Journal of Organometallic Chemistry, 335 (1987) C17–C19
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

A tris(alkyne)triosmium cluster with an open structure: crystal structure of $[Os_3(CO)_8(Me_2C_2)_3]$

Brian F.G. Johnson, Rajesh Khattar, Jack Lewis, and Paul R. Raithby
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain)

(Received September 4th, 1987)

Abstract

Reaction of $[Os_3(CO)_8(Me_2C_2)_2]$ with Me_2C_2 at 70 °C in toluene produces a tris(alkyne) substituted triosmium cluster, which has been shown crystallographically to contain a bent arrangement of osmium atoms. Two of the alkyne units are linked via a carbon–carbon bond to produce an osmacyclopentadiene ring, while the third alkyne unit remains independently coordinated to the cluster via two π-bonds.

Thermal reaction of $[M_3(CO)_{12}]$ ($M = Fe$, Ru or Os) with alkynes is often accompanied by carbon–carbon bond formation resulting from the coupling of two or more alkynes [1]. For the iron and ruthenium clusters this carbon–carbon bond formation is accompanied by the cleavage of a metal–metal edge. In the case of the osmium cluster, where the metal–metal bonds are stronger, edge cleavage has not been observed, but ligand fragmentation may occur. We have recently shown that it is possible to coordinate more than one alkyne ligand to a triosmium framework under mild conditions by labilising the starting clusters with MeCN ligands [2]. The major product under these conditions is $[Os_3(CO)_8(R_2C_2)_2]$ (**1**), in which the triangular metal framework is retained, and the alkylenic ligands coordinate as independent units. We now report that mild thermolysis of **1**, in the presence of excess alkyne results in metal–metal edge cleavage as well as carbon–carbon bond formation, contrasting with the behaviour of the parent carbonyl under thermolysis conditions, and affords the cluster $[Os_3(CO)_8(R_2C_2)_3]$ (**3**), which has an open metal framework.

It is known that in toluene at 80 °C the cluster $[Os_3(CO)_8(Me_2C_2)_2]$ (**1**), which has a closed triangular metal framework, promotes carbon–carbon bond formation, and this followed by the scavenging of a carbonyl ligand affords $[Os_3(CO)_9(Me_4C_4)]$ (**2**) [2]. The cluster **2** contains a triangular metal skeleton with two dimethylacetylene ligands which are linked via a carbon–carbon bond to produce an osmacyclopentadiene ring [3]. We have now found that if the pyrolysis of **1** is carried out in the presence of an excess of dimethylacetylene in the same solvent at 70 °C, a tris(al-

