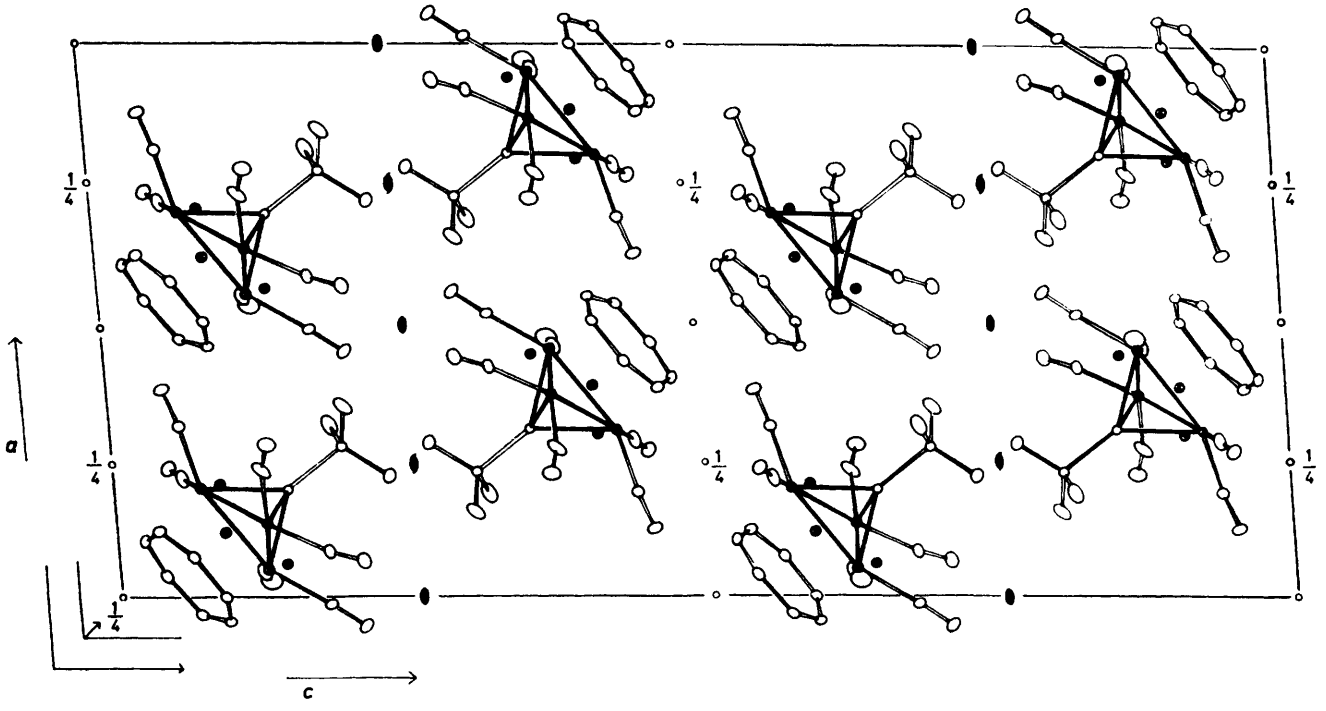


FIGURE 3 Contents of the monoclinic unit cell of (5), viewed along the *b* axis. Thermal ellipsoids are constructed at the 10% probability level

out of the C_7 plane *towards* the metal atom. This is a result of the ring π orbitals undergoing reorientation in order to maximise overlap with hybridised metal *d* orbitals. The observation that the hydrogens lie away from a metal triangle suggests that an opposite reorientation is required of the ring π orbitals, as might be expected.

