Journal of Organometallic Chemistry, 401 (1991) C46–C49
Elsevier Sequoia S.A., Lausanne
JOM 21478PC

Preliminary communication

Heptanuclear clusters of osmium: crystal structure of $[Os_7(CO)_{20}P(OMe)_3]$

Brian F.G. Johnson, Jack Lewis *, Julie Luniss
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (UK)

Dario Braga * and Fabrizia Grepioni
Dipartimento di Chimica "G. Ciamician", via Selmi 2, 40126 Bologna (Italy)

(Received October 17th, 1990)

Abstract

The structure of $[Os_7(CO)_{20}P(OMe)_3]$ has been determined by an X-ray diffraction study. The metal-atom skeleton consists of a capped octahedron, in which the capping Os-atom bears the $P(OMe)_3$ ligand and two terminal COs, while the other six Os-atoms bear three terminal COs each.

In earlier communications [1–3] we reported the preparation and structural characterisation of $[Os_7(CO)_{21}]$ (**1**), an orange-brown binary carbonyl isolated as one of the products of the pyrolysis of $[Os_3(CO)_{12}]$, $[Os_7H_2(CO)_{20}]$ (**2**), a red dihydride isolated from the reactions of $[Os_6(CO)_{16}(MeCN)_2]$ by reaction with $[OsH_2(CO)_4]$, and from the same reaction the pink $[Os_7H_2(CO)_{21}]$ (**3**) and the yellow $[Os_7H_2(CO)_{22}]$ (**4**). We subsequently repeated a more convenient synthesis of **2**, **3** and **4** from the reaction of the cluster $[Os_6(CO)_{18}]$ with Me_3NO in the presence of $[OsH_2(CO)_4]$. These clusters revealed a diverse range of molecular geometries accessible to heptaosmium systems. Thus, $[Os_7(CO)_{21}]$ possesses a monocapped octahedral metal arrangement, $[Os_7H_2(CO)_{20}]$ and edge-bridged bicapped tetrahedral arrangement, $[Os_7H_2(CO)_{21}]$ a monocapped square-based pyramid arrangement, and, finally in $[Os_7H_2(CO)_{22}]$ the geometry is best described as a triangle and a trigonal bipyramid sharing an edge.

Despite the apparent complexity of these structures there exist a clear and well-defined relationship between their polyhedral forms which has been rationalised in terms of simple electron counting procedures [3]. Nevertheless, we were keen to explore more fully the potential offered by this diversity of individual forms and have been systematically examining the displacement of CO by a variety of donor ligands. In this communication we report the synthesis and full structural characterisation of the new substituted heptanuclear cluster $[Os_7(CO)_{20}P(OMe)_3]$ (**5**).

0022-328X/91/$03.50

The complex 5 was prepared directly from the parent 1 by reaction first with Me_3NO/MeCN and then by addition of one equivalent of the phosphite ligand. The reaction presumably proceeds via the initial formation of the acetonitrile complex $[Os_7(CO)_{20}(MeCN)]$ (6) which was not characterised because of its rapid decomposition in the absence of excess MeCN. The red-brown cluster 5 was purified by TLC and crystals suitable for single crystal X-ray analysis grown from toluene *.

The structure of (5) is shown in Fig. 1. The metal polyhedron is strictly related to that of the parent $[Os_7(CO)_{21}]$ (1) [1], and can be described as a capped octahedron. The capping Os-atom bears the $P(OMe)_3$ ligand and two terminal COs; all remaining Os-atoms of the octahedral core bear three terminal ligands. The molecular symmetry approximates to C_s-m, with the mirror plane including the capping Os-atom and the P-atom and bisecting one of the octahedron equators. Deviation from this idealized symmetry is shown by the OMe groups.

