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Structure of a Hexanuclear Ruthenium Cluster: $Ru_6C(CO)_{15}(Ph_2PCH_2PPh_2)$*

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Abstract. $[Ru_6C(C_{25}H_{22}P_2)(CO)_{15}]$, $M_r = 1423{\cdot}1$, monoclinic, $C2/c$, $a = 14{\cdot}116\ (4)$, $b = 18{\cdot}132\ (4)$, $c = 35{\cdot}665\ (4)$ Å, $\beta = 101{\cdot}04\ (2)°$, $V = 8959{\cdot}6$ Å^3, $Z = 8$, $D_m = 2{\cdot}10\ (2)$, $D_x = 2{\cdot}109$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 20{\cdot}4$ cm^{-1}, $F(000) = 5456$, room temperature, final $R = 0{\cdot}052$ for 5234 reflections $[F > 6\sigma(F)]$. The asymmetric unit consists of one $[Ru_6C(CO)_{15}(Ph_2PCH_2PPh_2)]$ cluster in which the central C atom is coordinated to the six Ru atoms (mean Ru—C distance 2·055 Å) which form an octahedral cage. One CO group is edge bridging, the remainder being terminal. The bis(phosphine) ligand bridges an Ru—Ru edge, thus forming a five-membered Ru—Ru—P—C—P ring. One of the P atoms is coordinated to an Ru atom which is *trans* to a metal atom involved in the CO bridge with the second P atom bound to an Ru atom *cis* to both CO-bridged metal centres.

Introduction. $[Ru_6C(CO)_{17}]$ reacts with bidentate phosphines (P–P) under ambient conditions to give clusters of general formula $[Ru_6C(CO)_{15}(P–P)]$ in high yield. Two possible coordination modes for the phosphine are either chelating to one Ru centre or as a bidentate bridging ligand. Low-temperature ^{31}P NMR experiments on one such derivative, $[Ru_6C(CO)_{15}(Ph_2PCH_2PPh_2)]$, demonstrated that the P atoms are in non-equivalent positions in solution at 172K), but at the lowest temperature attainable (158K) the ^{13}CO groups undergo a selective site exchange which precludes establishing the structure of the complex.

Experimental. Air-stable black crystals were obtained from cyclohexane/methylene chloride and density measured by flotation ($CCl_4/C_2H_4Br_2$). Preliminary data were from photographic X-ray examination and accurate cell dimensions obtained from 25 reflections ($9{\cdot}4 < \theta < 13{\cdot}9°$) using an Enraf–Nonius CAD-4 diffractometer fitted with graphite monochromator and Mo radiation. The intensities of 8829 reflections were recorded (ω–2θ scan, $1{\cdot}5 < \theta < 25°$, h0→16, k0→21, l−12→42) using a crystal 0·3 × 0·2 × 0·15 mm. The standard reflections (3) showed no decay with time and

Table 1. *Atomic coordinates and isotropic temperature factors* (Å^2 × 10^3)

