Journal of Organometallic Chemistry, 249 (1983) C21—C24
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

THE SYNTHESIS AND X-RAY ANALYSIS OF $HOs_8(CO)_{22}I$

BRIAN F.G. JOHNSON, JACK LEWIS*, WILLIAM J.H. NELSON, MARIA 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 March 14th, 1983)

Summary

The hydrido-monoanion $[HOs_8(CO)_{22}]^-$ reacts reversibly with iodine to give the neutral species $HOs_8(CO)_{22}I$ (I); X-ray analysis of I has shown that the reaction is accompanied by an unprecedented change in overall cluster geometry.

The neutral cluster compound $HOs_8(CO)_{22}I$ (I) has been prepared quantitatively by reaction of the hydrido-anion $[HOs_8(CO)_{22}]^-$(II) with a stoichiometric amount of iodine in CH_2Cl_2 (eq. 1). The reaction is rapid and no evidence of any

$$[HOs_8(CO)_{22}]^- + I_2 \longrightarrow HOs_8(CO)_{22}I + I^- \qquad (1)$$

other species has been detected spectroscopically. With an excess of I^- the reverse reaction occurs, and the monoanion $[HOs_8(CO)_{22}]^-$ is regenerated.

X-ray analysis shows that the cluster I* has the structure shown in Fig. 1. Unexpectedly, although the usual I-bridged "butterfly" Os_4 unit produced in this type of reaction is present, there is no simple relationship between the overall cluster geometry of I and that found for the monoanion II (Fig. 2a) in the solid state [1]. However the metal arrangement in I has retained a basic unit similar to the Os_6 core of $Os_6(CO)_{18}$ attached to which are two edge bridging metal atoms Os(7) and Os(8). A μ-I ligand links Os(8) and Os(1), the "wingtips" of the "butterfly" metal arrangement on the cluster surface (Os(1), Os(4), Os(6), and Os(8)).

---

* Crystal data I: $C_{22}HIO_{22}\cdot H_2O$, $M = 2283.75$, Monoclinic, space group $P2_1/c$, a 14.386(2), b 11.037(1), c 24.629(3) Å, β 94.30(2)°, $Z = 4$, V 3899.54 $Å^3$, D_c 3.89 g cm^{-3}, $I/\sigma(I) \geq 3.0$, present R factor 0.0569 for 4644 reflections corrected for absorption (μ(Mo-K_α) 257.68 cm^{-1}). Data were collected on a Philips PW1100 diffractometer in the θ-range 3—20°.

0022-328X/83/$03.00 © 1983 Elsevier Sequoia S.A.