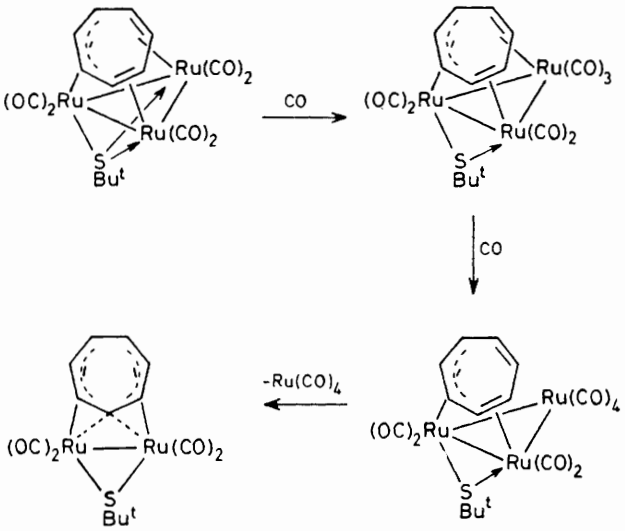
The Ru–C(ring) distances (Table 4) are consistent with η^3 bonding of carbons C(73)–C(74)–C(75) to the apical ruthenium Ru(1) and η^2 bonding of carbons C(76)–C(77) and C(71)–C(72) to the basal atoms Ru(2) and Ru(3) respectively of the isosceles Ru_3 triangle. This allows the representation of the molecular structure as (5). However, the planarity of the C_7 ring and the similarity [1.398(7)—1.434(7) Å] of the C–C distances within it encourage consideration of the ligand as being co-ordinated aromatic $C_7H_7^+$. If this is done, the corresponding formal one-electron reduction of the $Ru_3(CO)_6(\mu_3\text{-}SBu^t)$ fragment allows a common +II oxidation state for the ruthenium atoms. The identical Ru–S distances provide some support for this concept.

Both the ^1H and ^{13}C n.m.r. spectra of (5) provide evidence, in the form of single sharp resonances for the C_7H_7 ring, of fluxional rotation of the hydrocarbon relative to the Ru_3 triangle. The activation energy for the process is sufficiently low that no change in the ring resonances is observed at −100 °C, at which temperature rotation is clearly still rapid. However, at −100 °C the signal due to the methyl protons of the Bu^t group is broadened substantially (width at half-height = 12 Hz; *cf.* 2 Hz for C_7H_7 signal). We attribute this to hindered rotation about the S–C bond.

The cluster (5) is interesting in containing two very different ligands, μ_3-SBu^t and μ_3-(η^7-C_7H_7), each of which is capable of changing its co-ordination mode, to μ-SBu^t and μ-(η^7-C_7H_7) respectively. That is, from face- to edge-bridging of the Ru_3 triangle. In so doing a co-ordination site is made available, a feature previously discussed [9] for an SR ligand and clearly relevant to catalysis. Complex (5) was therefore of potentially high reactivity. In order to test this an acetone solution of (5) was subjected to 15 atm of CO at 70 °C, conditions which brought about formation of (4) in high yield. Both the C_7H_7 and SBu^t ligands are shifted to μ-bridging and a ruthenium is ejected, appearing as $[Ru_3(CO)_{12}]$. A possible mechanism for the conversion is presented in the Scheme, in which first SBu^t and then C_7H_7 is envisaged to allow entry of CO *via* a co-ordination change, but C_7H_7 could equally well precede SBu^t in this role. Although this is the first observation of a transition from μ_3- to μ-C_7H_7, a change in co-ordination of the cycloheptatrienyl ligand from η^7 to η^5 is thought to be involved in the substitution reactions of $[Mo(CO)_3(\eta^7\text{-}C_7H_7)]^+$.[21]

Like cycloheptatriene, cyclo-octatetraene reacts with (1) in boiling heptane, but cluster fragmentation now dominates and stable yellow crystalline $[Ru_2(CO)_4(\mu\text{-}SBu^t)\{\mu\text{-}(\eta^7\text{-}C_8H_9)\}]$ (8) is the major (*ca.* 60%) product isolated. The structural relationship to (4) is apparent from its i.r. spectrum, which has a characteristic pattern in the carbonyl region. The addition of hydrogen to the C_8 ring is revealed by the ^1H and ^{13}C n.m.r. spectra (Table 2), which show inequivalence of all nine protons and eight carbons of the C_8H_9 ligand.

