DALTON
FULL PAPER

Reactions of 1,2,3-triphenyl-1,2,3-triphosphaindan with activated triosmium carbonyl clusters: characterization and crystal structure of the products

Siau-Gek Ang,* Xinhua Zhong and How-Ghee Ang

Department of Chemistry, National University of Singapore, 119260, Singapore

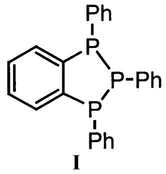
Received 31st October 2000, Accepted 8th February 2001
First published as an Advance Article on the web 8th March 2001

Reaction of 1,2,3-triphenyl-1,2,3-triphosphaindan (**I**) with $[Os_3(CO)_{11}(NCMe)]$ at room temperature afforded two clusters: mono-substituted trinuclear $[Os_3(CO)_{11}\{1\text{-}C_6H_4(PPh)_3\}]$ **1** and bridged bis-trinuclear $[\{Os_3(CO)_{11}\}_2\{\mu\text{-}1,3\text{-}\eta^2\text{-}C_6H_4(PPh)_3\}]$ **2**, which can also be prepared by further reaction of **1** with an equimolar amount of $[Os_3(CO)_{11}(NCMe)]$. The reaction at 100 °C gave, apart from cluster **2**, a di-substituted bridged cluster, $[Os_3(CO)_{10}\{\mu\text{-}1,3\text{-}\eta^2\text{-}C_6H_4(PPh)_3\}]$ **3**, and that at 140 °C formed a linked pentanuclear cluster, $[Os_2(CO)_6\{\mu_3\text{-}\eta^3\text{-}PPhC_6H_4(PPh)_2\}Os_3(CO)_{11}]$ **4** and a trinuclear cluster with only two M–M bonds, $[Os_3(CO)_9\{\mu_3\text{-}\eta^3\text{-}PPhC_6H_4(PPh)_2\}]$ **5** together with **3**. Similarly $[Os_3(CO)_{10}(NCMe)_2]$ reacted with **I** at room temperature to afford **3** in good yields. The conversion of cluster **1** into **3** can be achieved through pyrolysis of a solution of **1**. Cluster **4** exhibits stereochemical non-rigidity in the solution state and exists as two isomers at low temperature. All the new compounds were characterized by spectroscopic and analytical techniques and their structures established by X-ray crystallography.

Introduction

Phosphorus-containing carbonyl clusters of Group VIIIA metals (Fe, Ru, Os) play an important role in the chemistry of metal carbonyl clusters mainly due to their low tendency to fragment into monometallic species and consequently to their potential use in many stoichiometric and catalytic reactions.[1,2] Study of the reactions of compounds containing phosphorus–phosphorus bond(s) with metal carbonyls started from tetraalkyldiphosphane,[3,4] which resulted either in retention of the bond to give complexes with this ligand or in rupture to give dialkylphosphido metal carbonyl derivatives. The study of reactions between metal carbonyls and compounds containing such bond(s) has been extended to cyclic derivatives with phosphorus–phosphorus bond(s) in the ring and carbonyl clusters. Cowley and Hill[5] reported the reaction of tetrakis-(trifluoromethyl)-1,2-diphosphetene with $[Fe_2(CO)_9]$ to give products of stoichiometries $(CF_3)_2P_2C_2(CF_3)_2Fe(CO)_4$ and $(CF_3)_2P_2C_2(CF_3)_2Fe_3(CO)_{10}$. Ang[6–11] and others[12,13] found that cyclopolyphosphines $(PR)_n$ (R = Ph, Et, Bu^t or CF_3; $n = 4$ or 5) reacted with ruthenium or osmium carbonyl clusters to give cluster derivatives with phosphido/phosphidene substitution or coordination of the cyclopolyphosphine ligand. Pentaphenyl-1,2,3-triphospholene[14] was recently reported to react with osmium clusters to give some cluster derivatives with one or none of the phosphorus–phosphorus bonds cleaved.

The reactions of 1,2,3-triphenyl-1,2,3-triphosphaindan (**I**) with $[Fe_2(CO)_9]$ or $[Fe_3(CO)_{12}]$ have been reported by King and co-workers[15,16] to give compounds with coordination of ligand **I** either intact or with the cleavage of one phosphorus–phosphorus bond. In other cases, both the phosphorus–phosphorus bonds are ruptured with the extrusion of a PPh unit to form Fe_3P_3 clusters. This paper describes the reactions of **I** with activated triosmium carbonyl clusters $[Os_3(CO)_{11}(NCMe)]$ and $[Os_3(CO)_{10}(NCMe)_2]$ under different conditions. In the products obtained **I** acts as a mono- or a bi-dentate ligand with the ring intact to give mono- or di-substituted cluster derivatives **1**, **2** and **3**, or with one P–P bond cleaved to form bis(μ-phosphido) derivatives **4** and **5**.



