DALTON
FULL PAPER

Formation of new cluster derivatives of triphospholene *via* ligand substitution and cleavage of P–P bond(s)

How Ghee Ang, Siau Gek Ang and Xiao Wang

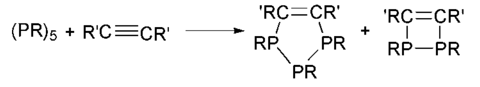
Department of Chemistry, National University of Singapore, Singapore 119260.
E-mail: chmanghg@nus.edu.sg

Received 16th March 2000, Accepted 2nd August 2000
First published as an Advance Article on the web 13th September 2000

At room temperature, triphospholene PhPPhPPhPCPh=CPh (L) underwent mono- and di-substitution reactions with $[Os_3(CO)_{11}(MeCN)]$ to afford the following derivatives: mono-substituted cluster $[Os_3(CO)_{11}$(2-PhPPhPPhPCPh=CPh)] **1**, di-substituted bridged cluster $[Os_3(CO)_{10}$(1,3-PhPPhPPhPCPh=CPh)] **2**, and linked cluster $[\{Os_3(CO)_{11}\}_2$(1,3-PhPPhPPhPCPh=CPh)] **3**. On the other hand, reactions with $[Os_3(CO)_{10}(MeCN)_2]$ gave two isomeric compounds: **2** and $[Os_3(CO)_{10}$(1,3-PhPPhPPhPCPh=CPh)] **4**, differing in the orientation of the phenyl group attached to the central unco-ordinated phosphorus atom. At elevated temperatures similar reactions result in cleavage of one P–P bond of the ligand to afford an open cluster $[Os_3(CO)_9(\mu_3\text{-}\eta^3$-PhPPhPCPh=CPhPPh)] **5**, and cleavage of two P–P bonds to give $[Os_3(CO)_9(\mu_3$-PPh)$(\mu_3\text{-}\eta^2$-PhPCPh=CPhPPh)] **6**, arising from the formation of the phosphinidene species. The clusters **1**, **2** and **4** can be converted sequentially on heating into **5** and then **6**.

Introduction

The first 1,2,3-triphospholene (**I**) and 1,2-diphosphetene (**II**)



I **II**

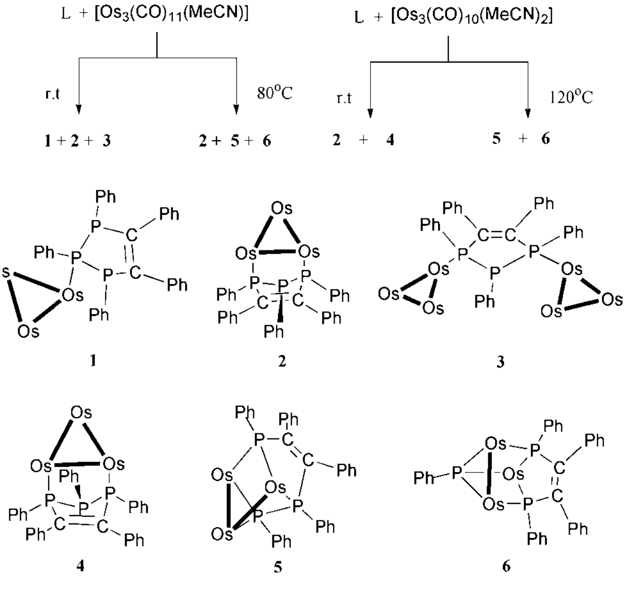
were obtained by Mahler in 1964 by pyrolysis of $(CF_3P)_{4,5}$ with an excess of $CF_3C{\equiv}CCF_3$ at 170 °C.[1] Mathey and co-workers reported the synthesis of several triphospholenes by the reaction of cyclopolyphosphine with substituted acetylene.[2]

In contrast to homo-cyclopolyphosphine, of which the diversified reactivity with transition-metal carbonyls has been the subject of many investigations,[3–10] the co-ordination chemistry of carbon–phosphorus heterocycles is poorly developed. When treated with metal carbonyl clusters, homo-cyclopolyphosphine can remain intact and act as a mono-, di- or tri-dentate ligand, or undergo ring cleavage, contraction, expansion or rupture. However, only a few co-ordination modes of **I** and **II** are known. Diphosphetene demonstrated η^1-phosphorus lone-pair co-ordination when treated with iron carbonyls as well as P–P bond cleavage.[11,12] Complete ring rupture also occurred to produce a phosphinidene complex.[12] A recent investigation by Zenneck and co-workers shows that 1,2-diphosphetene can also function as a four-electron donating flat ligand.[13] When 1,2,3,4,5-pentakis(trifluoromethyl)-1,2,3-triphospholene reacted with zerovalent platinum complexes[14] it co-ordinated as a normal olefin. When 1,2,3,4,5-pentaphenyl-1,2,3-triphospholene reacted with an excess of $[Cr(CO)_5(THF)]$ the 1,3-P atoms were the active centers and co-ordinated to the $Cr(CO)_5$ fragment.[13] However, no report has been made of the reaction of the triphospholene with metal carbonyl clusters. As an extension to our investigation of the co-ordination chemistry of homo-cyclopolyphosphine, we report here the reactions of 1,2,3,4,5-pentaphenyl-1,2,3-triphospholene (PhPPhPPhPCPh=CPh) with activated triosmium carbonyl clusters.

Results and discussion

Reactions and characterization

The reactions of PhPPhPPhPCPh=CPh (L) with $[Os_3(CO)_{11}(MeCN)]$ and $[Os_3(CO)_{10}(MeCN)_2]$ under different conditions are shown in Scheme 1. The reaction of L with one molar equivalent of $[Os_3(CO)_{11}(MeCN)]$ at room temperature overnight afforded mono-substituted cluster $[Os_3(CO)_{11}$(2-PhPPhPPhPCPh=CPh)] **1** as the major product and di-substituted cluster $[Os_3(CO)_{10}$(1,3-PhPPhPPhPCPh=CPh)] **2** as a minor product. The reaction of L with two molar equivalents of $[Os_3(CO)_{11}(MeCN)]$ under similar conditions afforded a small amount of a linked cluster $[\{Os_3(CO)_{11}\}_2$(1,3-PhPPhPPhPCPh=CPh)] **3** besides **1** and **2**. Raising the



Scheme 1 Reactions of L with $[Os_3(CO)_{12-n}(NCMe)_n]$ (n = 1 or 2).

