Journal of Organometallic Chemistry, 246 (1983) C69—C73
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

SYNTHESIS OF MIXED METAL DECAOSMIUM CARBIDO CLUSTERS: THE X-RAY STRUCTURES OF THE MONOANIONS $[Os_{10}C(CO)_{24}Cu(NCMe)]^-$ AND $[Os_{10}C(CO)_{24}AuPPh_3]^-$

BRIAN F.G. JOHNSON, JACK LEWIS, WILLIAM J.H. NELSON, MARIA D. VARGAS,
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain)
DARIO BRAGA and MARY MCPARTLIN
School of Chemistry, The Polytechnic of North London, London N7 8DB (Great Britain)

(Received January 7th, 1983)

Summary

The high nuclearity mixed metal cluster monoanions $[Os_{10}C(CO)_{24}Cu(NCMe)]^-$ (I) and $[Os_{10}C(CO)_{24}AuPPh_3]^-$ (II) have been obtained by reaction of the carbido-dianion $[Os_{10}C(CO)_{24}]^{2-}$ (III) with one equivalent of $[Cu(NCMe)_4][BF_4]$ and Ph_3PAuCl, respectively, in CH_2Cl_2. X-ray analysis of the $[PPh_3Me]^+$ salts of I and II show that the Cu and Au ligands have added to capping tetrahedra of the dianion III in μ_3- and μ_2-bridging positions, respectively.

The treatment of preformed cluster anions with appropriate mononuclear metal halides or cations has been shown to be an efficient route to mixed metal clusters in high yield [1—3].

We have obtained the mixed-metal cluster anions $[Os_{10}C(CO)_{24}Cu(NCMe)]^-$ (I) and $[Os_{10}C(CO)_{24}AuPPh_3]^-$ (II) by treating the dianion $[Os_{10}C(CO)_{24}]^{2-}$ (III) with one equivalent of $[Cu(NCMe)_4][BF_4]$ and $AuPPh_3Cl$ (in the presence of $TlPF_6$ as halide acceptor) respectively in CH_2Cl_2. These are the first high nuclearity mixed metal clusters of osmium to be isolated.

X-ray analysis* of the $[PPh_3Me]^+$ salts of I and II shows that the tetracapped-

---

*Crystal data: $[C_{27}H_3CuNO_{24}Os_{10}][C_{19}H_{18}P]$ (I), M = 3,088.3, triclinic, space group $P\bar{1}$, a 16.452(2), b 13.881(2), c 13.290(2) Å, α 82.12(1), β 93.23(1), γ 96.40(1)°, $Z = 2$, V 2,985.04 Å^3, D_c 3.47 g cm^{-3}, $I/\sigma(I) \geq 3.0$, present R factor = 0.0492 for 4325 reflections corrected for absorption (μ(Mo-K_α) 208.31 cm^{-1}). Data were collected on a Philips PW 1100 diffractometer in the θ-range 3—25°.

$[C_{43}H_{15}AuO_{24}Os_{10}P][C_{19}H_{18}P]$ (II), M = 3,322.84. Triclinic, space group $P\bar{1}$, a 17.296(3), b 15.403(3), c 15.191(3) Å, α 107.31(2), β 98.28(2), γ 89.99(2)°, $Z = 2$, V 3,822.06 Å^3, D_c 2.89 $I/\sigma(I) \geq 3.0$, present R factor = 0.055 for 5314 reflections corrected for absorption (μ(Mo-K_α 178.44 cm^{-1}). Data were collected on a Philips PW 1100 diffractometer in the θ-range 3—22°.