	x	*y*	*z*	*U*
Ru(1)	0·32246 (6)	0·50806 (5)	0·10917 (3)	27·5 (5)*
Ru(2)	0·17424 (6)	0·40948 (5)	0·13232 (3)	27·2 (5)*
Ru(3)	0·37966 (7)	0·37158 (5)	0·15412 (3)	33·0 (5)*
Ru(4)	0·39852 (6)	0·38205 (5)	0·07596 (3)	31·0 (5)*
Ru(5)	0·19569 (6)	0·41954 (5)	0·05322 (3)	30·6 (5)*
Ru(6)	0·25496 (7)	0·28645 (5)	0·09865 (3)	34·6 (5)*
P(1)	0·2383 (2)	0·6170 (2)	0·1165 (1)	30 (2)*
P(2)	0·1118 (2)	0·5165 (2)	0·1543 (1)	29 (2)*
C(1)	0·4211 (10)	0·5226 (7)	0·1519 (4)	45 (3)
O(1)	0·4846 (8)	0·5403 (6)	0·1759 (3)	73 (3)
C(2)	0·3802 (10)	0·5596 (8)	0·0745 (4)	54 (4)
O(2)	0·4182 (9)	0·5921 (6)	0·0536 (4)	81 (3)
C(3)	0·1757 (9)	0·3680 (7)	0·1794 (4)	42 (3)
O(3)	0·1683 (8)	0·3403 (6)	0·2084 (3)	67 (3)
C(4)	0·0503 (9)	0·3735 (7)	0·1136 (4)	40 (3)
O(4)	−0·0268 (8)	0·3490 (6)	0·1020 (3)	65 (3)
C(5)	0·3842 (10)	0·3681 (7)	0·2063 (4)	52 (3)
O(5)	0·3882 (8)	0·3651 (6)	0·2398 (4)	82 (3)
C(6)	0·5112 (11)	0·3604 (8)	0·1637 (4)	51 (4)
O(6)	0·5947 (9)	0·3552 (7)	0·1693 (4)	80 (3)
C(7)	0·3535 (9)	0·2606 (7)	0·1475 (4)	43 (3)
O(7)	0·3868 (8)	0·2064 (6)	0·1637 (3)	71 (3)
C(8)	0·5149 (11)	0·4323 (9)	0·0874 (4)	59 (4)
O(8)	0·5882 (9)	0·4656 (7)	0·0920 (3)	82 (3)
C(9)	0·3955 (10)	0·3884 (7)	0·0227 (4)	47 (3)
O(9)	0·4021 (9)	0·3913 (7)	−0·0094 (4)	84 (3)
C(10)	0·4576 (10)	0·2895 (8)	0·0790 (4)	48 (3)
O(10)	0·4983 (8)	0·2335 (6)	0·0818 (3)	75 (3)
C(11)	0·0738 (10)	0·4608 (7)	0·0477 (4)	46 (3)
O(11)	−0·0014 (8)	0·4892 (6)	0·0432 (3)	71 (3)
C(12)	0·2181 (9)	0·4722 (7)	0·0105 (4)	46 (3)
O(12)	0·2314 (8)	0·5068 (6)	−0·0155 (3)	67 (3)
C(13)	0·1485 (10)	0·3290 (8)	0·0281 (4)	51 (3)
O(13)	0·1129 (9)	0·2830 (6)	0·0075 (3)	79 (3)
C(14)	0·2810 (10)	0·2036 (7)	0·0719 (4)	50 (3)
O(14)	0·2991 (8)	0·1503 (6)	0·0560 (3)	78 (3)
C(15)	0·1614 (10)	0·2318 (8)	0·1149 (4)	52 (3)
O(15)	0·1032 (9)	0·1942 (7)	0·1248 (4)	91 (4)
C(16)	0·2861 (7)	0·3992 (5)	0·1048 (3)	22 (2)
C(17)	0·1152 (8)	0·5969 (6)	0·1239 (3)	29 (2)
C(21)	0·2954 (6)	0·6788 (4)	0·1545 (2)	37 (3)
C(22)	0·3945 (6)	0·6908 (4)	0·1586 (2)	56 (4)
C(23)	0·4415 (6)	0·7376 (4)	0·1873 (2)	72 (5)
C(24)	0·3894 (6)	0·7724 (4)	0·2118 (2)	63 (4)
C(25)	0·2904 (6)	0·7604 (4)	0·2076 (2)	55 (3)
C(26)	0·2433 (6)	0·7136 (4)	0·1790 (2)	46 (3)
C(31)	0·2096 (6)	0·6803 (4)	0·0756 (2)	40 (3)
C(32)	0·2278 (6)	0·7558 (4)	0·0798 (2)	57 (4)
C(33)	0·1969 (6)	0·8034 (4)	0·0491 (2)	73 (5)
C(34)	0·1480 (6)	0·7756 (4)	0·0143 (2)	78 (5)
C(35)	0·1298 (6)	0·7001 (4)	0·0101 (2)	75 (5)
C(36)	0·1606 (6)	0·6525 (4)	0·0408 (2)	50 (4)
C(41)	0·1631 (6)	0·5503 (4)	0·2019 (2)	32 (3)
C(42)	0·2585 (6)	0·5337 (4)	0·2182 (2)	50 (4)
C(43)	0·3011 (6)	0·5655 (4)	0·2530 (2)	68 (4)
C(44)	0·2483 (6)	0·6140 (4)	0·2714 (2)	70 (5)
C(45)	0·1529 (6)	0·6306 (4)	0·2550 (2)	71 (4)
C(46)	0·1103 (6)	0·5988 (4)	0·2203 (2)	49 (3)
C(51)	−0·0159 (5)	0·5070 (5)	0·1560 (2)	35 (3)
C(52)	−0·0872 (5)	0·5296 (5)	0·1255 (2)	54 (4)
C(53)	−0·1842 (5)	0·5164 (5)	0·1261 (2)	69 (4)
C(54)	−0·2100 (5)	0·4808 (5)	0·1574 (2)	67 (4)
C(55)	−0·1388 (5)	0·4582 (5)	0·1879 (2)	70 (4)
C(56)	−0·0417 (5)	0·4714 (5)	0·1872 (2)	54 (4)

