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Preliminary communication

Synthesis and X-ray structure of $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_9(C_8H_{12})$: a 60 electron tetrahedral triosmium-platinum cluster containing a carbonyl bridging an Os–Os edge

Paul Ewing and Louis J. Farrugia *

Department of Chemistry, The University, Glasgow G12 8QQ (Great Britain)

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Abstract

The 60 electron cluster $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_9(COD)$ (**1**) has been synthesized in high yield by treatment of $Os_3(\mu\text{-}H)_2(CO)_{10}$ with $Ru_3Pt(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}C{\equiv}CBu^t)(CO)_9(COD)$, (COD = 1,5-cyclooctadiene). Crystallographic analysis reveals a *closo* tetrahedral metal framework, with a carbonyl group bridging an Os–Os edge. Complex **1** is also formed as one of the products in the reaction between $Os_3(\mu\text{-}H)_2(CO)_{10}$ and $Pt(COD)_2$.

The unsaturated tetrahedral triosmium-platinum clusters $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)$ (**1**) [1], which possess 58 cluster valence electrons, react readily [2,3] with 2-electron donor ligands L to give saturated 60-electron adducts $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)(L)$ (**2**). Depending on the nature of the donor ligand these adducts either have a *closo* tetrahedral metal core, e.g. for L = μ-CH_2 (**2a**) [3] or adopt an open butterfly arrangement for L = PPh_3 [2] or L = CO (**2b**) [3]. In an effort to understand this divergent behaviour we have recently carried out [4] extended Hückel MO calculations on the interactions of the unsaturated model complex tetrahedro-$[Ru_3Pt(CO)_{10}(PH_3)]^{2-}$ (I) with CO and CH_2. The HOMO and LUMO of I (of π and σ symmetry, respectively) provide a suitable symmetry match for the frontier orbitals of the CH_2 fragment. However interaction of I with CO in the same configuration (i.e. giving a μ-CO unit with a similar geometry to the μ-CH_2 found in **2a**) leaves one of the CO π^* orbitals essentially unperturbed. We thus reasoned that this "adduct" with a μ-CO would seek further stabilisation of the CO π^* orbitals by forming a butterfly cluster such as **2b**, where all the CO ligands are terminally bound. We now report the synthesis and structure of a 60 electron tetrahedral Os_3Pt cluster closely related to **2b**, which has a carbonyl ligand bridging an Os–Os edge.

The spiked triangular cluster $Ru_3Pt(\mu\text{-}H)(\mu_4\text{-}\eta^2\cdot C{\equiv}CBu^t)(CO)_9(COD)$ (**3**) [5] reacts readily with $Os_3(\mu\text{-}H)_2(CO)_{10}$ in toluene to afford dark red-brown crystals of

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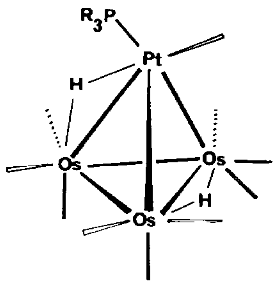

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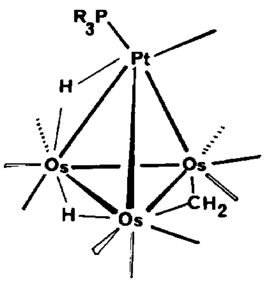
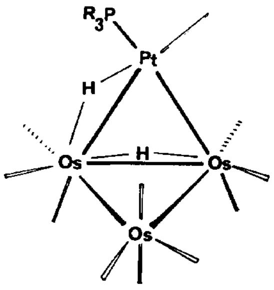
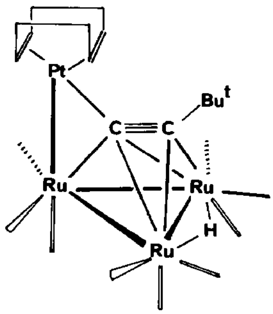


2a



2b



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the title complex $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_9(COD)$ (**4**). Yellow crystals of $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)(CO)_9$ [6] are also formed. Spectroscopic data for **4**: $\nu(CO)$ CH_2Cl_2, 2087m, 2062vs, 2038s, 2005s, 1980sh, 1940w,br, 1769w,br cm^{-1}: ^1H NMR; (CD_2Cl_2, 298 K) δ 5.52 (s,br, 4H, CH=CH, *J*(Pt–H) 53 Hz), 2.74–2.42 (m, 8H, CH_2), −21.78 (s, 2H, Os(μ-H)Os, *J*(Pt–H) 17.0, *J*(Os–H) 21.6 Hz); (CD_2Cl_2, 203 K) δ 5.70 (s,br, 2H, CH=CH, *J*(Pt–H) 61 Hz), 5.16 (s,br, 2H, CH=CH, *J*(Pt–H) 48 Hz), 2.90–2.20 (m, br, 8H, CH_2), −21.92 (s, 2H, Os(μ-H)Os, *J*(Pt–H) 17.3 Hz). The hydride resonance in the ^1H NMR spectrum of **4** is a sharp singlet throughout the temperature range 203–298 K, and displays coupling to ^{195}Pt and ^{187}Os. The two inequivalent sets of olefinic protons show two signals at 203 K (at δ 5.70 and 5.16 ppm), while at 298 K rapid rotation of the COD ligand renders these environments equivalent. A bridging carbonyl ligand is indicated by the stretch at 1769 cm^{-1} in the IR spectrum. An X-ray diffraction study on **4** was carried out to define the structure fully [12*].