The μ-(η^7-C_8H_9) ligand is rare and only three examples have been characterised structurally; $[Fe_2(CO)_6\{\mu\text{-}(\eta^7\text{-}C_8H_9)\}][BF_4]$,[22] $[Ru_3(CO)_6(\eta^5\text{-}C_8H_9)\{\mu\text{-}(\eta^7\text{-}C_8H_9)\}]$,[23] and $[Rh_2(\eta^3\text{-}C_8H_9)(\eta^4\text{-}C_8H_{12})\{\mu\text{-}(\eta^7\text{-}C_8H_9)\}]$.[24] In each of these the ligand adopts the same bonding mode, with



SCHEME

a mirror plane through the ring and including the metal–metal axis, so that the methylenic carbon is localised near one metal atom. A similar bonding mode has been suggested for $[Ru_2(CO)_4(\mu\text{-}I)(\eta^7\text{-}C_8H_9)\}]$ (9) on the basis of n.m.r. spectra.[2] The inequivalence of all the nuclei in the C_8H_9 ligand of (8) and, incidentally, of (9), can be traced to the bridging SBu^t and I ligands lying to one side of the vertical mirror plane through the hydrocarbon. This is a feature which has been established by *X*-ray diffraction for the related complexes (6).[11]

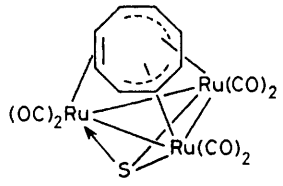
In an attempt to show that the C_8H_9 ligand arises by hydrogen transfer from the ruthenium cluster, a sample of (1) containing 33% of deuterium in the bridging site was prepared {from Bu^tSD and $[Ru_3(CO)_{12}]$} and treated with cyclo-octatetraene. Mass spectroscopy revealed that two thirds of this deuterium was transferred to the C_8 ring of the product (8) *i.e.* 22% incorporation. Because of the overlapping nature of several of the ^1H n.m.r. signals of (8), it was not possible to detect by this method whether the transferred deuterium was localised in the methylene group.

A minor product of the reaction of (1) with cyclo-octatetraene was $[Ru_3(CO)_6(\mu_3\text{-}S)\{\mu_3\text{-}(\eta^8\text{-}C_8H_8)\}]$ (10), a complex much better prepared from $[Ru_3H_2(CO)_9(\mu_3\text{-}S)]$ (2) and which is discussed below. Cleavage of substituents from sulphur in reactions with metal carbonyls is not uncommon.

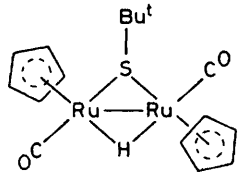
The propensity for μ-(η^7-C_8H_9) co-ordination was also

shown by the reaction of cyclo-octatriene with (1), which gave 28% of (8) as a result of H loss from the C_8H_{10} hydrocarbon.

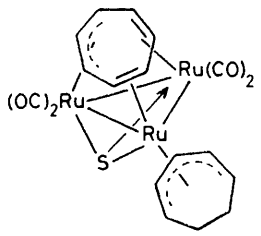
With cyclopentadiene the cluster (1) also fragments, to generate $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and *trans*-$[Ru_2(\mu\text{-}H)(CO)_2(\mu\text{-}SBu^t)(\eta\text{-}C_5H_5)_2]$ (11). The presence of a bridging



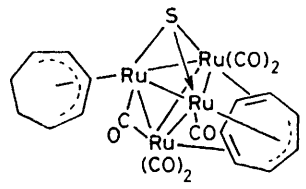
(10)



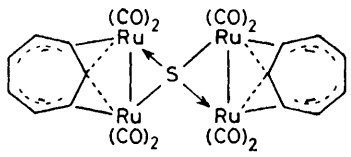
(11)



(12)



(13)



(14)

hydride ligand is established by the high-field ^1H n.m.r. shift of τ 24.2, and the two cyclopentadienyl resonances require a *trans* arrangement of these ligands with respect to the Ru–Ru axis. Unlike the di-μ-SR complexes $[Ru_2(CO)_2(\mu\text{-}SR)_2(\eta\text{-}C_5H_5)_2]$ discussed in Part 4 [1] of this series, the 18-electron rule predicts a metal–metal interaction in (11).

In concluding this section, it may be noted that the reactions of cycloheptatriene, cyclo-octatetraene, cyclo-octatriene, and cyclopentadiene with (1) all proceed at roughly the same rate in boiling heptane as their reactions with $[Ru_3(CO)_{12}]$. The presence of a capping SBu^t ligand with versatile co-ordination properties does not, therefore, appear significantly to enhance the reactivity of the Ru_3 cluster. Cluster fragmentation is, however, common and this involves irreversible alteration of μ_3-SBu^t bridging. It is accompanied by the release of a ruthenium carbonyl grouping, which appears as $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$, $[Ru_3(CO)_6(C_7H_9)(C_7H_7)]$, *etc.* The scheme proposed for the reaction of (5) with CO probably also serves as a model for cluster degradation by the cyclic polyolefins. Only with cycloheptatriene is retention of the Ru_3S skeleton favoured, and this may be attributed to the loss of three carbonyls and the one bridging hydride being nicely balanced electronically by C_7H_7 face-bridging.