An appreciable "swelling" of the whole metal cluster seems to accompany the replacement of one CO group from 1 by the $P(OMe)_3$ ligand, as can be seen from a comparison of the average Os–Os bond lengths within the octahedral core in 5 and 1 [2.870(2), 2.854(6) Å, respectively] and between those involving the outer Os-atom [2.866(2), 2.819(6) Å, respectively]. This effect can be accounted for in terms of the weaker π-acceptor ability of the $P(OMe)_3$ ligand with respect to CO, which results in an increased accumulation of electron density on the metal core, and in longer M–M bonds. This inference is to some extent substantiated by the fact that whereas in 1 Os–Os bonds involving the capping atom are, on the average, shorter than those within the Os_6-core (see above), in 5 almost identical values are observed. Nonetheless, in both species the capped triangular face is smaller than the opposite one [mean 2.850(2), 2.905(2); 2.835(6), 2.902(6) Å, in 5 and 1, respectively]. Unfortunately, the differences in Os–C and C–O distances between 5 and 1 [mean 1.85(4), 1.18(6); 1.89, 1.15 Å, respectively] cannot be used to support these considerations because of the systematic error [4] introduced into the CO structural parameters arising from the fact that fully anisotropic treatment of the C and O-atom thermal motion is prevented in both species by the poor quality of the X-ray data *.

Structural parameters involving the $P(OMe)_3$ ligand are within the values observed for other phosphito-substituted clusters. In particular, Os–P [2.27(1) Å], P–O [mean 1.58(3) Å] and O–C [mean 1.44(5) Å], in 5 can be compared with the values

---

* *Crystal data.* $C_{23}H_9O_{23}Os_7P$, $M = 2015.7$, monoclinic, space group $C2/c$, $a = 34.585(8)$, $b = 13.152(2)$, $c = 16.106(4)$ Å, $\beta = 101.74(2)°$, $U = 7172.9$ Å^3, $F(000) = 7021$, $Z = 8$, $D_{calcd} = 3.73$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.71069$ Å, μ(Mo-K_α) = 238.6 cm^{-1}. 6555 intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer by the $\omega/2\theta$ scan method, in the range $2 < \theta < 25°$. Final R value = 0.058, $R_w = 0.058$, for 3065 independent reflections $[I_o > 2\sigma(I_o)]$. Correction for decay under X-ray exposure (ca. 40%) and for absorption were applied, this latter by a combined use of azimuthal scanning of 6 high χ-reflections (transmission range 34-100%) and of the Walker and Stuart method [9] (correction range 0.6–1.0) once a complete structural model was obtained.

Because of the poor quality of the X-ray data only Os-atoms and the P-atom were allowed to vibrate anisotropically, while C-atoms and O-atoms were refined isotropically. The H-atoms of the methyl groups were added in calculated positions (C–H 1.08 Å) and refined "riding" on their respective C-atoms; a single isotropic thermal parameter was also refined [0.09(1) Å^2].

