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Structure of μ_6-Carbido-2,3-μ-carbonyl-1,1,1,2,2,3,3,4,4,4,5,5,5-tridecacarbonyl-6-(η^6-toluene)-*octahedro*-hexaruthenium(12 *Ru–Ru*)

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Abstract. $[Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}C_6H_5CH_3)]$, $M_r = 1102{\cdot}7$, orthorhombic, *Pnam* (non-standard setting of *Pnma*, No. 62, D_{2h}^{16}, equiv. positions used: $-x, y, z$: $-x, -y, \frac{1}{2}+z$: $\frac{1}{2}+x, \frac{1}{2}-y, z$: $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$ and centrosymmetric equivalents), $a = 12{\cdot}481\,(3)$, $b = 14{\cdot}385\,(3)$, $c = 15{\cdot}034\,(5)$ Å, $V = 2699\,(1)$ Å^3, $Z = 4$, $D_x = 2{\cdot}71$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 32{\cdot}8$ cm^{-1}, $F(000) = 2064$, $T = 298$ K, $R = 0{\cdot}039$ for 2770 observed reflections. The cluster has crystallographic mirror symmetry, with the carbido ligand significantly closer to the arene-bearing Ru atom: Ru(2)—C(1) = 1·937 (7) Å; the mean of the other Ru—C(carbide) distances is 2·067 (7) Å.

Introduction. Numerous examples of μ_6-carbido-*octahedro*-hexaruthenium clusters are now known (Bradley, 1983), and indeed $Ru_6(\mu_6\text{-}C)(CO)_{17}$ (1) was one of the first crystallographically characterized carbido clusters (Sirigu, Bianchi & Benedetti, 1969). The carbido ligand in this complex is close to the geometric centre of the Ru octahedron with a mean Ru—C distance of 2·05 (5) Å. However, another early structure on a mesitylene derivative of (1), namely $Ru_6(\mu_6\text{-}C)(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)$ (2) (Mason & Robinson, 1968) showed that the carbide ligand was displaced *ca* 0·2 Å towards the arene-bearing Ru atom. We have serendipitously prepared the title complex (3), a previously reported toluene analogue of (2) (Johnson, Johnston & Lewis, 1968), by treatment of $CoRu_3(\mu\text{-}H)(CO)_{13}$ with $HgPh_2$ in refluxing toluene. We herein report the structure of (3) and compare it with (2) and other derivatives of (1).

Experimental. Black prisms from hexane solution: crystal dimensions 0·35 × 0·40 × 0·25 mm; systematic absences: $h = 2n+1$ in $h0l$; $k+l = 2n+1$ in $0kl$; $k = 2n+1$ in $0k0$: Enraf–Nonius CAD-4F diffractometer; graphite monochromator; $\theta/2\theta$ scan mode; cell parameters refined by least-squares method on basis of 25 independent θ values, $11 \le \theta \le 13°$; intensities measured to $\theta = 27{\cdot}5°$ over range of *hkl* 0 to 16, −1 to 18, −1 to 19; $26\bar{6}$, $\bar{6}2\bar{5}$, $\bar{3}80$ measured every 2 h, no appreciable decomposition observed, 3944 reflections measured, 3216 independent data with 2770 having $I \ge 3{\cdot}0\sigma(I)$ considered observed and used in structure determination and refinement; R_{int} 0·039 after correction; corrections for Lorentz/polarization, absorption (*DIFABS;* Stuart & Walker, 1983; range of transmission factors on *F*, 0·908 to 1·637); solved by direct methods (*MITHRIL;* Gilmore, 1984) and subsequent full-matrix least squares; anisotropic thermal parameters for non-H atoms; H atoms included at fixed calculated positions with fixed isotropic ($U = 0{\cdot}05$ Å^2) thermal parameters; $w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma^2(F_o)]^{-1}$; max. Δ/σ 0·036, av. 0·005; $(\Delta\rho)_{\max}$ +1·05, $(\Delta\rho)_{\min}$ −2·63 e Å^{-3} in vicinity of heavy metal atoms; $R = 0{\cdot}039$, $wR = 0{\cdot}058$; $R(wR) = 0{\cdot}045(0{\cdot}061)$ for all data; $S = 3{\cdot}27$; atomic scattering factors including anomalous terms from *International Tables for X-ray Crystallography* (1974); calculations carried out on a Gould-SEL 32/37 mini-computer using the *GX* suite of programs (Mallinson & Muir, 1985).

