ELSEVIER

Journal of Organometallic Chemistry 489 (1995) C78–C80

Journal of Organometallic Chemistry

Preliminary communication

Synthesis and characterization of triosmium-dipalladium mixed-metal cluster. Crystal structure of $[\{(bipy)Pd\}_2Os_3(CO)_{12}]$

Suzanna Chan, Wing-Tak Wong *

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

Received 27 September 1994

Abstract

The cluster $[H_2Os_3(CO)_{10}]$ reacts with $[(bipy)Pd(CO_2Me)_2]$ to give $[\{(bipy)Pd\}_2Os_3(CO)_{12}]$, **1**, in moderate yield; an X-ray structure analysis of **1** reveals an edge bridging square metal core.

Keywords: Palladium; Osmium; Bipyridine; Carbonyl; Crystal structure

---

We are interested in the chemistry of osmium–palladium metal–metal bonded systems. Previously, we reported the reaction of $[(bipy)Pd(CO_2Me)_2]$ with $[Os_3(CO)_{10}(MeCN)_2]$ to give the novel complex $[Os_6Pd(CO)_{18}(bipy)]$ [1]. The compound has a closo metal framework consisting of an octahedron and a trigonal pyramid fused to one face. We now report the synthesis and characterization of another osmium–palladium cluster, $[\{(bipy)Pd\}_2Os_3(CO_{12}]$, **1**, which contains a rare open metal framework.

The complexes $[H_2Os_3(CO)_{10}]$ and $[(bipy)Pd(CO_2Me)_2]$ in 1 : 2 molar ratio were dissolved in CH_2Cl_2 (15 ml) and the solution was stirred under nitrogen. The reaction was monitored by IR spectroscopy. After 1.5 h of stirring at room temperature, the violet solution gradually changed to orange, and a red precipitate separated. The solution was taken to dryness in vacuo and the residue extracted with CH_2Cl_2 (2 × 10 ml) to remove most of the $[Os_3(CO)_{12},]$ and then with acetone (2 × 5 ml) to give a bright red solution of the title compound in 25% yield. The residue left behind, which was not identified, was brown in colour and poorly soluble in most organic solvents. The solid recovered from the acetone extract was recrystallized from acetone/chloroform at 0°C. Red rod-shaped crystals were obtained after a few days. The ^1H NMR spectrum of a solution of the product reveals the presence of bipy group but the absence of any metal hydride [2]. The IR spectrum shows a small hump at 1798 cm^{-1}, suggesting the presence of bridging carbonyl. Compound **1** is slightly air- and moisture-sensitive. In acetone solution it decomposes in air overnight to give $[Os_3(CO)_{12}]$ and a dark brown unidentified product. It decomposes on silica or alumina plates. Purification was performed by fractional crystallization. A single crystal suitable for X-ray analysis was chosen for determination of the molecular structure. A perspective view of **1** and some important bonding parameters are shown in Fig. 1.

Complex **1** crystallizes in the orthorhombic space group *F ddd* and the molecule possesses C_2 symmetry, with the two-fold axis passing through the apical Os(2) atom [3]. Half of the molecule is generated by the symmetry operation. The metal framework can be described as an isosceles triangle fused to a twisted rectangle, with one side shared. The maximum deviation of atoms from the best plane defined by the five metal atoms is 0.402 Å. Such an open structure is rare and resembles that of $[Ru_5(CO)_{14}(\mu_4\text{-}S)_2]$ [4] and $[Ru_5(CO)_{13}(\mu_4\text{-}PPh)(\mu_5\text{-}\eta^6\text{-}C_6H_4)]$ [5]. The molecule can be viewed as involving addition of two {(bipy)Pd} groups to the parent $[Os_3(CO)_{12}]$, with the daughter groups held by the bridging carbonyls. The supported Os–Pd bond length is 2.727(1) Å, which is comparable to the lengths of the unsupported Os–Pd bonds found

---

* Corresponding author.

