A New, Mixed Ruthenium–Nickel Cluster. Synthesis and *X*-Ray Crystal Structure of $(\eta^5\text{-}C_5H_5)NiRu_3(CO)_9C{\cdot}C(H)Bu^t$

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Summary The complex $(\eta^5\text{-}C_5H_5)NiRu_3(CO)_9C{\cdot}C(H)Bu^t$ has been synthesized and its structure determined by *X*-ray crystallography; an unusual co-ordination of one carbon atom to four metal atoms is observed in the complex.

THERE is an increasing interest now in the homo- and hetero-polynuclear metal carbonyl clusters.[1] Among many others, iron–nickel derivatives have been obtained[2] accompanied, in some cases, by C–H activation in the presence of organic ligands.[3] However, to our knowledge, no ruthenium–nickel derivatives have been reported until now.

We report here the synthesis and crystal structure of the tetranuclear complex $(\eta^5\text{-}C_5H_5)NiRu_3(CO)_9C{\cdot}C(H)Bu^t$ (I) which is obtained by treating $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$ with $HRu_3(CO)_9C_2Bu^t$ (II)[4] in refluxing n-octane and purified by preparative t.l.c. and crystallized from n-heptane at −10 °C.

The i.r. spectrum of (I) in the CO stretching region (n-heptane solution) shows bands at 2079s, 2054vs, 2040vs, 2008vs, 2002vs(sh), and 1979m cm^{-1}. Its mass spectrum is similar to that of (II).

Crystal data: (I), monoclinic, $a = 15{\cdot}514(11)$, $b = 17{\cdot}003(13)$, $c = 9{\cdot}138(8)$ Å, $\beta = 94{\cdot}6(1)^\circ$; space group $P2_1/n$ with $Z = 4$.

The intensities of all the reflections with θ in the range 2·5—27·0° were collected on an AED single-crystal diffractometer with Zr-filtered Mo-K_α radiation. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares to $R = 0{\cdot}035$, on the basis of 4038 independent observed reflections.†

The structure of (I), represented in the Figure, consists of a 'butterfly' arrangement of three Ru and one Ni atoms, bonded to nine terminal carbonyl groups (through the Ru atoms only), a cyclopentadienyl (Cp) group (through the Ni atom), and a rearranged t-butylacetylene group (through all the metal atoms). The metal–metal bond distances are: Ru(1)–Ru(2) = 2·826, Ru(1)–Ru(3) = 2·788, Ru(2)–Ru(3) = 2·834, Ru(1)–Ni = 2·571, and Ru(2)–Ni = 2·555 Å (e.s.d.s 0·001 Å).

The arrangement of the three Ru atoms and of the alkyne unsubstituted carbon atom, partly corresponding to the structure of (II),[5] indicates that, after Ni–Ni bond breaking, 'face bridging' of a Ni(Cp) fragment on Ru(1)–Ru(2)–C has occurred, to form the 'butterfly' cluster; this process requires the hydridic-hydrogen transfer.

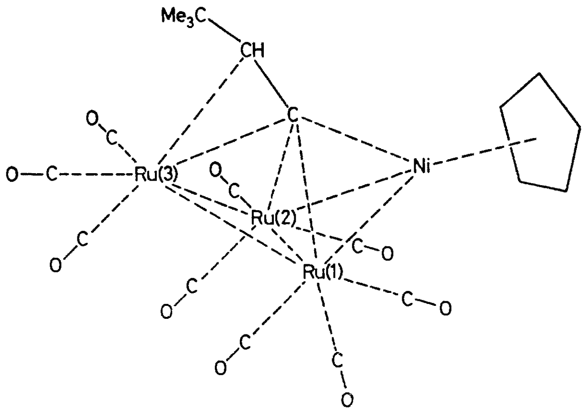

FIGURE. Structure of $(\eta^5\text{-}C_5H_5)NiRu_3(CO)_9C{\cdot}C(H)Bu^t$ (I).

Noteworthy is the bonding of the alkyne group to the cluster, with the terminal carbon atom interacting with all the metal atoms [Ru(1)–C = 2·156, Ru(2)–C = 2·177, Ru(3)–C = 2·156, Ni–C = 1·837, C–C(H) = 1·429, and Ru(3)–C(H) = 2·219 Å (e.s.d.s 0·005—0·011 Å)]. This is the first example of this type of co-ordination of an alkyne group to a tetranuclear metal cluster.

Although some carbido-carbonyls, in which a carbon atom at the centre of a regular polyhedron of metal atoms co-ordinates to five and six metal atoms, have been reported,[6] the only other comparable example of this type of carbon atom co-ordination is $[HFe_4(CO)_{13}]^-$ having an unusually bridging CO group.[7] This also indicates that the activation of CO and HC_2R alkyne groups on metal atom clusters is comparable.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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