Inorganica Chimica Acta, *89* (1984) L29–L30

Synthesis and Structural Characterization of a High Nuclearity Osmium–Platinum Cluster

CHRISTIANE COUTURE, DAVID H. FARRAR* and ROBERT J. GOUDSMIT

Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ont., Canada M5S 1A1

Received May 17, 1984

Reaction of $Os_6(CO)_{20}$ with $Pt(C_8H_{12})_2$ has resulted in the synthesis of $Os_6Pt_2(CO)_{17}(C_8H_{12})_2$. The structural features of this cluster have been determined by single crystal X-ray diffraction. The metal framework can be described as an octahedron of Os atoms with two face capping Pt atoms. The 1,5-cyclooctadiene ligands, bound to the capping Pt atoms, have been shown to be labile to substitution.

The interest in mixed-metal cluster chemistry has led to a great diversity of synthetic approaches [1, 2]. Commonly these involve either ionic or unsaturated synthons. Herein we report the synthesis of a new high-nuclearity mixed-metal cluster where the loss of labile ligands by the starting materials facilitates metal–metal bond formation.

Treatment of a toluene/acetonitrile solution of $Os_6(CO)_{20}$ [3] with $Pt(C_8H_{12})_2$ [4] under ethylene results in the formation of a mixture of compounds. Product separation was achieved using thin-layer chromatography (t.l.c.) (0.25 mm Merck Kieselgel 60F) eluting with hexanes/CH_2Cl_2 (2:1). While many of the products were unstable we did isolate a deep purple complex (R_f = 0.34; IR(νCO) cm^{-1}, 2070m, 2033s, 2021 m(sh), 1978 w) in approximately 15% yield. Crystals of adequate mosaicity were finally obtained by slow evaporation of a CH_2Cl_2 solution and the complex was shown to be $Os_6Pt_2(CO)_{17}(C_8H_{12})_2$ by single crystal X-ray diffraction.

Crystal Data

$C_{33}H_{24}Os_6Pt_2O_{17}$, M = 2223.93, triclinic, space group $P\bar{1}$, a = 10.110(3) Å, b = 12.894(2) Å, c = 16.997(3) Å, α = 101.26(1)°, β = 97.29(2)°, γ = 95.60(2)°, V = 2138.3 Å^3, D_c = 3.45 g cm^{-3}, Z = 2, μ(MoK$\bar{\alpha}$) = 244.3 cm^{-1}.

The crystal system and approximate cell dimensions were determined from Weissenberg X-ray photographs. Intensity data were measured on an Enraf-Nonius CAD4 diffractometer. Three standard reflections, monitored every 2.8 hours during data collection, showed an average decrease in intensity of 32%. The recorded data were corrected for decomposition, Lorentz and polarization effects and a standard deviation σ(I) was assigned to each intensity (I), using the programs of the Enraf-Nonius SDP system [5]. An empirical absorption correction was applied to the data based on psi scans for seven reflections with varying 2θ values. Of the total reflections processed, 3709 unique data with $I > 3\sigma(I)$ were used in the solution and refinement of the structure.

Solution of the structure proved difficult and it was eventually solved in the space group P1 using the direct methods routines in the program SHELX [6]. The centre of symmetry was then located and the appropriate shift applied to the atom coordinates. The refinement of 137 variables (anisotropic thermal parameters for the eight metal atoms, and isotropic thermal parameters for the 50 ligand non-hydrogen atoms) converged at agreement factor R = 0.11 [6]. A new absorption correction was applied to the data using the Gaussian method (12 × 10 × 4 grid) [5]. Further refinement resulted in convergence at the residuals R = 0.089 and R_w = 0.093 with weights given by $w^{-1} = \sigma(F)^2 + 0.0009F^2$. We were unable to locate the cyclooctadiene hydrogen atoms in a difference Fourier synthesis. The poor quality of the structure is ascribed to that of the crystals and to crystal decomposition. All attempts to obtain single crystals of a more suitable mosaicity have failed.

Metal–metal distances are given in Table I and a perspective view of the cluster showing the atom numbering scheme is presented in Fig. 1. The molecule may be regarded as a regular octahedron of osmium atoms with two face-capping $Pt(C_8H_{12})$ units. The 17 carbonyl ligands are linear and terminal. The osmium atom with the highest metal connecti-

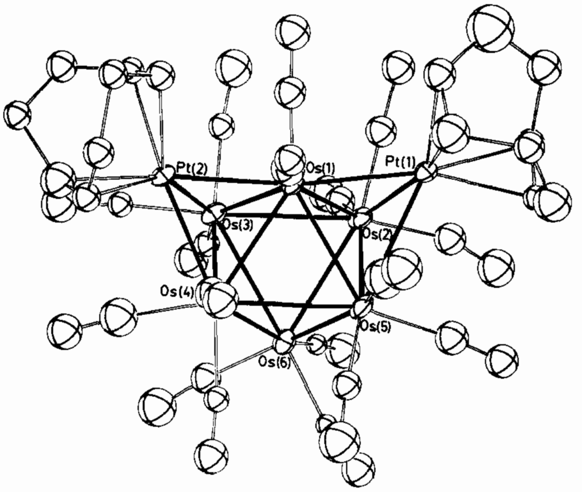

Fig. 1. Synthesis and structural characterization of a high nuclearity osmium-platinum cluster.

