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The First Undecaruthenium Hydrido Carbonyl Anion; Synthesis and Structural Characterisation of $[Ru_{11}H(CO)_{27}]^{3-}$

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The cluster trianion $[Ru_{11}H(CO)_{27}]^{3-}$ has been obtained from the thermolysis of $[Ru_3(CO)_{12}]$ in a methanol–water mixture; an X-ray structure analysis of the $[NEt_3(CH_2Ph)]^+$ salt shows that the metal core in the anion is a fragment of hexagonal close packing, which may be described alternatively as the condensation between two octahedra and two trigonal bipyramids sharing common triangular faces.

During the last 3 years there have been significant developments in the methods of synthesis and isolation of high-nuclearity osmium carbonyl complexes, and species containing up to 20 close-packed osmium atoms are now known.[1] The chemistry of high-nuclearity ruthenium clusters is less well developed, partly because of their greater lability compared to osmium analogues, which results in rapid formation of the most thermodynamically stable products.[2] As a result of these thermodynamic factors, the majority of the known high-nuclearity ruthenium clusters are carbide-[3] or nitride[4]-containing species, with the interstitial main-group atoms stabilising the large array of metal atoms. However, the first non-carbido decaruthenium cluster $[Ru_{10}H_2(CO)_{25}]^{2-}$ was obtained from the thermolysis of $[Ru_3(CO)_{12}]$ in the protic solvent ethanol.[5] The use of protic solvents is known to enhance the production of hydrido clusters, and the presence of hydride ligands, which occupy bridging in preference to terminal sites,[6] may help stabilise large metal cluster cores in the absence of interstitial main-group atoms. It was, therefore, decided to attempt further thermolysis reactions to generate high-nuclearity hydrido-clusters using a methanol–water solvent, since this mixture had proved successful previously in generating tetranuclear hydrido–ruthenium clusters.[7]

In order to attempt the preparation of high-nuclearity ruthenium hydrido-clusters, the complex $[Ru_3(CO)_{12}]$ (1 g) was dissolved in a methanol–water mixture (200 cm^3) and heated under reflux for 40 h, during which time the initial orange solution turned red and then black. At this point $[N(PPh_3)_2]Cl$ (1 g) was added to the hot solution, and as the mixture cooled a black precipitate formed. Separation of the mixture by thin-layer chromatography on silica (eluent: acetone–hexane 3:2) resulted in the isolation of four products {together with some unreacted $[Ru_3(CO)_{12}]$}: $[Ru_6H(CO)_{18}]^-$ **2**,[8] $[Ru_{10}H_2(CO)_{25}]^{2-}$ **3**,[5] $[Ru_8H_2(CO)_{21}]^{2-}$ **4**,[9] and the new trianion $[Ru_{11}H(CO)_{27}]^{3-}$ **1**[†] {isolated in *ca.* 15% yield as its $[N(PPh_3)_2]^+$ salt} in order of elution. When longer reaction times were employed the yield of the trianion **1** increased at the expense of **3**, consistent with the view that the structure of **1** was based on that of $[Ru_{10}H_2(CO)_{25}]^{2-}$ **3**.

The structure of the trianion $[Ru_{11}H(CO)_{27}]^{3-}$ **1** has been established by an X-ray analysis (Fig. 1).[‡] The metal core geometry (Fig. 2) may be described as the condensation of two octahedra [Ru(1), Ru(2), Ru(5), Ru(6), Ru(8), Ru(9) and Ru(1), Ru(2), Ru(3), Ru(5), Ru(7), Ru(11)], sharing the Ru(1), Ru(2), Ru(5) triangle, together with two trigonal bipyramids [Ru(1), Ru(2), Ru(3), Ru(4), Ru(9) and Ru(1), Ru(5), Ru(6), Ru(7), Ru(10)], sharing the common butterfly units Ru(1), Ru(2), Ru(3), Ru(9) and Ru(1), Ru(5), Ru(6), Ru(7). This leaves one butterfly unit uncapped [Ru(2), Ru(5), Ru(8), Ru(11)], and it is compelling to consider the addition of a further Ru atom over this face, to form a third trigonal bipyramid, to give a systematic build up to a symmetric twelve-atom core. The Ru_{11} core itself may also be considered as being built up from the Ru_{10} core in **3** by simply adding the eleventh Ru atom to the square face [Ru(1), Ru(4), Ru(7), Ru(8)] (Fig. 3). Furthermore, the metal framework in **1** may be viewed as being built up by the consecutive capping of the monoanion $[Ru_6H(CO)_{18}]^-$ **2**,[8] as are the other products in the reaction. It is, therefore, not unreasonable to assume that a capping mechanism for cluster build-up is viable in this solvent system, and it has already been shown that the decaruthenium dianion **3** may be synthesised from the redox condensation of **2** with $[Ru_3(CO)_{12}]$ in diglyme $[O(CH_2CH_2OMe)_2]$ at 140 °C.[5]

The metal core in anion **1** (Fig. 2) can be regarded as a fragment of a hexagonal close-packed metal lattice. This is in contrast with the face-centred cubic metal frameworks observed in the carbido- and nitrido-decaruthenium cluster anions.[3,4] These structural differences may be related to a difference in growth pattern in the production of the two types of cluster under thermolytic conditions, once high nuclearities are reached.