DOI: 10.1039/b002140g

Table 1 Infrared spectroscopic[a] and NMR[b] data for the complexes

Complex	IR(ν)/cm^{-1}	NMR (δ) ^{1}H	 ^{31}P-{^{1}H}
1	2106w, 2054m, 2037w, 2018s, 2001w, 1990w, 1976w	7.7(m,Ph)	68.0 [dd, 1P, J_1(PP) = 293.6, J_2(PP) = 17.2], 41.2 [dd, 1P, J_1(PP) = 254.1, J_2(PP) = 17.2], −50.1 [dd, J_1(PP) = 254.1, J_2(PP) = 293.6]
2	2095m, 2034w, 2019m, 2012s, 1982w, 1964w, 1955w	7.7(m,Ph)	58.7 [dd, 1P, J_1(PP) = 240.8, J_2(PP) = 248.0], 1.3 [d, 2P, J(PP) = 244.2]
3	2107w, 2058m, 2042w, 2024s, 2003w, 1994w, 1980w, 1970w	7.2(m, Ph)	14.6 [d, 1P, J(PP) = 285.5], 14.6 [d, 1P, J(PP) = 271.0], −20.2 [dd, 1P, J_1(PP) = 271.0, J_2(PP) = 285.5]
4	2098m, 2034w, 2018s, 1985w, 1965w, 1952w	7.2(m, Ph)	102.5 [t, 1P, J(PP) = 179.3], −39.9 [d, 2P, J(PP) = 179.3]
5	2072m, 2048s, 2019m, 2009s, 1997w, 1975w, 1958w, 1946w	7.1(m, Ph)	57.2 [dd, 1P, J_1(PP) = 232.7, J_2(PP) = 6.9], 0.09 [dd, 1P, J_1(PP) = 232.4, J_2(PP) = 41.8] −95.4 [dd, 1P, J_1(PP) = 42.0, J_2(PP) = 6.6]
6	2081w, 2062s, 2032s, 2018w, 1999m, 1995w, 1973w, 1955w	6.9(m, Ph)	−154.8 [d, 2P, J(PP) = 62.6], −242.3 [t, 1P, J(PP) = 62.6]

[a] Recorded in cyclohexane. [b] Recorded in $CDCl_3$, the coupling constants are in Hz.

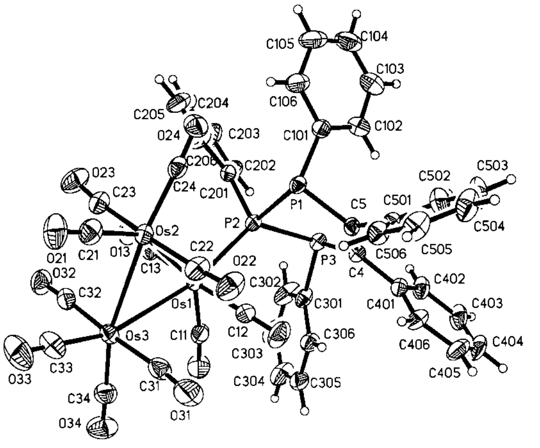


Fig. 1 Molecular structure of cluster **1**.

temperature to 80 °C afforded new compounds [$Os_3(CO)_9$-(μ_3-η^3-PhPPhPCPh=CPhPPh)] **5** and [$Os_3(CO)_9$(μ_3-PPh)(μ_3-η^2-PhPCPh=CPhPPh)] **6** with cleaved P–P and Os–Os bond(s) besides **2**. On the other hand, the room temperature reaction of L with [$Os_3(CO)_{10}(MeCN)_2$] afforded a pair of isomers **2** and [$Os_3(CO)_{10}$(1,3-Ph$\overline{\text{PPhPPhPCPh=C}}$Ph)] **4** while the reaction at 120 °C afforded **5** and **6**.

Clusters **1**–**6** are fully characterized by spectroscopic techniques (IR, ^{1}H, ^{31}P NMR) (Table 1) as well as elemental analyses. Single crystal X-ray analyses were also carried out to establish their molecular structures. Selected bond lengths (Å) and bond angles (°) are listed in Table 2.

Characterization of compounds 1 and 3

The molecular structure of compound **1** is shown in Fig. 1. The ligand L in **1** is intact and is bonded through its central phosphorus atom to the osmium triangle *via* an equatorial site. The central phosphorus atom of L lies nearly in the triosmium plane [P(2)–Os(1)–Os(2)–Os(3) 177.27°], while the other four atoms are also very roughly planar [P(3)–C(4)–C(5)–P(1) 11.11°]. The phenyl groups attached to the three phosphorus atoms adopt a *trans*,*cis* configuration. The Os(2)–Os(3) distance [2.9132(6) Å] is longer than Os(1)–Os(2) [2.9029(6) Å] which is *cis* to the ligand.

The molecular structure of compound **3**, as shown in Fig. 2, consists of two discrete osmium triangles linked at two equatorial sites by the ligand L through two phosphorus atoms. The phenyl groups attached to the three phosphorus atoms adopt a *trans*, *trans* configuration, with the two osmium triangles and the three phenyl groups occupying equatorial and axial sites of the ring respectively. Like most of the mono-substituted derivatives [$M_3(CO)_{11}L$] obtained from [$M_3(CO)_{12}$] (M = Os or Ru, L = Group 15 ligand), the Os(1)–Os(2) [2.9111(9) Å] and Os(4)–Os(5) [2.9343(11) Å] bonds *cis* to the phosphorus ligand are the longest Os–Os bonds in the respective triangles. This is attributed to the steric bulk of the Group 15 ligand.