Discussion. Final positional parameters are given in Table 1, with selected bond distances and angles in Table 2.* The molecular structure and atomic labelling scheme are shown in Fig. 1, with a stereoview in Fig. 2. The molecule has crystallographic mirror symmetry. The essentially regular octahedral array of Ru atoms has Ru—Ru distances ranging from 2·815 (1) to 2·955 (1) Å, with a mean value of 2·892 (1) Å. The carbonyl manifold is similar to that found in (1) and (2) with the Ru(3)—Ru(3′) edge symmetrically bridged by a CO ligand C(6)—O(6). There is also a weak semi-bridging interaction between C(7)—O(7) and Ru(3), with an Ru(4)—C(7)—O(7) angle of 166·3 (7)° and an Ru(3)···C(7) contact distance of 2·801 (7) Å. Other carbonyls are essentially linear. The Ru—C(arene) distances are normal, ranging from 2·221 (10) to 2·282 (9) Å [mean 2·25 (1) Å] and compare well with the mean corresponding distance of 2·24 (4) Å found in complex (2) (Mason & Robinson, 1968). The

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* Lists of structure factors, anisotropic thermal parameters, calculated hydrogen positional parameters, and a complete listing of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44822 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final positional parameters (fractional coordinates) with e.s.d.'s in parentheses, and equivalent isotropic thermal parameters,* U_{eq}(Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ru(1)	0·55441 (5)	0·44223 (4)	0·25000	0·021
Ru(2)	0·84986 (5)	0·55176 (4)	0·25000	0·023
Ru(3)	0·75394 (3)	0·39675 (3)	0·15639 (3)	0·022
Ru(4)	0·65933 (3)	0·58501 (3)	0·15190 (3)	0·022
O(2)	0·9510 (4)	0·3820 (4)	0·0406 (4)	0·058
O(3)	0·4600 (4)	0·3256 (4)	0·1013 (4)	0·058
O(4)	0·3410 (6)	0·5445 (6)	0·2500	0·066
O(5)	0·6690 (4)	0·2396 (4)	0·0440 (4)	0·060
O(6)	0·3214 (6)	0·2783 (5)	0·2500	0·051
O(7)	0·7540 (5)	0·0386 (4)	0·0323 (3)	0·061
O(8)	0·7884 (4)	0·2903 (3)	−0·1381 (4)	0·062
O(9)	1·0609 (4)	0·1178 (5)	−0·0761 (4)	0·068
C(1)	0·7085 (5)	0·4962 (5)	0·2500	0·018
C(2)	0·8769 (5)	0·3875 (5)	0·0855 (4)	0·038
C(3)	0·4999 (5)	0·3663 (5)	0·1554 (4)	0·036
C(4)	0·4230 (6)	0·5090 (7)	0·2500	0·037
C(5)	0·6980 (5)	0·3012 (4)	0·0853 (4)	0·033
C(6)	0·2955 (7)	0·1994 (6)	0·2500	0·033
C(7)	0·7823 (6)	0·0450 (5)	−0·0395 (4)	0·039
C(8)	0·8039 (5)	0·2120 (4)	−0·1426 (4)	0·036
C(9)	0·9815 (5)	0·1044 (5)	−0·1043 (5)	0·040
C(10)	−0·0750 (6)	0·6917 (7)	0·2500	0·043
C(11)	−0·0492 (4)	0·6486 (5)	0·3316 (5)	0·039
C(12)	0·0029 (5)	0·5615 (5)	0·3309 (5)	0·041
C(13)	0·0283 (6)	0·5170 (7)	0·2500	0·042
C(14)	0·0836 (8)	0·4228 (9)	0·2500	0·057

Table 2. *Selected bond lengths* (Å) *and bond angles* (°), *with e.s.d.'s in parentheses*

