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COMMUNICATION

Use of $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3]^+$ as a capping reagent in cluster build-up: synthesis and structural characterisation of $[Os_5Ru_2(CO)_{15}(\eta^5\text{-}C_5H_5)_2]$

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Ionic coupling of the mononuclear cation $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3]^+$ with the cluster dianion $[Os_5(CO)_{15}]^{2-}$ afforded the neutral heptanuclear cluster $[Os_5Ru_2(CO)_{15}(\eta^5\text{-}C_5H_5)_2]$ which has been shown by X-ray diffraction studies to contain a tricapped tetrahedral metal core.

There is considerable current interest in the chemistry of transition-metal clusters which contain cyclic, unsaturated organic ligands such as arenes and dienes.[1] This interest has been stimulated by the appealing analogy between the co-ordination of an organic group to a cluster and to a metal surface, and the relevance of the latter to heterogeneous catalytic processes.[2] The complexes obtained can be prepared by one of two synthetic routes, (*i*) where the co-ordination mode and level of unsaturation of the organic ligand is modified once it has been co-ordinated to the cluster[3] and (*ii*) where a cationic organometallic fragment containing the organic group is coupled to a carbonyl cluster anion.[4] For this second method of the synthesis the dicationic species '$M(\eta^6\text{-}C_6H_{6-n}R_n)^{2+}$' (M = Ru or Os; R = H or Me)[5,6] and '$Rh(\eta^5\text{-}C_5Me_5)^{2+}$' have been used extensively,[7] however, reactions with monocationic species such as '$Ru(\eta^5\text{-}C_5H_5)^{+}$' have not been attempted, and the only cluster systems containing '$Ru(\eta^5\text{-}C_5H_5)$' units have been prepared by the reaction of ruthenium-containing clusters with C_5H_6.[8]

There are some advantages in using a monocationic capping reagent in reactions with cluster dianions compared to using a dicationic species such as $[Ru(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$. With a monocation it is, in principle, possible to add one or two units to a dianionic cluster thereby increasing the nuclearity by two metal atoms. Also, because $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3]^+$ is less redox active than $[Ru(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ less redox chemistry should occur, and higher yields of the reaction products should be obtained.

In this communication we report the first use of '$[Ru(\eta^5\text{-}C_5H_5)]^{+}$', generated from $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3]^+$, as a capping reagent in the synthesis of higher-nuclearity clusters and the formation of the new mixed-metal heptanuclear cluster $[Os_5Ru_2(CO)_{15}(\eta^5\text{-}C_5H_5)_2]$ **1**.

In an ionic coupling reaction 2 molar equivalents of the monocation $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3]^+$, as its $[PF_6]^-$ salt (59 mg, 0.134 mmol),[9] were added to a dichloromethane solution (25 cm^3) of the osmium cluster dianion $[Os_5(CO)_{15}]^{2-}$, as its $[N(PPh_3)_2]^+$ salt (150 mg, 0.061 mmol),[10] and the mixture stirred at room temperature for *ca.* 15 min. During this time the solution turned green, and after removal of the solvent, the solid residue was purified by TLC, using CH_2Cl_2–hexane (80:20) as eluent. The cluster $[Os_5Ru_2(CO)_{15}(\eta^5\text{-}C_5H_5)_2]$ **1** was isolated as the sole product in 87% yield (90 mg, 0.053 mmol) and recrystallised from CH_2Cl_2–hexane. The complex was initially characterised from spectroscopic data.† The FAB mass spectrum exhibits a molecular ion peak at *m*/*z* 1703, and also shows fragments corresponding to the sequential loss of 15 carbonyl groups. The ^1H NMR spectrum, at room temperature, exhibits a singlet at δ 5.19 which is indicative of the protons on two equivalent $\eta^5\text{-}C_5H_5$ rings. This chemical shift is comparable with that observed for the protons on the $\eta^5\text{-}C_5H_5$ ligands in the mixed-metal cluster $[Ru_5RhC(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)_2]$ (δ 5.14).[8]

