

Preliminary communication

Synthesis and characterisation of linked triosmium clusters using the bis(diphenylphosphino)acetylene ligand

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Abstract

The reaction of $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$ with bis(diphenylphosphino)acetylene (dppa) at room temperature affords $[\text{Os}_3(\text{CO})_{11}]_2(\text{dppa})$ (**1**) in good yield, while $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ with an excess of dppa gives $[\text{Os}_3(\text{CO})_{10}(\text{dppa})]_3$ (**2**) and $[\text{Os}_3(\text{CO})_{10}(\text{dppa})]_4$ (**3**) in moderate yields. The structure of **1** has been determined by a single crystal X-ray diffraction study.

It has been shown that ruthenium carbonyl clusters containing the bis(diphenylphosphino)acetylene (dppa) ligand can be converted into a range of tetraruthenium and pentaruthenium clusters by a reaction which involve both C–P bond cleavage and the rearrangement of the dppa ligand [1,2] on heating. Although dppa is a potentially tridentate ligand, it normally coordinates via the two terminal phosphorus atoms. The rigidity of the linear $-\text{C}\equiv\text{C}-$ unit between two phosphorus centres forces the dppa ligand to form bonds two between different metal atoms which are not linked by a metal–metal bond. These observations prompted us to use the dppa ligand in the synthesis of some oligomeric osmium cluster compounds under mild conditions.

The reaction of $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$ with dppa (2:1 molar ratio) in dichloromethane at room temperature for 2 h, followed by careful chromatography on silica, yielded a dark yellow product (ca. 60%) which analyses as $[\text{Os}_3(\text{CO})_{11}]_2(\text{dppa})$ (**1**). The ^{31}P NMR spectrum of **1** exhibits a singlet resonance at -171.67 ppm [reference $\text{P}(\text{OMe})_3$: $\delta = 0$, downfield positive] shows a high field shift relative to the signal of the free dppa ligand [**3**] (107 ppm) on coordinating to the metal centres. The appearance of a singlet resonance is taken to indicate that the two P atoms are in equivalent environments. The ^1H NMR spectrum of **1** shows a multiplet at 7.48 ppm, and the FAB mass spectrum exhibits an envelope of molecular ions with peak at 2155. These spectroscopic data are consistent with the proposed formulation of **1**. An X-ray diffraction analysis was carried out on a single crystal obtained from slow

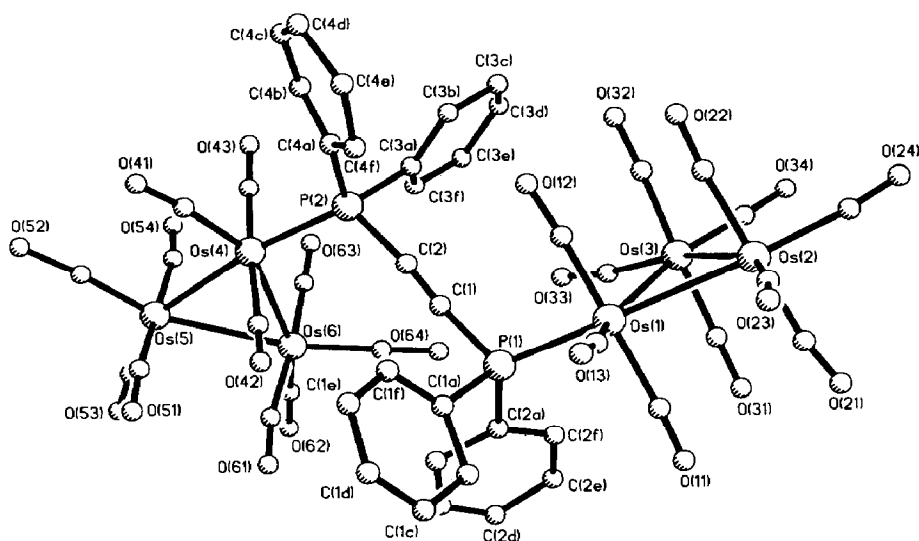


Fig. 1. The molecular structure of $[\text{Os}_3(\text{CO})_{11}]_2(\text{dppa})$ (**1**) showing the atom numbering scheme. Bond lengths: Os(1)–Os(2), 2.876(3); Os(1)–Os(3), 2.907(3); Os(2)–Os(3), 2.883(3); Os(4)–Os(5), 2.877(3); Os(4)–Os(6), 2.903(3); Os(5)–Os(6), 2.881(3); Os(1)–P(1), 2.336(11); Os(4)–P(2), 2.321(12); P(1)–C(1), 1.78(5); P(1)–C(1a), 1.87(4); P(1)–C(2a), 1.82(4); P(2)–C(2), 1.81(5); P(2)–C(3a), 1.92(4); P(2)–C(4a), 1.83(4); C(1)–C(2), 1.13(7) Å. Bond angles: Os(2)–Os(1)–Os(3), 59.8(1); Os(1)–Os(2)–Os(3), 60.6(1); Os(1)–Os(3)–Os(2), 59.6(1); Os(5)–Os(4)–Os(6), 59.8(1); Os(4)–Os(5)–Os(6), 60.6(1); Os(4)–Os(6)–Os(5), 59.7(1); Os(2)–Os(1)–P(1), 168.4(3); Os(3)–Os(1)–P(1), 108.8(3); Os(5)–Os(4)–P(2), 168.0(3); Os(6)–Os(4)–P(2), 108.6(3); Os(1)–P(1)–C(1), 115(1); Os(4)–P(2)–C(2), 115(1); P(1)–C(1)–C(2), 173(4); P(2)–C(2)–C(1), 173(4)°.