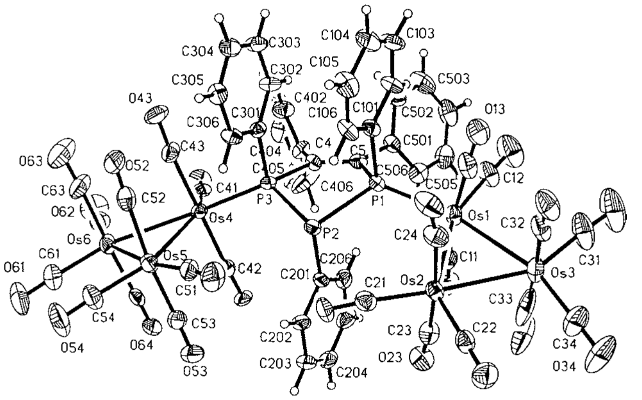


Fig. 2 Molecular structure of cluster **3**.

The IR absorption in the carbonyl region of compounds **1** and **3** is consistent with the pattern generally displayed by the mono-substituted cluster [$Os_3(CO)_{11}L$] (L is a phosphorus containing ligand). The ^{31}P-{^{1}H} NMR spectrum of **1** shows three sets of signals in a 1 : 1 : 1 ratio. The signal at δ −50.1(dd) shows two large coupling constants (J_1 = 254.1, J_2 = 293.6 Hz), indicating direct linkage to two phosphorus atoms, and is assigned to P(2). Both the signals at δ 68.0(dd) and at 41.2(dd) show coupling to P(2) as well as a normal long range coupling constant (J = 17.2 Hz), indicating that the two non-co-ordinated phosphorus atoms are not chemically equivalent.

The ^{31}P-{^{1}H} NMR spectrum of compound **3** shows two sets of signals at δ 14.6 and −20.2 in a 2 : 1 ratio. In the solid state structure of **3**, P(1) and P(3) are both connected to the osmium triangle, while P(2) is not. Thus P(1) and P(3) are in similar chemical environments. Therefore the two doublets at δ 14.6 are assigned to P(1) and P(3), that at δ −20.2 (dd) to P(2). Although P(1) and P(3) have the same chemical shift, they are magnetically non-equivalent (with osmium triangles attached to P(1) and P(3), it is unlikely that they are magnetically equivalent in solution on the NMR timescale). They exhibit different couplings to P(2).

Characterization of isomers 2 and 4

Isomeric compounds **2** and **4** are obtained by reaction of L with [$Os_3(CO)_{10}(MeCN)_2$] at room temperature. Their IR absorption in the carbonyl region differs in the shape and position of the strongest peak: for cluster **2** the strongest peak splits into two at 2019 and 2012 cm^{-1} while for **4** there is one peak at 2018 cm^{-1} (see Table 1). Single crystal X-ray analysis shows that they are

