Journal of Organometallic Chemistry, *444* (1993) C55–C56

JOM 23254PC

Preliminary Communication

Synthesis and X-ray structure of the octaosmium carbido cluster $Os_8C(CO)_{22}$

Angelo J. Amoroso, Brian F.G. Johnson, Jack Lewis, Chi-Keung Li, Paul R. Raithby and Wing-Tak Wong

University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (UK)

(Received September 14, 1992)

Abstract

Solid state vacuum pyrolysis of $Os_3H_3(CO)_9(\mu_3\text{-COMe})$ (**1**) gives the dark purple octanuclear carbido cluster $Os_8C(CO)_{22}$ (**2**) in *ca.* 15% yield. An X-ray analysis of **2** shows that the carbido-carbon is encapsulated in a trigonal prismatic cavity within the metal core.

Previous work from our group on the vacuum pyrolysis of $Os_3(CO)_{12}$ at high temperatures has indicated that one of the products is a deep purple compound which is obtained in very low yield (less than 5%). This product was formulated as $Os_8C(CO)_{22}$ on the basis of IR and EI mass spectroscopy [1]. Unfortunately, the full characterisation of the compound was hindered by the availability of the material and lack of good quality single crystals suitable for X-ray diffraction studies. Here we report a more reliable alternative synthetic route and re-examination of this compound.

We have been examining the use of $Os_3H_3(CO)_9(\mu_3\text{-COMe})$ as a potential source of carbido complexes, since cleavage of the C–O bond in the μ_3-COMe group would provide a reactive carbide. The vacuum pyrolysis of $Os_3H_3(CO)_9(\mu_3\text{-COMe})$ at 240°C for 12 h affords a range of compounds, including $Os_4H_4(CO)_{12}$ (12%), $Os_6(CO)_{18}$ (10%), $Os_7H_2C(CO)_{19}$ (50%), $Os_8C(CO)_{22}$ (15%), $Os_{10}H_2C(CO)_{24}$ (3%) and together with other uncharacterised products in low yield. After chromatographic separation on silica, $Os_8C(CO)_{22}$ (**2**) has been characterised by spectroscopic methods * (IR, FAB MS, ^{1}H NMR and ^{13}C NMR) and by a single crystal X-ray structure analysis **. It is noteworthy that the identification of the true molecular ion of **2** by mass spectrometry is difficult. The Electron Impact (EI) technique always shows the $[Os_8C(CO)_{21}]^+$ as the molecular ion. The Fast Atom Bombardment (FAB) gives the true molecular ion at m/z 2149 $\{Os_8C(CO)_{22}\}$ for the same batch of sample. In all cases the $[Os_8C(CO)_{21}]^+$ is the most intense ion fragment. There is no hydride signal in the range of δ −40 to 0. ^{13}C NMR of a ^{13}C enriched sample (*ca.* 20% enrichment) in CD_2Cl_2 at room temperature reveals a carbido carbon resonance at δ 377.1 and signals due to coordinated CO ligands in the range δ 160–196. However, the interpretation based on the observed solid state structure is difficult due to the decomposition of the product in solution.

The molecular structure of **2**, together with some important bond parameters, is shown in Fig. 1. The metal core may be described as a monocapped trigonal prism fused with a tetrahedron, sharing a common trigonal face. The carbido atom is approximately in the centre of the trigonal prism defined by Os(1), Os(2), Os(3), Os(4), Os(5) and Os(6), with average Os–C(carbido) distance 2.17(2) Å. The sixteen Os–Os distances are in the range 2.69–3.01 Å with a mean of 2.83 Å. An interesting observation in the interbasal distances in the prism decrease as the metal connectivity increases [Os(5)–Os(6), 2.974(3) Å for 3 M–M contacts; Os(1)–Os(2), 2.841(3) Å for 4 M–M; Os(3)–Os(4), 2.771(3) Å for 5 M–M]. This metal connectivity dependance is also apparent in the square-based pyramid [Os(1)–Os(7) and Os(2)–Os(7), 2.902(3) Å; Os(3)–Os(7)

Correspondence to: Professor The Lord Lewis.

* Spectroscopic data for **2**: IR ν(CO) (CH_2Cl_2): 2119w, 2089m, 2071s, 2042w, br, 2030m, 2019m cm^{-1}. FAB MS: M$^+$ (obs) m/z 2149 (calc), 2150. ^{13}C NMR (CD_2Cl_2): δ 377.1 carbide.

** Crystal data for **2**: $[Os_8C(CO)_{22}]\cdot CH_2Cl_2$, $C_{24}H_2O_{22}Cl_2Os_8$, $M = 2149.6$ (2234.8 including CH_2Cl_2), monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$ No. 14), $a = 17.653(7)$, $b = 11.183(3)$, $c = 19.273(5)$ Å, $\beta = 106.87(2)°$, $V = 3641(2)$ Å^3, $Z = 4$, $D_c = 4.077$ g cm^{-3}, $F(000) = 3856$, Mo K$_\alpha$ radiation, $\lambda = 0.71069$ Å, μ(Mo Kα) = 280.78 cm^{-1}, 2786 observed diffractometer data $[F > 3\sigma(F)]$. Structure solved by direct methods and Fourier difference techniques, refined by full-matrix least-squares analysis (Os atom anisotropic) to $R = 0.075$, $R_w = 0.073$. Atomic coordinates, bond lengths and angles, and the thermal parameters for **2** have been deposited at the Cambridge Crystallographic Data Centre.