diffusion of acetonitrile to a solution of **1** in $\text{CH}_2\text{Cl}_2/n$ -hexane mixture. The molecular structure of **1** is shown in Fig. 1 together with some important bond parameters*. Two discrete $[\text{Os}_3(\text{CO})_{11}]$ units in the molecule are linked together by a dppa ligand. The phosphorus atoms of the ligand coordinate to equatorial sites on one osmium atom in each triangular cluster unit. Os(1)–Os(3) and Os(4)–Os(6) distances [average 2.905(3) Å] are significantly longer than all other Os–Os distances [average 2.879(3) Å]. This may be due to the steric repulsion between the bulky dppa ligand and the adjacent equatorial carbonyl ligands. Unfortunately, the high e.s.d. of bond parameters arising from poor absorption correction precludes detailed analysis of the organic moiety.

The treatment of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ with an excess (3 fold) of dppa ligand in dichloromethane proceeds at room temperature over a period of 12 hours to

* *Crystal data:* $\text{C}_{48}\text{H}_{20}\text{O}_{22}\text{P}_2\text{Os}_6$, $M = 2151.8$, monoclinic, space group $P2_1/n$ (no. 14 non-standard setting), a 12.306(7), b 31.490(7), c 14.080(3) Å, β 90.27(1)°, $V = 5456$ Å³, $D_c = 2.619$ g cm⁻³, $Z = 4$, $F(000) = 3880$, $\lambda(\text{Mo-K}_\alpha)$ 0.71069 Å, $\mu(\text{Mo-K}_\alpha)$ 140.73 cm⁻¹. Yellow rectangular platelet, crystal dimensions: 0.10 × 0.44 × 0.52 mm, $\mu R = 2.49$. 7769 data measured on Nicolet R3mV four-circle diffractometer ($5.0 < 2\theta < 45.0^\circ$), corrected for absorption, 4156 unique observed reflections with $I > 3\sigma(I)$, structure solved by a combination of direct method and Fourier difference techniques and refined by full-matrix least-square analysis, with Os and P atoms assigned anisotropic displacement parameters; no allowance was made for H-atoms. The weighting scheme employed was $\omega = 1/[\sigma^2(F + 0.002F^2)]$. The final residuals were $R = 0.085$ and $R_w = 0.086$. The atomic coordinates for this work are available on request from the director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, CB2 1EW (U.K.).

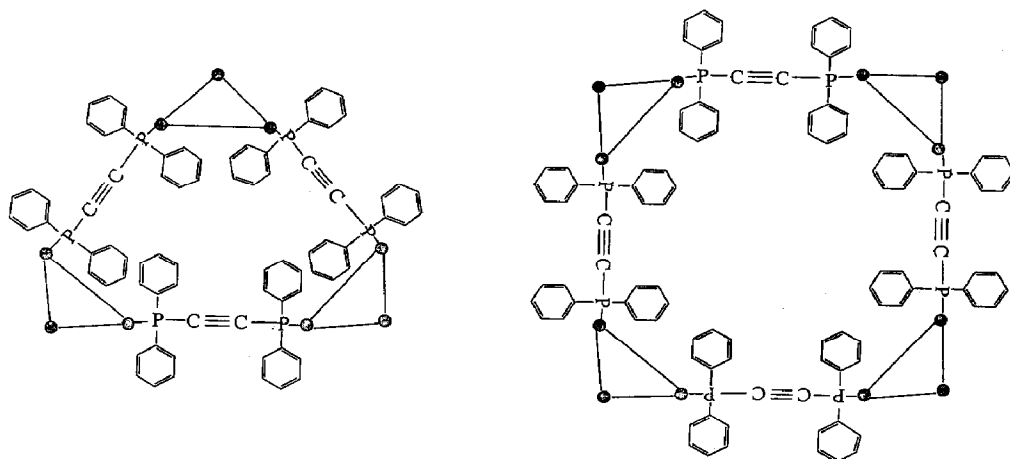


Fig. 2. Possible structures of $[\text{Os}_3(\text{CO})_{10}(\text{dppa})]_3$ and $[\text{Os}_3(\text{CO})_{10}(\text{dppa})]_4$.

Table 1

Compound	IR($\nu(\text{co})$, cm^{-1} , hexane)	FAB MS	^{31}P NMR	^1H NMR
$[\text{Os}_3(\text{CO})_{11}]_2(\text{dppa})$	2109m, 2057s, 2021vs, 1991w.	2155	-171.67 s	7.46 m
$[\text{Os}_3(\text{CO})_{10}(\text{dppa})]_3$	2088w, 2070w, 2059w, 2033m, 2004vs, 1974m.	3735.6	-174.16 s	7.50 m
$[\text{Os}_3(\text{CO})_{10}(\text{dppa})]_4$	2087w, 2030m, 2006vs, 1974m	4979.6	-	7.50 m

produce oligomeric species $[\text{Os}_3(\text{CO})_{10}(\text{dppa})]_3$ (**2**) (30%) and $[\text{Os}_3(\text{CO})_{10}(\text{dppa})]_4$ (**3**) (15%) which have been characterised on the basis of the FAB mass spectral analysis (molecular ions at 3735 and 4979 respectively). The ^{31}P NMR spectrum of **2** shows a singlet resonance at -174.16 ppm which indicates that the phosphorus atoms are in identical environments and hence a symmetrical arrangement of the phosphino-acetylene in the trimer is expected. Possible structures of the oligomers are shown in Fig. 2.

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