

### Preliminary communication

## A PLATINA-ALLENYL LIGAND COORDINATED TO A TRIOSMIUM CLUSTER: X-RAY STRUCTURE OF THE ACETYLIDE COMPLEX $\text{Os}_3\text{Pt}(\mu\text{-H})(\mu_4\text{-}\eta^2\text{-C}\equiv\text{CPh})(\text{CO})_{10}(\text{PCy}_3)$

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### Summary

The spiked triangular triosmium-platinum cluster complex  $\text{Os}_3\text{Pt}(\mu\text{-H})(\mu_4\text{-}\eta^2\text{-C}\equiv\text{CPh})(\text{CO})_{10}(\text{PCy}_3)$  has been synthesised by treatment of the unsaturated  $\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}(\text{PCy}_3)$  with  $\text{LiC}\equiv\text{CPh}$  followed by protonation. Crystallographic analysis reveals an unusual twisted configuration of the  $\mu_4\text{-}\eta^2\text{-C}\equiv\text{CPh}$  ligand about the triosmium framework such that the complex may be regarded as a platina-allenyl moiety coordinated to an  $\text{Os}_3(\mu\text{-H})(\text{CO})_9$  unit.

The  $58e^-$  unsaturated cluster compounds  $\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}(\text{PR}_3)$  (**1**) [1] have a tetrahedral platinum-triosmium framework, and have been shown to be highly reactive towards 2 electron donors L giving the  $60e^-$  adducts  $\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}(\text{PR}_3)(\text{L})$  [2]. These adducts either have a butterfly metal arrangement for  $\text{L} = \text{PPh}_3$ ,  $\text{R} = \text{Ph}$  [2a] and  $\text{L} = \text{CO}$ ,  $\text{R} = \text{Cy}$  ( $\text{Cy} = \text{cyclo-C}_6\text{H}_{11}$ ) [2b], or are tetrahedral  $\text{L} = 2\text{H}$ ,  $\text{R} = \text{Cy}$ , and  $\text{L} = \text{CH}_2$ ,  $\text{R} = \text{Cy}$  [2b]. In view of current interest in multisite cluster bound acetylene derived ligands [3] as models (both from a chemical reactivity [4] and theoretical perspective [5]) of adsorbed alkynes on transition metal surfaces [6], we were interested in synthesising derivatives of **1** with the  $2e^-$  donor acetylide anion  $\text{RC}\equiv\text{C}^-$ . Treatment of dark green **1a** ( $\text{R} = \text{Cy}$ ) with  $\text{PhC}\equiv\text{C}^- \text{Li}^+$  at  $-20^\circ\text{C}$  rapidly gave an orange solution. The nature of the initial (presumably anionic) products are still under investigation, but in the hope of obtaining neutral species the reaction mixture was treated with excess  $\text{CF}_3\text{COOH}$ . A yellow compound characterised as  $\text{Os}_3\text{Pt}(\mu\text{-H})(\mu_4\text{-}\eta^2\text{-C}\equiv\text{CPh})(\text{CO})_{10}(\text{PCy}_3)$  (**2**) was isolated in ca. 10% yield. Spectroscopic data for **2**;  $\nu(\text{CO})$  cyclohexane, 2086m, 2062s, 2042vs, 2022m, 1993m, 1964w  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR,  $\text{CDCl}_3$ ,  $\delta$  7.39–7.03 ( $\text{C}_6\text{H}_5$ , 5H), 1.75–0.88 ( $\text{C}_6\text{H}_{11}$ , 33H),  $-20.42$  ( $\text{Os}(\mu\text{-H})\text{Os}$ , 1H). An X-ray diffraction study