I

Results and discussion

Reactions (Scheme 1) of 1,2,3-triphenyl-1,2,3-triphosphaindan (**I**) with the activated osmium cluster $[Os_3(CO)_{11}(NCMe)]$ in 1 : 1 molar ratio at different temperatures yielded a series of phosphorus complexed osmium clusters **1–5**. From the reaction at room temperature, a mono-substituted trinuclear cluster $[Os_3(CO)_{11}\{1\text{-}C_6H_4(PPh)_3\}]$ **1** and a bridged bis-trinuclear cluster, $[\{Os_3(CO)_{11}\}_2\{\mu\text{-}1,3\text{-}\eta^2\text{-}C_6H_4(PPh)_3\}]$ **2**, were isolated in relatively high yields (37 and 30% respectively). Using an excess of ligand or cluster in this reaction led to the same products but with different yields (1 : 1 cluster : ligand ratio favors formation of cluster **1**, while, a 2 : 1 ratio gave cluster **2** in highest yield). When the reaction temperature was raised to 100 °C, cluster **2** and a di-substituted bridged trinuclear cluster $[Os_3(CO)_{10}\{\mu\text{-}1,3\text{-}\eta^2\text{-}C_6H_4(PPh)_3\}]$ **3** were formed in moderate yields (30 and 20% respectively), while cluster **1** was not found. This is because **1** can be converted into **3** at this temperature. The reaction temperature was further raised to 140 °C, to give low yields of cluster **3**, a linked pentanuclear cluster $[Os_2(CO)_6\{\mu_3\text{-}\eta^3\text{-}PPhC_6H_4(PPh)_2\}Os_3(CO)_{11}]$ **4** consisting of a dinuclear $[Os_2(CO)_6]$ and a trinuclear $[Os_3(CO)_{11}]$ unit held together by the triphosphaindan ligand with one P–P bond cleaved, and a trinuclear cluster with only two M–M bonds $[Os_3(CO)_9\{\mu_3\text{-}\eta^3\text{-}PPhC_6H_4(PPh)_2\}]$ **5**. Cluster **1** is shown to be the precursor of **2**. It reacted further with $[Os_3(CO)_{11}(NCMe)]$ in 1 : 1 molar ratio at room temperature to give cluster **2** in high yields (52%). Cluster **3** could also be obtained in high yields (55%) from the reaction of **I** with $[Os_3(CO)_{10}(NCMe)_2]$ in 1 : 1 molar ratio at room temperature.

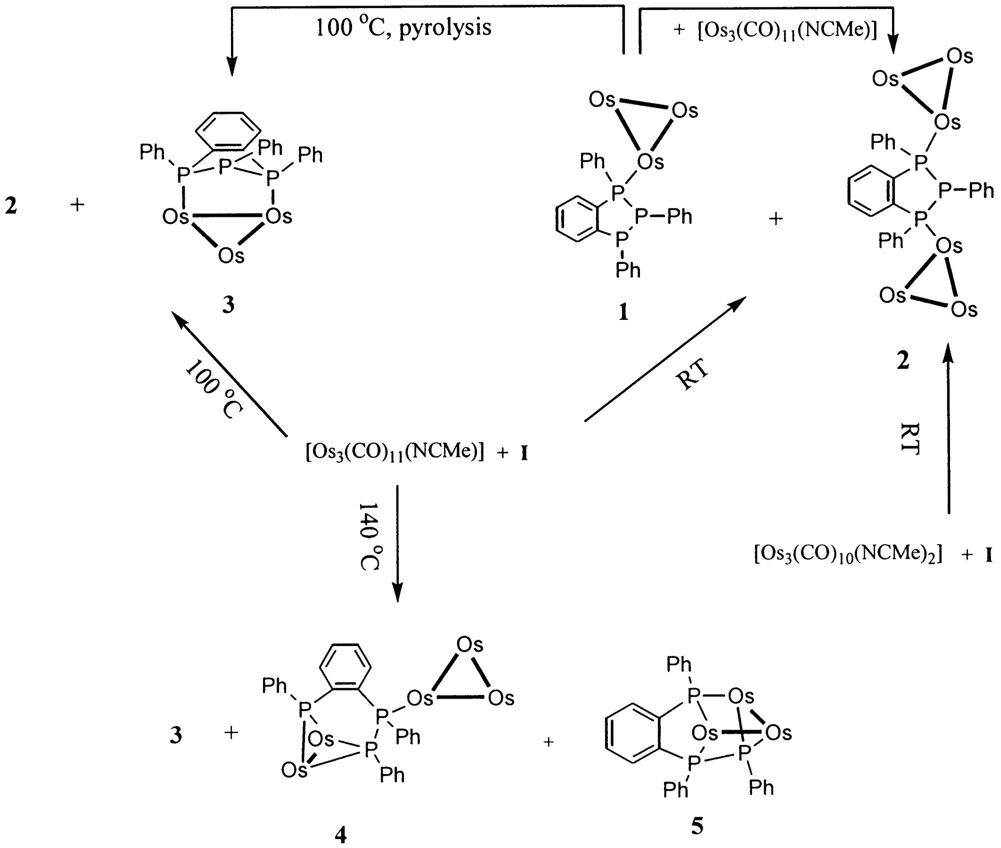
All the new compounds obtained were fully characterized by FAB mass spectrometry, elemental analysis, IR, ^1H and ^{31}P

DOI: 10.1039/b008766l

Table 1 Spectroscopic data for clusters **1** to **5**

Complex	IR, ν(CO)[a]/cm^{-1}	^{1}H NMR, δ (J/Hz)[b]	^{31}P-{^{1}H} NMR, δ (J/Hz)[c]	MS, m/z[d]
1	2106m, 2055s, 2035w, 2019vs, 2002w, 1988w, 1980w	8.3–6.7 (m, Ph)	22.3 (d, 267.0, 1P, P^3) 13.1 (d, 256.0, 1P, P^1) −36.2 (dd, 267.0, 256.0, 1P, P^2)	1279 (1279)
2	2106m, 2057s, 2037w, 2023vs, 2008w, 1990w, 1975w	8.3–6.8 (m, Ph)	13.3 (dd, 264.5, 2P, P^2, P^3) −23.9 (dd, 264.5, 1P, P^2)	2158 (2158)
3	2093s, 2033w, 2020w, 2008vs, 1974w, 1962w, 1952w	7.6–6.8 (m, Ph)	48.8 (dd, 253, 1P, P^2) −2.4 (dd, 253.0, 2P, P^1, P^3)	1251 (1251)
4[e]	2109m, 2074m, 2058s, 2046m, 2038w, 2021vs, 2004w, 1987w	7.8–6.6 (m, Ph)	6.9 (dd, 223.2, 83.2, 1P, P^1) −4.6 (d, 83.2, 1P, P^3) −49.5 (d, 223.2, 1P, P^2)	1827 (1827)
5	2071s, 2047vs, 2013vs, 2006s, 1990w, 1978w, 1963w, 1937w	8.0–6.6 (m, Ph)	32.0 (dd, 217.4, 7.6, 1P, P) −9.3 (dd, 217.4, 26.7, 1P, P) −107.4 (dd, 26.7, 7.6, 1P, P)	1223 (1223)

[a] In CH_2Cl_2. [b] In $CDCl_3$ with $SiMe_4$ as reference. [c] In $CDCl_3$ with 85% H_3PO_4 as reference. [d] Simulated values given in parentheses. [e] NMR recorded at 55 °C.