Table 2 Selected bond lengths (Å) and bond angles (°) for the complexes

Complex						
1	Os(1)–Os(2)	2.9029(6)	P(3)–P(2)	2.217(2)	Os(1)–P(2)	2.366(2)
	Os(1)–Os(3)	2.8834(8)	P(1)–C(5)	1.822(6)	P(3)–C(301)	1.837(7)
	Os(3)–Os(2)	2.9132(6)	C(5)–C(4)	1.342(7)	P(2)–C(201)	1.820(6)
	P(1)–P(2)	2.247(2)	P(3)–C(4)	1.842(6)	P(1)–C(101)	1.840(7)
	Os(2)–Os(1)–Os(3)	60.46(2)	P(1)–P(2)–P(3)	92.61(8)	P(3)–C(4)–C(5)	118.6(5)
	Os(1)–Os(2)–Os(3)	59.44(2)	P(2)–P(3)–C(4)	94.4(2)	P(1)–C(5)–C(4)	122.8(5)
	Os(2)–Os(3)–Os(1)	60.10(2)	C(5)–P(1)–P(2)	94.6(2)	P(2)–Os(1)–Os(2)	102.29(4)
	P(2)–Os(1)–Os(3)	162.56(4)				
2	Os(1)–Os(2)	2.8728(5)	Os(1)–Os(3)	2.8909(4)	Os(2)–Os(3)	2.8738(4)
	Os(1)–P(1)	2.3350(13)	Os(3)–P(3)	2.3376(14)	P(1)–P(2)	2.208(2)
	P(2)–P(3)	2.223(2)	P(1)–C(5)	1.861(5)	P(3)–C(4)	1.851(5)
	C(4)–C(5)	1.341(7)	P(1)–C(101)	1.823(5)	P(2)–C(201)	1.824(6)
	P(3)–C(301)	1.826(5)				
	Os(1)–Os(2)–Os(3)	60.406(9)	P(1)–P(2)–P(3)	82.13(7)	C(5)–P(1)–P(2)	99.6(2)
	Os(2)–Os(3)–Os(1)	59.780(10)	P(2)–P(3)–C(4)	98.7(2)	P(1)–C(5)–C(4)	114.8(4)
	Os(2)–Os(1)–Os(3)	59.814(10)	P(3)–C(4)–C(5)	115.2(4)	P(1)–Os(1)–Os(3)	89.62(3)
	P(3)–Os(3)–Os(1)	90.85(3)				
3	Os(1)–Os(2)	2.9111(9)	Os(1)–Os(3)	2.8974(10)	Os(2)–Os(3)	2.8898(11)
	Os(4)–Os(5)	2.9343(11)	Os(4)–Os(6)	2.9001(10)	Os(5)–Os(6)	2.8897(9)
	Os(1)–P(1)	2.367(3)	Os(4)–P(3)	2.365(3)	P(1)–P(2)	2.226(5)
	P(2)–P(3)	2.217(5)	P(1)–C(5)	1.875(13)	P(3)–C(4)	1.856(12)
	C(4)–C(5)	1.36(2)	P(1)–C(101)	1.827(13)	P(2)–C(201)	1.838(14)
	P(3)–C(301)	1.837(7)				
	Os(1)–Os(2)–Os(3)	59.93(3)	Os(5)–Os(6)–Os(4)	60.90(2)	P(1)–C(5)–C(4)	119.6(10)
	Os(2)–Os(3)–Os(1)	60.40(2)	P(1)–Os(1)–Os(3)	158.44(9)	P(3)–Os(4)–Os(6)	162.93(9)
	Os(5)–Os(4)–Os(6)	59.37(2)	P(1)–Os(1)–Os(2)	99.69(9)	P(3)–Os(4)–Os(5)	105.43(8)
	Os(2)–Os(1)–Os(3)	59.814(10)	P(1)–P(2)–P(3)	93.1(2)	P(2)–P(3)–C(4)	98.6(4)
	Os(4)–Os(5)–Os(6)	59.72(2)	C(5)–P(1)–P(2)	98.5(5)	P(3)–C(4)–C(5)	120.5(10)
4	Os(1)–Os(2)	2.8930(8)	P(1)–P(2)	2.244(5)	C(4)–C(5)	1.360(18)
	Os(1)–Os(3)	2.8893(7)	P(2)–P(3)	2.221(5)	P(1)–C(101)	1.829(13)
	Os(2)–Os(3)	2.8870(7)	P(1)–C(5)	1.864(12)	P(2)–C(201)	1.835(15)
	Os(1)–P(1)	2.347(3)	P(3)–C(4)	1.863(14)	P(3)-C(301)	1.830(14)
	Os(2)–P(3)	2.355(3)				
	Os(1)–Os(2)–Os(3)	59.983(17)	P(3)–Os(2)–Os(1)	90.12(8)	P(2)–P(3)–C(4)	88.8(4)
	Os(2)–Os(3)–Os(1)	60.111(18)	P(1)–Os(1)–Os(2)	90.16(8)	C(5)–P(1)–P(2)	88.0(4)
	Os(2)–Os(1)–Os(3)	59.905(17)	P(1)–P(2)–P(3)	81.38(16)	P(3)–C(4)–C(5)	114.9(9)
	P(1)–C(5)–C(4)	114.2(10)				
5	Os(1)–Os(2)	2.9731(5)	Os(2)–Os(3)	2.9286(5)	Os(1)–P(3)	2.438(2)
	Os(1)–P(1)	2.377(2)	Os(2)–P(2)	2.331(2)	Os(3)–P(2)	2.367(2)
	Os(3)–P(3)	2.435(2)	P(2)–P(1)	2.203(3)	P(1)–C(5)	1.842(9)
	C(4)–C(5)	1.351(12)	C(4)–P(3)	1.871(9)		
	Os(1)–Os(2)–Os(3)	83.281(14)	Os(1)–P(3)–Os(3)	107.16(10)	C(4)–P(3)–Os(1)	103.6(3)
	Os(1)–P(1)–C(5)	106.7(3)	P(1)–Os(1)–P(3)	75.10(4)	Os(2)–P(2)–Os(3)	77.13(7)
	C(5)–C(4)–P(3)	116.5(7)	P(1)–C(5)–C(4)	112.7(6)		
6	Os(2)–Os(3)	2.9608(5)	Os(1)–P(1)	2.4248(12)	Os(1)–P(2)	2.4424(12)
	Os(1)–P(3)	2.4244(12)	Os(2)–P(1)	2.4514(12)	Os(2)–P(2)	2.3690(13)
	Os(3)–P(2)	2.3610(13)	Os(3)–P(3)	2.4382(13)	P(1)–C(5)	1.854(5)
	P(1)–C(101)	1.829(5)	C(4)–C(5)	1.339(6)	P(3)–C(4)	1.850(5)
	P(3)–C(301)	1.830(5)	P(2)–C(201)	1.825(5)		
	P(1)–Os(1)–P(3)	75.10(4)	Os(1)–P(1)–Os(2)	102.41(4)	C(5)–C(4)–P(3)	116.2(3)
	P(1)–C(5)–C(4)	115.5(3)	Os(1)–P(2)–Os(3)	104.79(5)	Os(1)–P(3)–Os(3)	103.01(4)
	C(4)–P(3)–Os(1)	104.6(2)	Os(1)–P(1)–C(5)	103.9(2)	Os(1)–P(2)–Os(2)	104.34(5)
	Os(2)–P(2)–Os(3)	77.51(4)				

isomers, differing in the orientation of the phenyl group attached to the central phosphorus atom of the ligand ring (Fig. 3).

The molecular structure of compound **2** is shown in Fig. 4. The ligand of cluster **2** acts as bidentate, occupying the equatorial sites of the osmium triangle plane and chelating across an Os–Os edge through P(1) and P(3). The two phosphorus atoms lie in the same plane as the osmium triangle [P(1)–Os(1)–Os(3)–Os(2) −178.04°], while P(1), P(3), C(4) and C(5) are also nearly planar [P(1)–C(5)–C(4)–P(3) −2.84°]. P(2) folds away from this plane on the opposite side of the osmium triangle. The phenyl group attached to P(2) points away from the osmium triangle [Os(1)–P(1)–P(2)–C(201) −178.39°], thus the ligand has a *cis*, *cis* configuration with regard to the three phenyl groups attached to the three phosphorus atoms.

The molecular structure of compound **4** is shown in Fig. 5. Like cluster **2**, the two phosphorus atoms P(1) and P(3) are in the same plane as the osmium triangle, and the four atoms

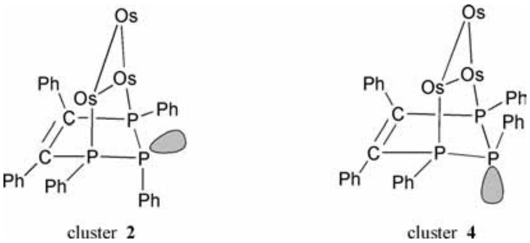


Fig. 3 Isomeric compounds **2** and **4**.

