The Crystal Structure of $C_{12}H_{16}Ru_4(CO)_{10}$: an Open Ru_4 Cluster Containing a Novel Three-carbon Bridging Group

By ROSEMARY BELFORD, M. I. BRUCE,* M. A. CAIRNS, M. GREEN, HELEN P. TAYLOR, and P. WOODWARD
(*Department of Inorganic Chemistry, The University, Bristol* BS8 1TS)

Summary The electron-deficient complex $C_{12}H_{16}Ru_4(CO)_{10}$ is shown to contain an open Ru_4 cluster; the monocyclic C_{12} ring is attached to the cluster by a conventional π-allyl bond to one ruthenium atom, and by a novel bridging C_3 unit, which is π-bonded to the two apical metal atoms, and σ-bonded to each of the "hinge" metal atoms.

TREATMENT of $HRu_3(CO)_9C_{12}H_{15}$ (I)[1] with $Ru_3(CO)_{12}$ gave a reddish brown complex (II), which could also be isolated from the initial reaction between $Ru_3(CO)_{12}$ and cyclododeca-1,5,9-triene. Compound (II) has a complex ν(CO) pattern; analysis and m.s. indicate the presence of four ruthenium atoms and ten carbonyl groups, high-resolution measurements suggesting the formula $C_{12}H_nRu_4(CO)_{10}$ (n = 15 or 16). In contrast to (I), there is no high-field resonance in the region τ 10—40.

Crystals of $C_{22}H_{16}O_{10}Ru_4$ are monoclinic, a = 15·51, b = 16·71, c = 10·11 Å, β = 93°0′; space group $P2_1/n$, with Z = 4. The intensities of 1106 reflections were measured visually from precession photographs $hk0$—$hk5$ (Mo-K_α radiation). The ruthenium atoms were located by the symbolic addition method; the other atoms by conventional electron-density difference synthesis. The structure (see Figure) has been refined by least-squares analysis to R = 0·090.

The four ruthenium atoms define a "butterfly" configuration in which two isosceles triangles share a basal "hinge" Ru(1)–Ru(2) of length 2·852(6) Å. This is significantly longer than the other distances in the metal cluster: Ru(3)–Ru(2) = 2·780(5), Ru(3)–Ru(1) = 2·772(6), Ru(4)–Ru(2) = 2·816(3), Ru(4)–Ru(1) = 2·776(6) Å. The nonbonded distance Ru(1)–Ru(4) = 3·665(8) Å. The atoms Ru(1), Ru(2), and Ru(3) each carry three terminal carbonyl groups; Ru(4) only one. The mean Ru–C distance is 1·88 Å, and the mean C–O distance is 1·17 Å.

The C_{12} ring remains intact (though with bond rearrangement) and is attached to the metal cluster by a novel type of linkage. Atoms C(1) and C(11) are σ-bonded to the hinge atoms of the metal cluster: Ru(1)–C(11) = 2·16(5), Ru(2)–C(1) = 2·12(5) Å. These two carbon atoms, together with C(12), form a C_3 system which is equidistant from both Ru(3) and Ru(4): C(11)–Ru(3) = 2·49(7), C(11)–Ru(4) = 2·18(4), C(12)–Ru(3) = 2·23(6), C(12)–Ru(4) = 2·27(5), C(1)–Ru(3) = 2·30(4), C(1)–Ru(4) = 2·21(6) Å. The five atoms C(5), C(6), C(7), Ru(1), and Ru(2) thus all lie approximately on the hinge mirror-plane of the cluster. Furthermore, atoms C(5), C(6), and C(7) also lie within bonding distance of Ru(4): C(5)–Ru(4) = 2·11(6), C(6)–Ru(4) = 2·20(8), C(7)–Ru(4) = 2·25(11) Å. The remaining carbon atoms in the ring are joined by normal C–C single bonds.

Although because of lack of data the carbon atoms are not as well delineated as might be wished (C–C distances vary between 1·37 and 1·74 Å with a mean standard deviation of 0·08 Å), nevertheless the only reasonable interpretation of the bonding situation is that atoms C(11)–C(12)–C(1) form a symmetrical π-allyl bridge between Ru(3) and Ru(4) while at the same time C(11) and C(1) are σ-bonded to Ru(1) and Ru(2), respectively. Atoms C(5)–C(6)–C(7) form a π-allyl system bonded to Ru(4) in the usual way.

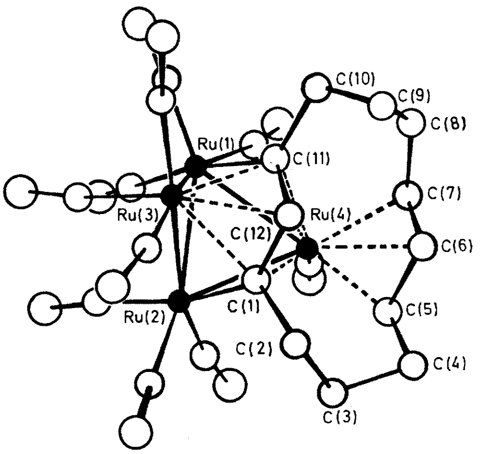

FIGURE. *Structure of* $C_{12}H_{16}Ru_4(CO)_{10}$

The ^1H n.m.r. spectrum of (II) shows a singlet at τ 4·02, and a triplet (J 10 Hz) at τ 6·22, which are assigned to H(12) and H(6), respectively. Two complex multiplets at τ 7·2 and 8·2 result from the remaining protons of the methylene groups.

A formal electron count shows that the complex is electron-deficient, and furthermore no conventional valence-bond description accounts for the observed structure. Churchill and Veidis[2] have observed that stereochemical requirements of attached ligands often result in violations of the "rare-gas rule" in tetrahedral clusters. In complex (II), interaction of ruthenium d-orbitals with bonding and non-bonding orbitals of the bridging allyl group results in multicentre orbitals containing paired electrons; this also accounts for the diamagnetism of the complex.

The common feature of a doubly σ-bonded C_3 unit to three metal atoms in (I) and (II) suggests that the formation of (II) from (I) and $Ru_3(CO)_{12}$ involves interaction of an incoming ruthenium atom with one of the free double bonds in (I). The processes which occur, not necessarily in order, include disproportionation of the Ru_3 cluster, hydrogen isomerisation involving the metal-bonded hydrogen atom in (I), with formation of two $(CH_2)_3$ chains, and linkage of the fourth ruthenium atom to the cluster.

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[1] M. I. Bruce, M. A. Cairns, A. Cox, M. Green, M. D. H. Smith, and P. Woodward, *Chem. Comm.*, 1970, 735.
[2] M. R. Churchill and M. V. Veidis, *Chem. Comm.*, 1970, 529.