Scheme 1 All CO groups on Os atoms are omitted for clarity.

NMR spectroscopies, and single-crystal X-ray crystallography. The IR, FAB mass data, ^{1}H and ^{31}P-{^{1}H} NMR chemical shifts and coupling constants are listed in Table 1. The positive FAB mass spectra of these compounds exhibit isotopic peak envelopes at the corresponding molecular weight values which are followed by a series of peaks due to loss of carbonyl ligands. The carbonyl stretching vibrations of all the compounds fall in the region between 2150 and 1900 cm^{-1}, indicating that all the carbonyl groups are terminal. ^{1}H NMR spectra of all the compounds show resonance signals in the range δ 6.6–8.3, which is characteristic for phenyl protons. Proton-decoupled phosphorus-31 (^{31}P-{^{1}H}) NMR spectroscopy is very useful for elucidating the structures of the compounds obtained in this study since the $^1J_{PP}$ values for directly bonded phosphorus atoms are relatively large (≈200 Hz), while $^2J_{PP}$ and $^3J_{PP}$ are much smaller (usually less than 50 Hz), and thus readily identifiable from the spectra. For this reason the ^{31}P NMR spectra can be used to determine whether the P–P bond(s) in **I** remain intact or whether one (or both) is no longer present in the products. The ^{31}P NMR spectra of all the clusters were interpreted and assigned.

Spectroscopic and structural characterization of clusters 1, 2 and 3

The ^{31}P-{^{1}H} NMR spectrum of cluster **1** shows an AMX spin pattern [δ_A 22.3 (d, 267.0); δ_M 13.1 (d, 256.0), δ_X −36.2 (dd, 267.0, 256.0 Hz)], which is consistent with a species in which the P–P bonds of the triphosphaindan remain intact. From the non-equivalence of the outer phosphorus atoms in ligand **I**, we conclude that the central phosphorus atom is not bonded to the osmium group. The elemental analysis data are in accordance with the formula $C_6H_4(PC_6H_5)_3{\cdot}Os_3(CO)_{11}$ and its positive FAB MS reveals an intense molecular envelope centered at m/z 1279. We therefore deduce that only one of the outer phosphorus atoms is bonded to the triosmium group. The

Table 2 Selected bond lengths (Å) and angles (°) for clusters **1**, **2** and **3**

	1[a]	**2**	**3**[b]
Os(1)–Os(2)/Os(4)–Os(5)	2.8742(8)/2.9230(7)	2.8790(5)/2.8769(5)	2.8764(7)
Os(1)–Os(3)/Os(4)–Os(6)	2.9103(7)/2.8769(8)	2.9133(5)/2.9304(5)	2.9033(8)
Os(2)–Os(3)/Os(5)–Os(6)	2.8891(8)/2.8888(11)	2.8826(5)/2.8763(6)	2.8764(7)
Os(1)–P(1)/Os(4)–P(4)	2.349(3)/2.350(3)	2.348(2)/2.348(2)	2.324(2)
P(1)–P(2)/P(4)–P(5)	2.213(4)/2.213(4)	2.221(3)	2.212(3)
P(2)–P(3)/P(5)–P(6)	2.194(4)/2.200(4)	2.221(3)	2.212(3)
Os(1)–Os(2)–Os(3)/Os(4)–Os(5)–Os(6)	60.66(2)/59.34(2)	60.749(12)/61.242(12)	60.22(2)
Os(2)–Os(3)–Os(1)/Os(5)–Os(6)–Os(4)	59.42(2)/60.92(2)	59.563(13)/59.390(12)	59.691(11)
Os(3)–Os(1)–Os(2)/Os(6)–Os(4)–Os(5)	59.92(2)/59.74(2)	59.688(13)/59.368(13)	59.691(11)
P(1)–P(2)–P(3)/P(4)–P(5)–P(6)	95.75(14)/96.24(14)	93.71(11)	83.75(16)
Os(3)–Os(1)–P(1)/Os(6)–Os(4)–P(4)	104.51(7)/105.04(7)	101.37(5)/104.46(5)	90.61(5)

[a] Two independent molecules contained in the unit cell. [b] Os(3) and P(3) correspond to Os(1′) and P(1′) respectively.

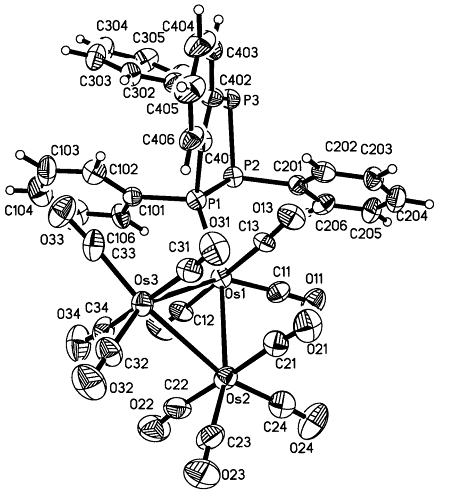


Fig. 1 Molecular structure of cluster **1** showing the atom-labelling scheme for non-hydrogen atoms.

IR spectrum is similar to that of mono-substituted triosmium cluster derivatives: $[Os_3(CO)_{11}(PR_3)]$ (R = Ph,[17] Me[18] or Et[19]). In the ^{31}P NMR spectrum the δ_X signal can be unambiguously assigned to the central phosphorus atom P(2). δ_M is assigned to the coordinated outer phosphorus atom P(1) based on the reason that the magnitude of the $^1J_{PP}$ coupling constant will be reduced when the lone pair electrons of the three-coordinated phosphorus atom are removed by complexation.[20] δ_A is then assigned to the uncoordinated outer phosphorus atom P(3). **1** is not thermally stable at high temperature. When pyrolysed at 100 °C, it is almost completely converted into cluster **3**.