0022-328X/83/$03.00

octahedral geometry of the dianion III is retained in both clusters, with the hetero-metal atom in each case bonded to Os atoms of a capping tetrahedron as shown in Figs. 1 and 2 respectively. Formally the cations $[Cu(NCMe)]^+$ and $[AuPPh_3]^+$ may be regarded as donating no electrons to the cluster so, on the basis of total electron count, no change in metal core geometry is expected. However, the 24 CO ligands on the surface of the dianion III form a close packed array and in all previous derivatives with more than this number of surface ligands the metal core has been opened up. For example in $[Os_{10}C(CO)_{24}I]^-$ the addition of extra electrons by the iodide ligand causes the breaking of an Os—Os

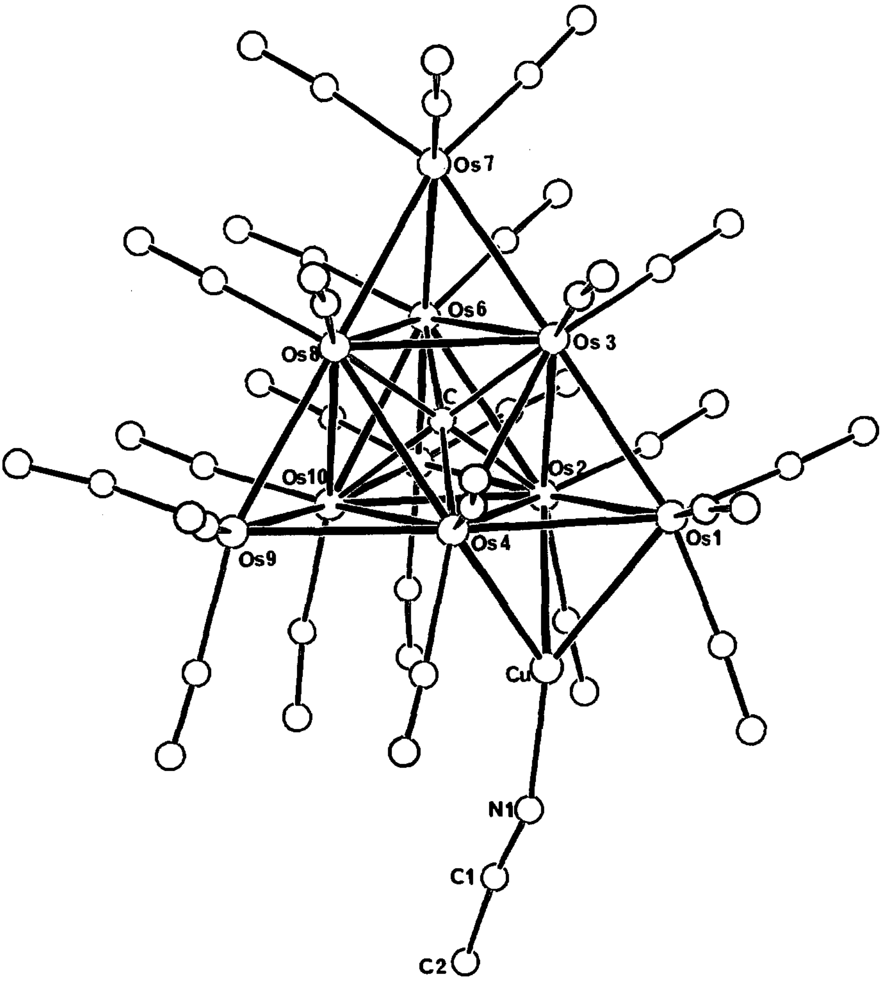

Fig. 1. The structure of the monoanion $[Os_{10}C(CO)_{24}Cu(NCMe)]^-$ (I). Important bond lengths are: Os—Os: (1)—(2) 2.808, (1)—(3) 2.778, (1)—(4) 2.880, (2)—(3) 2.884, (2)—(4) 3.012, (2)—(5) 2.801, (2)—(6) 2.872, (2)—(10) 2.885, (3)—(4) 2.883, (3)—(6) 2.857, (3)—(7) 2.793, (3)—(8) 2.868, (4)—(8) 2.849, (4)—(9) 2.854, (4)—(10) 2.964, (5)—(6) 2.761, (5)—(10) 2.799, (6)—(7) 2.782, (6)—(8) 2.844, (6)—(10) 2.859, (7)—(8) 2.799, (8)—(9) 2.770, (8)—(10) 2.904, (9)—(10) 2.788; maximum e.s.d. 0.002 Å;
Cu—Os(1) 2.688(8), Cu—Os(2) 2.676(9), Cu—Os(4) 2.547(7), Cu—N(1) 1.93(4), N(1)—C(1) 1.17(4), C(91)—C(92) 1.42(4), mean Os—C (carbido) 2.04(3) Å.