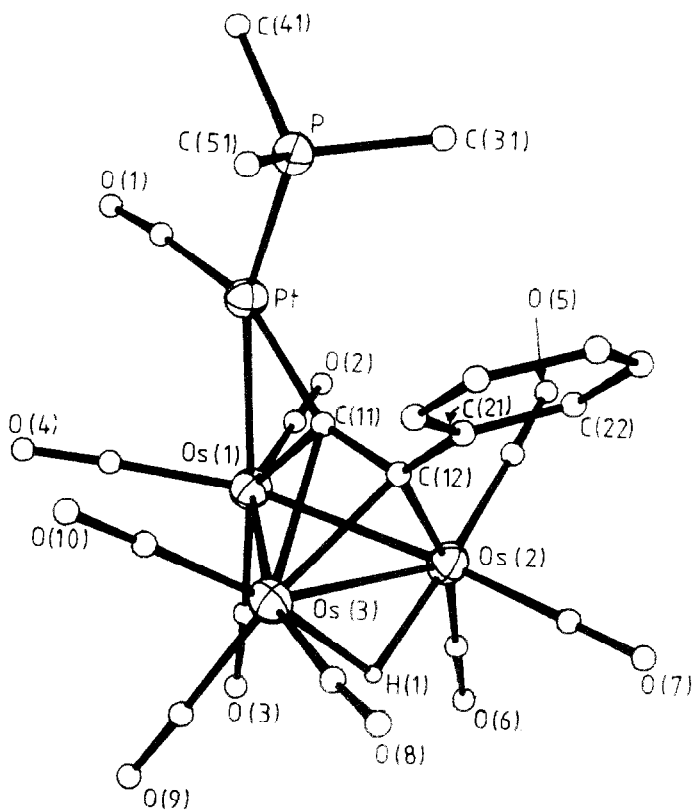


Fig. 1. Molecular structure of  $\text{Os}_3\text{Pt}(\mu\text{-H})(\mu_4\text{-}\eta^2\text{C}\equiv\text{CPh})(\text{CO})_{10}(\text{PCy}_3)$  (**2**). Important bond lengths and angles: Os(1)–Os(2) 2.845(1), Os(1)–Os(3) 2.824(1), Os(2)–Os(3) 2.838(1), Os(1)–Pt 2.712(1), C(11)–Pt 2.00(1), C(11)–Os(1) 2.15(1), C(11)–Os(2) 2.59(1), C(11)–Os(3) 2.40(1), C(11)–C(12) 1.34(1), C(12)–Os(2) 2.15(1), C(12)–Os(3) 2.23(1), Pt–P 2.328(3) Å; C(11)–C(12)–C(21) 128.6(9), Pt–C(11)–Os(1) 81.6(4), Os(1)–C(11)–Os(3) 76.6(3), Os(2)–C(12)–Os(3) 80.8(4), Pt–C(11)–C(12) 152.7(8), Os(1)–C(11)–C(12) 124.4(8)°. Cyclohexyl groups on P omitted for clarity, only contact carbons shown

was carried out to determine the detailed structure\*.

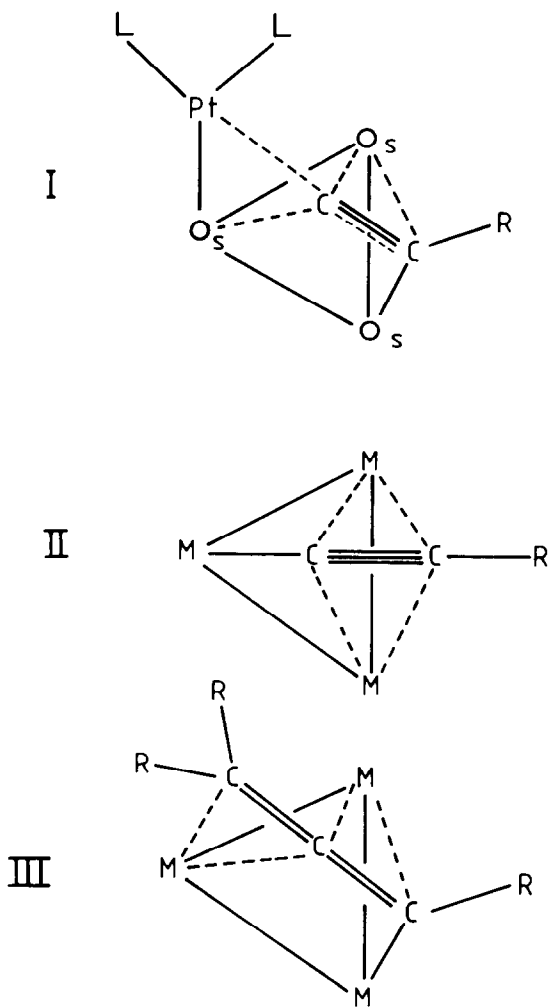
A view of **2** is shown in Fig. 1. The metal skeleton consists of an equilateral triosmium triangle, with a platinum atom coordinated in an axial position on Os(1) (angle between Pt–Os(1) and Os<sub>3</sub> triangle 101.7°) resulting in a spiked triangular