The proposed structure of cluster **1** is further confirmed by single crystal X-ray diffraction analysis. The asymmetric unit consists of $\mathbf{1}\cdot 0.25CH_2Cl_2\cdot 0.25C_6H_{14}$. Two independent molecules are contained in the unit cell. The molecular structure is shown in Fig. 1 together with the atomic numbering scheme. Important bond distances and angles are listed in Table 2. The geometry of **1** is based on $Os_3(CO)_{12}$ with one of the equatorial carbonyls replaced by the outer phosphorus atom P(1) of ligand **I**. The structure is typical for $[Os_3(CO)_{11}(PR_3)]$ (PR_3 = phosphine or phosphite) complexes with the axial carbonyls perpendicular to the Os_3 triangle. As in other bulky ligand substituted triosmium clusters,[8,21,22] the Os–Os bond *cis* to the phosphorus atom, Os(1)–Os(3) [2.9103(7) Å], is the longest and significantly longer than the average of the other two bonds [2.8816(8) Å] in **1**. This is attributed to the steric repulsion between the bulky ligand and the adjacent equatorial carbonyl ligands (C(13)–Os(1)–Os(2) is 91.9(3)°, while P(1)–Os(1)–Os(3) is 104.51(7)°). The P–Os distance of 2.349(3) Å in **1** falls in the range (2.238(1) to 2.478(1) Å) for Os–P bond lengths in the $[Os_3(CO)_{11}(PR_3)]$ clusters previously reported.[22,23] The geometry of the triphosphaindan portion in **1** is similar to that of the free ligand.[24] The phenyl group attached to P(2) is *trans* to those at P(1) and P(3). Unlike the free ligand, the bicyclic phosphaindan nuclei in **1** are not coplanar.

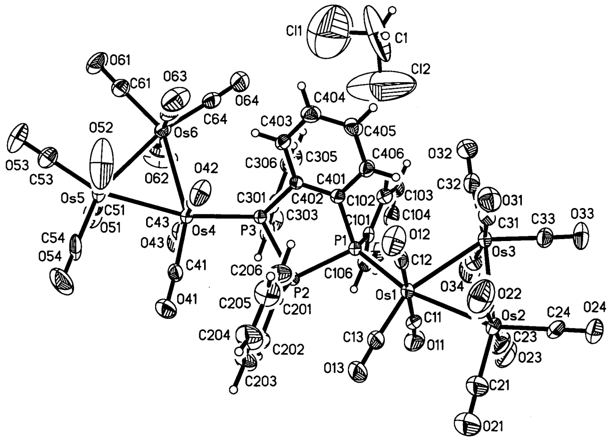


Fig. 2 Molecular structure of cluster $\mathbf{2}\cdot CH_2Cl_2$. Details as in Fig. 1.

The ^{31}P-{^1H} NMR spectrum of cluster **2** exhibits a second-order AB_2 spin pattern [δ_A −23.9 (t, 264.5); δ_B 13.3 (d, 264.5 Hz)] similar to that of the free ligand **I**.[25] Because of the presence of a large coupling constant (264.5 Hz), which lies within the typical $^1J_{PP}$ range, we can deduce that the two P–P bonds of **I** remain intact. δ_A corresponds to the central phosphorus atom, δ_B to the equivalent two outer phosphorus atoms. The resonance centered at δ 32.5 for free **I** corresponding to the equivalent outer phosphorus atoms is shifted upfield to δ 13.3 for **2** whereas that at δ −39.4 for **I** corresponding to the central phosphorus atom is shifted downfield to δ −23.9. From the ^{31}P NMR spectrum we can deduce that in **2** either both outer phosphorus atoms or the central phosphorus atom is bonded to the triosmium group. The result of elemental analysis demonstrates that the formula is $C_6H_4(PPh)_3\cdot\{Os_3(CO)_{11}\}_2$ and the corresponding FAB MS exhibits a molecular ion peak at *m*/*z* 2158, which leads to the conclusion that both outer phosphorus atoms are bonded to two discrete triosmium groups. The close similarities in the patterns of the IR ν(CO) frequencies of **2** to those of known compounds $[\{Os_3(CO)_{11}\}_2\{\mu\text{-}\eta^2\text{-}(PPh)_5\}]$[9] and $[\{Os_3(CO)_{11}\}_2\{\mu\text{-}\eta^2\text{-}Ph_2PCCPPh_2\}]$[26] provided further evidence for this proposal.

Single-crystal X-ray diffraction confirmed this proposed structure. The asymmetric unit of cluster **2** consists of $\mathbf{2}\cdot CH_2Cl_2$. The molecular structure is depicted in Fig. 2 together with the atomic labeling scheme and relevant structural parameters are listed in Table 2. The structure consists of two discrete

Table 3 Selected bond lengths(Å) and angles(°) for clusters **4** and **5**

	4	**5**		**4**	**5**
Os(1)–Os(2)	2.8178(4)	2.8900(2)	Os(3)–P(2)	2.369(2)	2.3693(11)
Os(2)–Os(3)		2.9633(2)	Os(3)–P(3)		2.4078(11)
Os(1)–Os(3)		3.9296	P(1)–P(2)	2.213(3)	2.1900(6)
Os(3)–Os(4)	2.9142(5)				
Os(3)–Os(5)	2.8884(4)		Os(1)–P(1)–Os(2)	72.79(6)	76.08(3)
Os(4)–Os(5)	2.8764(5)		Os(1)–P(3)–Os(2)/Os(3)	72.95(6)	108.87(4)
Os(1)–P(1)	2.378(2)		Os(1)–Os(2)–Os(3)		84.333(7)
Os(1)–P(3)	2.363(2)	2.3667(11)	Os(3)–Os(4)–Os(5)	59.840(11)	
Os(2)–P(1)	2.371(2)	2.4231(11)	Os(4)–Os(5)–Os(3)	60.730(11)	
Os(2)–P(3)	2.377(2)	2.3232(11)	Os(5)–Os(3)–Os(4)	59.430(12)	