There is a ca. 35% disorder of the anion corresponding to a second orientation of the cluster in which all the atoms are coincident with those in the first orientation except CO(41) and the Cu ligand.

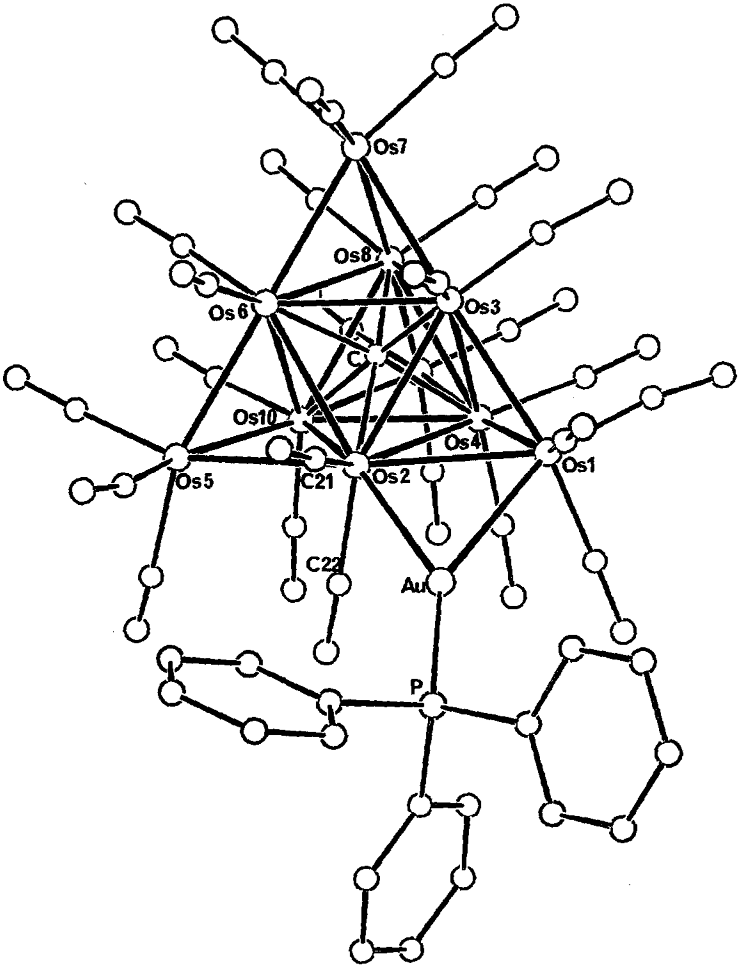

Fig. 2. The structure of the monoanion $[Os_{10}C(CO)_{24}AuPPh_3]^-$ (II). Important bond lengths are: Os—Os: (1)—(2) 2.962, (1)—(3) 2.780, (1)—(4) 2.776, (2)—(3) 2.895, (2)—(4) 2.909, (2)—(5) 2.876, (2)—(6) 2.875, (2)—(10) 2.906, (3)—(4) 2.900, (3)—(6) 2.877, (3)—(7) 2.805, (3)—(8) 2.861, (4)—(8) 2.877, (4)—(9) 2.807, (4)—(10) 2.867, (5)—(6) 2.762, (5)—(10) 2.772, (6)—(7) 2.786, (6)—(8) 2.871, (6)—(10) 2.878, (7)—(8) 2.788, (8)—(9) 2.777, (8)—(10) 2.886, (9)—(10) 2.799; maximum e.s.d. 0.002 Å; Au—Os(1) 2.851(2), Au—Os(2) 2.781(2), Au—P 2.27(1), mean Os—C (carbido) 2.04(3) Å.

bond of one of the capping tetrahedra and the extra ligand is readily accommodated bridging the wingtips of the resultant 'butterfly' indentation on the metal surface [4].