Reactions of $[Ru_3H_2(CO)_9(\mu_3\text{-}S)]$ (2).—Extension of the argument contained in the last sentence of the previous section suggested that three carbonyls and the two bridging hydride ligands of (2) might be replaced by a face-bridging 8π-electron cyclo-octatetraene ligand. This proved to be the case in that heating (2) in boiling octane with cyclo-octatetraene gave $[Ru_3(CO)_6(\mu_3\text{-}S)\{\mu_3\text{-}(\eta^8\text{-}C_8H_8)\}]$ (10) in 50% yield as the single isolated product. This orange crystalline complex was identified by elemental analyses and mass, i.r., and n.m.r. spectra (Tables 1 and 2). Like (5) its mass spectrum has a molecular ion and ions corresponding to the loss of six carbonyl groups, but the i.r. spectrum is more complicated with four carbonyl bands of appreciable intensity rather than two. Whether this is a reflection of a less symmetrical molecular structure than that of (5) is uncertain.

Strong evidence that the complex contains a face-bridging C_8H_8 ligand is provided by the ^{13}C n.m.r. spectrum, which exhibits a high-field shift for the hydrocarbon at 48.0 p.p.m. This may be compared with values of 68.9 p.p.m. for the μ-$(\eta^8$-$C_8H_8)$ ring in $[Ru_2(CO)_5(C_8H_8)]$ and of *ca.* 98 p.p.m. for the η^4-C_8H_8 ring in $[Ru(CO)_3(C_8H_8)]$.[25] It seems clear that the ^{13}C shift of a fluxional cyclo-octatetraene ligand is a useful aid in determining the number of metal atoms to which it is bonded. It was seen earlier that this also holds for C_7H_7, shifts of *ca.* 60 and 40 p.p.m. appearing characteristic of μ-$(\eta^7$-$C_7H_7)$ and μ_3-$(\eta^7$-$C_7H_7)$ bonding respectively. The face-bridging C_8H_8 ring in (10) is clearly undergoing fluxional rotation, in view of the single n.m.r. shift, and this continues even at −100 °C, at which temperature the ^1H and ^{13}C spectra are unchanged.

By analogy with the structure of (5) we represent the structure of (10) as illustrated, with the cyclo-octatetraene being η^3,η^3,η^2 co-ordinated to the ruthenium atoms, which are now capped by a four-electron S rather than five-electron SBu^t ligand. This implies the presence of an isosceles Ru_3 triangle, as in (5). Only two other examples of a face-bonded cyclo-octatetraene have been discovered, in structurally established $[Co_3(CO)_6(\mu_3\text{-}CPh)\{\mu_3\text{-}(\eta^6\text{-}C_8H_8)\}]$ [26] and $[Ni_3(CO)_3(CF_3C_2CF_3)\{\mu_3\text{-}(\eta^8\text{-}C_8H_8)\}]$.[27] In the former the hydrocarbon is bound through η^2 interactions to three cobalt atoms, but the latter contains an η^8-co-ordinated ring whose planarity provoked speculation over its nature as aromatic 6π-electron $C_8H_8^{2+}$. The same arguments could probably be applied to (10).

The reaction of cycloheptatriene with (2) also proceeds well in boiling octane, and produces three new cluster compounds containing three or four ruthenium atoms: $[Ru_3(CO)_4(\mu_3\text{-}S)(\eta^5\text{-}C_7H_9)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$ (12), $[Ru_4(CO)_6(\mu_3\text{-}S)(\eta^5\text{-}C_7H_9)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$ (13), and $[Ru_4(CO)_8(\mu_4\text{-}S)\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}_2]$ (14). The major product (16% yield) is (12), which retains the Ru_3S unit, but evidently some cluster fragmentation and reconstitution must also occur. The complexes are crystalline, not very soluble

in saturated hydrocarbons, and were identified by elemental analyses and spectroscopic data (Tables 1 and 2). Each of (12) and (14) displayed a molecular ion in its mass spectrum and ions corresponding to the loss of the appropriate number of carbonyl ligands, but (13) was much less volatile and the heaviest ion observed was due to $C_7H_7^+$.