Figure 1 shows a view of **4** with the crystallographic labelling. The Os_3Pt skeleton is a distorted tetrahedron with Pt–Os distances ranging from 2.714(1)–2.811(1) Å, and Os–Os separations from 2.837(1)–2.952(1) Å. A carbonyl ligand symmetrically bridges (Os(1)–C(1) 2.17(2), Os(2)–C(1) 2.10(2) Å) the Os(1)–Os(2) bond, which is

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* Reference number with asterisk indicates a note in the list of references.

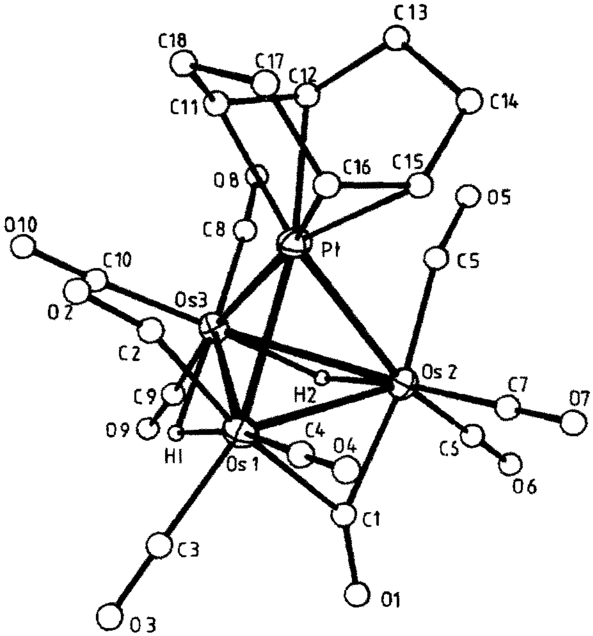

Fig. 1. Molecular structure of $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_9(COD)$ (4). Important bond lengths and angles: Os(1)–Pt 2.730(1), Os(2)–Pt (2.811(1), Os(3)–Pt 2.714(1), Os(1)–Os(2) 2.837(1), Os(1)–Os(3) 2.919(1), Os(2)–Os(3) 2.952(1), Os(1)–C(1)(1) 2.17(2), Os(2)–C(1) 2.10(2), Pt...C(2) 2.50(2), Pt...C(5) 2.63(2), Pt–C(11) 2.19(2), Pt–C(12) 2.20(2), Pt–C(15) 2.30(2), Pt–C(16) 2.30(2) Å, Os(1)–C(1)–O(1) 135.7(1), Os(2)–C(1)–O(1) 141.0(1), Os(1)–C(2)–O(2) 160.7(2), Os(2)–C(5)–O(5) 163.2(2), mean remaining Os–C–O 177.3(2)°.

the shortest such vector in **4**. As expected from the ^1H NMR data, the two hydride ligands (HYDEX [7]) bridge the equivalent remaining Os–Os edges. In addition weak semibridges to the Pt atom are formed by the carbonyls C(2)–O(2) (C(2)... Pt 2.50(2) Å, Os(1)–C(2)–O(2) 160.7(2)°) and C(5)–O(5) (C(5)... Pt 2.63(2) Å, Os(2)–C(5)–O(5) 163.2(2)°). The COD ligand is asymmetrically bonded to the Pt atom, with the olefinic bond lying over the Pt–Os(3) edge (C(11)–C(12)) having significantly shorter Pt–C distances (2.19(2), 2.20(2) Å) than the olefinic bond lying over the Pt–Os(1)–Os(2) face (C(15)–C(16); Pt–C 2.30(2) Å). A similar feature is found in the closely related complex $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_9(COD)$ recently reported by Norén and Sundberg [8].

The presence of a carbonyl ligand bridging an Os–Os bond is a relatively rare phenomenon in osmium cluster chemistry [9*], though bridging carbonyls are common in ruthenium clusters. This may be related to a size effect, since clusters containing a carbonyl bridged Re–Re bond are extremely rare [10*], whilst many examples of clusters with CO bridged Ir–Ir bonds are known [11]. The formation of **4** from $Os_3(\mu\text{-}H)_2(CO)_{10}$ and **3** involves a transfer of a Pt(COD) unit. We have examined the reaction of $Os_3(\mu\text{-}H)_2(CO)_{10}$ with $Pt(COD)_2$ by ^1H NMR spectroscopy, and although a high field signal due to **4** is observed, there are other signals at δ −12.37 (J(Pt–H) 24.3 Hz) and −20.45 in significant amounts, due to unidentified co-products. We have not yet been able to isolate pure **4** from this reaction mixture, since **4** is not very stable in solution and cannot be chromatographed on Florosil or alumina without decomposition. The synthetic route involving complex **3**, with fractional recrystallisation of the reaction mixture, is preferred.