In order to establish the molecular structure of cluster **1** and establish the geometry of the metal core and the positions of the '$Ru(\eta^5\text{-}C_5H_5)$' units a crystal structure determination was undertaken. The molecular structure‡ is shown in Fig. 1 which includes some selected bond parameters. The metal framework may be described as a bicapped trigonal bipyramid, with the two '$Ru(\eta^5\text{-}C_5H_5)$' units at the two apical sites of the trigonal bipyramid, or as four Os_3Ru tetrahedra sharing four common faces. In the latter case the metal core can be viewed as being related to that observed in $[Os_7(CO)_{17}(\eta^6\text{-}C_6H_6)]$,[6] which itself is derived from that of the bicapped tetrahedral core found in the parent binary carbonyl $[Os_6(CO)_{18}]$.[13] In terms of the eighteen-electron rule, as with the two osmium cluster examples, it is not possible formally to assign each metal atom 18 electrons although the total electron count of 96e$^-$ for the cluster is consistent with the Mingos condensed polyhedral count for the structure.[14] If the two $\eta^5\text{-}C_5H_5$ rings each donate five electrons and the two bridging carbonyl ligands, C(12)O(12) and C(13)O(13), donate one to each of the bridged metal atoms, then Os(2) and Os(4) are each associated with 17e$^-$, Os(1), Ru(1) and Ru(2) with 18e$^-$, and Os(3) and Os(5) with 19e$^-$. The two '$Ru(\eta^5\text{-}C_5H_5)$' units have not simply clipped on as caps to the Os_5 trigonal-bipyramidal core, occupying 17e$^-$ sites, as might be expected, but the formation of **1** has involved a metal-core rearrangement in which the two '$Ru(\eta^5\text{-}C_5H_5)$' units occupy two of the three 18e$^-$ sites. This is consistent with the fact that the $\eta^5\text{-}C_5H_5$ groups are much better donors and poorer π acceptors than carbonyl groups, and so the '$Ru(\eta^5\text{-}C_5H_5)$' units are better suited to sites of higher formal electron density. The two bridging carbonyl ligands, which are better acceptors than terminal carbonyl ligands, are associated with the two ruthenium centres and the formally 18e$^-$ Os atom, Os(1); in this way the higher electron density provided by the '$Ru(\eta^5\text{-}C_5H_5)$' units can be balanced. Similar effects have been

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† IR (CH_2Cl_2): ν(CO) 2074w, 2055s, 2024vs, 2007s, 1987s and 1933 (br) m cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.19 (s, 10 H). Positive-ion FAB mass spectrum: *m*/*z* 1703 (calc. 1702 based on ^{190}Os and ^{101}Ru) (Found: C, 17.65; H, 0.55. Calc. for $C_{25}H_{10}O_{15}Os_5Ru_2$: C, 17.65; H, 0.6%).

‡ Crystal data: $C_{25}H_{10}O_{15}Os_5Ru_2$, $M = 1703.47$, green plate, crystal dimensions 0.12 × 0.31 × 0.33 mm, monoclinic, space group $P2_1/n$ (alternative setting $P2_1/c$, no. 14), $a = 11.692(4)$, $b = 17.699(6)$, $c = 14.984(6)$ Å, $\beta = 92.88(4)°$, $U = 3097(2)$ Å^3, $D_c = 3.654$ Mg m^{-3}, $Z = 4$, $F(000) = 2992$, Mo-Kα radiation, $\lambda = 0.710\,73$ Å, μ(Mo-Kα) = 21.45 mm^{-1}, $T = 293(2)$ K. Siemens *R3mV* four-circle diffractometer, 4425 reflections collected in the range $2.54 \le \theta \le 22.54°$, 4053 unique absorption-corrected data ($R_{int} = 0.039$). Structure solved by direct methods (Os and Ru atoms) (SHELXTL PLUS[11]) and refined with Os, Ru and O atoms anisotropic by full-matrix least squares based on F^2 (SHELXL 93[12]); H atoms were not included in the refinement. Refinement converged at $R1 = 0.0686$, $wR2 = 0.1268$ for 2336 unique data with $F > 4\sigma(F)$, and $R1 = 0.1505$ and $wR2 = 0.1645$ (all data), goodness of fit = 1.089, weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0514P)^2 + 146.12P]$ where $P = (F_o^2 + 2F_c^2)/3$. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/315.