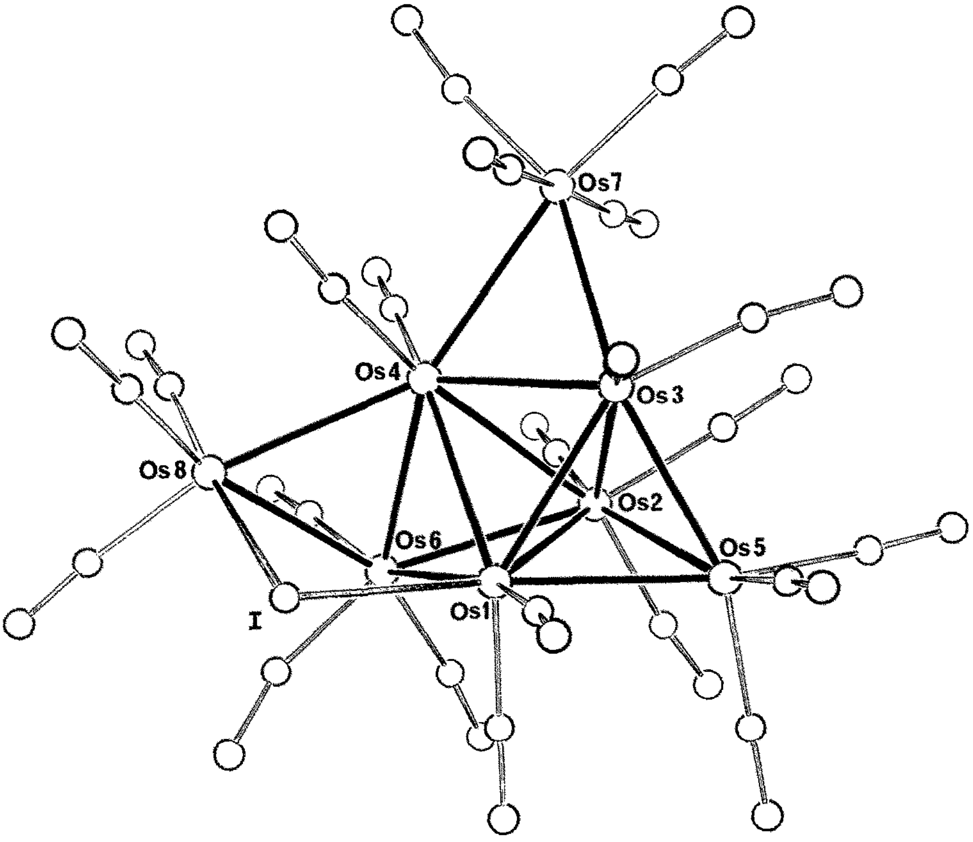

Fig. 1. The structure of the $HIOs_8(CO)_{22}$ cluster. Important bond lengths (Å) are: Os—Os: (1)—(2) 2.764, (1)—(3) 2.803, (1)—(4) 2.868, (1)—(5) 2.795, (1)—(6) 2.814, (2)—(3) 2.894, (2)—(4) 2.868, (2)—(5) 2.890, (2)—(6) 2.800, (3)—(4) 2.699, (3)—(5) 2.695, (3)—(7) 2.742, (4)—(6) 2.782, (4)—(7) 2.904, (4)—(8) 2.882, (6)—(8) 2.870, maximum e.s.d. 0.002 Å; Os(1)—I 2.753(2), Os(8)—I 2.736(2).

The hydrogen ligand was not detected in the X-ray analysis and it proved unusually difficult to locate by the indirect methods which were found successful in the past [1,3]. Computer diagrams of space-filling models [4] of the molecule revealed only one "hole" in the close-packed surface ligands corresponding to the H-ligand being located in an asymmetric μ_3-site above the face Os(1)—Os(3)—Os(4), which surprisingly has rather short bond lengths (Os—Os 2.699—2.868 Å).

The apparently massive rearrangement of the metal core and ligands required to go from the structure (Fig. 2a) previously revealed by X-ray analysis for II to that (Fig. 2b) found for I, is without precedent for the reaction of a higher cluster with iodine. We believe that the greater flexibility observed in these Os_8 systems compared to the Os_{10} systems is related to the fact that no interstitial carbide atom is present to "bind" the metal core together. Consistent with this idea we have found that the dianion $[Os_8(CO)_{22}]^{2-}$, which has a bicapped octahedral metal geometry [5], is broken down on reaction with iodine [6]. The metal core geometry in I shows a strong resemblance to that recently found for