In the monoanion I the Cu atom lies between three carbonyl ligands and is attached to the Os metal skeleton in a slightly asymmetric μ_3-bonding mode (Cu—Os(4) 2.547 and mean of Cu—Os(1) and Cu—Os(2) 2.68 Å). The very congested coordination site selected by the $[CuNCMe]^+$ ligand may be related to an observation by Mingos [5], from EHMO calculations on MPH_3 fragments, that a coordinated Cu atom can accept back donation of electron density into its empty and relatively low lying p_x and p_y orbitals. The mean Cu—C (carbonyl) distances of 2.39 Å may be taken to also indicate some bonding interaction between the Cu atom and the surrounding CO ligands; the coordination round the

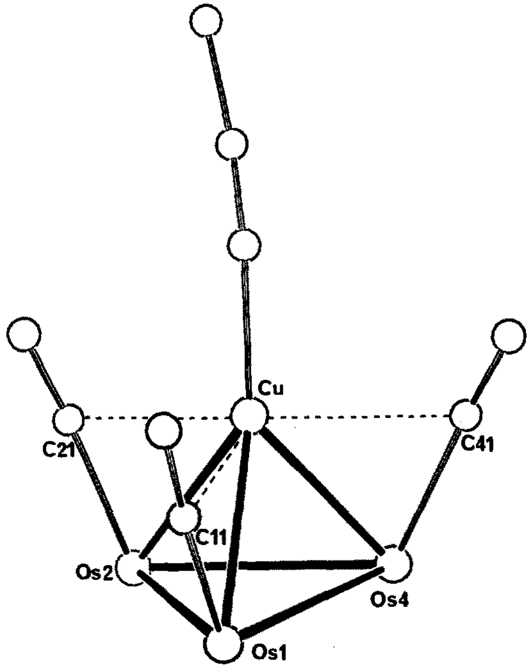

Fig. 3. The coordination sphere of the Cu atom in the monoanion I. Important distances are: Cu—C(11) 2.40(3), Cu—C(21) 2.30(4), Cu—C(41) 2.46(6) Å.

Cu atom is shown in Fig. 3. The three CO ligands have retained their linearity (mean Os—C—O 177°) and the geometry is reminiscent of the η^2-μ_2 type of CO bridging first observed in $[Mn_2(CO)_5(Ph_2PCH_2PPh_2]$ [6]. However no evidence has been found to date in the IR spectrum* of I for carbonyl—copper bonding.

There is a certain similarity between the structure of I and the bis-$Cu(NCMe)^+$ adduct of $[Ru_6C(CO)_{16}]^{2-}$, $Ru_6C(CO)_{16}\{Cu(NCMe)\}_2$ (IV) which has recently been reported. In IV one Cu atom adopts a μ_3-position above one of the triangular faces of the Ru_6C core forming a tetrahedral capping group similar to the capping $Os(CO)_3$ groups in III; the second Cu ligand bridges a triangular face of the $CuRu_3$ cap. Short Cu···C distances (minimum 2.471 Å) similar to those observed in I were also noticed in the structure of IV.

The monoanion $[Os_{10}C(CO)_{24}Cu(NCMe)]^-$ (I) also adds a second $[Cu(NCMe)]^+$ cation, by reaction with 1 equivalent of $[Cu(NCMe)_4][BF_4]$, to give the neutral compound $Os_{10}C(CO)_{24}\{Cu(NCMe)\}_2$ (V) which was characterised by microanalysis. It would be interesting to know if there is a Cu—Cu bond present in this compound similar to that in IV, but it has proved impossible to obtain crystals for X-ray analysis because V is insoluble in most solvents, and dissociates to the monoanion I in donor solvents.