Elsevier Science S.A.
SSDI 0022-328X(94)05281-6

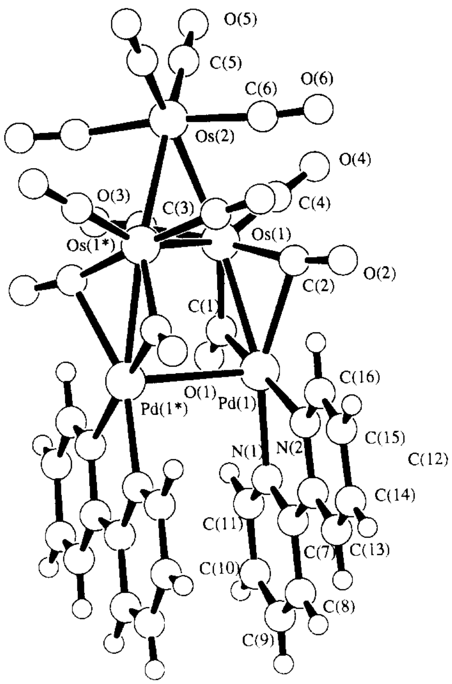

Fig. 1. Molecular structure of **1**, showing the atom numbering scheme, with selected bond distances (Å) and angles (°): Os(1)–Os(1*), 2.912(1); Os(1)–Os(2), 2.851(1); Os(1)–Pd(1), 2.727(1); Pd(1)–Pd(1*), 2.973(2); Os(1)–C(1), 2.02(2); Os(1)–C(2), 1.96(2); Pd(1)–C(1), 1.98(2); Pd(1)–C(2), 2.34(2); Pd(1)–N(1), 2.18(1); Pd(1)–N(2), 2.26(1); N(1)–C(7), 1.36(2); N(1)–C(11), 1.33(2); N(2)–C(12), 1.38(2); N(2)–C(16), 1.32(2); C(7)–C(8), 1.45(2); C(7)–C(12), 1.45(2); C(8)–C(9), 1.40(2); C(9)–C(10), 1.35(2); C(10)–C(11), 1.40(2); C(12)–C(13), 1.39(2); C(13)–C(14), 1.31(2); C(14)–C(15), 1.42(2); C(15)–C(16), 1.37(2). Os(1*)–Os(1)–Os(2), 59.3(1); Os(1)–Os(2)–Os(1*), 61.4(1) Os(1*)–Os(1)–Pd(1), 86.1(1); Os(1)–Pd(1)–Pd(1*), 84.9(1); Os(2)–Os(1)–Pd(1), 141.9(1); Os(1)–C(1)–O(1), 144(1); Os(1)–C(2)–O(2), 167(1); Pd(1)–C(1)–O(1), 129(1); Pd(1)–C(2)–O(2), 113(1); Os(1)–C(1)–Pd(1), 86.1(7); Os(1)–C(2)–Pd(1), 78.2(6); N(1)–Pd(1)–N(2), 75.6(5).

in [$Os_6Pd(CO)_{18}$(bipy)] (2.740(2)–2.808(2) Å) [1]. The Pd(II)–Pd(II) distance is 2.973(2) Å, which lies within the usual range for Pd(II)–Pd(II) bonds (2.950–3.311 Å) [6,7]. The shared Os(1)–Os(1*) edge of the polygons has a length of 2.912(1) Å, which is 0.061 Å longer than the other two Os–Os bonds in the Os triangle (cf. 2.877(2) Å in [$Os_3(CO)_{12}$] [8]). This may suggest an electron excess on the two osmium atoms. As in [$Ru_5(CO)_{14}(\mu_4\text{-}S)_2$] [4], dative metal–metal bonding is proposed for the Os–Pd bonds, with osmium as the electron donor. Under such condition, the osmium atoms have 19 electrons while the palladium atoms have 16 electrons, and this accounts for the weakening of the Os–Os bond. Such electronic imbalance condition is further reflected by the presence of incipient bridging carbonyls [9] C(2)–O(2) and C(2*)–O(2*), which are tilted slightly towards the palladium atoms [Os(1)–C(2)–O(2) = 167°, Pd(1)...C(2) = 2.34(2)Å] as in [$Ru_5(CO)_{14}(\mu_4\text{-}S)_2$] [4], and [$Os_7(\mu\text{-}H)_2C(CO)_{19}$] [10].

Alternatively, the relatively short Pd...Pd distance in **1** can be viewed as the result of the Pd linking to the Os–Os edge and the π-stacking of the bipy ligands. In this interpretation, there is no need for a Pd–Pd bond, and the compound has 76 valence electrons, with 5 formal metal–metal bonds, in accordance with Effective Atomic Number (EAN) rule.