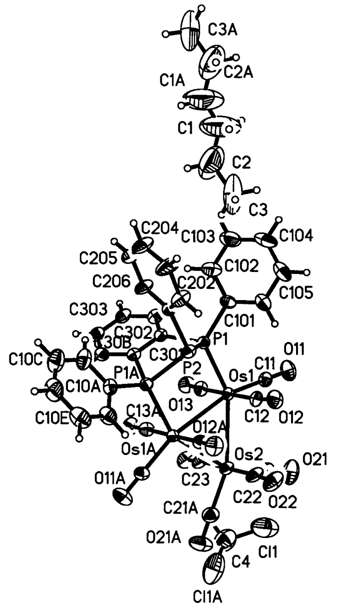


Fig. 3 Molecular structure of cluster **3**·CH_2Cl_2·C_6H_{14}. Details as in Fig. 1.

triosmium triangles linked at two equatorial sites through P(1) and P(3) atoms. As in the case of **1**, the Os–Os bonds *cis* to the phosphorus atoms, Os(1)–Os(3) [2.9133(5) Å] and Os(4)–Os(6) [2.9304(5) Å], are the longest and significantly longer than the average length of the other four bonds [2.8780(7) Å]. Owing to the coordination of P(1) and P(3) to heavy triosmium atoms, the average P–P bond length (2.223 Å) and the P–C distance of the phosphorus atoms to the fused phenyl ring (1.843 Å) in **2** are a little longer than the corresponding bonds in the "free" ligand (2.209, 1.823 Å respectively). The geometry of the triphosphaindan portion in **2** is similar to that of the "free" ligand. The phenyl group at P(2) is *trans* to those on P(1) and P(3). Another feature of **2** is that P(1), P(3) and the fused phenyl ring are almost coplanar while P(2) lies out of this plane. Cluster **2** is thermally stable. When pyrolysis of it in toluene solution was carried out at 100 °C overnight no decomposition was observed. **2** can be formed from **1** by treating the latter with a stoichiometric quantity of $[Os_3(CO)_{11}(NCMe)]$ at room temperature, giving 52% yield.

The ^{31}P-{^1H} NMR spectrum of cluster **3** shows the same AB_2 spin pattern [δ_A 48.8 (t, 253.0); δ_B −2.4 (d, 253.0 Hz)] as that for **2**. This indicates that the triphosphaindan portion in **3** remains intact as in **2**. Compared to the ^{31}P NMR spectrum of the free ligand **I**, the chemical shift of the two equivalent coordinated P(1) and P(3) atoms in **3** (from the crystal structure) is shifted upfield to δ −2.4 from 32.5 for **I** whereas the chemical shift of the uncoordinated P(2) atom in **3** is shifted downfield to δ 48.8 from −39.4. Elemental analysis data show that only one ligand is coordinated to one triosmium group. Comparing the IR spectrum of **3** with those of known compounds $[Os_3(CO)_{10}\{\mu\text{-}\eta^2\text{-}(PPh)_5\}]$[9] and $[Os_3(CO)_{10}\{\mu\text{-}\eta^2\text{-}(PhP(CH_2)_nPPh)\}]$ ($n = 2$–4),[26,27] we deduce that the outer phosphorus atoms in the triphosphaindan portion bridge across an Os–Os edge of the triosmium triangle in a μ-η^2-coordination mode in **3**.

Single-crystal X-ray diffraction analysis confirmed the proposed structure given in Fig. 3 with selected bond distances and angles listed in Table 2. In this compound triphosphaindan acts as a bidentate ligand, occupying equatorial sites on the osmium triangle plane and bridging over an Os–Os edge through the outer phosphorus atoms P(1) and P(1′). The bicyclic triphosphaindan nucleus is roughly planar with only P(2) atom out of the plane. Excluding P(2), the triphosphaindan plane is approximately perpendicular to the triosmium plane. Unlike the free ligand, in which the phenyl group on the central phosphorus atom P(2) is *trans* to those on the two side phosphorus atoms P(1) and P(1′), the phenyl groups bonded to the three phosphorus atoms in **3** are all above the triphosphaindan plane with a *cis*, *cis* configuration. To accommodate the short Os–Os distance and to coordinate to the osmium atom, the angle of P(1)–P(2)–P(1′) (83.75°) in **3** is much smaller than that in the free ligand (97.3°), which reflects a large torsional strain of the ring. The molecule of **3** has mirror symmetry through the plane of Os(2), P(2) and the center of the fused phenyl ring. The bridged Os–Os distance (2.9033 Å) in **3** is a little longer than the non-bridged Os–Os distance (2.8764 Å), which is in accordance with observations in diphosphine triosmium cluster derivatives $[Os_3(CO)_{10}\{\mu\text{-}\eta^2\text{-}(PhP(CH_2)_nPPh)\}]$ ($n = 2$–4),[27,28] but contrary to what is found in $[Os_3(CO)_{10}\{\mu\text{-}\eta^2\text{-}(PPh)_5\}]$.[9]

Spectroscopic and structural characterization of clusters 4 and 5

The ^{31}P-{^1H} NMR spectrum of cluster **4** (recorded at 55 °C in $CDCl_3$) exhibits an AMX spin pattern (δ_A 6.9 (dd, 223.2, 83.2); δ_M −4.6 (d, 83.2) and δ_X −49.5 (d, 223.2 Hz)). The appearance of six sets of resonances in the low-temperature-limiting spectrum implies the presence of two interconverting isomers (**4a**, **4b**) as discussed below. The ratio of the two isomers is estimated to be about 5 : 1 in dichloromethane at −75 °C from the ^{31}P NMR spectrum. On recrystallization only crystals of one isomer are obtained, but there is insufficient information to identify it as **4a** or **4b**. The molecular structure of the crystalline form has been established by X-ray crystallography and is shown in Fig. 4 together with the atomic numbering scheme. In the structure the half hexane solvent molecule in the asymmetric unit is poorly defined. The important bond lengths and angles are listed in Table 3. The cluster can be viewed as a binuclear $Os_2(CO)_6$ unit linked to a triosmium triangle $Os_3(CO)_{11}$ through a triphosphaindan ligand with one P–P bond cleaved. Both phosphorus atoms (P(1), P(3)) from the broken P–P bond bridge over the binuclear $Os_2(CO)_6$ unit *via* bis(μ-phosphido) mode to form a butterfly configuration with a dihedral angle of 80.6°. The other phosphorus atom P(2) bonds to the triosmium triangular cluster *via* an equatorial site. The triosmium unit points to the side of the fused phenyl group. The Os–Os distance of the binuclear unit