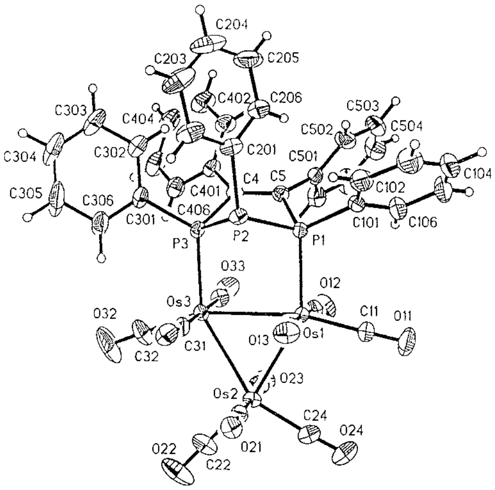


Fig. 4 Molecular structure of cluster **2**.

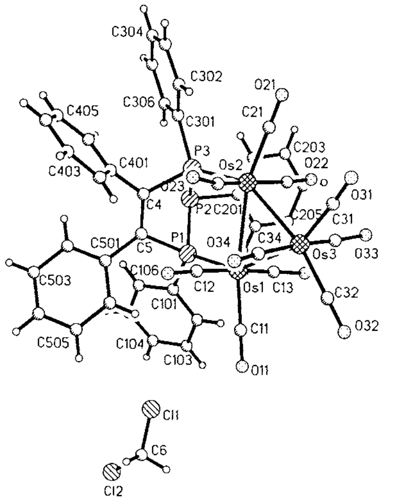


Fig. 5 Molecular structure of cluster **4**.

P(3), C(4), C(5) and P(1) of the ligand are also roughly planar [P(3)–C(4)–C(5)–P(1) 1.33°]. P(2) also folds away from this P(3)–C(4)–C(5)–P(1) plane on the opposite side of the osmium triangle. However, unlike **2**, the phenyl group attached to P(2) is on the same side of the osmium triangle [Os(1)–P(1)–P(2)–C(201) 49.98°]. Thus in **4** the ligand has a *trans*, *trans* configuration with regard to the three phenyl groups attached to the three phosphorus atoms.

The chemical shifts and coupling constants for the ^{31}P-{^{1}H} NMR spectra are listed in Table 1. Cluster **2** shows signals at δ 58.7(dd) and 1.3(d) in a 1 : 2 ratio. In the solid state structure P(1) and P(3) are both connected to osmium atoms while P(2) is not, thus P(1) and P(3) are chemically more similar. The doublet of doublets at δ 58.7 is assigned to P(2), showing different couplings to P(1) and P(3) ($J_1 = 240.8$, $J_2 = 248.0$ Hz). The two doublets at δ 1.3 are overlapping, showing an average coupling constant of 244.2 Hz. The ^{31}P-{^{1}H} NMR spectrum of cluster **4** shows a triplet at δ 102.5 and a doublet at δ −39.9 in a 1 : 2 ratio.

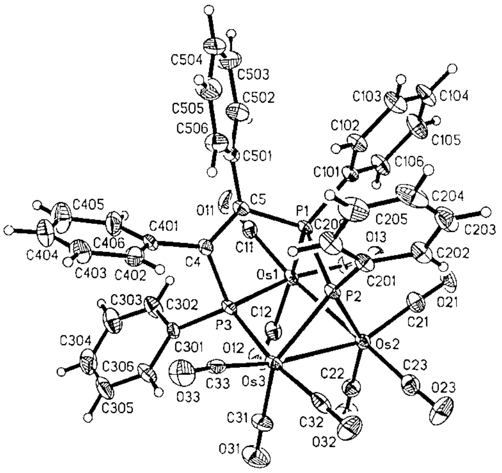


Fig. 6 Molecular structure of cluster **5**.

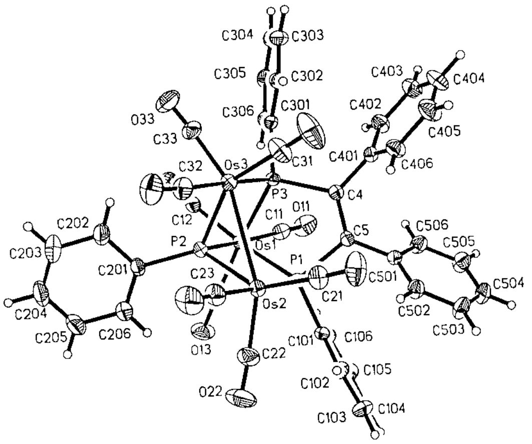


Fig. 7 Molecular structure of cluster **6**.

The first signal is assigned to P(2), the second to P(1) and P(3).

Positive ion FAB-MS spectra of clusters **2** and **4** were obtained using 3-nitrobenzyl alcohol as matrix. Cluster **2** shows an abundant quasi-molecular ion $[M + H]^+$ at *m*/*z* 1353 (based on ^{190}Os) and significant fragment ions formed by loss of up to ten CO ligands ($[M - 2CO]^+$ at *m*/*z* 1296, $[M - 3CO]^+$ at *m*/*z* 1268, *etc.*). **4** also shows an abundant quasi-molecular ion ($[M + H]^+$) at *m*/*z* 1353 (based on ^{190}Os) and significant fragment ions formed by successive loss of ten CO ligands.