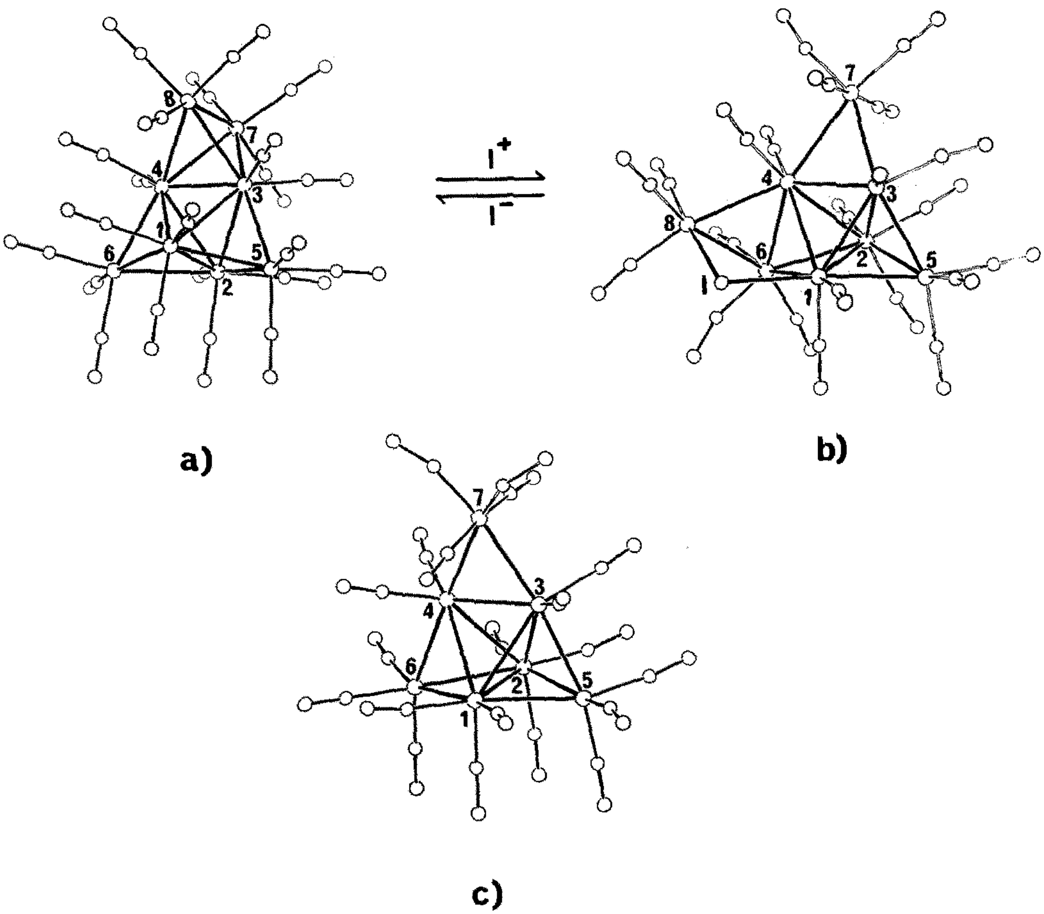

Fig. 2. Comparison of the structures of (a) $[HOs_8(CO)_{22}]^-$ [5], (b) $HOs_8(CO)_{22}I$, and (c) $H_2Os_7(CO)_{20}$ [7].

$H_2Os_7(CO)_{20}$ which is shown in Fig. 2(c) [7]. "Butterfly" arrangements on cluster surfaces have been found several times [8] before but have always arisen from the simple opening of an M_4 tetrahedron in the cluster. The unusual geometries of $[HOs_8(CO)_{22}]^-$ and $HOs_8(CO)_{22}I$ and their ready interconversion (Fig. 2a and 2b) cannot be explained by current skeletal electron counting procedures [2,9] nor were they predicted by recent comprehensive cluster geometry analyses using molecular orbital calculations [10].

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.

References

1 D. Braga, K. Henrick, B.F.G. Johnson, J. Lewis, M. McPartlin, W.J.H. Nelson and M.D. Vargas, J. Chem. Soc., Chem. Commun., (1982) 419.
2 R. Mason, K.M. Thomas and D.M.P. Mingos, J. Am. Chem. Soc., 95 (1973) 3802.

3 M.R. Churchill and J. Wormald, J. Am. Chem. Soc., 93 (1971) 5670; M. McPartlin, C.R. Eady, B.F.G. Johnson and J. Lewis, J. Chem. Soc., Chem. Commun., (1976) 883; P.F. Jackson, B.F.G. Johnson, J. Lewis, M. McPartlin and W.J.H. Nelson, J. Chem. Soc., Chem. Commun., (1978) 920; R.G. Teller and R. Bau, Struct. Bonding (Berlin), 44 (1981) 1.

4 Schakal Program, E. Keller, University of Freiburg, 1978.

5 P.F. Jackson, B.F.G. Johnson, J. Lewis and P.R. Raithby, J. Chem. Soc., Chem. Commun., (1980) 60.

6 B.F.G. Johnson, J. Lewis and M.D. Vargas, unpublished results.

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

8 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; D. Braga, K. Henrick, B.F.G. Johnson, J. Lewis, M. McPartlin, W.J.H. Nelson, and J. Puga, ibid., (1982) 1083; G.R. Johns, B.F.G. Johnson, J. Lewis, W.J.H. Nelson and M. McPartlin, J. Organomet. Chem., 171 (1979) C14.

9 K. Wade, Adv. Inorg. Chem. Radiochem., 18 (1976) 1.

10 J.W. Lauher, J. Am. Chem. Soc., 100 (1978) 5305; J. Organomet. Chem., 213 (1981) 25; G. Ciani and A. Sironi, ibid., 197 (1980) 233.