Orange $[Ru_3(CO)_4(\mu_3\text{-}S)(\eta^5\text{-}C_7H_9)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$ (12) is assigned the structure illustrated on the basis of ^1H and ^{13}C n.m.r. spectra. The ^1H n.m.r. spectrum contains signals characteristic of an $\eta^5\text{-}C_7H_9$ cycloheptadienyl ligand on a ruthenium cluster, as occurs in $[Ru_3(CO)_6(\eta^5\text{-}C_7H_9)\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}]$,[10] and a sharp singlet due to a fluxional C_7H_7 ring. The ^{13}C n.m.r. spectrum reveals this ring to have a ^{13}C shift of 39.1 p.p.m., very close to that (38.7 p.p.m.) of the face-bonded ligand in (5), and a similar bonding mode can be assigned with confidence. Only terminal carbonyl absorption is seen in the i.r. spectrum, and with the aid of the 18-electron rule the instantaneous structure (12) is deduced. At −110 °C the ^1H n.m.r. spectrum of (12) shows some broadening of the C_7H_7 signal and splitting of the C_7H_9 resonances. Similar behaviour for a C_7H_9 ring in $[Ru_3(CO)_6(\eta^5\text{-}C_7H_9)\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}]$ was attributed to restricted rotation.[28] The broadening of the C_7H_7 signal of (12) indicates a higher barrier to rotation in this complex than in (5).

The small yield and low solubility of blue-black $[Ru_4(CO)_6(\mu_3\text{-}S)(\eta^5\text{-}C_7H_9)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$ (13) prevented a ^{13}C n.m.r. spectrum from being obtained, but since C_7H_7 adopts a face-bonding posture in the clusters (6) and (12) we believe this is most likely also the case for (13). Some evidence in support of this conclusion is provided by the ^1H n.m.r. spectra of (12) and (13), which have the C_7H_7 signal at τ 6.56 and 6.61 respectively. However, the $\mu\text{-}(\eta^7\text{-}C_7H_7)$ ligand in (4) resonates in the same region and this comparison is therefore not as decisive as with ^{13}C n.m.r. information. Again, an $\eta^5\text{-}C_7H_9$ ligand is clearly present (Table 2). Electron counting suggests the structure (13), illustrated, which is in accord with the observation of a bridging-carbonyl absorption in the i.r.

Only terminal carbonyl groups are present in orange $[Ru_4(CO)_8(\mu_4\text{-}S)\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}_2]$ (14) and only fluxional C_7H_7 rings, which are equivalent, with a common signal in the ^1H n.m.r. spectrum at τ 5.74. The ^{13}C n.m.r. criterion of co-ordination mode clearly points to μ-bridging of C_7H_7 in this complex, since the shift is 64.3 p.p.m., at much lower field than that for (5), (12), or (13). The structure (14) seems most likely, in which sulphur, acting as a six-electron ligand, is tetrahedrally placed between four ruthenium atoms. The relationship to (4) is obvious, and there is also a parallel with the complex $[Fe_4(CO)_{12}(\mu_4\text{-}S)(\mu\text{-}SMe)_2]$.[29]

It may be noted that the reactions of $[Ru_3H_2(CO)_9(\mu_3\text{-}S)]$ with cyclic polyolefins require more vigorous conditions (boiling octane *versus* boiling heptane) than those of $[Ru_3H(CO)_9(\mu_3\text{-}SBu^t)]$. Although sulphur can bridge two metal atoms the only evidence for it comes in complex (14), which may arise *via* dimerisation of an $Ru_2(CO)_4(\mu\text{-}S)\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}$ unit. Again, therefore, there is little to justify the idea of enhanced cluster reactivity as a consequence of the capping ligand having a variable co-ordination ability. The stability of the $Ru_3(\mu_3\text{-}S)$ unit is shown by its consistent presence in the products of the reactions of (2).