Characterization of compounds 5 and 6

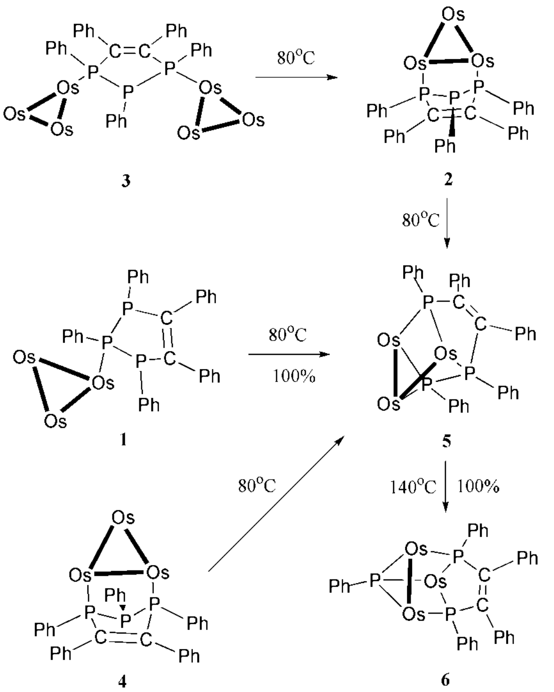
The molecular structure of compound **5** is shown in Fig. 6. The three osmium atoms form an isosceles triangle, with two metal–metal bonds [Os(1)–Os(2) 2.9731(5), Os(2)–Os(3) 2.9286(5) Å] and one open edge [Os(1) · · · Os(3) 3.9133 Å]. One P–P edge of the five membered ring of the ligand is broken. One phosphorus atom bridges the open edge of the osmium triangle while the central phosphorus atom bridges a bonded edge Os(2)–Os(3). The P–Os distances of the bonded edges of the osmium triangle [P(2)–Os(2) 2.331(2), P(2)–Os(3) 2.367(2) Å] are slightly shorter than those of the non-bonded Os · · · Os edge [P(3)–Os(1) 2.438(2), P(3)–Os(3) 2.435(2) Å]. The Os–Os bond distances [Os(1)–Os(2) 2.9731(5), Os(2)–Os(3) 2.9286(5) Å] are longer than those in $[Os_3(CO)_{12}]$ [2.877(3) Å].

The molecular structure of compound **6** is shown in Fig. 7. It contains three osmium atoms, with only one Os–Os bond [Os(2)–Os(3) 2.9608(5) Å]. The Os(1) · · · Os(3) and Os(1) · · · Os(2) distances, 3.8057 and 3.8005 Å respectively, are approximately 1 Å longer than normal Os–Os bonds *cf.* $[Os_3(CO)_{12}]$. The central phosphorus atom of the ligand breaks away from the ring and holds the three osmium atoms together by bonding to each of them, while the other two phosphorus atoms bridge the two open edges of the osmium triangle. The bond length of P(2)–Os(1) [2.4424(12) Å] is slightly longer than that of P(2)–Os(2) [2.3690(13) Å] and P(2)–Os(3) [2.3610(13) Å]. That means the distances between the capping phosphorus atom and the two bonded osmium atoms are shorter than those between the capping phosphorus atom and the non-bonded osmium atoms.

The ^{31}P-{^{1}H} NMR spectrum of cluster **5** shows three sets of signals: δ −95.4 (dd, $J_1 = 42.0$, $J_2 = 6.6$), 57.2 (dd, $J_1 = 232.7$, $J_2 = 6.9$) and 0.09 (dd, $J_1 = 232.4$, $J_2 = 41.8$ Hz). From the coupling constant values we can deduce that one P–P bond in the cyclic ligand has been cleaved, *i.e.* the PhPCPh=CPhPPhPPh fragment exists. It is easy to assign the signal at δ −95.4 (dd) to P(3), the atom which bridges the non-bonded Os···Os edge. It is rather difficult to assign the other peaks to either P(1) or P(2). The ^{31}P-{^{1}H} NMR spectrum of **6** shows two sets of signals at δ −154.8 (d, 2P) and −242.3 (t, 1P). The first is assigned to the two phosphorus atoms that bridge the two non-bonded osmium atoms, while the second is assigned to the phosphorus atom that caps the three osmium atoms.

Conversion of cluster derivatives

The conversion of cluster derivatives is summarized in Scheme 2. Heating **1** at 80 °C overnight enables the complete conversion into **5**, while **2** and **4** can also be partially converted into **5**. Complete conversion from **5** to **6** can be achieved by heating **5** at 140 °C overnight. Heating **3** at 80 °C resulted in the formation of **2**, **5** and [Os$_3$(CO)$_{12}$]. The reaction pathways involve the cleavage of P–P bond(s), attack of the phosphorus lone pair(s) on the osmium atoms, and cleavage of an Os–Os bond.



Scheme 2 Conversion of the cluster derivatives.

Conclusion

The reactions of the five-membered heterocyclic PhPPhPPhPCPh=CPh with [Os$_3$(CO)$_{12-n}$(NCMe)$_n$] ($n = 1$ or 2) under different conditions afford a series of new clusters **1**–**6**. In **1**, **2**, **3** and **4** the ligands are all intact with different configurations with respect to the phenyl groups attached to the three P atoms: *trans*, *cis* in **1**, *cis*, *cis* in **2**, *trans*, *trans* in **3** and *trans*, *trans* in **4**. **2** and **4** are isomers, differing in the orientation of the phenyl group attached to the central unco-ordinated phosphorus atom of the ligand ring: in **2** it bends away from the osmium triangle while in **4** it points towards the osmium triangle.

Unlike clusters **1**, **2**, **3** and **4**, which are structurally similar to those obtained with the five-membered homo-cyclopolyphosphine (PPh)$_5$, clusters **5** and **6**, derived from cleavage of P–P bond(s), are structurally different. Transformation of clusters **1**, **2** and **4** to **5** and then to **6** is a result of progressive cleavage of the P–P bonds and the Os–Os bonds leading finally to the incorporation of 'Os(CO)$_3$' and 'PhP' units in the structural framework of **6**.