0022-328X/87/$03.50

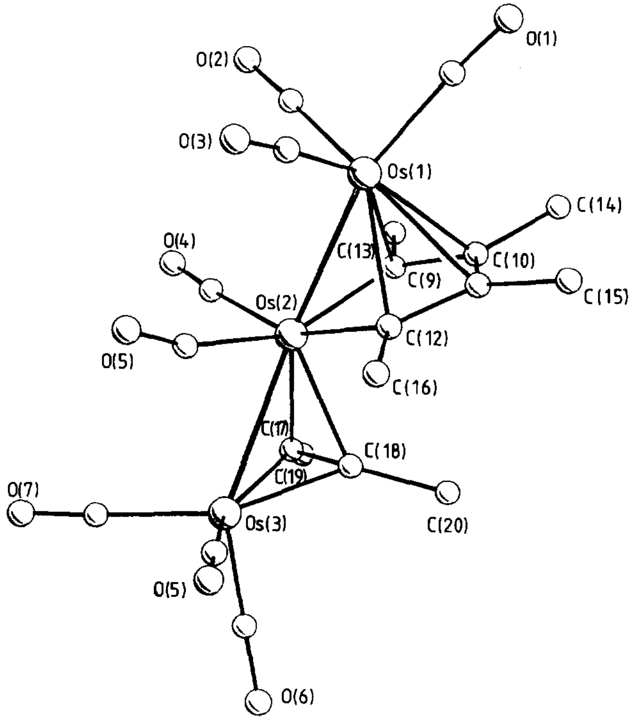

Fig. 1. The molecular structure of $[Os_3(CO)_8(Me_2C_2)_3]$ (3). Bond lengths (dimensions for the second independent molecule are given in square brackets): Os(2)–Os(1), 2.733(1) [2.736(1)]; Os(3)–Os(2), 2.812(1) [2.811(1)]; C(9)–Os(1), 2.32(2) [2.33(2)]; C(10)–Os(1), 2.31(2) [2.25(2)]; C(11)–Os(1), 2.30(2) [2.33(3)]; C(12)–Os(1), 2.30(2) [2.31(2)]; C(9)–Os(2), 2.04(2) [2.11(2)]; C(12)–Os(2), 2.09(2) [2.08(2)]; C(17)–Os(2), 2.22(2) [2.20(2)]; C(18)–Os(2), 2.17(2) [2.22(2)]; C(17)–Os(3), 2.11(2) [2.06(3)]; C(18)–Os(3), 2.06(2) [2.07(2)] Å; bond angles: Os(3)–Os(2)–Os(1), 151.9(1) [153.1(1)]°.

kyne) cluster with a formulation $[Os_3(CO)_8(Me_2C_2)_3]$ (3) is obtained in 40% yield. The complex 3 has been fully characterised spectroscopically *. In order to establish its geometry, a single crystal structure analysis was undertaken.

The crystal structure of 3 contains two independent but structurally similar molecules per asymmetric unit. The structure ** of 3 is shown in Fig. 1, which also includes some important bond parameters. In each molecule the three osmium

---

* Spectroscopic data (IR in CH_2Cl_2, ^1H NMR in $CDCl_3$): $\nu(CO)$: 2080s, 2044vs, 2017s, 2003s, 1953s,br and 1905w cm^{-1}; M^+: m/z 962; ^1H NMR: δ 2.51(s, 6H), 2.42(s, 6H), 2.39(s, 6H). No change in ^1H NMR spectrum was observed on cooling to $-60\,°C$.

** Crystal data for 3: $C_{20}H_{18}O_8Os_3$, $M = 956.94$, monoclinic, space group $P\,2_1/a$ (alt. $P\,2_1/c$, No. 14), a 17.517(3), b 10.118(1), c 26.428(3) Å, β 92.69(2)°, V 4678.8 Å^3, $Z = 8$, D_c 2.716 g cm^{-3}, λ(Mo-K_α) 0.71069 Å, μ(Mo-K_α) 162.85 cm^{-1}, F (000) 3440. 9431 Intensities measured ($5 \leq 2\theta \leq 45°$) on a Stoe-Siemens four circle diffractometer. Structure solved by a combination of direct methods and Fourier difference techniques, and refined by blocked full-matrix least-squares to $R = 0.055$ and $R_w = 0.055$ for 4348 unique observed reflections [$F > 4\sigma(F)$]. The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by the full literature citation.

atoms define a bent arrangement. Two of the dimethylacetylene ligands have undergone carbon–carbon bond formation to produce an organic ligand containing a chain of four carbon atoms. This organic ligand forms two π-bonds to Os(1) and two σ-bonds to Os(2), thereby forming an osmacyclopentadiene ring. The C(10)–C(11) bond of an osmacyclic ring lies almost perpendicular to the Os(1)–Os(2) edge. A similar type of bonding mode has been previously observed in $[Os_3(CO)_7(Ph_2C_2)_3]$ [4]. The third alkyne unit forms a π-bond each to the Os(2) and Os(3) atoms and the C(17)–C(18) bond lies approximately perpendicular to the Os(2)–Os(3) edge. The alkylenic ligands in this molecule adopt a coordination arrangement similar to that recently observed in the mixed-metal cluster $[Co_2W(CO)_8(\mu\text{-}C_4Et_4)(\mu\text{-}C_2Et_2)]$ [5]. Seven of the eight carbonyl ligands are terminally bound to the Os atoms, but the eighth [C(5)O(5)] forms an incipient bridge to Os(3) (Os(3) ··· C(5), 2.69(2) [2.68(2)] Å). This reflects the formal electron imbalance within the metal framework; Os(1) is formally associated with 19 electrons, Os(2) is associated with 18 electrons, and Os(3) is electron-poor, with only 17 electrons. Overall, however, the alkyne ligands donate a total of ten electrons to the cluster unit, and in terms of electron counting the complex **3** is a 50 electron cluster, consistent with the presence of two metal–metal bonds.

