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Preliminary communication

REACTIONS OF THE HEXARUTHENIUM CARBIDE CLUSTER $Ru_6C(CO)_{17}$ WITH SOME π-ACID LIGANDS; DIRECT LOCATION OF THE μ-HYDRIDE LIGAND IN $HRu_6C(CO)_{15}(SEt)_3$ BY X-RAY ANALYSIS

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Summary

Reaction of $Ru_6C(CO)_{17}$ with $P(OMe)_3$ has given a series of substitution products $Ru_6C(CO)_{17-n}[P(OMe)_3]_n$ (n = 1, 2, 3 or 4), but reaction with PPh_3 gives only the mono- and di-substituted derivatives; with EtSH the complexes $H_2RuC(CO)_{15}(EtS)_2$ and $HRu_6C(CO)_{15}(EtS)_3$ (I) are formed and X-ray analysis of I has allowed direct location of the μ-H ligand and shows that the extra electrons donated by the thiols have caused an opening up of the octahedral cluster.

Dodecacarbonyltriruthenium undergoes thermal decomposition in vacuo to produce the carbido complex $Ru_6C(CO)_{17}$ [1]. It has been shown that the source of the carbido atom is CO and that CO_2 is produced as pyrolysis takes place [2]. In the octahedral hexaruthenium cluster $Ru_6C(CO)_{17}$ the central carbido atom is completely surrounded by a close-packed array of metal atoms and carbonyl ligands [3] and so far attempts to directly study the chemistry of this carbido atom have been unsuccessful.

We report the reaction of $Ru_6C(CO)_{17}$ with a number of neutral ligands of potential π-acid character, which by donating electrons directly to the metal core might cause an opening up of the ruthenium octahedron and hence expose the central carbido atom. Whereas the phosphorus ligands $P(OMe)_3$ or PPh_3 simply replace CO groups and appear to leave the metal geometry intact, attack by EtSH has produced rearrangement of the ruthenium atoms and the hydrido product $HRuC(CO)_{15}(EtS)_3$ (I) has been shown by X-ray analysis to have the open structure shown in Fig. 1.

Reaction of $Ru_6C(CO)_{17}$ with $P(OMe)_3$ gives a series of complexes $Ru_6C(CO)_{17-n}[P(OMe)_3]_n$ (n = 1, 2, 3 or 4); with PPh_3 the two complexes

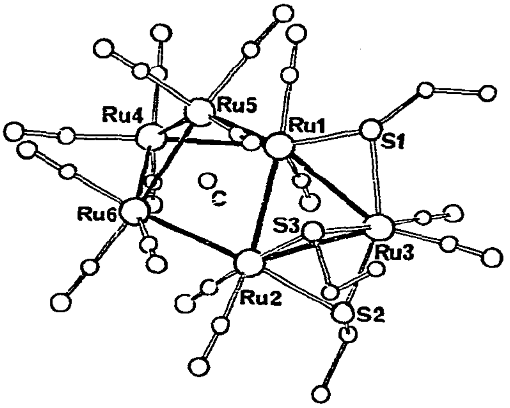

Fig. 1. The structure of $HRu_6(CO)_{15}(SC_2H_5)_3C$, principal bond lengths (Å) are:

Ru(1)—Ru(2)	3.049	Ru(1)—Ru(3)	3.052	Ru(1)—Ru(4)	2.840	Ru(1)—Ru(5)	2.903
Ru(2)—Ru(3)	3.012	Ru(2)—Ru(6)	2.908	Ru(4)—Ru(5)	2.855	Ru(4)—Ru(6)	2.875
Ru(5)—Ru(6)	2.816	Ru(1)—S(1)	2.401	Ru(3)—S(1)	2.331	Ru(2)—S(2)	2.417
Ru(2)—S(3)	2.414	Ru(3)—S(2)	2.356	Ru(3)—S(3)	2.422	Ru(1)—C	1.956
Ru(2)—C	2.130	Ru(4)—C	2.150	Ru(5)—C	2.132	Ru(6)—C	2.001

The e.s.d.'s average Ru—Ru 0.001, Ru—S 0.002, and Ru—C 0.004 Å.
Relevant non-bonded contacts are Ru(2)—Ru(5) 4.011 and Ru(2)—Ru(4) 3.961 Å.

