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Synthesis and Crystal Structure of $(\eta\text{-}C_5H_5)NiRu_3(CO)_8(C_6H_9)$. A New Complex Obtained by Insertion of a Nickel Atom into a Ru_3 Cluster

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We previously reported the reaction of the hydride $HRu_3(CO)_9C_2Bu^t$ (I) [1] with $[(\eta\text{-}C_5H_5)Ni(CO)]_2$, which yielded the tetranuclear compound $(\eta\text{-}C_5H_5)NiRu_3(CO)_9C{\cdot}C(H)Bu^t$ (II) [2], until now the first ruthenium–nickel cluster described.

We give now a preliminary report on the synthesis and crystal structure of a new tetranuclear ruthenium–nickel complex, $(\eta\text{-}C_5H_5)NiRu_3(CO)_8(C_6H_9)$ (III), which was obtained by treating $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ with the hydride $HRu_3(CO)_9(C_6H_9)$ [3] (IV), 'allyl' isomer, in refluxing n-octane, purified by preparative t.l.c., and crystallized from n-heptane/$CHCl_3$ at −10 °C.

The i.r. spectrum of (III) in the CO stretching region (n-heptane solution) shows bands at 2049 s, 2013 vs, 1981 s, 1964 s, 1859 m, 1837 s, cm^{-1}. The mass spectrum shows the molecular ion at 735 m/e, gradual loss of 8 CO groups, then demolition of the organic moiety; doubly charged ions, corresponding to CO loss, are observed.

The crystals of (III) are monoclinic, $a = 10.525(9)$, $b = 20.487(13)$, $c = 9.891(7)$ Å, $\beta = 92.11(7)°$, $V = 2131$ Å^3, $Z = 4$, $d_{calc} = 2.29$ g cm^{-3}, space group $P2_1/n$.

4918 reflections in the range $3 < \theta < 27°$ were recorded on an AED single-crystal diffractometer using the Zr-filtered MoKα radiation; 2963 of these (having $I > 2\sigma(I)$) were used in the structure analysis. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares to $R = 0.062$.

The structure of (III), represented in Fig. 1, is characterized by a butterfly arrangement of three Ru and one Ni atoms, bonded to eight carbonyls (through the Ru atoms only), to a cyclopentadienyl group (through the Ni atom) and to a 1-methyl-3-ethyl-allyl unit (through all the metals). The Ni atom occupies a corner of the hinge-side of the cluster and is bound to all the Ru atoms. The metal–metal bond distances are: Ru(1)–Ru(2) = 2.708, Ru(1)–Ru(3) = 2.693, Ru(1)–Ni = 2.664, Ru(2)–Ni = 2.595, Ru(3)–Ni = 2.611 Å (e.s.d's 0.002 Å). Six carbonyls are terminal (mean Ru–C bond 1.89 Å) and two are bridging (the former bridges Ru(2) and Ru(1) with Ru–C bonds of 1.987 and 2.280 Å, the latter bridges Ru(3) and Ru(1) with Ru–C bonds of 1.994 and 2.173 Å).

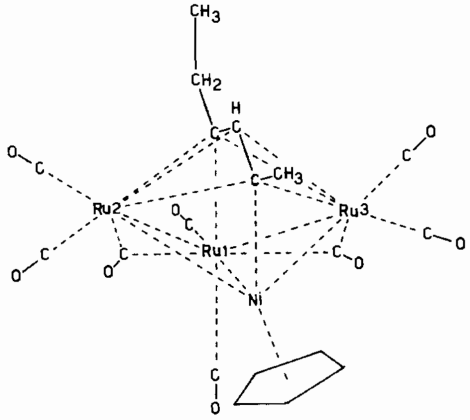

Fig. 1. The structure of $(\eta\text{-}C_5H_5)NiRu_3(CO)_8(C_6H_9)$.

In the organic ligand the C_1 and C_3 allylic atoms are σ-bonded to the hinge atoms of the cluster: C_1–Ni = 1.877and C_3–Ru(1) = 2.169 Å. These two carbon atoms, together with the central allylic C_2 atom, form a three carbons system η-interacting with both Ru(2) and Ru(3) metals so that the carbon atoms are equidistant from these metals (mean Ru–C distance 2.301 Å). The substituted allyl unit does not present appreciable modifications with respect to the one in the starting compound (IV), although the coordination to the cluster is different.

In complex (I) the Ni atom does not occupy a hinge position in the cluster, so that the formation of the tetrametallic derivative can be explained with the 'addition' of a $(\eta\text{-}C_5H_5)Ni$ fragment to one face of the tetrahedral Ru_3C core of (I). The position of the Ni atom in the present compound (III) can only be explained with the opening of the Ru_3 cluster of (IV), and 'insertion' of $(\eta\text{-}C_5H_5)Ni$ into a Ru–Ru, as well as into a Ru–C (σ) bond. Two isomers can be envisaged for (III) when considering that either the Ru–C(Et) or the Ru–C(Me) bond in (IV) can be involved in this process. This question is now under investigation.

Thus, although for both (I) and (III) the formation of the 'butterfly' cluster – a quite common structure for tetra-metallic derivatives [4] – involves a Ru–C-

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(σ) bond, two different mechanisms must be proposed for the two reactions, showing considerable versatility of the (η-C_5H_5)Ni fragment as a ligand.

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