Clusters with an open structure are rare in triosmium chemistry. Other crystallographically characterised triosmium clusters with an open structure are $[Os_3(CO)_{12}I_2]$ [6], $[Os_3(CO)_{12}(SiCl_3)_2]$ [7], $[Os_3(CO)_9E_2]$ [8,9] (E = S or Se), $[Os_3H(CO)_{10}(PEt_3)(CF_3CCHCF_3)]$ [10], $[CpOs_3(CO)_{10}Cl]$ [11], and $[Os_3(CO)_9(PhC_2)_2]$ [12]. To our knowledge, the cluster **3** is the first structurally authenticated example of an alkyne substituted triosmium cluster with an open structure.

Acknowledgements. We thank the Nehru Trust, the Cambridge Commonwealth Trust, and the Committee of Vice-Chancellors and Principals for financial support (to R.K.) and Johnson Matthey PLC is for the generous loan of OsO_4.

References

1 R.P. Dodge and V. Schomaker, J. Organomet. Chem., 3 (1965) 274; G. Cetini, O. Gambino, E. Sappa and M. Valle, Atti. Acad. Sci., Torino, 101 (1967) 813; G. Cetini, O. Gambino, E. Sappa, and M. Valle, J. Organomet. Chem., 17 (1969) 437; R.P. Ferrari, G.A. Vaglio, O. Gambino, and G. Cetini, J. Chem. Soc., Dalton Trans., (1972) 1998.; G. Ferraris and G. Gervasio, J. Chem. Soc., Dalton Trans., (1972) 1057.
2 B.F.G. Johnson, R. Khattar, F.J. Lahoz, J. Lewis, and P.R. Raithby, J. Organomet. Chem., 319 (1987) C51.
3 G. Ferraris and G. Gervasio, J. Chem. Soc., Dalton Trans., (1974) 1813.
4 G. Ferraris and G. Gervasio, J. Chem. Soc., Dalton Trans., (1973) 1933.
5 L.J. Farrugia and M.J. Went, J. Chem. Soc., Chem. Commun., (1987) 973.
6 N. Cook, L. Smart and P. Woodward, J. Chem. Soc., Dalton Trans., (1977) 1744.
7 A.C. Willis, G.N. van Buuren, R.K. Pomeroy and F.W.B. Einstein, Inorg. Chem., 22 (1983) 1162.
8 R.D. Adams, I.T. Horvâth, B.E. Segmüller, and L.-W. Yang, Organometallics, 2 (1983) 144.
9 B.F.G. Johnson, J. Lewis, P.G. Lodge, and P.R. Raithby, Acta Crystallogr., B37 (1981) 1731.
10 Z. Dawoodi, M.J. Mays, and P.R. Raithby, J. Chem. Soc., Chem. Commun., (1979) 721.
11 M.A. Gallop, B.F.G. Johnson, J. Lewis, and P.R. Raithby, J. Chem. Soc., Chem. Commun., (1986) 706.
12 A.J. Deeming, M.S.B. Felix, P.A. Bates, and M.B. Hursthouse, J. Chem. Soc., Chem. Commun., (1987) 461.