Experimental

General comments

The reactions were carried out in evacuated reaction tubes using vacuum-line techniques. All solvents were dried using appropriate drying agents and distilled prior to use. The compounds PhPPhPPhPCPh=CPh,[2] [Os$_3$(CO)$_{11}$(MeCN)][15,16] and [Os$_3$(CO)$_{10}$(MeCN)$_2$][17] were prepared by literature methods. The products of the reactions were separated by thin-layer chromatography on 20 × 20 cm glass plates coated with 0.3 mm of Merck Kieselgel 60 GF$_{254}$ using mixtures of dichloromethane and hexane in various proportions as eluents. Infrared spectra were recorded as solutions in 0.5 mm KBr cells on a Bio-Rad FTS 160 FT-IR spectrophotometer, and ^{1}H and ^{31}P NMR spectra on a Bruker ACF-300 NMR MHz spectrometer using SiMe$_4$(^{1}H) and H$_3$PO$_4$(^{31}P) as references. Fast Atom Bombardment (FAB) mass spectra were obtained on a Finnigan MAT 95 XL(T) mass spectrometer.

Reaction of PhPPhPPhPCPh=CPh with [Os$_3$(CO)$_{11}$(MeCN)]

(a) At room temperature. The ligand L (60 mg, 0.120 mmol) was added to a solution of [Os$_3$(CO)$_{11}$(MeCN)] (111 mg, 0.120 mmol) in dichloromethane (10 ml). The mixture was stirred at room temperature overnight during which time it changed from yellow to orange. The solvent was removed under vacuum and TLC of the residue using dichloromethane–hexane (1 : 4) as eluent afforded compounds **1** ($R_f = 0.23$, 32.6 mg, 19.7%) (Found: C, 36.95; H, 2.03; P, 6.43. C$_{43}$H$_{25}$O$_{11}$Os$_3$P$_3$ requires: C, 37.39; H, 1.82; P, 6.72%) and **2** ($R_f = 0.13$, 8 mg, 4.9%) (Found: C, 37.08; H, 2.29; P, 6.19. C$_{42}$H$_{25}$O$_{10}$Os$_3$P$_3$ requires: C, 37.28; H, 1.86; P, 6.87%).

The ligand L (63 mg, 0.124 mmol) reacted with [Os$_3$(CO)$_{11}$(MeCN)] (228 mg, 0.248 mmol) under similar conditions to afford compounds **1** (59.7 mg, 34.8%), **2** (15 mg, 8.9%) and **3** ($R_f = 0.13$, 8 mg, 2.8%) (Found: C, 28.72; H, 1.35; P, 3.78. C$_{54}$H$_{25}$O$_{22}$Os$_6$P$_3$ requires: C, 28.70; H, 1.11; P, 4.11%).

(b) At 80 °C. [Os$_3$(CO)$_{11}$(MeCN)] (112 mg, 0.122 mmol), ligand L (61.2 mg, 0.122 mmol) and dichloromethane (10 ml) were mixed in a Carius tube. After the mixture was degassed, the Carius tube was sealed in vacuum, placed in an iron pipe, and heated in an oven at 80 °C for 17 h. The solution turned from yellow to orange. Excess of solvent was removed under vacuum. TLC of the residue using dichloromethane–hexane (1 : 4) as eluent afforded compounds **2** (24.1 mg, 14.6%) and **5** ($R_f = 0.38$, 39.5 mg, 13.64%) (Found: C, 37.34; H, 2.07; P, 6.49. C$_{41}$H$_{25}$O$_9$Os$_3$P$_3$ requires: C, 37.16; H, 1.90; P, 7.01%) and **6** ($R_f = 0.47$, 5 mg, 3.1%) (Found: C, 36.93; H, 2.12; P, 6.63. C$_{41}$H$_{25}$O$_9$Os$_3$P$_3$ requires: C, 37.16; H, 1.90; P, 7.01%).

Reaction of PhPPhPPhPCPh=CPh with [Os$_3$(CO)$_{10}$(MeCN)$_2$]

(a) At room temperature. The ligand L (88 mg, 0.176 mmol) was added to a solution of [Os$_3$(CO)$_{10}$(MeCN)$_2$] (164 mg, 0.176 mmol) in dichloromethane (10 ml). The mixture was stirred at

Table 3 Crystal data and data collection parameters for compounds **1**–**6**

	1	**2**	**3**	**4**	**5**	**6**
Formula	$C_{43}H_{25}O_{11}Os_3P_3$	$C_{42}H_{25}O_{10}Os_3P_3$	$C_{54}H_{25}O_{22}Os_6P_3$	$C_{42}H_{25}O_{10}Os_3P_3\cdot CH_2Cl_2$	$C_{41}H_{25}O_9Os_3P_3$	$C_{41}H_{25}O_9Os_3P_3$
Formula weight	1381.14	1353.13	2259.85	1438.06	1325.12	1325.12
T/K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a/Å	11.309(2)	12.195(2)	12.9826(12)	17.538(2)	9.50960(10)	13.366(3)
b/Å	13.627(3)	18.653(2)	15.074(4)	19.03240(10)	11.56210(10)	19.244(3)
c/Å	15.910(2)	18.832(2)	17.282(2)	13.540(2)	20.1480(2)	16.430(2)
α/°	111.977(14)		108.455(9)		82.1810(10)	
β/°	104.098(11)	90.030(11)	100.079(12)	91.959(5)	82.5320(10)	102.984(10)
γ/°	90.74(2)		98.27(2)		68.51(0)	
V/Å^3	2190.4(7)	4283.8(10)	3085.8(9)	4516.8(9)	2034.34(3)	4118.0(11)
Z	2	4	2	4	2	4
μ/mm^{-1}	8.847	9.044	12.456	8.698	9.518	9.404
Reflections collected	14342	27323	19944	40762	12851	26240
Independent reflections	10218	10546	14222	11286	9449	10247
	$R_{int} = 0.0255$	$R_{int} = 0.0425$	$R_{int} = 0.0311$	$R_{int} = 0.0538$	$R_{int} = 0.0511$	$R_{int} = 0.0292$
Final $R1$, $wR2$ indices [$I > 2\sigma I$]	0.0359, 0.0775	0.0322, 0.0727	0.0625, 0.1625	0.0727, 0.1892	0.0551, 0.1358	0.0275, 0.0576
(all data)	0.0586, 0.0879	0.0480, 0.0809	0.0949, 0.01846	0.1001, 0.2079	0.0683, 0.1429	0.0439, 0.0667