The ligand framework in the structure of anion **1** is asymmetric, and includes the presence of seven bridging

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[†] Spectroscopic data **1**: IR (CH_2Cl_2) ν(CO) 2051s (sh), 1993vs and 1751m (br) cm^{-1}; ^1H NMR (CD_2Cl_2) δ −5.47 (s) and 7.70 (m); mass spectrum (negative ion FAB) *m/z* 1866 {$[Ru_{11}H(CO)_{27}]^-$} and 2409 {$[N(PPh_3)_2Ru_{11}H(CO)_{27}]^-$}.

[‡] Crystal data for $[NEt_3(CH_2Ph)]_3[Ru_{11}H(CO)_{27}]$, $C_{66}H_{67}N_3O_{27}Ru_{11}$, $M = 2446.0$, triclinic, space group $P\bar{1}$ (no. 2), $a = 13.714(3)$, $b = 13.991(3)$, $c = 21.387(5)$ Å, $\alpha = 85.55(2)$, $\beta = 81.46(2)$, $\gamma = 74.77(2)°$, $U = 3912.4(14)$ Å^3, $Z = 2$, $D_c = 2.076$ g cm^{-3}, $F(000) = 2368$, Mo-Kα radiation, $\lambda = 0.710\,73$ Å, μ(Mo-Kα) = 21.36 cm^{-1}, crystal dimensions 0.12 × 0.13 × 0.18 mm, 6431 unique observed diffractometer data [$F > 4\sigma(F)$]. Structure solved by direct methods and Fourier difference techniques, refined by full-matrix least-squares analysis (Ru and O anisotropic) to $R = 0.0655$, $R' = 0.0711$, $w^{-1} = \sigma^2(F) + 0.002F^2$, program used SHELXTL PLUS.[10] Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, Issue 1, pp. xx–xxv.

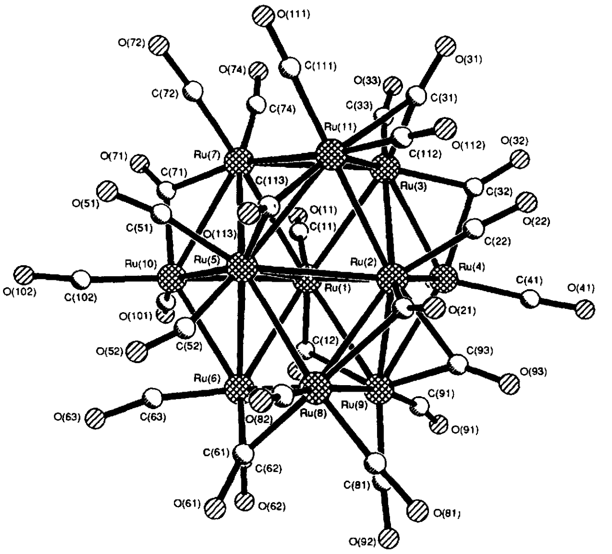

Fig. 1 The structure of the $[Ru_{11}H(CO)_{27}]^{3-}$ **1** anion showing the atom numbering scheme. Selected bond distances (Å): Ru(1)–Ru(2) 2.788(3), Ru(1)–Ru(3) 2.861(3), Ru(1)–Ru(4) 2.869(3), Ru(1)–Ru(5) 2.796(2), Ru(1)–Ru(6) 2.825(3), Ru(1)–Ru(7) 2.883(2), Ru(1)–Ru(9) 2.774(3), Ru(1)–Ru(10) 2.798(3), Ru(2)–Ru(4) 2.807(3), Ru(2)–Ru(5) 2.950(2), Ru(2)–Ru(8) 2.827(3), Ru(2)–Ru(9) 2.786(2), Ru(2)–Ru(11) 2.861(2), Ru(3)–Ru(4) 2.772(2), Ru(3)–Ru(7) 2.983(3), Ru(3)–Ru(11) 2.875(3), Ru(4)–Ru(9) 2.834(3), Ru(5)–Ru(6) 2.902(2), Ru(5)–Ru(7) 2.855(3), Ru(5)–Ru(8) 2.865(3), Ru(5)–Ru(10) 2.848(3), Ru(5)–Ru(11) 2.872(3), Ru(6)–Ru(8) 2.831(3), Ru(6)–Ru(9) 2.842(3), Ru(6)–Ru(10) 2.830(3), Ru(7)–Ru(10) 2.865(3), Ru(7)–Ru(11) 3.085(3) and Ru(8)–Ru(9) 3.093(3)