The dihedral angle between the bipyridine group and the best plane formed by the five metal atoms is 68.4°. The atoms in the bipyridine groups are coplanar, with a maximum deviation of 0.06 Å. The bipyridine rings are seen to stack almost in parallel along the *c*-axis, with a dihedral angle of about 7° between the bipyridine groups within a molecule. The intramolecular separation of the bipyridine groups is 3.45 Å, while the intermolecular separation is 3.49 Å. These π–π stacking distances for the rings are comparable to those found in 4-pheny-1,2-dithia-3,5-diazolium bis-(maleonitrile-dithiolato)platium(II) [11] and 2-(4-pentanoyloxy-phenyl)-6-pentanolyloxybenzoxazole [12].

We thank the Hong Kong Research Grants Council, the University of Hong Kong, and the Croucher Foundation (S.C.) for financial support.

References and notes

[1] S. Chan and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, (1994) 1605.

[2] Spectroscopic data for 1: IR ν(CO) (CH_2Cl_2): 2081w, 2068m, 2035s, 2020s, 1998s, 1798br w cm^{-1}. ^1H nmr. (acetone-D_6): δ 7.57 (m, 1H), δ 7.92 (m, 1H), δ 8.06 (m, 2H), δ 8.30 (m, 1H), δ 8.49 (m, 2H), δ 9.14 (m, 1H). −ve FAB MS (with thioglycerol as matrix) *m/z* 1431 (1432 calcd.)

[3] Crystal data for **1**: $C_{32}H_{16}N_4O_{12}Pd_2Os_3$, $M = 1431.90$, orthorhombic, space group *Fddd* (No. 70), $a = 29.838(10)$, $b = 39.614(7)$, $c = 13.469(3)$Å, $U = 15920(15)$Å^3, $Z = 16$, $D_c = 2.389$gcm^{-3}, $F(000) = 10432$, Mo Kα radiation, $\lambda = 0.71069$Å, μ(Mo-Kα) = 104.84cm^{-1}, bright red rod of dimensions of 0.15 × 0.15 × 0.32 mm, 2856 unique data measured at 298 °C on a Rigaku AFC7R diffractometer ($2\theta_{max} = 45°$), absorption corrected by ψ-scan method, 1515 observed [$I > 3\sigma(I)$]. Structure solved by direct methods (SIR88) [13] and Fourier techniques (DIRDIF92) [14], refined by full-matrix least-squares analysis (Os and Pd anisotropic) to $R = 0.031$, $R_w = 0.028$, $w = 4Fo^2/[\sigma^2(Fo^2)]$; program used TEXSAN [15]. Atomic coordinates, thermal parameters and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

[4] R.D. Adams, J.E. Babin, and M. Tasi, *Inorg. Chem.*, *26* (1987) 2807.

[5] S.A.R. Knox, B.R. Lloyd, A.G. Orpen, J.M. Vinas and M. Weber, *J. Chem. Soc., Chem. Commun.*, (1987) 1498.

[6] M. Krumm, I. Mutikainen, and B. Lippert, *Inorg. Chem.*, *30* (1991) 884.

[7] A.J. Blake, A.J. Holder, Y.V. Roberts, and M. Schröder, *J. Chem. Soc., Chem. Commun.*, (1993) 260.

[8] E.R. Corey and L.F. Dahl, *Inorg. Chem.*, *1* (1962) 521.

[9] F.A. Cotton, *Prog. Inorg. Chem.*, *21* (1976) 1.

[10] A.J. Amoroso, B.F.G. Johnson, J. Lewis, P.R. Raithby, and W.-T. Wong, *J. Chem. Soc., Chem. Commun.*, (1990) 1209.

[11] W. Clegg and S.L. Birkby, *Acta Cryst. C50* (1994) 28.
[12] R. Centore, *Acta Cryst., C50* (1994) 260.
[13] SIR88: M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna and D. Viterbo, *J. Appl. Cryst., 22* (1989) 389.
[14] DIRDIF92: P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. Garcia-Granda, R.O. Gould, J.M.M. Smith and C. Smykalla, The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.
[15] TEXSAN: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 and 1992).