A Novel Allyl-ruthenium Cluster: the σ-1,3-h^2-π-1,2,3-h^3-Cyclododeca-1,6,9-trienyl Ligand as a Five-electron Donor

By M. I. BRUCE,* M. A. CAIRNS, A. COX, M. GREEN, M. D. H. SMITH, and P. WOODWARD
(*Department of Inorganic Chemistry, The University, Bristol* BS8 1TS)

Summary Reactions of cyclododeca-1,5,9-trienes with $Ru_3(CO)_{12}$ lead to dehydrogenation and isomerisation with the formation of four cluster complexes: in the major product, $HRu_3(CO)_9(C_{12}H_{15})$, the monocyclic ligand is attached to the cluster by an unusual allylic bonding arrangement involving only three carbon atoms.

WE have investigated the reaction of $Ru_3(CO)_{12}$ with cyclododeca-1,5,9-trienes. It has been shown that the product of the analogous reaction with $Fe(CO)_5$[1] is an $Fe(CO)_3$ complex of bicyclo[6,4,0]dodeca-9,11-diene.[2]

Dodecacarbonyltriruthenium reacts slowly with either all-*trans*-, all-*cis*-, or *cis*, *cis*, *trans*-cyclododeca-1,5,9-triene in refluxing petroleum ether (b.p. 80—100°) to give four complexes. These were separated by column chromatography and characterised by elemental analysis, high resolution mass, i.r. and ^1H n.m.r. spectrometry as yellow $HRu_3(CO)_9(C_{12}H_{15})$ (I), m.p. 138°, ν(CO) 2096s, 2070vs, 2045vs, 2027vs, 2015s, 2007vs, 1995m, 1973m cm^{-1}; orange $HRu_3(CO)_9(C_{12}H_{17})$ (II), m.p. 150° (decomp.), ν(CO) 2087m, 2058s, 2033vs, 2017s, 2009w, 2002m, 1994w, 1990w, 1982sh, 1972w cm^{-1}; brown $HRu_3(CO)_7(C_{24}H_{33})$ (III), m.p. 194° (decomp.), ν(CO) 2054s, 2018vs, 1998s, 1965s cm^{-1}; and dark red $Ru_4(CO)_{10}(C_{12}H_{16})$ (IV), m.p. 143° (decomp.), ν(CO) 2075s, 2034vs, 2006m, 1997s, 1992s, 1975sh, 1956w cm^{-1}.

Hydrogenation of the principal product (I) gave α-$H_4Ru_4(CO)_{12}$ and cyclododecane, demonstrating that, in contrast with the iron system, ring closure had not occurred. This is confirmed by an X-ray crystallographic study.

Crystals of $C_{21}H_{16}O_9Ru_3$ (I) are monoclinic, $a = 11{\cdot}18$, $b = 15{\cdot}52$, $c = 15{\cdot}48$ Å, $\beta = 114°5'$, space group $P2_1/a$, with $Z = 4$. The intensities of 1419 reflections were measured on a Supper–Pace 0·01° incrementing autodiffractometer using equi-inclination geometry, ω-scan, and Mo-K_α radiation. The structure (Figure) was solved by the conventional heavy-atom method and has been refined to $R = 0{\cdot}080$ (weighted $R = 0{\cdot}058$).

The three ruthenium atoms define an isosceles triangle in which Ru(1)–Ru(3) = 2·773(3), Ru(2)–Ru(3) = 2·779(3), and Ru(1)–Ru(2) = 2·921(3) Å. Each ruthenium atom carries three carbonyl groups, and among these nine CO ligands the mean Ru–C distance is 1·85 Å, and the mean C–O distance 1·19 Å. Atoms C(1), C(2), and C(3) are all equidistant from Ru(3) at $2{\cdot}15_3$ Å, while C(1) and C(3) are at a distance of $2{\cdot}04_3$ Å from Ru(2) and Ru(1) respectively. There is no other linkage between the ring and the Ru_3 cluster.

These data are consistent with there being π-bonding between Ru(3) and the allylic carbon atoms C(1), C(2), and C(3), with C(1) and C(3) also being σ-bonded to Ru(2) and Ru(1), respectively. This establishes a novel bonding arrangement for a hydrocarbon to a metal cluster, which is different from that found in certain binuclear allyl–iron carbonyl compounds.[3,4] Adapting Cotton's nomenclature,[5] the C(1)–C(2)–C(3) unit may be described as a σ-1,3-*dihapto*-π-1,2,3-*trihapto*-allyl group.