* Equivalent isotropic temperature factor, $U_{eq} = \frac{1}{3}$ trace **U**.

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* μ_6-Carbido-μ-carbonyl-tetradecacarbonyl-μ-[(P,P,P',P'-tetraphenyl)methylenebis(phosphine)]-*octahedro*-hexaruthenium.

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

Ru(1)–Ru(2)	2·986 (1)	Ru(2)–Ru(6)	2·870 (1)
Ru(1)–Ru(3)	2·975 (1)	Ru(3)–Ru(4)	2·857 (1)
Ru(1)–Ru(4)	2·875 (1)	Ru(3)–Ru(6)	2·838 (1)
Ru(1)–Ru(5)	2·897 (1)	Ru(4)–Ru(5)	2·903 (1)
Ru(2)–Ru(3)	2·936 (1)	Ru(4)–Ru(6)	2·898 (1)
Ru(2)–Ru(5)	2·900 (1)	Ru(5)–Ru(6)	2·938 (1)
Ru(1)–P(1)	2·345 (3)	Ru(2)–P(2)	2·328 (3)
Ru(1)–C(16)	2·04 (1)	P(1)–C(17)	1·843 (11)
Ru(2)–C(16)	2·02 (1)	P(1)–C(21)	1·822 (7)
Ru(3)–C(16)	2·05 (1)	P(1)–C(31)	1·840 (7)
Ru(4)–C(16)	2·07 (1)	P(2)–C(17)	1·822 (11)
Ru(5)–C(16)	2·06 (1)	P(2)–C(41)	1·819 (7)
Ru(6)–C(16)	2·09 (1)	P(2)–C(51)	1·825 (7)
Terminal CO's			
Ru–C(min.)	1·83 (1)	C–O(min.)	1·16 (2)
Ru–C(max.)	1·93 (1)	C–O(max.)	1·19 (2)
Ru–C(mean)	1·86 (3)	C–O(mean)	1·17 (2)
Bridging CO			
Ru(3)–C(7)	2·05 (1)	C(7)–O(7)	1·19 (2)
Ru(6)–C(7)	2·06 (1)		
Ru–Ru–Ru on triangular faces (24)	min. 58·4 (1)		
	max. 62·5 (1)		
Ru–Ru–Ru on square sections (12)	min. 88·6 (1)		
	max. 91·4 (1)		
Ru(2)–Ru(1)–P(1)	94·4 (1)	Ru(1)–Ru(2)–P(2)	85·6 (1)
Ru(1)–P(1)–C(17)	111·2 (4)	Ru(2)–P(2)–C(17)	114·3 (4)
Ru(1)–P(1)–C(21)	116·1 (3)	Ru(2)–P(2)–C(41)	119·1 (3)
Ru(1)–P(1)–C(31)	118·5 (3)	Ru(2)–P(2)–C(51)	111·9 (3)
P(1)–C(17)–P(2)	112·1 (6)	Ru(3)–C(7)–O(7)	135·1 (11)
Ru(3)–C(7)–Ru(6)	87·3 (5)	Ru(6)–C(7)–O(7)	137·5 (11)
Terminal CO's			
Ru–C–O (min.)	168 (1)		
Ru–C–O (max.)	179 (1)		
Ru–C–O (mean)	176 (3)		

