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Triosmium carbonyl cluster derivatives containing pentameric phenyl cyclopolyphosphine

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Abstract

The reactions of the pentaphenylcyclopentaphosphine with $[Os_3(CO)_{10}(NCCH_3)_2]$ afforded a pair of inversion isomers, (**1**) and (**2**). $[Os_3(CO)_{11}(C_6H_5P)_5]$ (**3**) and $[\{Os_3(CO)_{11}\}_2(C_6H_5P)_5]$ (**4**) were obtained by the treatment of the same ligand with $[Os_3(CO)_{11}(NCCH_3)]$. The four new triosmium clusters have been shown by X-ray crystallography to contain an intact cyclopolyphospine ring in each case.

Keywords: Osmium; Phosphorus; Cyclopolyphosphine; Cluster; Crystal structure

Although there are numerous examples of cyclopolyphosphine ligands coordinated to mononuclear transition metal complexes [1,2], relatively little attention has been paid to transition metal carbonyl clusters in which a cyclopolyphosphine ligates. In recent publications involving the reactions of tetrameric cyclophosphorus, $({}^tBuP)_4$, with ruthenium carbonyl cluster, several ruthenium cluster derivatives were obtained, each containing one or more phosphido group(s) showing extensive disruption of the cyclic phosphorus ring [3,4]. We now report the reactions between triosmium carbonyl clusters and pentameric phenylcyclopentaphosphine ligand, which afford several cluster derivatives where the phosphorus ring structure remains intact.

The cyclic phosphorus, $(C_6H_5P)_5$, was allowed to react with an equivalent molar amount of the activated trinuclear cluster $[Os_3(CO)_{10}(NCCH_3)_2]$ in dichloromethane at 80°C overnight. The orange compound (**1**) (yield 15.3%) and the yellow compound (**2**) (yield 17.3%) were obtained by thin-layer chromatography (TLC) of the product using CH_2Cl_2/hexane (30%/70%) as eluent. The structures of the two compounds, which were recrystallised from a mixed solvent of dichloromethene and hexane, have been determined by X-ray analysis to be a pair of isomers which have the same molecular formula $[Os_3(CO)_{10}(C_6H_5P)_5]$. The yellow compound $[Os_3(CO)_{11}(C_6H_5P)_5]$, (**3**) (yield 47.8%) and the orange linked compound, $[\{Os_3(CO)_{11}\}_2(C_6H_5P)_5]$, (**4**) (yield 44.7%) were obtained by the treatment of $(C_6H_5P)_5$ with a two-fold molar ratio of $[Os_3(CO)_{11}(NCCH_3)]$ in dichloromethane at room temperature and subsequent purification by thin-layer chromatography (TLC) using CH_2Cl_2/hexane (30%/70%) as eluent. All four clusters were characterised by IR, ^1H NMR, ^{31}P NMR and element analysis [5*]. X-ray crystallographic study [6*] of clusters (**1**)–(**4**) established the overall structures illustrated in Figs. 1–4, respectively. Selected bond lengths and angles are given in Tables 1–4.

In the molecular structures of (**1**) and (**2**), as shown in Fig. 1 and Fig. 2, the $(C_6H_5P)_5$ moiety acts as a bidentate ligand, taking up the equatorial sites of the osmium triangular planes and chelating across an Os–Os edge, through the two P atoms in the 1,3-positions of the phosphorus ring. The solid structures of (**1**) and (**2**) differ essentially in the orientations adopted by the aromatic rings attached to the uncoordinated phosphorus atoms. For example, in (**1**) the phenyl group of phosphorus 2 is over the phosphorus ring on the same side as the triosmium plane, while in (**2**) this group lies below the phosphorus ring on the opposite side from the triosmium plane. The phosphorus rings cannot flip freely after chelating to the two osmium atoms because

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Table 2
Selected bond lengths (Å) and angles (°) of **2**

Os(1)–Os(2)	2.890(1)	Os(1)–Os(3)	2.901(1)
Os(2)–Os(3)	2.874(1)		
P(1)–P(2)	2.227(3)	P(1)–P(5)	2.224(4)
P(2)–P(3)	2.219(3)	P(3)–P(4)	2.259(3)
P(4)–P(5)	2.214(3)		
Os(1)–P(1)	2.324(3)	Os(3)–P(3)	2.339(3)
Os(2)–Os(1)–Os(3)	59.5(1)	Os(1)–Os(2)–Os(3)	60.4(1)
Os(1)–Os(3)–Os(2)	60.1(1)		
P(2)–P(1)–P(5)	99.93(1)	P(1)–P(2)–P(3)	87.4(1)
P(2)–P(3)–P(4)	111.3(1)	P(3)–P(4)–P(5)	98.1(1)
P(1)–P(5)–P(4)	98.1(1)		

(b) The angle (87.3°) of P(1)–P(2)–P(3) in (**1**) is almost equal to the angle (87.4°) of P(1)–P(2)–P(3) in (**2**). These two angles are much smaller than the average angle of free ligand because the two phosphorus atoms of 1,3-position in the phosphorus rings must move closer to fit the short Os–Os distance in the triosmium cluster after forming the coordination compound so that the P ring is more puckered.