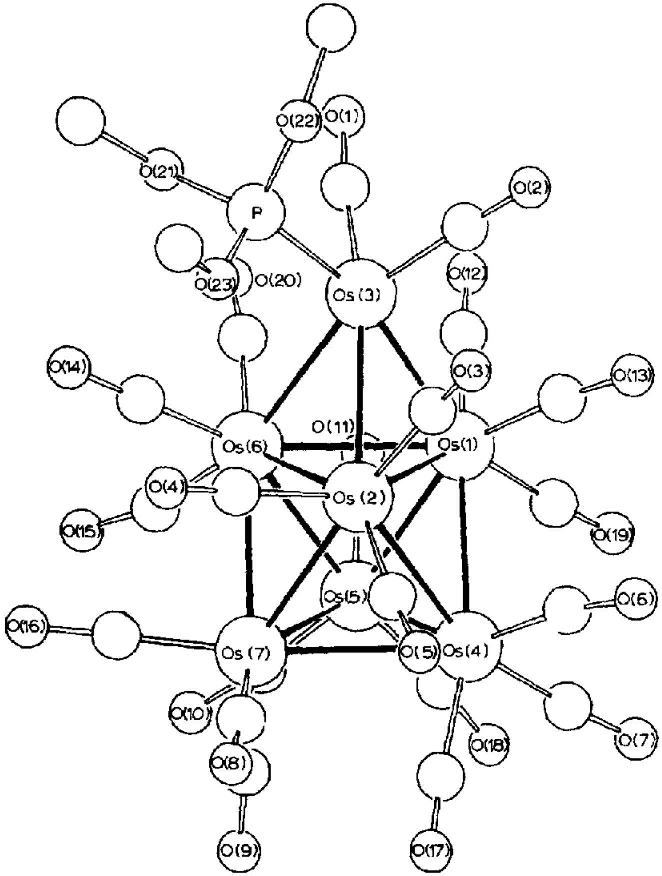

Fig. 1. The molecular structure of $[Os_7(CO)_{20}P(OMe)_3]$ (5). The C-atoms of the CO groups and of the $P(OMe)_3$ ligand bear the same numbering as the corresponding O-atoms. H-atoms of the methyl groups are omitted for clarity. Relevant bond distances and angles include: Os(2)–Os(1) 2.853(2), Os(3)–Os(1) 2.837(2), Os(4)–Os(1) 2.846(2), Os(5)–Os(1) 2.844(2), Os(6)–Os(1) 2.848(2), Os(3)–Os(2) 2.868(2), Os(4)–Os(2) 2.876(2), Os(6)–Os(2) 2.848(2), Os(7)–Os(2) 2.861(2), Os(6)–Os(3) 2.892(2), Os(5)–Os(4) 2.928(2), Os(7)–Os(4) 2.892(2) ,Os(7)–Os(5) 2.894(2), Os(7)–Os(6) 2.887(2), Os(6)–Os(5) 2.873(2); mean $Os–C_{CO}$ 1.85(4); C–O 1.18(6); Os–P 2.27(1) Å; Os–C–O 173°.

reported for $[Os_6(CO)_{17}\{P(OMe)_3\}_4]$ [5] [mean Os–P 2.24(1) Å], $[Os_{10}C(CO)_{23}\{P(OMe)_3\}(\mu\text{-}I)_2]$ [6] [Os–P 2.25(1)Å], $[Os_{10}(CO)_{21}\{P(OMe)_3\}_4]$ [6] (two isomers) [mean Os–P 2.25(1), 2.30(1); mean P–O 1.56(3), 1.58(3) Å for the two isomers, respectively], $[Os_5(CO)_{16}\{P(OMe)_3\}_3]$ [7] [mean Os–P 2.27(2), mean P–O 1.59(9), mean O–C 1.48(9) Å], and $[Os_3(CO)_6\{P(OMe)_3\}_6]$ [8] [mean Os–P 2.237(7), mean P–O 1.61, mean O–C 1.42 Å].

Obviously the two clusters 1 and 5 are isoelectronic, and since they contain the same number of ligands of a similar type (i.e. simple two-electron donors) the observation that both possess the same monocapped octahedral geometries is in complete accord with our simple views of electron-counting procedures [3]. However, the results once again serve to emphasise the significant stereochemical demands placed on heptanuclear metal clusters by hydrido-ligands [3].

Acknowledgments. We thank prof. V. Bertolasi, University of Ferrara, for the use of the CAD4 diffractometer.

References

1 C.R. Eady, B.F.G. Johnson, J. Lewis, R. Mason, P.H. Hitchcock and K.M. Thomas, J. Chem. Soc., Commun., (1977) 385.

2 E.J. Ditzel, H.D. Holden, B.F.G. Johnson, J. Lewis, A. Saunders and M.J. Taylor, J. Chem. Soc., Chem. Commun., (1982) 1373.

3 B.F.G. Johnson, J. Lewis, M. McPartlin, J. Morris, G.L. Powell, P.R. Raithby and M.D. Vargas, J. Chem. Soc., Dalton Trans., (1986) 429.

4 D. Braga and T.F. Koetzle, J. Chem. Soc., Chem. Commun., (1987) 144.

5 R.J. Goudsmit, B.F.G. Johnson, J. Lewis, P.R. Raithby and K.H. Whitmire, J. Chem. Soc., Chem. Commun., (1982) 641.

6 R.J. Goudsmit, P.F. Jackson, B.F.G. Johnson, J. Lewis, W.J.H. Nelson, J. Puga, M.D. Vargas, D. Braga, K. Henrick, M. McPartlin and A. Sironi, J. Chem. Soc., Dalton Trans., (1985) 1795.

7 D.H. Farrar, B.F.G. Johnson, J. Lewis, P.R. Raithby and M.J. Rosales, J. Chem. Soc., Dalton Trans., (1982) 2051.

8 R.F. Alex, F.W.B. Einstein, R.H. Jones and R.K. Pomeroy, Inorg. Chem., 26 (1987) 3175.

9 N. Walker and D. Stuart, Acta Crystallogr., A39 (1983) 158.