0022-328X/93/$6.00

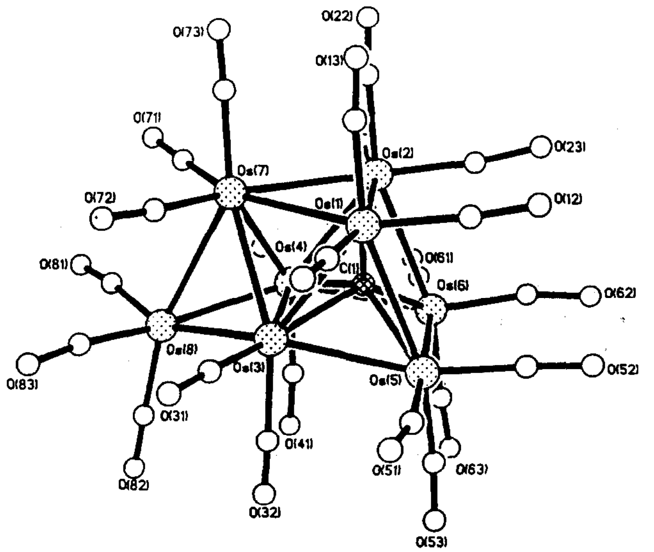
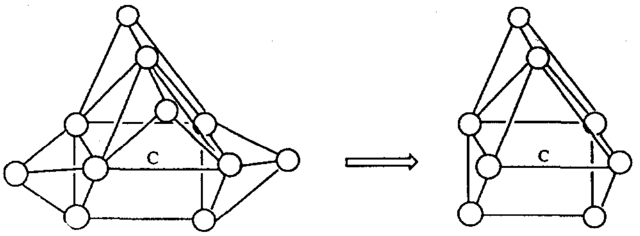


Fig. 1. The molecular structure of $[Os_8C(CO)_{22}]$ (**2**) showing the atom numbering scheme. Bond lengths (Å): Os(1)–Os(2), 2.841(4); Os(1)–Os(5), 2.971(3); Os(2)–Os(4), 2.767(3); Os(2)–Os(7), 2.920(4); Os(3)–Os(5), 2.759(3); Os(3)–Os(8), 2.695(3); Os(4)–Os(7), 2.804(3); Os(5)–Os(6), 2.974(3); Os(1)–C(1), 2.18(4); Os(3)–C(1), 2.15(5); Os(5)–C(1), 2.16(4); Os(1)–Os(3), 2.763(3); Os(1)–Os(7), 2.920(3); Os(2)–Os(6), 2.927(3); Os(3)–Os(4), 2.771(3); Os(3)–Os(7), 2.803(3); Os(4)–Os(6), 2.749(3); Os(4)–Os(8), 2.692(3); Os(7)–Os(8), 3.006(3); Os(2)–C(1), 2.18(4); Os(4)–C(1), 2.15(3); Os(6)–C(1), 2.18(5). Bond angles (°): Os(1)–C(1)–Os(2), 81(1); Os(2)–C(1)–Os(3), 131(2); Os(2)–C(1)–Os(4), 79(1); Os(1)–C(1)–Os(5), 84(1); Os(3)–C(1)–Os(5), 80(1); Os(1)–C(1)–Os(6), 143(2); Os(3)–C(1)–Os(6), 134(2); Os(5)–C(1)–Os(6), 86(1); Os(1)–C(1)–Os(3), 79(2); Os(1)–C(1)–Os(4), 131(2); Os(3)–C(1)–Os(4), 80(1); Os(2)–C(1)–Os(5), 142(2); Os(4)–C(1)–Os(5), 134(2); Os(2)–C(1)–Os(6), 84(2); Os(4)–C(1)–Os(6), 79(1).



$[Os_{11}C(CO)_{27}]^{2-}$ $[Os_8C(CO)_{22}]$

Fig. 2. Structural comparison of the dianion $[Os_{11}C(CO)_{27}]^{2-}$ and $[Os_8C(CO)_{22}]$.

and Os(4)–Os(7), 2.804(3) Å]. A structurally very similar compound, $Rh_8C(CO)_{19}$ has been reported to have a monocapped trigonal prism, plus one edge-bridging atom [2]. However, no apparent correlation between bond distances and coordination numbers or metal connectivity can be established in this structure. The Os(8) atom asymmetrically caps one triangular face of the square-based pyramid with one long and two short bonds [3.006(3) Å and 2.692(3) Å, 2.695(3) Å]. Similar asymmetric capping $Os(CO)_3$ groups can be found in the $[Os_9H(CO)_{24}]^-$ anion [3]. The molecule of **2** possesses an approximately C_s symmetry. All 22 carbonyl ligands are terminally bonded and all bond parameters are within the expected ranges. The complex **2** can be considered to be derived from $[Os_{11}C(CO)_{27}]^{2-}$ by the removal of three $Os(CO)_3$ capping groups as shown in Fig. 2. However, the high e.s.d.s of bond parameters in the structure of the $[Os_{11}C(CO)_{27}]^{2-}$ precludes meaningful comparison of bond parameters between the two compounds [4].

Acknowledgements

We thank the Royal Commisson for the Exhibition of 1851, the committee of Vice-Chancellors and Principals (W.T.W.), SERC (A.J.A.) and the Croucher Foundation (C.K.L.) for financial support.

References

1 C. R. Eady, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.* (1975) 2606.

2 V. G. Albano, M. Sansoni, P. Chini, S. Martinengo and D. Strumolo, *J. Chem. Soc., Dalton Trans.* (1975) 305.

3 A. J. Amoroso, B. F. G. Johnson, J. Lewis, P. R. Raithby and W.-T. Wong, *J. Chem. Soc., Chem. Commun.* (1991) 814.

4 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.