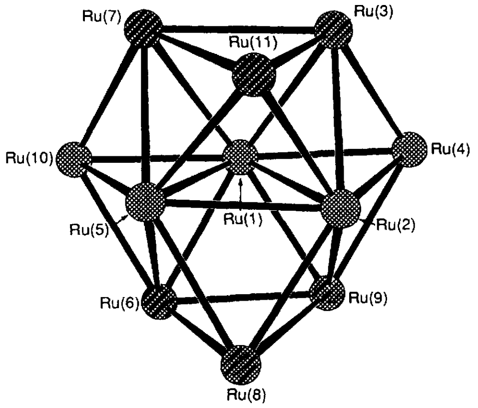

Fig. 2 The structure of the metallic core in the $[Ru_{11}H(CO)_{27}]^{3-}$ **1** anion

carbonyls. The ^1H NMR spectrum indicates the presence of a hydride ligand. However, potential-energy calculations[11] using the crystallographically determined structure failed to locate a suitable site for this ligand on the surface of the cluster. In view of the position of the signal at δ −5.47, which is similar to the value found for the interstitial hydride in **2**,[8] it is possible that the hydride occupies an interstitial site in one of the Ru_6 octahedra.

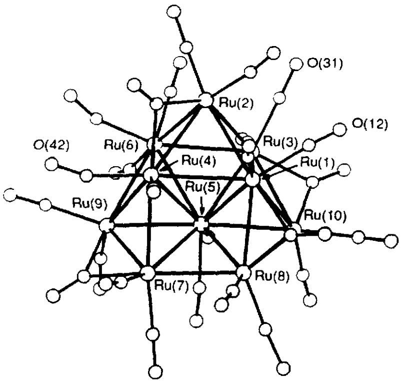

Fig. 3 The structure of the known dianion $[Ru_{10}H_2(CO)_{25}]^{2-}$ **3**

In terms of electron counting the trianion **1** is a 146-electron system, which is consistent with the count obtained using[12] the 'condensation principle' for the condensation of two octahedra with two trigonal bipyramids. When comparing the metal framework in **1** to that found in other eleven-metal systems, there is little similarity to the square pyramid-based geometry in $[Os_{11}C(CO)_{27}]^{2-}$,[13] but there is a closer relationship to the three fused octahedra found in $[Cs_{11}O_3]^{5+}$.[14]

Acknowledgements

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References

1 B. F. G. Johnson, L. H. Gade, J. Lewis and W. T. Wong, *Mat. Chem. Phys.*, 1991, **29**, 85.
2 M. D. Vargas and J. N. Nicholls, *Adv. Inorg. Chem. Radiochem.*, 1987, **30**, 123.
3 P. J. Bailey, B. F. G. Johnson, J. Lewis, M. McPartlin and H. R. Powell, *J. Organomet. Chem.*, 1989, **377**, C17; C. E. Anson, P. J. Bailey, M. J. Duer, B. F. G. Johnson, J. Lewis, G. Conole, M. McPartlin and H. R. Powell, *J. Organomet. Chem.*, 1990, **383**, 441; C.-M. T. Hayward, J. R. Shapley, M. R. Churchill, C. Bueno and A. L. Rheingold, *J. Am. Chem. Soc.*, 1982, **104**, 7347.
4 P. J. Bailey, G. C. Conole, B. F. G. Johnson, J. Lewis, M. McPartlin, A. Moule and D. A. Wilkinson, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1706.
5 P. J. Bailey, E. Charalambous, J. Hoyle, B. F. G. Johnson, J. Lewis and M. McPartlin, *J. Chem. Soc., Chem. Commun.*, 1990, 1443.
6 D. M. P. Mingos and D. J. Wales, *Introduction to Cluster Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1990.
7 B. F. G. Johnson and J. Lewis, *Adv. Inorg. Chem. Radiochem.*, 1981, **24**, 225.
8 C. R. Eady, B. F. G. Johnson, J. Lewis, M. C. Malatesta, P. Machin and M. McPartlin, *J. Chem. Soc., Chem. Commun.*, 1976, 945.
9 T. Chihara, Y. Matsura and H. Yamazaki, *J. Chem. Soc., Chem. Commun.*, 1988, 886.
10 Program version 4.0 SHELXTL PLUS, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1990.
11 A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1980, 2509.
12 D. M. P. Mingos, *J. Chem. Soc., Chem. Commun.*, 1983, 706.
13 S. R. Drake, B. F. G. Johnson, J. Lewis, W. J. H. Nelson, M. D. Vargas, T. Adatia, D. Braga, K. Henrick, M. McPartlin and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1989, 1455.
14 A. Simon, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 159.

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