JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 14
1987

The First Heptaruthenium Cluster: *X*-Ray Crystal Structure of $Ru_7(CO)_{18}(\mu_4\text{-}PPh)_2$, a Molecule Consisting of Fused Square Pyramidal Polyhedra

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The first heptaruthenium cluster $Ru_7(CO)_{18}(\mu_4\text{-}PPh)_2$ has been obtained from the pyrolysis of the phosphido complex $(\mu\text{-}H)Ru_3(CO)_{10}(\mu\text{-}PPh_2)$ in toluene; *X*-ray analysis has revealed a novel condensed metal framework based on two square pyramidal Ru_5 fragments sharing a common face.

Mingos[1] has recently outlined a generalised principle for electron counting in condensed polyhedral clusters. We report herein the isolation and structural characterisation of $Ru_7(CO)_{18}(\mu_4\text{-}PPh)_2$ (**1**), the first heptaruthenium species to be crystallographically identified and a member of the interesting series of condensed high nuclearity clusters characterised by the sharing of a triangular face between square pyramidal metal fragments. Few high nuclearity ruthenium clusters are known,[2] although ten[3] and eight atom[4,5] polyhedra have recently been described.

Pyrolysis of a solution of $(\mu\text{-}H)Ru_3(CO)_{10}(\mu\text{-}PPh_2)$ (0.62 mmol) in toluene (40 ml) at 120 °C for 2 h gave a complex mixture from which five products were separated and purified by preparative t.l.c. on silica gel with C_7H_{16}–C_6H_6 as eluant. In order of elution, these compounds were: $Ru_4(CO)_{13}(\mu_3\text{-}PPh)$[6] (37%), $Ru_5(CO)_{15}(\mu_4\text{-}PPh)$[7] (7%), $(\mu_3\text{-}H)Ru_5(CO)_{13}(\mu_4\text{-}PPh)(\mu_2\text{-}PPh_2)$ (7%) which has also been structurally characterised,[8] deep green (**1**) (2%) [i.r. ν(CO) CCl_4, 2089vw, 2064vs, 2054s, 2049m,sh, 2021m, 2009w, 1983w, 1976w, 1938w cm^{-1}; ^{31}P {^1H} n.m.r. $CDCl_3$, δ 457.5 s], and a dark brown compound whose structure is under investigation. To establish the structure of (**1**) an *X*-ray analysis was carried out.† An ORTEP plot of the structure is shown in Figure 1.

The seven ruthenium atoms define a condensed polyhedron consisting of two square pyramidal Ru_5 units sharing a triangular face [Ru(1), Ru(2), Ru(2′)]. A crystallographic two-fold axis passes through Ru(1) and the mid-point of the Ru(2)–Ru(2′) bond relating the two halves of the molecule.

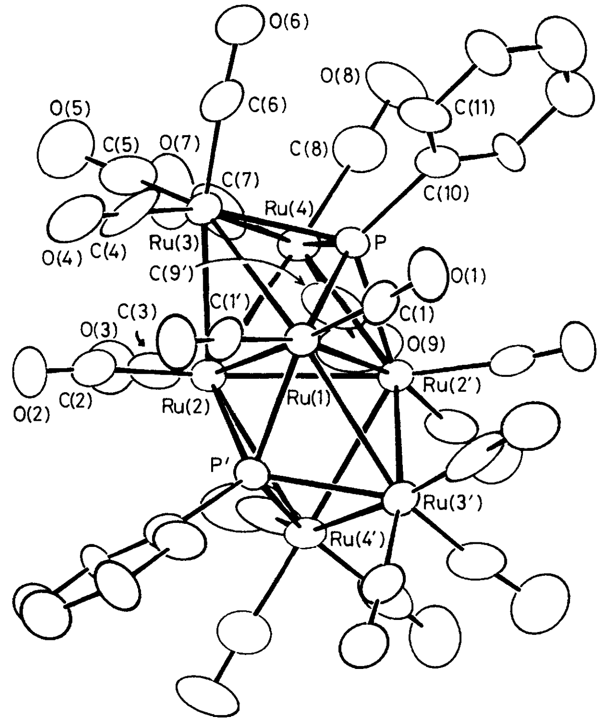

Figure 1. An ORTEP II plot of the molecular structure of $Ru_7(CO)_{18}(\mu_4\text{-}PPh)_2$ showing the atomic numbering. Important bond lengths not given in the text (Å): Ru(1)–Ru(2), 2.865(2); Ru(1)–Ru(3), 2.825(2); Ru(2)–Ru(2′), 2.899(2); Ru(2)–Ru(3), 2.791(2); Ru(2)–Ru(4), 2.848(2); Ru(2)–Ru(4′), 2.906(2); Ru(3)–Ru(4), 2.867(2); Ru(1)–P, 2.366(4); Ru(2′)–P, 2.326(4); Ru(3)–P, 2.374(5); Ru(4)–P, 2.346(5).

† *Crystal data:* $Ru_7P_2O_{18}C_{30}H_{10}\cdot 2CH_2Cl_2$, M = 1597.72, black hexagonal prisms from CH_2Cl_2, monoclinic, space group *C2/c*, a = 11.718(6), b = 17.701(6), c = 22.943(9) Å, β = 94.74(4)°, U = 4743(3) Å^3, Z = 4, D_c = 2.237 g cm^{-3}, $\mu(Mo\text{-}K_\alpha)$ = 24.72 cm^{-1}, $F(000)$ = 2880. The structure solution (MULTAN) and refinement were based on 2139 observed [$I \geqslant 3\sigma(I)$] reflections, measured on a Syntex $P2_1$ diffractometer with Mo-K_α (λ = 0.71069 Å) radiation using the θ–2θ scan method. With all non-hydrogen atoms having anisotropic thermal parameters, the structure has been refined to R and R_w values of 0.065 and 0.080 respectively. The asymmetric unit contains one disordered molecule of dichloromethane of solvation. A best fit model for the disorder had three sites for the carbon atom and four for chlorine with partial occupancies refined to reflect a total of one molecule of CH_2Cl_2.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Alternatively, if the μ_4-phosphinidene groups are considered as part of the skeleton, two octahedral Ru_5P fragments are fused at an Ru_3 face. There is in fact a rather striking resemblance between (**1**) and the condensed polyhedron of $Rh_9(CO)_{19}^{3-}$, where two Rh_6 octahedra share a common face.[9] Although homoheptanuclear clusters are known[2,10] they are still relatively rare, particularly in comparison with penta-, hexa-, and octa-nuclear species. Compound (**1**) appears to be the first example of an Ru_7 cluster. The central ruthenium atoms, Ru(1), Ru(2), and Ru(2'), bear two terminal carbonyl groups whereas in the upper and lower Ru_2P faces each Ru atom has three carbonyl groups. The Ru–Ru bond lengths range from 2.791(2) Å for Ru(2)–Ru(3), with the average basal–basal Ru–Ru distance (2.891 Å) being somewhat longer than the average apical–basal distance (2.851 Å). In terms of electron counting, the polyhedral electron count of 100 predicted for two square pyramids (2×74 e) sharing a triangular face (-48 e) is in agreement with the number of cluster valence electrons for $Ru_7(CO)_{18}(PPh)_2$. The molecule (**1**) is a member of the growing class of metallophosphorus clusters[11] containing metals and phosphorus atoms in the skeletal framework. The use of capping phosphinidene groups as in (**1**) can be expected to lead to the stabilisation of other high nuclearity ruthenium clusters, a topic we are currently exploring.

We are grateful to NSERC for financial support of this work.

Received, 27th March 1987; Com. 390

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