In the structure of II the gold atom bridges the edge of a capping tetrahedron and the bridged Os—Os bond (2.962 Å) is significantly longer than any other

---

*Spectroscopic data: ν(CO) (cm^{-1}): I (CH_2Cl_2) 2082w, 2051vs, 2043ssh, 2001s, 1991m, 1976mw, and 1934w;
II (CH_2Cl_2) 2081w, 2050s, 2040m, and 1999s.

M—M bond in the molecule (Fig. 2). Similar lengthening of Os—Os bonds by Au ligands has been observed before in tetranuclear osmium clusters where the bonding mode of the [AuPPh$_3$] ligand has been shown to be similar to that of a bridging hydride, both ligands being 1e donors. This comparison cannot be extended to the structure of II because in the analogous hydride monoanion [HOs$_{10}$C(CO)$_{24}$]$^-$ the hydride ligand is interstitial [7].

Mingos has shown that for [AuPH$_3$] fragments, unlike their Cu analogues, the p_x and p_y orbitals are relatively high lying and cannot accept electron density effectively. The edge-bridging position adopted by the [AuPPh$_3$] ligand in II reduces contact between the Au atom and the close packed carbonyls, compared to the copper carbonyl interactions in I, but there are nevertheless two relatively short Au—carbonyl distances (Au—C(21) 2.661 and Au—C(22) 2.668 Å). In the monoanion [RuC(CO)$_{15}$NO(AuPPh$_3$)]$^-$, where the surface ligand density is relatively low, a μ_3-bridging position is adopted by the Au ligand [8].

Unlikely the reaction of I to give V, the monoanion II does not react with further AuPPh$_3$Cl in the presence of TlPF$_6$ so that the bis-gold neutral molecule has not been obtained.

In the mixed metal monoanions I and II the [Cu(NCMe)]$^+$ and [AuPPh$_3$]$^+$ groups dissociate readily in coordinating solvents to regenerate the dianion III, but both compounds appear to be indefinitely stable in dry chlorinated hydrocarbon solvents.

Acknowledgments

We thank the S.E.R.C. (D.B.), I.C.I. (W.J.H.N.) and C.N.Pq. (Brazil) (M.D.V.) for financial support. We would also like to thank D.A. Kaner and S.N.A.B. Syed-Mustaffa for their advice and interest in this work.

References

1 C.W. Bradford, W. van Bronswijk, R.J.H. Clark and R.S. Nyholm, J. Chem. Soc. A, (1970) 2889; V.G. Albano, D. Braga, S. Martinengo, P. Chini, M. Sansoni and D. Strumolo, J. Chem. Soc., Dalton Trans., (1980) 52.
2 B.F.G. Johnson, D.A. Kaner, J. Lewis, P.R. Raithby and M.J. Taylor, J. Chem. Soc., Chem. Commun., (1982) 314.
3 J.S. Bradley, R.L. Pruett, E. Hill, G.B. Ansell, M.E. Leonowicz and M.A. Modrick, Organometallics, 1 (1982) 748.
4 D.H. Farrar, P.G. Jackson, B.F.G. Johnson, J. Lewis, W.J.H. Nelson, M.D. Vargas and M. McPartlin, J; Chem. Soc., Chem. Commun., (1981) 1009.
5 D.E. Evans and D.M.P. Mingos, J. Organometal. Chem., 232 (1982) 171.
6 C.J. Commons and B.F. Hoskins, Aust. J. Chem., 28 (1975) 1663.
7 P.F. Jackson, B.F.G. Johnson, J. Lewis, M. McPartlin and W.J.H. Nelson, J. Chem. Soc., Chem. Commun., (1982) 49.
8 D. Braga, W. Clegg, B.F.G. Johnson, J. Lewis, M. McPartlin, W.J.H. Nelson, J. Puga and P.R. Raithby, J. Organometal. Chem., 243 (1983) C13.