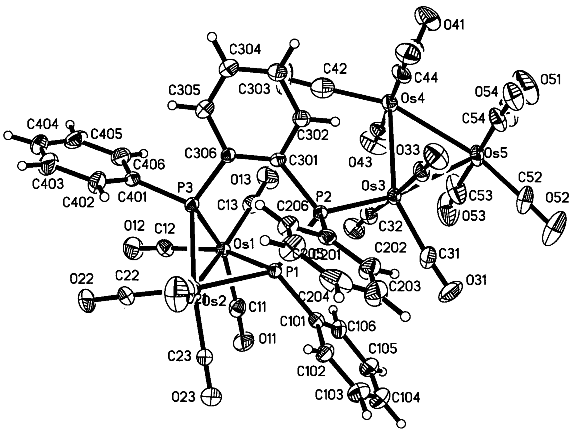


Fig. 4 Molecular structure of crystalline form cluster **4**. Details as in Fig. 1.

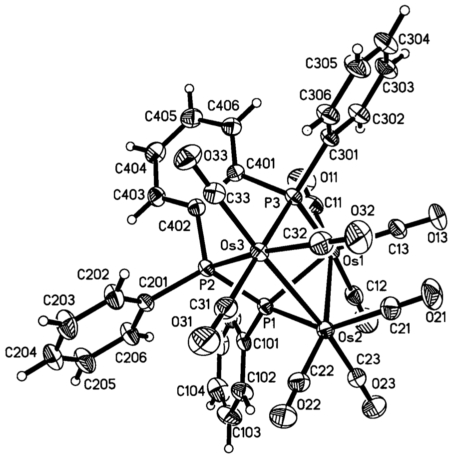


Fig. 5 Molecular structure of cluster **5**. Details as in Fig. 1.

[2.8178(4) Å] is shorter than the average Os–Os bond distance of the triosmium triangular unit [2.8930(5) Å] and of $[Os_3(CO)_{12}]$ (2.877 Å).[29] The distance of the existing P–P bond P(1)–P(2) is 2.213(3) Å, which is almost the same as that in the free ligand (2.209 Å).

The ^{31}P-{^1H} NMR spectrum of cluster **5** exhibits an AMX spin pattern [δ_A 32.0 (dd, 217.4, 7.6); δ_M −9.3 (dd, 217.4, 26.7); δ_X −107.4 (dd, 26.7, 7.6 Hz)]. δ_A and δ_M have a large value coupling constant of 217.4 Hz, which corresponds to a $^1J_{PP}$ value of two directly bonded phosphorus atoms. The third phosphorus resonance δ_X does not contain any large coupling, which means that this phosphorus atom is not directly bonded to either of the other two, indicating that one of the P–P bonds in the triphosphaindan has been cleaved. Together with the crystal structure, the resonance at δ −107.4 can be assigned to P(3). It is difficult to assign the remaining two resonances for P(1) and P(2). The upfield shift of P(3) also serves as a probe for the absence of M–M bonding between Os(1) and Os(3) with which P(3) bonds.[30] Single crystal X-ray diffraction analysis gave the structure of **5**, shown in Fig. 5 together with the atomic numbering scheme. Selected bond distances and angles are listed in Table 3. Cluster **5** consists of a triangular array of three osmium atoms with only two M–M bonds. One P–P bond in triphosphaindan is cleaved and two phosphorus atoms act as bridging phosphido ligands, one across a Os–Os edge, the other linking two non-bonding osmium atoms. The other phosphorus atom P(2) acts as a σ-donor ligand. The Os(1)–Os(2) distance (2.8900(2) Å) is evidently shorter than that of Os(2)–Os(3) (2.9633(2) Å), although both pairs are within bonding distance, while the Os(1) and Os(3) atoms are at a non-bonding distance of 3.9296 Å. The intact P–P bond distance [2.1900(6) Å] is almost the same as that in the "free" ligand (2.209 Å). Since P(3) bridges two discrete Os atoms, the distance between it and the fused phenyl ring, P(3)–C(401) [1.851(4) Å], is longer than the other corresponding P(2)–C(402) distance [1.818(4) Å] and that in the free ligand (1.823 Å).

Phosphorus-31 NMR spectrum and fluxional behavior of cluster 4

At room temperature the resonance signals of the ^{31}P NMR spectrum of cluster **4** broaden owing to its non-rigidity in the solution state. Variable-temperature ^{31}P-{^1H} NMR spectra of **4** were acquired as shown in Fig. 6. The appearance of six sets of resonances in the low-temperature-limiting spectrum signifies the presence of two isomers (**4a** and **4b**) in **4**. Their ratio is estimated to be about 5 : 1 in dichloromethane at −75 °C from the ^{31}P NMR spectrum. The three resonances with higher integration intensity are assigned to isomer **4a**: P(1) δ 13.3 (dd, 211.6, 82.4); P(2), −47.3 (d, 211.6); P(3), −3.2 (d, 82.4 Hz). The assignment of that at δ 13.3 to P(1) is based on the large $^2J_{PP}$ coupling (82.4 Hz) between two phosphido bridges (the value for $[Pd_2(\mu\text{-}PBu^t{}_2)(\mu\text{-dppm})(PMe_3)_2]^+$ is as high as 199.5 Hz[31]). The remaining three resonances with lower integration intensity are assigned to isomer **4b**. Even though the signals of P(1) and P(3) in **4b** partly overlap, the respective chemical shifts and coupling constants for different phosphorus atoms can still be deduced from their coupling relationship: P(1) δ −6.9 (dd, 167.5, 85.5); P(2) −57.5 (dd, 167.5, 30.5); P(3) −6.0 (dd, 85.5, 30.5 Hz). Warming the solution of **4** results in broadening of the sharp peaks to humps which coalesce at about 255 K and finally merge into three pairs of sharp resolved peaks (corresponding to the average signals of isomers **4a** and **4b**) with integration ratio of 1 : 1 : 1 at high temperature. The free energy of activation for this fluxional process is estimated to be 46 kJ mol^{-1} from the coalescence temperature.[32] When the temperature is lowered the same spin pattern appears at the original positions again, indicating no decomposition of cluster **4** during the variable-temperature studies.