Ru(1)—Ru(3)	2·934 (1)	Ru(1)—Ru(4)	2·848 (1)
Ru(2)—Ru(3)	2·896 (1)	Ru(2)—Ru(4)	2·839 (1)
Ru(3)—Ru(3′)	2·815 (1)	Ru(3)—Ru(4)	2·955 (1)
Ru(4)—Ru(4′)	2·950 (1)	Ru(1)—C(1)	2·074 (7)
Ru(2)—C(1)	1·937 (7)	Ru(3)—C(1)	2·085 (5)
Ru(4)—C(1)	2·046 (5)	Ru(1)—C(3)	1·918 (7)
Ru(1)—C(4)	1·901 (9)	Ru(3)—C(2)	1·873 (7)
Ru(3)—C(5)	1·875 (6)	Ru(3)—C(6)	2·041 (7)
Ru(4)—C(7)	1·928 (7)	Ru(4)—C(8)	1·889 (7)
Ru(4)—C(9)	1·919 (7)	Ru(2)—C(10)	2·221 (10)
Ru(2)—C(11)	2·243 (7)	Ru(2)—C(12)	2·268 (7)
Ru(2)—C(13)	2·282 (9)	C(10)—C(11)	1·411 (9)
C(11)—C(12)	1·412 (10)	C(12)—C(13)	1·410 (9)
C(13)—C(14)	1·521 (16)	Ru(3)···C(7)	2·801 (7)
Ru(1)—C(1)—Ru(3)	89·8 (3)	Ru(1)—C(1)—Ru(4)	87·5 (3)
Ru(2)—C(1)—Ru(3)	92·0 (3)	Ru(2)—C(1)—Ru(4)	90·9 (3)
Ru(3)—C(1)—Ru(3′)	84·9 (3)	Ru(3)—C(1)—Ru(4)	91·3 (1)
Ru(4)—C(1)—Ru(4′)	92·3 (3)	Ru(3)—C(6)—O(6)	136·2 (2)
Ru(4)—C(7)—O(7)	166·3 (7)		

Other Ru—C—O mean 176·4 (9)

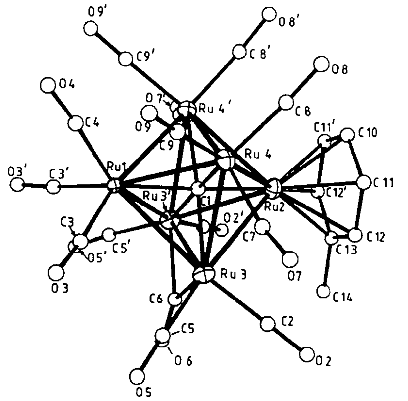

Fig. 1. Molecular structure of complex (3).

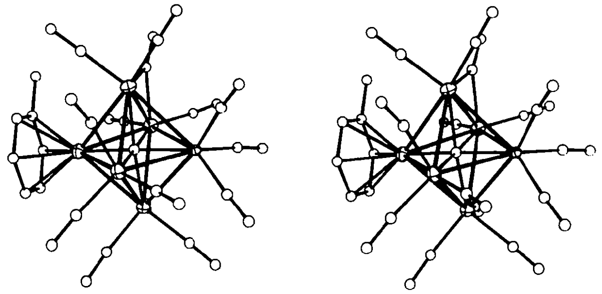

Fig. 2. Stereoview of complex (3).

carbido ligand is displaced towards the arene-bearing Ru(2) atom by *ca* 0·13 Å from the mean of the remaining Ru—C(carbide) separations [2·067 (7) Å]. This effect seems to be a feature of the arene-substituted complexes (2) and (3), since other derivatives of (1) appear to have symmetrically disposed carbides. Thus in the complexes $Ru_6(\mu_6\text{-}C)(CO)_{16}(L)$ for $L = PPh_2Et$ the Ru—C(carbido) separations range from 2·010 (7) to 2·089 (7) Å (Brown, Evans & Webster, 1981), while with $L = CNBu^t$ this range is 2·032 (8)–2·074 (8) Å (Adams, Mathur & Segmüller, 1983). $Ru_6(\mu_6\text{-}C)(CO)_{14}(C_{14}H_{14})$ shows a range of 2·022 (2)–2·076 (2) Å for this parameter (Ansell & Bradley, 1980*b*), while in the anionic species $[Ru_6(\mu_6\text{-}C)(CO)_{16}]^{2-}$ a range 2·029 (13)–2·064 (13) Å is observed (Ansell & Bradley, 1980*a*).

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