Synthesis and Crystal Structure of a New Mixed-metal Cluster, $(\eta\text{-}C_5H_5)_3Ni_3Os_3(CO)_9$. An Example of a High Yield Pyrolytic Synthesis

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Summary The new, neutral mixed-metal cluster $(\eta\text{-}C_5H_5)_3Ni_3Os_3(CO)_9$ has been obtained in good yield from a simple pyrolytic reaction; the metal-atom arrangement has been shown by *X*-ray crystallography to be a face-capped trigonal bipyramid.

WE have recently investigated the pyrolytic synthesis of mixed-metal carbonyl complexes, in particular from the reactions of cyclopentadienyl–nickel derivatives with the iron triad metal carbonyls both in the absence and presence of alkynes.[1–4] In the absence of alkynes, $(\eta\text{-}C_5H_5)_2Ni_2Fe_2(CO)_7$ is obtained in low yield[1] when iron carbonyls are allowed to react with $(\eta\text{-}C_5H_5)_2Ni$ or $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ in hydrocarbon solvents. The reaction of $Ru_3(CO)_{12}$ or $H_4Ru_4(CO)_{12}$ with the same nickel derivatives yielded a black compound in 2—5% yield, tentatively identified as $(\eta\text{-}C_5H_5)NiRu_3(CO)_9$ on the basis of elemental and i.r., ^1H n.m.r., and mass spectral analyses.[2] This unsaturated species seemed to us to be of interest in view of possible catalytic applications, but unfortunately we were not able to obtain crystals suitable for an *X*-ray structure determination.

In an attempt to obtain the osmium homologue of $(\eta\text{-}C_5H_5)NiRu_3(CO)_9$, we allowed $Os_3(CO)_{12}$ to react with a 2:1 molar excess of $[\eta\text{-}C_5H_5)Ni(CO)]_2$ in refluxing octane under a nitrogen atmosphere for 40 min, but the complex

$(\eta\text{-}C_5H_5)_3Ni_3Os_3(CO)_9$ (**1**) was obtained in 40% yield with respect to the osmium instead of the expected tetrametallic complex. The dark-brown complex (**1**), air stable, was purified from the reaction mixture by preparative t.l.c. plates (Kieselgel P.F.) and shows ν_{CO}(hexane) 2020 m, 2005 vs, 1960 s, 1745 m, and 1600 s cm^{-1}, $\tau(CDCl_3)$ 7·75(s), considerably to high-field compared with other known cyclopentadienyl derivatives, and it decomposes in the mass spectrometer. Black, thin prismatic crystals of (**1**) were obtained by cooling saturated heptane–$CHCl_3$ solutions at −10 °C for some days.

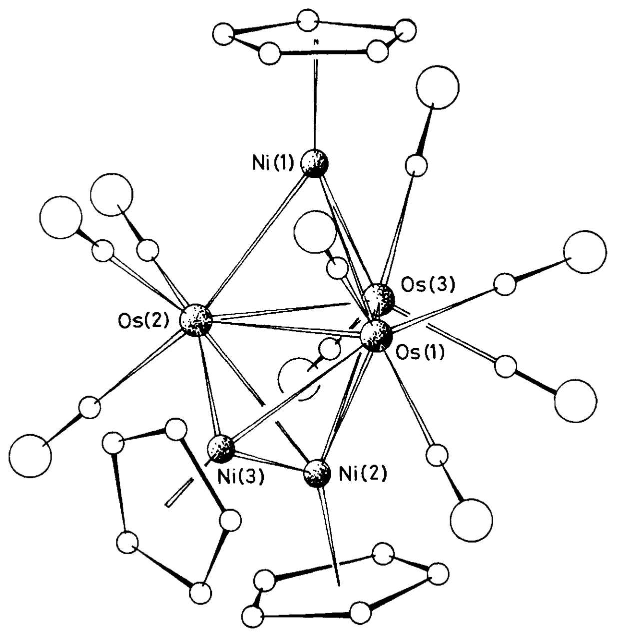

FIGURE. The molecular structure of $(\eta\text{-}C_5H_5)_3Ni_3Os_3(CO)_9$ (**1**). Bond lengths: Os(1)–Os(2) = 2·775(6), Os(1)–Os(3) = 2·777(6), Os(2)–Os(3) = 2·755(6), Os(1)–Ni(1) = 2·64(1), Os(1)–Ni(2) = 2·58(1), Os(1)–Ni(3) = 2·58(1), Os(2)–Ni(1) = 2·63(1), Os(2)–Ni(2) = 2·59(1), Os(2)–Ni(3) = 2·60(1), Os(3)–Ni(1) = 2·61(1), Os(3)–Ni(2) = 2·66(1), Ni(2)–Ni(3) = 2·54(2) Å.

Crystal data: $C_{24}H_{15}Ni_3O_9Os_3$, M = 1194·11, tetragonal, space group $P\bar{4}2_1c$, a = 19·28(1), c = 15·31(1) Å, U = 5662(5) $Å^3$, Z = 8, D_c = 2·78 g cm^{-3}; $\mu(\text{Mo-}K_\alpha)$ = 153·21 cm^{-1}. The intensities of 2214 independent reflections were collected on a Siemens AED diffractometer (with θ in the range 3—23°), using Nb-filtered Mo-K_α radiation and the θ—2θ scan technique. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares on the basis of 924 observed reflections [having $I \geqslant 2\sigma(I)$] to an R value of 5·8%.†

The structure of (**1**) is represented in the Figure. The metal cluster can be described as a trigonal bipyramid with the Os atoms in the equatorial positions and two Ni atoms in the apical positions; a third Ni atom caps one face of the bipyramid. The Os–Os bond distances are quite normal; the Os–Ni lengths range from 2·58 to 2·66 Å, comparable to those found in the tetrametallic complex $[NiOs_3H_2(CO)_{10}(PPh_3)_2]$ [2·605(1), 2·668(1), and 2·733(1) Å],[5] the only other Ni–Os mixed cluster to have been reported.

Trigonal bipyramidal arrangements of metal atoms are known both for homometallic[6] and heterometallic[7] clusters; a face-capped Os_6 cluster has been reported[8] which shows structural analogies with (**1**). However many of the above clusters are anionic and the heterometallic clusters contain only one or two heterometals. To our knowledge, (**1**) is the first reported complex with a neutral mixed three-to-three metal atom arrangement.

It is noteworthy also that this complex has been obtained in high yield, considering the very simple synthesis and purification; usually, many species in low yields are obtained from pyrolytic syntheses.[1–4,9]

The three cyclopentadienyl ligands are η-bonded, one to each Ni atom. The Ni atoms are non-equivalent and so the presence of only one signal in the ^1H n.m.r. spectrum is surprising and probably indicates a rearrangement in solution. The Ni(2) atom does not obey the effective atomic number rule; this has been already found for the $(\eta\text{-}C_5H_5)Ni$ ligand.[1–4]

Nine carbonyls are bound to the Os atoms, three to each metal.

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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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