The 60 electron tetrahedral complex **4** is conceptually closely related to the 60 electron butterfly adduct **2b**, by replacement of the CO and PR_3 ligands on the Pt atom in **2b** with a COD unit. The isolation of **4** demonstrates that the factors governing the structures adopted by the 60 electron adducts **2** are finely balanced and may depend on the nature of the ancilliary ligands on the Pt atom, as well as on the two electron donors L. **4** readily reacts with CO with displacement of the COD ligand to give $Os_3Pt(\mu\text{-}H)_2(CO)_{12}$, which has a single hydride resonance in the ^1H NMR spectrum at δ -19.22 (CD_2Cl_2), J(Pt–H) 22.6 Hz. Further characterisation of this product and of other species derived from **4** are under investigation.

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References

1 L.J. Farrugia, J.A.K. Howard, P. Mitrprachachon, F.G.A. Stone and P. Woodward, J. Chem. Soc. Dalton Trans., (1981) 155.

2 L.J. Farrugia, J.A.K. Howard, P. Mitrprachachon, F.G.A. Stone and P. Woodward, J. Chem. Soc. Dalton Trans., (1981) 162.

3 L.J. Farrugia, M. Green, D.R. Hankey, M. Murray, A.G. Orpen and F.G.A. Stone, J. Chem. Soc. Dalton Trans., (1985) 177.

4 P. Ewing and L.J. Farrugia, Nouv. J. Chim., in press.

5 P. Ewing and L.J. Farrugia, to be published.

6 E. Sappa, O. Gambino, L. Milone and G. Cetini, J. Organomet. Chem., 39 (1972) 169.

7 A.G. Orpen, J. Chem. Soc. Dalton Trans., (1980) 2509.

8 B. Norén and P. Sundberg, J. Chem. Soc. Dalton Trans., (1987) 3103.

9 Out of 454 structures (from the Cambridge Crystallographic Data Base) containing 3 or more Os atoms, only 13 structures report such an interaction. For example see: M.R. Churchill and H.J. Wasserman, Inorg. Chem., 21 (1982) 825; M.R. Churchill and H.J. Wasserman, J. Organomet. Chem., 248 (1983) 365; P.A. Dawson, B.F.G. Johnson, J. Lewis, D.A. Kaner and P.R. Raithby, J. Chem. Soc. Chem. Commun., (1980) 961; R.D. Adams, J.E. Babin, R. Mathab and S. Wang, Inorg. Chem., 25 (1986) 1623.

10 There are to our knowledge only two reported structures (a) $[Re_6C(CO)_{18}(\mu\text{-}CO)]^{2-}$; P.L. Stanghellini, R. Rossetti, G. D'Alphonso and G. Longoni, Inorg. Chem., 26 (1987) 2769; (b) $[Re_7C(CO)_{21}(\mu\text{-}CO)]^-$: T. Beringhelli, G. D'Alphonso, M. De Angelis, G. Ciani and A. Sironi, J. Organomet. Chem., 322 (1987) C21. The complex $[HRe_5(\mu_5\text{-}C)(CO)_{16}]^{2-}$ contains a semibridging carbonyl: T.J. Henly, S.R. Wilson and J.R. Shapley, Organometallics, 6 (1987) 2618.

11 (a) R.D. Pergola, F. Demartin, L. Garlaschelli, M. Manassero, S. Martinengo and M. Sansoni, Inorg. Chem., 26 (1987) 3487; (b) D. Braga and F. Grepioni, J. Organomet. Chem., 336 (1987) C9 and refs. therein.

12 *Crystal data*: $C_{18}H_{14}O_{10}Os_3Pt$, $M = 1156.0$, triclinic, space group $P\bar{1}$ (C_i^1 No. 2), a 9.384(2), b 9.411(7), c 14.055(4) Å, α 84.92(4), β 88.07(2), γ 63.52(5)°, $Z = 2$, $U = 1107(1)$ Å^3, D_c 3.47 g cm^{-3}, $F(000) = 1016$, μ(Mo-K_α) 236.2 cm^{-1}. The structure solution (Patterson, Fourier methods) and refinement (full matrix least squares, all non-hydrogen atoms apart from C(4) and C(7) were anisotropic) was based on 3189 independent observed ($I > 3\sigma(I)$) (4285 measured) absorption and extinction corrected data (Enraf–Nonius CAD4F diffractometer, max θ 25°). Final R and R_w values are 0.042 and 0.053.

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 CV2 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.