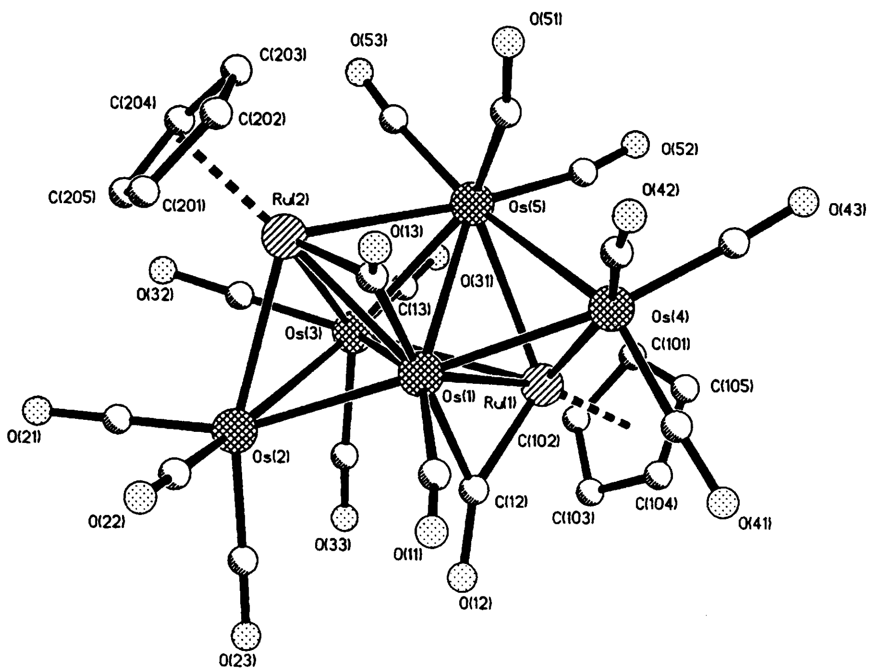

Fig. 1 Molecular structure of $[\mathrm{Os_5Ru_2(CO)_{15}(\eta^5\text{-}C_5H_5)_2}]$ **1** showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): Os(1)–Ru(1) 2.604(4), Os(1)–Ru(2) 2.610(4), Os(1)–Os(2) 2.692(3), Os(1)–Os(3) 2.757(2), Os(1)–Os(4) 2.686(3), Os(1)–Os(5) 2.759(2), Os(2)–Ru(2) 2.735(4), Os(2)–Os(3) 2.884(2), Os(3)–Ru(1) 2.857(4), Os(3)–Ru(2) 2.844(4), Os(3)–Os(5) 2.770(3), Os(4)–Ru(1) 2.736(4), Os(4)–Os(5) 2.880(3), Os(5)–Ru(1) 2.815(4), Os(5)–Ru(2) 2.837(4), Ru(1)–C(101) 2.22(4), Ru(1)–C(102) 2.22(4), Ru(1)–C(103) 2.19(4), Ru(1)–C(104) 2.17(5), Ru(1)–C(105) 2.19(5), Ru(2)–C(201) 2.18(4), Ru(2)–C(202) 2.23(4), Ru(2)–C(203) 2.31(4), Ru(2)–C(204) 2.30(4), Ru(2)–C(205) 2.22(4), Os(1)–C(12) 2.02(3), Os(1)–C(13) 2.02(3), Ru(1)–C(12) 1.99(3), Ru(2)–C(13) 2.08(4), Ru(1)–Cp(1)(centroid) 1.887 and Ru(2)–Cp(2)(centroid) 1.913; Os(1)–C(12)–Ru(1) 81.0(13) and Os(1)–C(13)–Ru(2) 79.0(12)

observed in the osmium arene clusters $[\mathrm{Os_6(CO)_{15}(\eta^6\text{-}C_6H_6)}]$ and $[\mathrm{Os_7(CO)_{17}(\eta^6\text{-}C_6H_6)}]$,[6] but in the case of **1** any possibility of arene migration over the cluster surface can be eliminated because of the positions of the rutheniums in the mixed-metal cluster. The fact that the '$\mathrm{Ru(\eta^5\text{-}C_5H_5)}$' units do not occupy the 19e$^-$ sites may have a steric origin. In the related cluster $[\mathrm{Ru_6(\eta^2\text{-}\mu_4\text{-}CO)_2(CO)_{13}(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)}]$[15] the $\mathrm{Ru(\eta^6\text{-}C_6H_3Me_3)}$ unit, which is a good donor group, does occupy one of the 19e$^-$ centres in the formally bicapped tetrahedral core, but the core opens out to generate a structure in which two edges of the central tetrahedron are bridged by Ru atoms and two of the carbonyls co-ordinate in the novel η^2-μ_4 mode. A similar structural rearrangement might be required if '$\mathrm{Ru(\eta^5\text{-}C_5H_5)}$' units were to occupy 19e$^-$ sites in **1**.

The crystal structure of cluster **1** shows that the molecules are separated by normal van der Waals distances, with the cyclopentadienyl rings packing facing carbonyl groups, so that there is no cyclopentadienyl–cyclopentadienyl stacking.