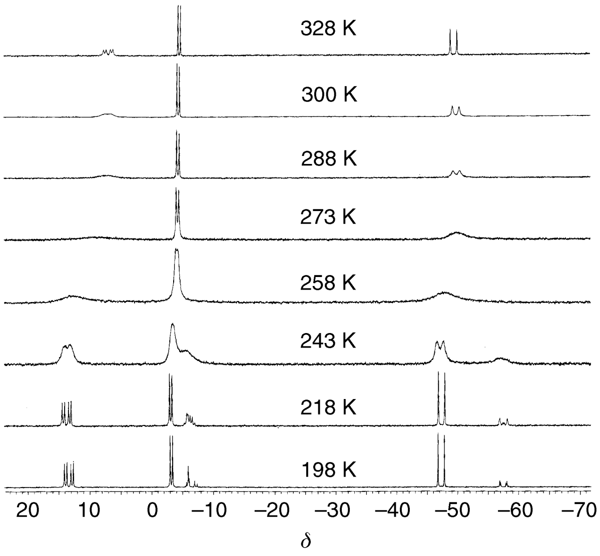
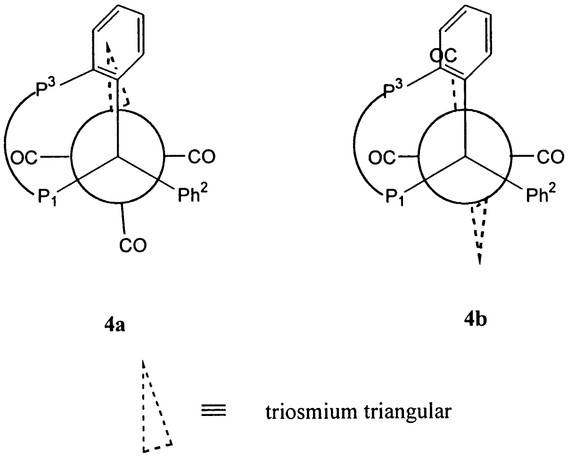


Fig. 6 VT-^{31}P NMR spectra of cluster **4a**.

In the crystal form, because the two phosphides bridge across the same Os–Os edge to form a butterfly configuration, the conformation of this unit is rather rigid. Under the conditions for dynamic NMR investigations no ligand dissociation is observed, thus an intermolecular process involving dissociation–association of ligand is ruled out for cluster **4**. The well known pairwise terminal–bridge carbonyl exchange mechanism[33] and trigonal-twist mechanism[34] also fail to explain the dynamic process because both carbonyl migration mechanisms do not affect the chemical shifts of the phosphorus atoms. For the quadruply substituted phosphorus atoms, room temperature cannot overcome the high energy barrier for conformational inversion. So the non-rigidity does not originate from the inversion of phosphorus atoms. It could arise from rotation of the single P(2)–Os(3) bond. Normally, the energy barrier for a single bond rotation is very low. The high energy barrier in this case may be due to the bulky triosmium triangle and the steric crowding of the fused phenyl ring and the phenyl rings bonded to phosphorus atoms. When the triosmium triangle in the crystalline form rotates 180° around the Os(3)–P(2) bond a new isomer with the triosmium group opposite to fused phenyl is obtained (the Newman projections are shown below, viewing from P(2) to Os(3)). This rotation results in a change of the orientation of the phenyl groups bonding to P(1) and P(2) and thus causes the change in the chemical shifts of the phosphorus atoms. This can serve as a reasonable explanation for the fluxionality of cluster **4**. To the best of our knowledge, this is the first example of isomerism based on single bond rotation of this type in metal cluster compounds. In clusters **1** and **2** fluxionality was not observed. The mechanism for the fluxionality of **4** is currently under further investigation.



viewing from P(2) to Os(3)

Conclusion

The reactions of cyclocarbaphosphine 1,2,3-triphenyl-1,2,3-triphosphaindan (**I**) with the activated triosmium cluster $[Os_3(CO)_{11}(NCMe)]$ or $[Os_3(CO)_{10}(NCMe)_2]$ form mono- or di-substituted trinuclear clusters **1** and **3** and bridged bis-trinuclear mono-substituted cluster **2** at room or moderate temperature (100 °C). Ligand **I** acts as a mono- or bi-dentate ligand with only the outer phosphorus atoms coordinating to clusters while the central phosphorus does not bond. When the reaction is performed under more severe conditions (140 °C) the rupture of one P–P bond in **I** occurs while the P–C bonds remain intact and cleavage of M–M bond(s) in the cluster is also observed. The fragments generated from the cleavage of ligand and cluster are stabilized with the formation of new P–M bonds to afford new cluster derivatives **4** and **5**. The ligand **I** is potentially a good phosphido source for stabilizing cluster fragments at high temperature with rupture of one P–P bond. Unlike the reaction with iron clusters, no extrusion of a PPh unit is observed. Cluster **1** is the precursor for both **2** and **3**. When **1** reacts further with an equimolar amount of $[Os_3(CO)_{11}(NCMe)]$ cluster **2** is formed. Cluster **3** can be obtained by pyrolysis of **1** at 100 °C, while **1** has no direct relation with **4** and **5**. In cluster **4** the mono-substituted trinuclear unit can undergo rotation around the P–Os bond and two conformational isomers are observed at low temperature. The chemical shift for phosphido bridging between non-interacting M atoms has a higher-field value than that for bridging between interacting M atoms.