\* *Crystal data:*  $\text{C}_{36}\text{H}_{39}\text{O}_{10}\text{Os}_3\text{P}$ ,  $M = 1428.37$ , triclinic, space group  $P\bar{1}$  ( $C_1^1$  No. 2),  $a$  9.816(1),  $b$  11.414(2),  $c$  19.971(4) Å,  $\alpha$  76.14(2),  $\beta$  77.83(1),  $\gamma$  87.68(1)°,  $Z = 2$ ,  $V = 2123.5(6)$  Å<sup>3</sup>,  $D_c$  2.24 g cm<sup>-3</sup>,  $F(000) = 1312$ ,  $\mu(\text{Mo-K}\alpha) 123.6$  cm<sup>-1</sup>. The structure solution (Patterson, Fourier methods) and refinement (full matrix least squares, all non hydrogen atoms apart from disordered solvent molecule were anisotropic) was based on 5444 independent observed ( $I > 3\sigma(I)$ ) (10861 measured) reflections (Enraf–Nonius CAD4F diffractometer, max  $\theta$  25°). Final  $R$  and  $R_w$  values are 0.031 and 0.042.

Full listings of atomic coordinates, thermal parameters, bond lengths and angles for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. Tables of structure factors are available from the authors on request.

arrangement. The 62 electron count for **2** (assuming the  $\mu_4\text{-}\eta^2\text{C}\equiv\text{CPh}$  group is a  $5e^-$  donor) is consistent with a  $16e^-$  Pt atom, and a similar spiked geometry is observed in the complex  $\text{Os}_3\text{Pt}(\mu\text{-H})_2(\mu_4\text{-C})(\text{CO})_{10}(\text{PCy}_3)$  [7] also having 62 valence electrons.

Although the overall coordination mode of the  $\mu_4\text{-}\eta^2\text{C}\equiv\text{CPh}$  group in **2** is somewhat similar to that recently reported for the same ligand in  $\text{Fe}_2\text{Ni}_2(\mu\text{-PPh}_2)(\mu_4\text{-}\eta^2\text{C}\equiv\text{CPh})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)_2$  (**3**) [8], there are some notable differences. In particular the C(11)–C(12) vector is not perpendicular to the Os(2)–Os(3) axis but is twisted by  $10.0^\circ$ , so that the C(11)–Os(2) distance of  $2.59(1)\text{\AA}$  is ca.  $0.20\text{\AA}$  longer than the C(11)–Os(3) separation, and may be considered non-bonding (I). In cluster compounds containing the  $\mu_3\text{-C}\equiv\text{CR}$  ligand a symmetric  $\eta^2 (\perp)$  bonding mode (II) is usual [3a,9]. The  $\mu_4\text{-}\eta^2\text{-C}\equiv\text{CPh}$  group in complex **3** is bonded in a  $\mu_3\text{-}\eta^2 (\perp)$



fashion to the Fe<sub>2</sub>Ni triangle (angle between C–C axis and Ni(2)–Fe(2) vector 89.5° [8]). By contrast in the recently reported complex Ru<sub>5</sub>(μ-H)(μ-PPh<sub>2</sub>)(μ<sub>4</sub>-η<sup>2</sup>-C≡CPh)(CO)<sub>13</sub> the acetylide ligand may be described as μ<sub>3</sub>-η<sup>2</sup> (||) bonded to the Ru<sub>3</sub> triangle, since the intervector angle between C(14)–C(15) and Ru(1)–Ru(3) is 1.0° [10]. The geometry observed in **2** is intermediate with an intervector angle between C(11)–C(12) and Os(2)–Os(1) of 20.5°.

Since the fragment PtL<sub>2</sub> is isolobal with CH<sub>2</sub> [11], it may be profitable to view the PtL<sub>2</sub>C=CPh unit as a platina-allenyl moiety. In the complexes Ru<sub>3</sub>(μ-H){μ<sub>3</sub>-η<sup>3</sup>-CH(Me)=C=C(Et)}(CO)<sub>10</sub> (**4**) [12], and Ru<sub>3</sub>(μ-PPh<sub>2</sub>)<sub>3</sub>{μ<sub>3</sub>-η<sup>3</sup>-CH<sub>2</sub>=C=C(Pr<sup>i</sup>)}(CO)<sub>8</sub> [4a] the central carbon atom of the μ<sub>3</sub>-η<sup>3</sup>-allenyl ligand is only bonded to two metal atoms in the triangle (III), as appears to be the case for C(11) in complex **2**.

The C(11)–C(12) distance of 1.34(1) Å is slightly longer than the corresponding distance in **3**, (1.313(8) Å) [8], and somewhat shorter than observed in **4** (1.365(8) Å) [12], though due to high esd's little significance can be attributed to these values. The Pt–C(11) distance of 2.00(1) Å is similar to observed Pt–carbene separations [13] and is consistent with the above analogy.

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