Preliminary communication

Cyclooct-1-ene-5-yne tetraruthenium undecacarbonyl

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SUMMARY

$Ru_4(CO)_{11}C_8H_{10}$ has the four metal atoms in a "butterfly" conformation; the carbonyl groups are all terminally bonded, the cyclooct-1-ene-5-yne ligand being coordinated to the four ruthenium atoms via "σ" "π" and "μ" bonds.

The reactions of cycloocta-1,5-diene with the tetrameric cluster, α-$H_4Ru_4(CO)_{12}$, are summarised in the accompanying report[1]. Two of the products, $Ru_4(CO)_{11}C_8H_{10}$ and $H_2Ru_3(CO)_9C_8H_{12}$, have been examined by X-ray diffraction methods; the analysis of the tetranuclear complex is essentially complete and is described here.

The crystals (cyclohexane) are monoclinic, space group $P2_1/n$, with $a = 10.499(2)$, $b = 14.764(3)$, $c = 14.724(3)$ Å, $\beta = 90.88°$; $Z = 4$, $D_c = D_m = 2.43$ g·cm^{-3}. 2157 reflexions with $F_{obs}^? > 3.0$ $\sigma(F^2)$ have been observed by four-circle diffractometry (Mo-Kα, graphite monochromator) and heavy atom Fourier methods have provided the structural arrangement; least squares analysis has converged R to 0.059 for the data which are presently uncorrected for (small) absorption effects. The stereochemistry is shown in Fig.1; e.s.d.'s in the bond lengths average 0.002 Å (Ru—Ru), 0.015 Å (Ru—C) and 0.025 Å (C—C and C—O).

The geometry is very similar to that of $Co_4(CO)_{10}(C_2H_5C\equiv CC_2H_5)^2$ in that the four metal atoms are in a butterfly conformation; each acetylenic carbon atom C_1 and C_2 forms one metal—carbon "σ" bond of average length 2.16 Å (to Ru_1 and Ru_2) and two "μ" bonds of length 2.21 Å (to Ru_3 and Ru_4)★. Only the "hinge" bond (Ru_1—Ru_2)

★ These symmetry designations of the bonds are intended only to be descriptive and consistent with earlier suggestions[2]; the symmetry of the individual bonds is low.
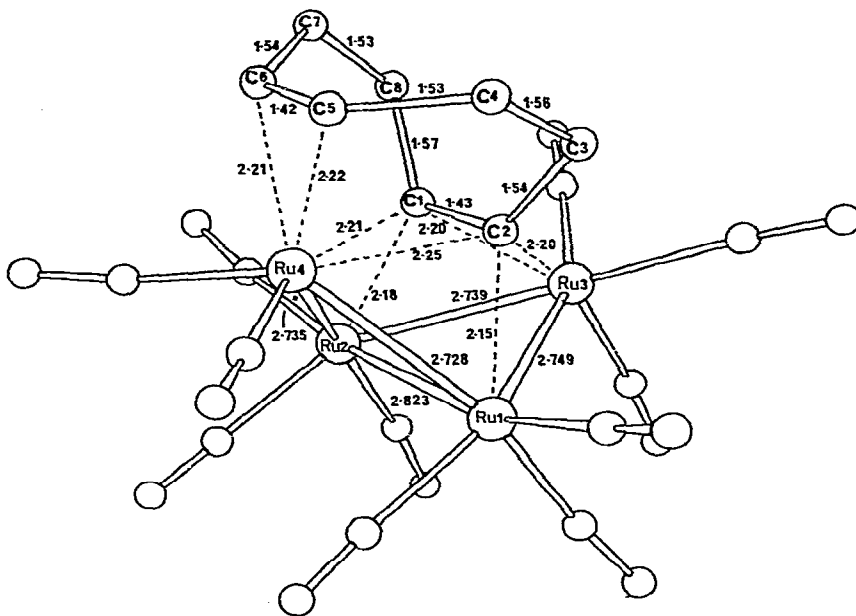
Fig.1. Stereochemistry of $Ru_4(CO)_{11}C_8H_{10}$.

has a bond length which is significantly different from the average length (2.47 Å) of the remaining metal—metal bonds; the dihedral angle between the two planes containing $Ru_1-Ru_2-Ru_4$ and $Ru_1-Ru_2-Ru_3$ respectively is 112°.

The conformation of the macrocyclic ligand is obviously dictated by the bonding and steric requirements of the cluster. The equality, within experimental error, of the bonds, C_1-C_2 and C_5-C_6, is evidence for considerable charge transfer between the cluster and the acetylenic bond. In the present complex the "μ" bonds are only 0.05 Å longer than the metal—carbon "σ" bonds, the corresponding difference being 0.09 Å in $Co_4(CO)_{10}(C_2H_5C\equiv CC_2H_5)$ and up to 0.25 Å in several benzyne complexes of osmium clusters[3]; the variations can be related, inter alia, to the nature of the other ligands coordinated to the metals, and to the need to preserve a high degree of cyclic delocalisation in coordinated benzyne.

REFERENCES

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