The Structure of a Ruthenium Carbonyl 'Carbide' Cluster

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THE preparation and characterisation of a new cluster compound, $Ru_6C(CO)_{17}$, and related molecules, $Ru_6C(CO)_{14}$(arene), have been described by Johnson, Johnston, and Lewis.[1] The complete structure of the mesitylene derivative, $RuC(CO)_{14}(C_6H_3Me_3)$, which is isoelectronic with $Rh_6(CO)_{16}$,[2] has now been determined by *X*-ray diffraction methods and is shown in the Figure.

The crystals are monoclinic with $a = 9\cdot465$, $b = 15\cdot825$, $c = 10\cdot563$ Å, $Z = 2$; space group $P2_1$ or $P2_1/m$. The structure determination was based on Patterson and Fourier methods. Full-matrix least-squares refinement of positional and isotropic thermal atomic parameters in the space group $P2_1/m$ (the molecule is then required to have strict C_s symmetry) has reduced the discrepancy index to a present value of 0·084 for 1195 reflexions (counter diffractometer data; $F^2{}_{obs}/\sigma(F^2{}_{obs}) \geqslant 3\cdot0$). The e.s.d's. in the bond lengths are 0·007 (Ru–Ru), 0·04 (Ru–C) and 0·06 Å (C–O).

The 'carbide' atom lies very close to the centre of the slightly distorted octahedron of ruthenium atoms. The mean Ru–C (carbide) distance is 2·04 Å and the maximum deviation from this is 0·16 Å (4σ). Each of three ruthenium atoms [Ru(1), (3), (6)] has three terminally co-ordinated carbon monoxide groups; two ruthenium atoms [Ru(2), (5)] are bridged by a single carbon monoxide group and have two terminal CO's, the sixth

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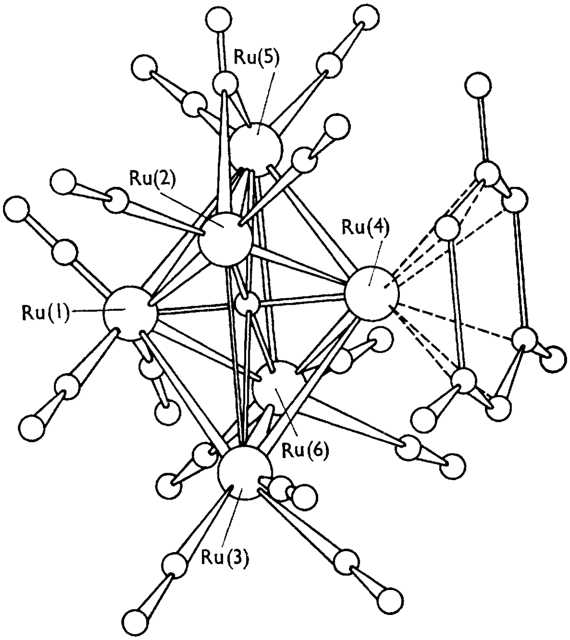
ruthenium atom [Ru(4)] is bonded only to the arene, the carbide atom, and four adjacent rutheniums. The ruthenium atoms are therefore all effectively eight co-ordinate (regarding the arene as a six-electron donor). The mean Ru–C (arene) bond length is 2·24, Ru–C (terminal carbonyl) 1·92, and Ru–C (bridged carbonyl) 2·06 Å.



Ru(1)–Ru(2)	2·864 Å
Ru(1)–Ru(3)	2·901
Ru(2)–Ru(3)	2·956
Ru(2)–Ru(4)	2·864
Ru(2)–Ru(5)	2·853
Ru(3)–Ru(4)	2·854
Ru(3)–Ru(6)	2·857

Ru(1)–C (centre)	2·12 Å
Ru(2)–C (centre)	2·04
Ru(3)–C (centre)	2·07
Ru(4)–C (centre)	1·88

Both the Ru–Ru and the metal-carbon (arene) bond distances[3] imply a covalent radius for Ru(0) of 1·45 ± 0·02 Å [the Ru–Ru bond length is close to that of 2·848 Å in Ru$_3$(CO)$_{12}$];[4] the mean Ru–C (carbide) distance of 2·04 Å is, therefore, less than the sum of metal and neutral carbon σ-bond radii.

One electron-transfer to each of the carbonyl-bridged ruthenium atoms, from the central carbon atom, would give those atoms, like the remaining ruthenium atoms, an 'inert-gas configuration'. The covalent radius of C^{2+} can be calculated as 0·60 Å (using Slater's rules) so that the sum of covalent radii (Ru + C^{2+}) becomes 2·05 Å, identical to within 0·01 Å with the observed mean value.

This extremely simple scheme must not be taken too literally. It should be emphasized that a molecular-orbital description of the bonding is identical in so far as it would not involve *d* orbitals on the central carbon atom to any significant extent. The six d_{z^2} metal orbitals pointing to the centre of the octahedron can be combined to give molecular orbitals of A_{1g}, E_g, and T_{1u} symmetry; the A_{1g} and T_{1u} orbitals are well situated to overlap with the carbon *s* and *p* orbitals respectively.

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