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer, using calcium fluoride cells of 1.0-mm path length, and were calibrated *via* the absorption of polystyrene film at 1 601 cm^{-1}. Proton n.m.r. spectra were obtained on a JEOL PS-100 instrument operating at 100 MHz and ^{13}C n.m.r. spectra with a JEOL PFT-100 spectrometer operating at 25.15 MHz in the Fourier-transform mode. Mass spectra were recorded using an AEI MS902 instrument.

Reactions were performed under nitrogen atmospheres, using solvents dried by distillation from lithium aluminium hydride or calcium hydride (for dichloromethane). Separation of products was achieved by column chromatography and further purification was by crystallisation from hexane–dichloromethane.

Physical, analytical, and spectroscopic data for new compounds are collected in Tables 1 and 2.

Preparations.—$[Ru_3H(CO)_9(\mu_3\text{-}SBu^t)]$ (1). A heptane (250 cm^3) solution of $[Ru_3(CO)_{12}]$ (1.84 g, 2.87 mmol) and Bu^tSH (0.8 g, 8.8 mmol) was heated at reflux for 10 min. The solution was then evaporated to dryness under reduced pressure and the residue introduced to an alumina column. Elution with hexane gave a yellow band which produced 1.28 g (69%) of yellow crystalline $[Ru_3H(CO)_9(\mu_3\text{-}SBu^t)]$ (1) [m.p. 120 °C (decomp.); ν(CO) (hexane) 2 089w, 2 063s, 2 039s, 2 017s, 2 006m, and 1 975w cm^{-1}; ^1H n.m.r. ($CDCl_3$) τ 8.50 (s, 9 H) and 28.20 (s, 1 H); Found: C, 24.2; H, 1.6%. *M*, 647. $C_{13}H_{10}O_9Ru_3S$ requires C, 24.2; H, 1.6%. *M*, 647].

If the reaction is allowed to proceed for longer than 10 min a variety of other sulphur–ruthenium complexes is produced. Brief examination revealed these to include $[Ru_2(CO)_6(\mu\text{-}SBu^t)_2]$, $[Ru_3(CO)_9(\mu\text{-}SBu^t)_2]$, $[Ru_3(CO)_7(\mu\text{-}SBu^t)_4]$, and $[Ru_3(CO)_6(\mu\text{-}SBu^t)_3(\mu_3\text{-}SBu^t)(\mu_3\text{-}S)]$.

$[Ru_3H(CO)_{10}(\mu\text{-}SBu^t)]$ (3; R = Bu^t). An acetone (10 cm^3) solution of (1) (100 mg, 0.15 mmol) was subjected to 15 atm of CO at 40 °C for 15 h in an autoclave. After evaporation of solvent, chromatography on alumina, and elution with hexane, gave a single yellow band from which 60 mg (57%) of red crystalline $[Ru_3H(CO)_{10}(\mu\text{-}SBu^t)]$ (3; R = Bu^t) were obtained [m.p. 97 °C (decomp.); ν(CO) (hexane) 2 103w, 2 062s, 2 054s, 2 025s, 2 002m, and 1 993w cm^{-1}; ^1H n.m.r. ($CDCl_3$) τ 8.75 (s, 9 H) and 27.4 (s, 1 H); Found: C, 25.1; H, 1.5%. *M*, 675. $C_{14}H_{10}O_{10}Ru_3S$ requires: C, 25.0; H, 1.5%. *M*, 675].

$[Ru_3H_2(CO)_9(\mu\text{-}S)]$ (2).—The most convenient synthesis of (2) is from $[Ru_3(CO)_{12}]$ and H_2S,[5] details of which are given here for the first time. Hydrogen sulphide was bubbled slowly through a boiling heptane (400 cm^3) solution of $[Ru_3(CO)_{12}]$ (2.0 g, 3.1 mmol) for 1 h. The reaction mixture was then evaporated to dryness and the yellow powder obtained chromatographed on alumina. Elution with hexane–dichloromethane (9 : 1) developed a yellow band from which was obtained 1.3 g (71%) of yellow crystalline $[Ru_3H_2(CO)_9(\mu_3\text{-}S)]$ (2).