(c) The bridged Os(1)–Os(3) distance of 2.901(1) Å in (**2**) is slightly longer than that of 2.876(2) Å in (**1**) which is similar to the Os–Os distance in their parent cluster $[Os_3(CO)_{12}]$ (2.877 Å) [8].

The structure of (**3**) comprises an isosceles triangle of osmium atoms in which the bulky cyclopolyphosphine ligand acts as a monodentate ligand, bonding to Os(1) by taking up an equatorial site. The longest Os–Os bond (2.917 Å) in (**3**) is much longer than the other two bond lengths (2.881 Å). These bonds are longer than the average Os–Os bond length of the parent cluster $[Os_3(CO)_{12}]$ (2.877 Å). The average angle (98.2°) of P–P–P is much closer to that (100.0°) of free ligand.

As shown in Fig. 4, the cyclopolyphosphine in the cluster (**4**) links through two phosphorus atoms at the 1 and 3 positions to two triosmium triangles at the equatorial roles. Because of this link pattern, the average distance (2.241 Å) of P–P is much longer than that (2.217 Å) of free ligand and even longer than that (2.228 Å) of (**3**). The other feature is that the Os(1)–Os(3) and Os(4)–Os(5) distances (mean 2.913 Å) are significantly longer than all other Os–Os distances (mean 2.876 Å) because of the steric repulsion between the bulky ligand and the adjacent equatorial carbonyl ligands. This may be like the case in $[\{Os_3(CO)_{11}\}_2$-(dppa)] [9] [dppa = bis(diphenylphosphinoacetylene] in which the longer Os–Os distances were attributed to the proximity of the phenyl rings of dppa to the adjacent equatorial carbonyl groups on each Os atom.

Table 3
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P(4)–P(5)	2.217(4)		
Os(1)–P(1)	2.345(3)		
Os(2)–Os(1)–Os(3)	59.6(1)	Os(1)–Os(2)–Os(3)	60.8(1)
Os(1)–Os(3)–Os(2)	59.6(1)		
P(2)–P(1)–P(5)	97.7(2)	P(1)–P(2)–P(3)	102.9(2)
P(2)–P(3)–P(4)	103.8(2)	P(3)–P(4)–P(5)	94.5(2)
P(1)–P(5)–P(4)	94.7(2)		

Table 4
Selected bond lengths (Å) and angles (°) of **4**

Os(1)–Os(2)	2.883(1)	Os(1)–Os(3)	2.931(1)
Os(2)–Os(3)	2.875(1)	Os(4)–Os(6)	2.872(1)
Os(4)–Os(5)	2.928(1)	Os(5)–Os(6)	2.873(1)
P(1)–P(2)	2.273(5)	P(1)–P(5)	2.279(8)
P(2)–P(3)	2.241(8)	P(3)–P(4)	2.215(6)
P(4)–P(5)	2.195(6)		
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Os(2)–Os(1)–Os(3)	59.3(1)	Os(1)–Os(2)–Os(3)	61.2(1)
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Os(4)–Os(5)–Os(6)	59.3(1)	Os(4)–Os(6)–Os(5)	61.3(1)
P(2)–P(1)–P(5)	102.0(2)	P(1)–P(2)–P(3)	103.6(3)
P(2)–P(3)–P(4)	94.3(3)	P(3)–P(4)–P(5)	95.9(2)
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We thank the National University of Singapore for financial support and for a research studentship (to Q.Z.).