$Ru_6C(CO)_{16}PPh_3$ and $Ru_6C(CO)_{15}(PPh_3)_2$ are obtained. These products have been fully characterised by analytical and spectroscopic techniques. In all these complexes CO ligands have been directly replaced by phosphorus ligands, so that each cluster maintains 86-valence electrons and the enclosing octahedron of ruthenium atoms is maintained round the central carbido atom.

With EtSH, which is capable of acting as a multi-electron donor cluster opening occurs, and two products have been identified, viz. $H_2Ru_6C(CO)_{15}(EtS)_2$ and $HRu_6C(CO)_{15}(EtS)_3$ (I). The orange-red crystal of the latter have been fully characterised by X-ray analysis. Crystals of $C_{22}H_{16}S_3O_{15}Ru_6$ are monoclinic, spacegroup $P2_1/c$, a 9.915, b 15.323, c 26.658 Å, β 119.90°, U 3511 Å^3, $Z = 4$. Intensity data were collected with a Philips PW1100 four-circle diffractometer using Mo-K_α radiation from a graphite monochromator, and were corrected for absorption (μ(Mo-K_α) 25 cm^{-1}). Full matrix refinement of positional and anisotropic thermal parameters of all non-hydrogen atoms, using 7354 reflections with $I/\sigma(I) \geqslant 3.0$, has given an R value of 0.030.

The hydrogen atoms were located from a limited difference Fourier ($\theta \leqslant 20°$) which showed maxima at reasonable positions (C—H 0.9 to 1.04 Å) for all methyl and methylene hydrogen atoms. In addition a hydrido ligand bridging Ru(4) and Ru(5) was clearly resolved (Ru—H 1.82, and 1.75 Å). The only other maxima (ca. 0.5 e A^{-3}) were within 1 Å of the metal atoms. The structure of the cluster compound is shown in Fig. 1.

It can be seen that addition of electrons from the three bridging thiol groups has destroyed the octahedral arrangement of the six ruthenium atoms round the central carbon atom present in $Ru_6C(CO)_{17}$. A relationship between the observed structure and the original Ru_6 octahedron is illustrated in Fig. 2. The two Ru—Ru edges bridged by the thiol ligands, Ru(1)—Ru(3) and Ru(2)—Ru(3),

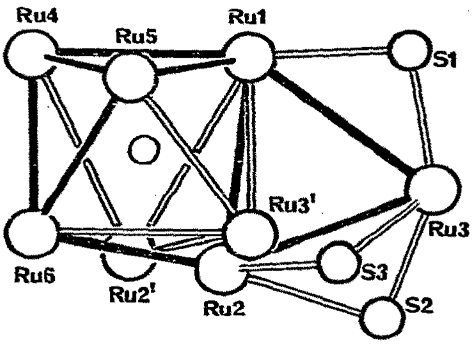

Fig. 2. The relationship of the ruthenium atoms in $[HRu_6(CO)_{15}(SC_2H_5)_3C]$ to the original Ru_6 octahedron in $[Ru_6(CO)_{17}C]$.

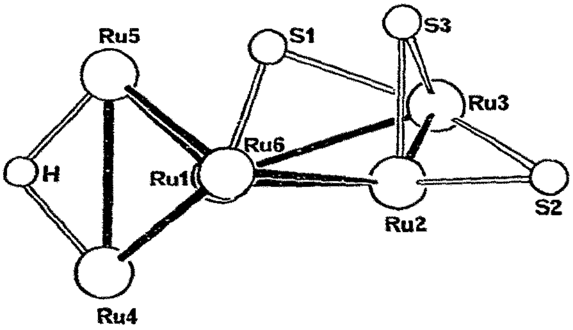

Fig. 3. The arrangement of the ruthenium and bridging sulphur atoms in $[HRu_6(CO)_{15}(SC_2H_5)_3C]$ viewed perpendicular to the equatorial plane of the bi-pyramid.

have swung out from the rest of the cluster, with Ru(1)—Ru(2) acting as a hinge, so that Ru(3) is no longer bonded to the central carbido atom. Ru (2) while remaining bonded to the central atom has moved to a site intermediate between its original position Ru(2)' and the original Ru(3) position Ru(3)' (Fig. 2). Thus the carbido atom in the thiolato-bridged cluster has a distorted trigonal by-pyramidal coordination defined by five ruthenium atoms with the remaining Ru atom, Ru(3), bridging a non-equatorial edge, Ru(1)—Ru(2).

The orientation of the bridging triangle Ru(1)—Ru(2)—Ru(3) is shown in Fig. 3.

References

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