It is interesting to note that the reaction of 1 equivalent of $[\mathrm{Ru(\eta^5\text{-}C_5H_5)(MeCN)_3}]^+$ with the hydrido monoanionic cluster[16] $[\mathrm{Os_5H(CO)_{15}}]^-$ does not yield the expected product $[\mathrm{Os_5RuH(CO)_{15}(\eta^5\text{-}C_5H_5)}]$, and the only product is the green, neutral species $[\mathrm{Os_5Ru_2(CO)_{15}(\eta^5\text{-}C_5H_5)_2}]$ **1** in 43% yield. This suggests that the introduction of one '$\mathrm{Ru(\eta^5\text{-}C_5H_5)}$' unit, under the reaction conditions, leads to ready deprotonation of the product, although the anion $[\mathrm{Os_5Ru(CO)_{15}(\eta^5\text{-}C_5H_5)}]^-$ has not been isolated and a further coupling reaction to afford **1** takes place.

Acknowledgements

We gratefully acknowledge the financial support of the Cambridge Overseas Trust, the Overseas Research Scheme, and ICI plc (to C. A. M.), and the European Union for a Human Capital and Mobility grant (to M. C. R. de A.). We thank Johnson Matthey plc for a generous loan of osmium and ruthenium salts.

References

1 B. F. G. Johnson, J. Lewis, M. A. Gallop and M. Martinelli, *Faraday Discuss., R. Soc. Chem.*, 1991, **92**, 241; H. Wadepohl, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 247; D. Braga, P. J. Dyson, F. Grepioni and B. F. G. Johnson, *Chem. Rev.*, 1994, **94**, 1585.

2 G. A. Somorjai, *J. Phys. Chem.*, 1990, **94**, 1013; H. P. Steinruck, W. Huber, T. Pache and D. Menzel, *Surf. Sci.*, 1989, 218; H. P. Steinruck, P. Heinmann, W. Huber, P. Jokob, T. Pache and D. Menzel, *J. Electron Spectrosc. Relat. Phenom.*, 1990, **52**, 51.

3 M. P. Goméz-Sal, B. F. G. Johnson, J. Lewis, P. R. Raithby and A. H. Wright, *J. Chem. Soc., Chem. Commun.*, 1985, 1682; A. J. Blake, P. J. Dyson, B. F. G. Johnson, C. M. Martin, J. G. M. Nairn, E. Parisini and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1993, 981; A. J. Edwards, M. A. Gallop, B. F. G. Johnson, J. U. Köhler, J. Lewis and P. R. Raithby, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1093.

4 J. Lewis, C.-K. Li, P. R. Raithby and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, 1993, 999.

5 J. Lewis, C.-K. Li, M. C. Ramirez de Arellano, P. R. Raithby and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, 1993, 1359.

6 J. Lewis, C.-K. Li, C. A. Morewood, M. C. Ramirez de Arellano, P. R. Raithby and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, 1994, 2159.

7 R. K. Henderson, P. A. Jackson, B. F. G. Johnson, J. Lewis and P. R. Raithby, *Inorg. Chim. Acta*, 1992, **198–200**, 393; J. R. Galsworthy, C. E. Housecroft, D. M. Matthews, R. Ostrander and A. L. Rheingold, *J. Chem. Soc., Dalton Trans.*, 1994, 69.

8 P. J. Bailey, A. J. Blake, P. J. Dyson, B. F. G. Johnson, J. Lewis and E. Parisini, *J. Organomet. Chem.*, 1993, **452**, 175.

9 T. P. Gill and K. R. Mann, *Organometallics*, 1982, **1**, 485.

10 C. R. Eady, J. J. Guy, B. F. G. Johnson, J. Lewis, M. C. Malatesta and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 1976, 807.

11 SHELXTL PLUS, PC Release 4.0, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1990.

12 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.

13 R. Mason, K. M. Thomas and D. M. P. Mingos, *J. Am. Chem. Soc.*, 1973, **95**, 3802.

14 D. M. P. Mingos, *J. Chem. Soc., Chem. Commun.*, 1983, 706.

15 C. E. Anson, P. J. Bailey, G. Conole, B. F. G. Johnson, J. Lewis, M. McPartlin and H. R. Powell, *J. Chem. Soc., Chem. Commun.*, 1989, 442.

16 G. R. John, B. F. G. Johnson, J. Lewis, M. McPartlin and W. J. H. Nelson, *J. Organomet. Chem.*, 1979, **171**, C14.

Received 13*th September* 1996; *Communication* 6/06327F