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[5] IR [ν(CO), cyclohexane/cm^{-1}]: **1** 2098m, 2036m, 2023s, 2016vs, 1982m, 1967w, 1950w; **2** 2095(m), 2036(m), 2025(s), 2012(vs), 1980(m), 1965(w), 1954(w); **3** 2107(m), 2056(s), 2036(m), 2020(vs), 2001(w), 1989(m), 1977(w), 1957(vw); **4** 2106m, 2058s, 2035m, 2024s, sh, 2022vs, 2004m, 1991m, 1981w. ^{1}H NMR (CD_2Cl_2, $SiMe_4$ reference): **1** δ 7.37(m); **2** δ 7.35(m); **3** δ 7.43(m); **4** δ 7.35(m). ^{31}P NMR (CD_2Cl_2, 85%H_3PO_4 reference): **1** δ 109.6 (m, 1P), δ 4.0 (m, 1P), δ −3.7 (m, 1P), δ −63.3 (m, 2P); **2** δ 62.5 (m, 1P), δ 15.3 (m, 2P), δ −15.6 (m, 1P), δ −41.5 (m, 1P); **3** δ 15.4 (m, 1P), δ −0.50 (m, 1P), δ −16.8 (m, P), δ −30.90 (m, 1P), δ −31.54 (m, 1P); **4** δ 36.9 (q, 1P), δ 20.5 (m, 1P), δ −0.2 (q, 1P), δ −19.9 (m, 1P), δ −35.6 (m, 1P). Element analysis: **1** Found: C, 34.82; H, 1.67; P, 10.80; calc.: C, 34.52; H, 1.80; P, 11.14%; **2** Found: C, 34.47; H, 1.70; P, 10.43; calc.: C, 34.52; H, 1.80; P, 11.14%; **3** Found: C, 34.70; H, 1.76; P, 10.96; calc.: C, 34.91; H, 1.75; P, 10.80%; **4** Found: C, 27.16; H, 1.09, P, 6.75; calc.: C, 27.20; H, 0.98; P. 6.58%.

[6] Crystal data $Os_3(CO)_{10}(C_6H_5P)_5$ **1**: $C_{40}H_{25}O_{10}Os_3P_5$, Monoclinic, $P2_1/c$, $a = 10.614(5)$ Å, $b = 38.85(2)$ Å, $c = 10.916(5)$ Å, $\beta = 108.93(4)°$, $M = 1391.1$, $U = 4258(4)$ Å^3, $Z = 4$, $d_{(calc)} = 2.170$ g cm^{-3}, $F(000)$ 2592, absorption coefficient = 91.74 cm^{-1}. 4546

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unique, observed, $[F > 4.0\ \sigma(F)]$, an empirical (ψ-scan) absorption correction was applied. $R = 0.0392$, $R_w = 0.0502$ $[w^{-1} = \sigma^2(F) + 0.0043F^2]$. $Os_3(CO)_{10}(C_6H_5P)_5$ **2**: $C_{40}H_{25}O_{10}Os_3P_5$, Triclinic $P\bar{1}$, $a = 11.747(3)$ Å, $b = 11.883(3)$ Å, $c = 16.120(4)$ Å, $\alpha = 92.30(2)°$, $\beta = 97.61(2)°$, $\gamma = 103.88(2)°$, $M = 1391.1$, $U = 2159.3(8)$ Å^3, $Z = 2$, $d_{calc} = 2.139$ g cm^{-3}, $F(000)$ 1296, absorption coefficient = 90.45 cm^{-1}. 6319 unique, observed, $[F > 4.0\ \sigma(F)]$, an empirical (ψ-scan) absorption correction was applied. $R = 0.0451$, $R_w = 0.0556$ $[w^{-1} = \sigma^2(F) + 0.0015F^2]$. $Os_3(CO)_{11}$-$(C_6H_5P)_5$ **3**; $C_{41}H_{25}O_{11}Os_3P_5$, Monoclinic, $P2_1/c$, $a = 10.273(2)$ Å, $b = 20.655(4)$ Å, $c = 21.207(7)$ Å, $\beta = 97.07(3)°$, $M = 1419.1$, $U = 4466(2)$ Å^3, $Z = 4$, $d_{(calc)} = 2.111$ g cm^{-3}, $F(000)$ 2648, absorption coefficient = 87.51 cm^{-1}. 5111 unique, observed, $[F > 4.0\ \sigma(F)]$, an empirical (ψ-scan) absorption correction was applied. $R = 0.0437$, $R_w = 0.0401$ $[w^{-1} = \sigma^2(F) + 0.0002F^2]$. $[\{Os_3(CO)_{11}\}_2(C_6H_5P)_5]$ **4**: $C_{52}H_{25}O_{22}Os_6P_5$, Triclinic, $P\bar{1}$, $a = 12.216(2)$ Å, $b = 16.706(3)$ Å, $c = 17.802(3)$ Å, $\alpha = 67.23(2)°$, $\beta = 71.30(2)°$, $\gamma = 69.03(2)°$, $M = 2297.8$, $U = 3051.4(9)$ Å^3, $Z = 2$, $d_{(calc)} = 2.496$ g cm^{-3}, $F(000)$ 2088, absorption coefficient = 126.24 cm^{-1}. 11160 unique, observed, $[F > 4.0\ \sigma(F)]$, an empirical (ψ-scan) absorption correction was applied. $R = 0.0938$, $R_w = 0.0742$ $[w^{-1} = \sigma^2(F) + 0.0010F^2]$.

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