an empirical ψ-scan absorption correction was applied. (Transmission: max. 99·8, min. 80·4%.) Systematic absences: hkl, $h+k \neq 2n$; $h0l$, $l \neq 2n$. After data reduction 7885 unique reflections, $R_{\rm int} = 0{\cdot}009$, of which 5262 with $F > 6\sigma(F)$ were used in the structure determination. The normalized structure factors (E's) suggested a centrosymmetric space group and $C2/c$ (No. 15) was used in the analysis and refinement. The Ru atoms were located using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and repeated structure factor and electron density syntheses located the remaining non-H atoms. H atoms bonded to C were introduced in geometrically calculated positions [d(C–H) = 1·08 Å] with a common refined temperature factor, and the phenyl C atoms were treated as a rigid group [d(C–C) = 1·395 Å]. The structure-factor listing showed a number with poor agreement and having a large value for l, and the worst of these (28) were omitted since it was thought they resulted from instrumental problems associated with the long c axis. Full-matrix least-squares refinement minimizing $\sum w(\Delta F)^2$ converged to $R = 0{\cdot}052$ {250 parameters, 5234 reflections, anisotropic (Ru, P) and isotropic (O, C, H) atoms, $w = 1/[\sigma^2(F) + 0{\cdot}0005F^2]$, max. $\Delta/\sigma = 0{\cdot}6$, $wR = 0{\cdot}077$}. The residual electron density was in the range 1·2 to −1·0 e Å^{-3}. Scattering factors for neutral atoms and anomalous-dispersion corrections were taken from *SHELX*76 (Sheldrick, 1976) and *International Tables for X-ray Crystallography* (1974) (Ru only). All calculations were carried out using *SHELX*76 (Sheldrick, 1976), *MULTAN*80 (Main *et al.*, 1980), *ORTEP* (Johnson, 1965) and *PLUTO* (Motherwell & Clegg, 1978) on ICL2970 or CDC7600 computers. The final positional parameters are given in Table 1 and pertinent bond lengths and angles in Table 2.[*]

Discussion. The molecular structure of the title compound contains an octahedron of Ru atoms with an interstitial carbide with a similar ligand arrangement to that reported for the parent cluster [$\mathrm{Ru_6C(CO)_{17}}$]

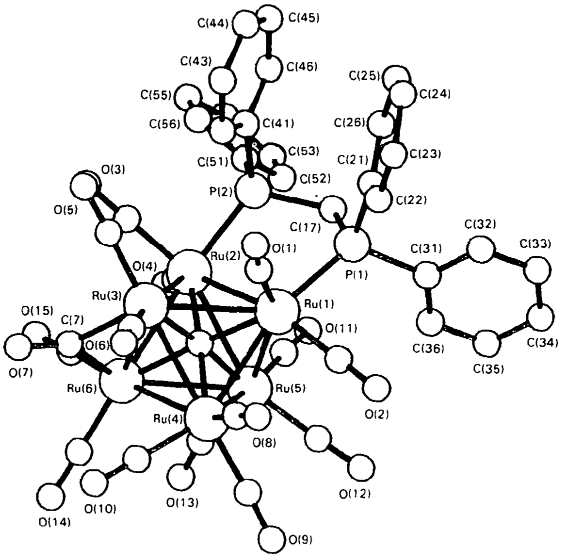

Fig. 1. Perspective view of the discrete molecule showing the atom-numbering scheme. Atoms are drawn with arbitrary size and H atoms are omitted for clarity.

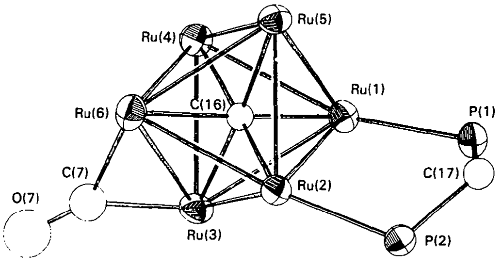

Fig. 2. View of the molecule showing the stereochemical relationship between the phosphine and μ-carbonyl group. Atoms are drawn with 50% probability thermal ellipsoids and all phenyl C atoms and terminal CO groups are omitted for clarity.