At the present stage of refinement, atoms C(9) and C(10) are the least well-defined, and the C–C distances around the ring (Table) have standard deviations of *ca.* 0·05 Å. These distances nevertheless suggest that, besides the allylic linkage between C(1), C(2), and C(3), ethylenic links occur between C(6)–C(7), and between C(9)–C(10). This is further confirmed by computation of the mean planes through atoms C(5), C(6), C(7), and C(8), and through atoms C(8), C(9), C(10), and C(11), which show that each of these groups is substantially planar.

Bond distances in the C_{12} *ring* (*average standard deviation* 0·05 Å)

C(1)–C(2)	1·27 Å	C(7)–C(8)	1·77 Å
C(2)–C(3)	1·39	C(8)–C(9)	1·52
C(3)–C(4)	1·68	C(9)–C(10)	1·15
C(4)–C(5)	1·56	C(10)–C(11)	1·86
C(5)–C(6)	1·60	C(11)–C(12)	1·63
C(6)–C(7)	1·24	C(12)–C(1)	1·64

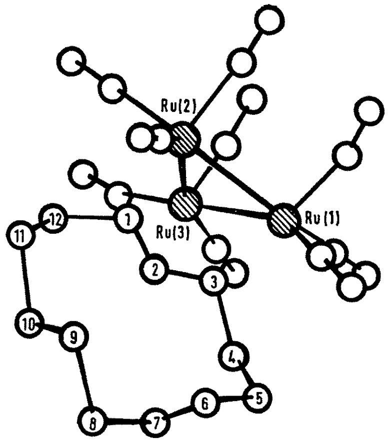

FIGURE. *Structure of* $HRu_3(CO)_9(C_{12}H_{15})$

The ^1H n.m.r. spectrum of (I) demonstrates the presence of a hydrogen atom bonded to ruthenium, the spectrum consisting of a doublet at τ 3·81, a complex multiplet at 4·67, a broad absorption between 6·8—8·5, and a doublet at high field (30·24). Decoupling experiments show that the protons at τ 3·81 and at τ 30·24 are coupled together ($J_{HH} = 2{\cdot}7$ Hz). Coupling of this type has not been observed previously.

In view of the unusual nature of the cluster environment it is not possible to assign an unequivocal location to the ruthenium-bonded hydrogen atom that gives rise to the high-field resonance. The two most obvious locations are (i) attached to Ru(3), *i.e.* a terminal Ru–H, or (ii) bridging between Ru(1) and Ru(2). The terminal location requires that Ru(3) be eight-co-ordinate. The significantly longer Ru(1)–Ru(2) bond distance might suggest the bridging location, as might the chemical shift. The coupling between this hydrogen and the proton on C(2) does not allow a conclusion to be drawn.

In terms of electron accounting it is necessary to consider the cluster as a whole. Then all ligands supply the required 30 electrons: 9 terminal CO groups (18), 3 Ru–Ru bonds (6), the C(1)–C(2)–C(3) system ($3\pi + 2\sigma$), and Ru–H (1).

Complex (I), besides featuring an unusual allylic form of bonding, contains the largest ring system yet to have been bonded to a metal cluster.

The formation of this complex involves dehydrogenation and hydrogen isomerisation of cyclododeca-1,5,9-triene, and further investigations into this type of reaction, and into the formation of $Ru_4(CO)_{10}(C_{12}H_{16})$ (IV) from $HRu_3(CO)_9(C_{12}H_{15})$ (I), will be reported later.

(*Received, April* 21*st*, 1970; *Com.* 582.)

---

[1] W. Fröhlich, Ph.D. Thesis, University of Munich, 1961; quoted by E. O. Fischer and H. Werner, *Angew. Chem.*, 1963, **75**, 62 *Angew. Chem. Internat. Edn.*, 1963, **2**, 85.

[2] P. Hardt, Ph.D. Thesis, T. H. Aachen, 1964.

[3] R. E. Davies, *Chem. Comm.*, 1968, 248.

[4] P. F. Lindley and O. S. Mills, *J. Chem. Soc.* (*A*), 1970, 38.

[5] F. A. Cotton, *J. Amer. Chem. Soc.*, 1968, **90**, 6230.