---

*Author to whom correspondence should be addressed.

0020-1693/84/$3.00

TABLE I.

Metals	Distance (Å)	Metals	Distance (Å)
Pt(1)–Os(1)	2.645(3)	Os(2)–Os(3)	2.922(3)
Pt(1)–Os(2)	2.787(4)	Os(2)–Os(5)	2.935(3)
Pt(1)–Os(5)	2.966(4)	Os(2)–Os(6)	2.875(4)
Pt(2)–Os(1)	2.659(3)	Os(3)–Os(4)	2.855(3)
Pt(2)–Os(3)	3.068(3)	Os(3)–Os(6)	2.909(3)
Pt(2)–Os(4)	2.762(3)		
Os(1)–Os(2)	2.783(3)	Os(4)–Os(5)	2.923(3)
		Os(4)–Os(6)	2.846(3)
Os(1)–Os(3)	2.815(4)		
Os(1)–Os(4)	2.788(4)	Os(5)–Os(6)	2.900(4)
Os(1)–Os(5)	2.796(3)		

vity, Os(1), has two carbonyl ligands bonded to it while the remaining osmium atoms each have three carbonyl ligands. Thus the osmium atoms are eight co-ordinate with the exception of Os(6) which is seven co-ordinate. Considering the olefinic groups of the 1,5-cyclooctadiene ligands as unidentate, two-electron ligands result in the platinum atoms being fomally five co-ordimate.

In terms of overall electron counting $Os_6Pt_2(CO)_{17}(C_8H_{12})$ is a 110-electron system, and the observed structure is in agreement with that proposed by Wade's skeletal electron counting scheme when extended to included clusters which have n metal atoms and n or (n – 1) skeletal electron pairs [7, 8]. The bicapped-octahedral cluster core geometry is the same as that found for the isoelectronic osmium cluster anion $[Os_8(CO)_{23}]^{2-}$ [9] and that postulated for the neutral cluster $Os_8(CO)_{23}$ [8]. This is somewhat unusual as mixed metal clusters containing PtL_2 fragments (where L is a two-electron ligand) tend to have fewer electrons than do their osmium analogues [10]. The fragment PtL_2 is in fact isolobal with $Os(CO)_4$ [11], not $Os(CO)_3$, and as such could be predicted to be edge-bridging rather than face-capping. Examination of the Pt–Os distances reveals that the platinum atoms are significantly closer to opposite edges of the octahedron (1–2 and 1–4) and not symmetrically capping the triangular faces, even assuming liberal bond errors due to the poor quality of the data.

Reaction of $Os_6Pt_2(CO)_{17}(C_8H_{12})_2$ with 1,2-diphenylphosphino-ethane (diphos) in CH_2Cl_2 at 25 °C affords $Os_6Pt_2(CO)_{17}(diphos)_2$ (IR(ν_{CO}) cm^{-1}, 2063m, 2025s, 2016m(sh), 1965w) where the bidentate phosphine ligands have replaced both cyclooctadiene groups. Thus while the cluster is structurally similar to $Os_8(CO)_{23}$ the lability to substitution associated with d^{10} Pt systems has been retained.

Acknowledgements

We thank the University of Toronto and the Natural Sciences and Engineering Council of Canada for operating and equipment grants, and Johnson Matthey and Co. Ltd. for their loan of Pt salts.

References

1 F. G. A. Stone, *Angew. Chem. Int. Ed. Engl., 23,* 89 (1984).
2 W. L. Gladfelter and G. L. Geoffrey, *Adv. Organomet. Chem., 18,* 207 (1980).
3 D. H. Farrar, B. F. G. Johnson, J. Lewis, J. N. Nicholls, P. R. Raithby and M. J. Rosales, *J. Chem. Soc., Chem. Comm.,* 273 (1981).
4 J. L. Spencer, *Inorg. Synth., 19,* 213 (1979).
5 Enraf-Nonius Structure Determination Package, SDP-PLUS, B. A. Frenz and Associates, College Station, TX, U.S.A.
6 G. Sheldrick, University of Cambridge, England, 1976.
7 K. Wade, *J. Chem. Soc., Chem. Comm.,* 792 (1971).
8 C. R. Eady, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.,* 2606 (1975).
9 P. F. Jackson, B. F. G. Johnson, J. Lewis and P. R. Raithby, *J. Chem. Soc., Chem. Comm.,* 60 (1980).
10 D. G. Evans and D. M. P. Mingos, *J. Organomet. Chem., 240,* 321 (1982).
11 R. Hoffmann, *Angew. Chem. Int. Ed. Engl., 21,* 711 (1982).