Reactions of $[Ru_3H(CO)_9(\mu_3\text{-}SBu^t)]$ (1).—(*a*) *With cycloheptatriene.* A mixture of (1) (0.5 g, 0.77 mmol) and cycloheptatriene (0.8 g, 8.7 mmol) was heated in boiling heptane (350 cm³) for 16 h. Chromatography on alumina, eluting with hexane–dichloromethane (20 : 1), gave a yellow band which afforded 14 mg (4%) of yellow crystalline $[Ru_2(CO)_4(\mu\text{-}SBu^t)\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}]$ (4). Further elution with hexane–dichloromethane (9 : 1) developed a second yellow band which gave 62 mg (12%) of $[Ru_3(CO)_6(\mu_3\text{-}SBu^t)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$ (5) as yellow crystals. Finally, elution with hexane–dichloromethane (4 : 1) provided an orange band from which a few mg of dark red crystals were obtained, identified as the known $[Ru_3(CO)_6(\eta^5\text{-}C_7H_9)\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}]$ [10] by i.r. and mass spectra and analysis (Found: C, 36.5; H, 2.4%. *M*, 655. $C_{20}H_{16}O_6Ru_3$ requires C, 36.6; H, 2.4%. *M*, 655).

(*b*) *With cyclo-octatetraene.* A mixture of (1) (0.35 g, 0.54 mmol) and cyclo-octatetraene (0.55 g, 5.3 mmol) was heated in boiling heptane (250 cm³) for 16 h. Chromatography on alumina gave four yellow bands on eluting with hexane. The first three of these contained cyclo-octatetraene, an unidentified carbonyl complex in very low yield, and (1). The fourth gave 167 mg (61%) of yellow crystalline $[Ru_2(CO)_4(\mu\text{-}SBu^t)\{\mu\text{-}(\eta^7\text{-}C_8H_9)\}]$ (8). Elution with hexane–dichloromethane (4 : 1) removed a yellow band containing a small amount of $[Ru_3(CO)_6(\mu_3\text{-}S)\{\mu_3\text{-}(\eta^8\text{-}C_8H_8)\}]$ (10), identified by i.r. spectroscopy.

(*c*) *With cyclo-octatriene.* A heptane (100 cm³) solution of (1) (0.3 g, 0.47 mmol) and cyclo-octatriene (0.5 g, 4.7 mmol) was heated at reflux for 17 h. Chromatography as in (*b*) then separated 67 mg (28%) of $[Ru_2(CO)_4(\mu\text{-}SBu^t)\{\mu\text{-}(\eta^7\text{-}C_8H_9)\}]$ (8), identified by i.r. and ^1H n.m.r. spectra.

(*d*) *With cyclopentadiene.* A heptane (100 cm³) solution of (1) (0.22 g, 0.33 mmol) and cyclopentadiene (0.8 g, 12.1 mmol) was heated at reflux for 20 h. Chromatography on alumina, eluting with hexane–dichloromethane (9 : 1), then gave two yellow bands. From these were obtained, respectively, 76 mg (48%) of red crystalline $[Ru_2(\mu\text{-}H)(CO)_2(\mu\text{-}SBu^t)(\eta\text{-}C_5H_5)_2]$ (11) and 44 mg (20%) of orange $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$, the latter identified by i.r. and ^1H n.m.r. spectra.

Reactions of $[Ru_3H_2(CO)_9(\mu_3\text{-}S)]$ (2).—(*a*) *With cycloheptatriene.* A mixture of (2) (0.43 g, 0.71 mmol) and cycloheptatriene (0.89 g, 9.7 mmol) was heated in octane (200 cm³) at reflux for 6 h. Chromatography on alumina, eluting with hexane–dichloromethane (1 : 1), provided two yellow bands which yielded 23 mg (5%) of orange crystalline $[Ru_4(CO)_8(\mu_4\text{-}S)\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}_2]$ (14) and 72 mg (16%) of orange crystalline $[Ru_3(CO)_4(\mu_3\text{-}S)(\eta^5\text{-}C_7H_9)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$ (12) in turn. Further elution with neat dichloromethane gave a blue band from which 10 mg (2%) of blue-black crystalline $[Ru_4(CO)_6(\mu_3\text{-}S)(\eta^5\text{-}C_7H_9)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$ (13) were obtained.