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[*] Lists of structure factors, anisotropic thermal parameters, calculated H-atom positions and complete geometric details have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44250 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(Sirigu, Bianchi & Benedetti, 1969). As shown in Figs. 1 and 2, the phosphine acts as a bridging ligand spanning the Ru(1)—Ru(2) edge. Ru(2) has the same regiochemical relationship with respect to the bridging CO ligand [C(7)O(7)] as the first phosphine substitution site adopted in $[Ru_6C(CO)_{16}(PPh_2Et)]$ (Brown, Evans & Webster, 1981), and the substitution site on Ru(2) is twisted away from the bridging CO side of the molecule to allow coordination of the second P atom to what appears to be the second-preference substitution site [on Ru(1)]. Indeed, in both phosphine- and arene-substituted derivatives, *e.g.* $[Ru_6C(CO)_{14}(C_7H_7)_2]$ (Ansell & Bradley, 1980) and $[Ru_6C(CO)_{11}(C_6H_6)_2]$ (Gomez-Sal, Johnson, Lewis, Raithby & Wright, 1985), the non-carbonyl ligands avoid coordination to the Ru atoms involved in the μ-CO bridge. The P NMR data at 172K, with two distinct ^{31}P environments, are consistent with this structure being maintained in solution.

The shortest Ru—Ru distance is that bridged by the μ-CO group, whilst the longest [Ru(1)—Ru(2)] is spanned by the $Ph_2PCH_2PPh_2$ ligand. However, the spread of metal–metal bond lengths in this compound (0·15 Å) is less than that of $[Ru_6C(CO)_{17}]$ (0·20 Å) and $[Ru_6C(CO)_{16}(PPh_2Et)]$ (0·26 Å), so there is little evidence for the phosphine destabilizing a metal–metal bond. The carbido site [C(16)] is slightly displaced towards Ru(1) and Ru(2), but the mean Ru—C(carbide) distance is very similar to that of the parent cluster.

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Structure of Tris(η^5-cyclopentadienyl)ytterbium(III)*

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Abstract. $[Yb(C_5H_5)_3]$, $M_r = 368{\cdot}32$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}988\,(3)$, $b = 8{\cdot}312\,(3)$, $c = 18{\cdot}176\,(6)$ Å, $V = 1206{\cdot}8\,(7)$ Å^3, $Z = 4$, $D_x = 2{\cdot}027$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}709261$ Å, $\mu = 76{\cdot}97$ cm^{-1}, $F(000) = 700$, $T = 295$ K, $R = 0{\cdot}037$ for 2244 unique observed reflections. The structure consists of Yb-centred, strictly mononuclear $(\eta^5\text{-}C_5H_5)_3Yb^{III}$ units and is not identical with the structures of the corresponding Tm and Lu complexes. The average Yb—C distance is 2·639 Å, and the Yb atom lies only 0·05 Å above the plane spanned by the centres of the three C_5 pentagons.

Introduction. In contrast to the series of strictly isomorphic tetrahydrofuran (THF) adducts $(\eta^5\text{-}C_5H_5)_3M^{III}$.THF, with M = lanthanoid (La–Lu) and Y (Ni, Deng & Qian, 1985) or U (Wasserman, Zozulin, Moody, Ryan & Salazar, 1983), the parent base-free tris(cyclopentadienyl)lanthanoid(III) complexes, $(C_5H_5)_3Ln^{III}$, display substantial structural variations with Ln (Eggers, Hinrichs, Kopf, Jahn & Fischer, 1986, and references therein). In view of the unexpectedly drastic structural changes experienced on going from $(\eta^5\text{-}C_5H_5)_3Tm^{III}$ to $[(\eta^5\text{-}C_5H_5)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}C_5H_5)Lu^{III}]_\infty$

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* Coordination Behaviour in Base-Free Tris(cyclopentadienyl) Complexes of Rare Earth Elements. V. Part IV: Eggers, Hinrichs, Kopf, Jahn & Fischer (1986).

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