room temperature overnight during which time it changed from yellow to orange. The solvent was removed under vacuum and TLC of the residue using dichloromethane–hexane (1 : 4) as eluent afforded compounds **2** (4.6 mg, 1.9%) and **4** ($R_f = 0.36$, 18.6 mg, 7.8%) (Found: C, 36.52; H, 1.97; P, 6.00. $C_{42}H_{25}O_{10}Os_3P_3$ requires: C, 37.28; H, 1.86; P, 6.87%).

(b) At 120 °C. $[Os_3(CO)_{10}(MeCN)_2]$ (113.7 mg, 0.122 mmol), ligand L (61.2 mg, 0.122 mmol) and dichloromethane (10 ml) were added in a Carius tube. The reaction at 120 °C for 14 h afforded compounds **6** (10.1 mg, 6.25%) and **5** (52.1 mg, 32.2%).

Conversions

From compound 1 to 5. **1** (20 mg) and 5 ml of dichloromethane were added in a Carius tube. After the mixture was degassed, the Carius tube was sealed in vacuum, placed in an iron pipe and heated in an oven at 80 °C for 16 h. Removal of the solvent afforded compound **5** (yield: 100%).

From compounds 2 and 4 to 5. **2** (20 mg) and 5 ml of dichloromethane were added in a Carius tube. After the mixture was degassed, the Carius tube was sealed in vacuum, placed in an iron pipe and heated in an oven at 80 °C for 16 h. Only 30% of compound **2** was converted into **5**. Under similar conditions **4** was changed to a mixture containing **5**.

From compound 5 to 6. **5** (20 mg) and 5 ml of *p*-xylene were added in a Carius tube. After the mixture was degassed, the Carius tube was sealed in vacuum, placed in an iron pipe and heated in an oven at 140 °C for 16 h. Removal of the excess of solvent afforded compound **6** (yield: 100%).

From compound 3 to 2. **3** (4 mg) and 5 ml of dichloromethane were added in a Carius tube. After the mixture was degassed, the Carius tube was sealed in vacuum, placed in an iron pipe, and heated in an oven at 80 °C for 18 h. Removal of the solvent afforded compounds **2** (68.8%) and **5** (31.2%).

Crystallography

Crystal data and details of data collection for compounds **1**–**6** are given in Table 3. Data collection was carried out on a Siemens CCD SMART system. The structures of all the complexes were solved by direct methods and remaining non-hydrogen atoms located in Fourier difference maps. Full-matrix least-squares refinements were carried out with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed on calculated positions (C–H 0.96 Å) and assigned isotropic thermal parameters riding on their parent atoms. Refinements were carried out on a Silicon Graphic workstation using SHELXTL IR1S Version 5.04 software package.[18] The data for crystal structures of **3**, **4** and **5** all show high residual electron peaks close to the metal atoms. For **4**, atoms C13, C23 and C33 had to be refined isotropically.

CCDC reference number 186/2127.

See http://www.rsc.org/suppdata/dt/b0/b002140g/ for crystallographic files in .cif format.

Acknowledgements

We thank the National University of Singapore for financial support and for research scholarships (to Xiao Wang).

References

1 W. Mahler, *J. Am. Chem. Soc.*, 1964, **86**, 2306.
2 C. Charrier, J. Guilhem and F. Mathey, *J. Org. Chem.*, 1981, **46**, 3.
3 B. O. West, in *Homoatomic rings, Chains and Macromolecules of the Main Group Elements*, ed. A. L. Rheingold, Elsevier, Amsterdam, 1977, p. 409.
4 M. Baudler and K. Blinka, *Chem. Rev.*, 1993, **93**, 1623.
5 C. S. Cundy, M. Green, F. G. A. Stone and T. R. Alison, *J. Chem. Soc. A*, 1968,1776.
6 B. F. G. Johnson, T. M. Layer, J. Lewis, P. R. Raithby and W. T. Wong, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 973.
7 E. Charalambous, L. Heuer, B. F. G. Johnson, J. Lewis, W. S. Li, M. McPartin and A. D. Massey, *J. Organomet. Chem.*, 1994, **468**, C9.
8 H. G. Ang, S. G. Ang, W. L. Kwik and Q. Zhang, *J. Organomet. Chem.*, 1994, **485**, C6.
9 H. G. Ang, L. L. Koh and Q. Zhang, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 2757.
10 H. G. Ang, S. G. Ang and Q. Zhang, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 2773.
11 A. H. Cowley and K. E. Hill, *Inorg. Chem.*, 1974, **12**, 1446.
12 I. G. Phillips, R. G. Ball and R. G. Cavell, *Inorg. Chem.*, 1988, **27**, 2269.
13 F. W. Heinemann, S. Kummer, U. Seiss-Brandl and U. Zenneck, *Organometallics*, 1999, **18**, 2021.
14 I. G. Phillips, R. G. Ball and R. G. Cavell, *Inorg. Chem.*, 1987, **26**, 4074.
15 J. N. Nicholls and M. D. Vargas, *Inorg. Synth.*, 1990, **28**, 232.
16 B. F. G. Johnson, J. Lewis and D. A. Pippard, *J. Chem. Soc.*, *Dalton Trans.*, 1981, 407.
17 J. N. Nicholls and M. D. Vargas, *Inorg. Synth.*, 1990, **28**, 234.
18 SHELXTL reference manual, version 5.1, Bruker AXS, Inc., Madison, WI, 1997.