(*b*) *With cyclo-octatetraene.* A mixture of (2) (0.4 g, 0.68 mmol) and cyclo-octatetraene (0.92 g, 8.8 mmol) was heated in octane at reflux for 24 h. Chromatography on alumina afforded only one band, eluted with hexane–dichloromethane (4 : 1), and this gave 212 mg (51%) of orange crystals of $[Ru_3(CO)_6(\mu_3\text{-}S)\{\mu_3\text{-}(\eta^8\text{-}C_8H_8)\}]$ (10).

Reaction of $[Ru_3(CO)_6(\mu_3\text{-}SBu^t)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$ (5) *with* CO.—An acetone (10 cm³) solution of (5) (150 mg, 0.23 mmol) was subjected to 15 atm of CO at 70 °C in an autoclave for 17 h. Evaporation of solvent, followed by chromatography of the residue on alumina, gave a yellow band with hexane. This contained a small amount of $[Ru_3(CO)_{12}]$, identified by i.r. spectroscopy. A second yellow band, eluted with hexane–dichloromethane (20 : 1), provided 76 mg (67%) of $[Ru_2(CO)_4(\mu\text{-}SBu^t)\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}]$ (4).

Crystal-structure Determination of $[Ru_3(CO)_6(\mu_3\text{-}SBu^t)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$ (5).—The crystal used for data collection, of dimensions *ca.* 0.55 × 0.6 × 0.2 mm, was chosen from among the transparent yellow parallelepipeds which grow from diethyl ether. Intensity measurements were made in the range $2.9 \leqslant 2\theta \leqslant 50°$ at 200 K on a Syntex $P2_1$ four-circle diffractometer. The intensity recorded in a preliminary 2-s count for each reflection led to a variable scanning rate, proportional to the magnitude of this prescan count at the Bragg position. The crystal temperature was maintained at 200 K by a stream of cold dry nitrogen gas, collinear with the ϕ axis of the diffractometer. Of the total 5 188 measurements recorded, 3 860 were unique and satisfied the criterion $I \geqslant 2\sigma(I)$, where $\sigma(I)$ is the standard deviation of the measured intensity based on counting statistics. Corrections were made for the effects of Lorentz and polarisation, but not for that of *X*-ray absorption. The intensities of the standard reflections, which were used to monitor the crystal and experimental stability, showed no appreciable variation throughout data collection.

Crystal data. $C_{17}H_{16}O_6Ru_3S$, *M* 651.6, Monoclinic, space group *C*2/*c*, $a = 14.875(6)$, $b = 8.902(6)$, $c = 30.977(2)$ Å, $\beta = 94.785(4)°$, $U = 4\,087(4)$ Å³, $D_m = 2.10$, $Z = 8$, $D_c = 2.12$ g cm⁻³, $F(000) = 2\,512$, Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 22.6 cm⁻¹.

Structure solution and refinement. The corrected, unique data were used to calculate a sharpened Patterson synthesis, from which the positions of the three ruthenium atoms were apparently located. A subsequent electron-density difference synthesis revealed positions for the S and Bu^t carbon atoms, but the refinement did not converge readily. At this stage there were significant residuals in the difference synthesis which suggested alternative positions for the three ruthenium atoms, coplanar with but rotated through 60° from the original triangle. This led to the trial of a disordered model in which the ruthenium atoms can occupy two alternative sites in the ratio 2 : 1, but 'share' the ordered ligand atoms. Further refinement of this model enabled all non-hydrogen and the ring-hydrogen atoms to be located. The methyl-hydrogen atoms, which could not be located directly from the density maps, were included in their calculated positions and refined according to the riding model of Busing and Levy.[30] All non-hydrogen atoms were refined using anisotropic thermal parameters and convergence was achieved at $R(R') = 0.041(0.040)$. The weighting scheme was $w = |\sigma^2(F) + \alpha|F|^2|^{-1}$ with $\alpha = 0.000\,14$, which gave approximately constant $w\Delta^2$ over the range of observations ($\Delta = |F_o - F_c|$). In the final cycles of refinement there were no significant shift-to-error ratios and the final electron-density difference synthesis showed no peaks $\geqslant$ *ca.* 1.0 e Å⁻³. Atomic scattering factors used were those of ref. 31, with appropriate correction for anomalous dispersion.

Computational work was carried out on the South Western Universities Computer Network, using the SHELX [32] system of programs. The observed and calculated structure factors, together with the thermal parameters for all atoms, are listed in Supplementary Publication No. SUP 23113 (21 pp.).*

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

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