Experimental

All reactions described above were carried out *in vacuo* using double-tube vessels equipped with Teflon taps. Analytical grade solvents were purified by distillation over appropriate drying agents and in a nitrogen atmosphere prior to use. Products were separated by TLC using laboratory-prepared 20 × 20 cm glass plates coated to a thickness of 0.3 mm with Merck Kieselgel $60F_{254}$ silica gel using a mixed solvent of dichloromethane and hexane in various proportions as eluent. The starting materials $[Os_3(CO)_{12}]$, $[Os_3(CO)_{11}(NCMe)]$ and $[Os_3(CO)_{10}(NCMe)_2]$ were prepared by literature methods.[35,36] Samples for elemental analysis were evacuated *in vacuo* at 60 °C for two hours beforehand. Elemental analysis was carried out at the Microanalytical Laboratory, Department of Chemistry, National University of Singapore. Infrared spectra were recorded as solutions in a 0.5 mm KBr cell on a Bio-Rad FTS-165 spectrometer, ^1H and ^{31}P NMR spectra on Bruker 300 or 500 MHz Fourier-Transform spectrometers using $SiMe_4$ (for ^1H) and 85% H_3PO_4 (for ^{31}P) as references and mass spectra on a Finnigan MAT 95 instrument by the fast atom bombardment technique, using α-nitrobenzyl alcohol or thioglycerol as the matrix solvent.

All single crystals for X-ray diffraction analysis were obtained by slow evaporation of a saturated CH_2Cl_2–hexane solution in a −20 °C refrigerator for several days or by slow diffusion of hexane into dichloromethane solution in a −20 °C refrigerator. Crystal data and details of the measurement for clusters **1**–**5** are given in Table 4. Diffraction intensities were collected at 293 K on a Siemens CCD SMART diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and ω–2θ scan technique. The structures were solved by direct methods and the refinement was by the full-matrix least-squares method with all non-hydrogen atoms refined anisotropically. All computations were carried out using a SHELXTL IRIS software package.[37]

CCDC reference numbers 158406–158410.

See http://www.rsc.org/suppdata/dt/b0/b008766l/ for crystallographic data in CIF or other electronic format.

Synthesis of 1,2,3-triphenyl-1,2,3-triphosphaindan (I)

This compound was prepared *via* modification of the literature methods.[25] 6.0 g of $(PPh)_5$[38] and 1.4 g of potassium in 100 ml THF were refluxed till the potassium disappeared completely to obtain a clear red solution. The resultant solution was cooled to −40 °C and 1,2-dichlorobenzene (2.7 g) in THF (10 ml) added within 20 min. The mixture became brown and was set aside at room temperature for 2 h. It was then boiled under reflux for 10 min, the THF evaporated under reduced pressure, and ether (50 ml) added followed by dilute hydrochloric acid (50 ml). The precipitated solid was collected and recrystallized from acetone to give the required compound (2.0 g, 27%). ^{31}P-{^1H} NMR: δ 32.5 (d, 265, 2P) and −39.4 (t, 265 Hz, 1P).

Reactions of $[Os_3(CO)_{11}(NCMe)]$ with I

(a) At room temperature. The compound $[Os_3(CO)_{11}(NCMe)]$ (155 mg, 0.17 mmol) and **I** (68 mg, 0.17 mmol) were placed in the inner tube of a double-tube reaction vessel and degassed *in vacuo*. Freshly distilled dichloromethane (10 ml) was placed in the outer tube. After degassing with three freeze–pump–thaw cycles the solvent was then transferred to the inner tube with the reactants. The reaction mixture changed gradually to light red from yellow after 2 h. The reaction system was stirred at room temperature overnight. The resultant red solution was evaporated to dryness under reduced pressure. The residue was dissolved in the minimum volume of CH_2Cl_2 and separated by

Table 4 Summary of crystal data and data collection parameters for clusters **1**–**5**

	1	**2**	**3**	**4**	**5**
Formula	$C_{35}H_{19}O_{11}Os_3P_3\cdot 0.25CH_2Cl_2\cdot 0.25C_6H_{14}$	$C_{46}H_{19}O_{22}Os_6P_3\cdot CH_2Cl_2$	$C_{34}H_{19}O_{10}Os_3P_3\cdot CH_2Cl_2\cdot C_6H_{14}$	$C_{41}H_{19}O_{17}Os_5P_3\cdot 0.5C_6H_{14}$	$C_{33}H_{19}O_9Os_3P_3$
M	1321.79	2242.65	1422.10	1870.56	1222.99
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/m$	$P\bar{1}$	$P2_1/c$
a/Å	15.7875(2)	16.9581(2)	10.8812(19)	9.8065(2)	16.17700(10)
b/Å	33.0071(4)	12.7231(2)	17.490(3)	13.7544(2)	11.9969(2)
c/Å	16.28320(10)	26.7882(3)	12.7076(19)	19.6895(3)	19.4553(2)
α/°				100.5680(10)	
β/°	101.47	96.2830(10)	107.135(17)	94.87	113.9670(10)
γ/°				109.5980(10)	
U/Å^3	8315.8(2)	5754.09(13)	2311.1(6)	2428.57(7)	3450.21(7)
Z	8	4	2	2	4
μ(Mo-Kα)/cm^{-1}	71.07	71.07	71.07	71.07	71.07
No. reflections collected	54537	36954	14824	22961	21779
No. reflections observed	20704	14253	5875	11757	8461
R (observed data)	0.0545	0.0456	0.0496	0.0401	0.0253
R' (observed data)	0.1056	0.0872	0.1041	0.0847	0.0505

TLC using CH_2Cl_2–hexane (1 : 3 v/v) as eluent. Two major bands of yellow cluster [$Os_3(CO)_{11}${1-$C_6H_4(PPh)_3$}] **1** (R_f = 0.56, 78 mg, 37%) and yellow cluster [{$Os_3(CO)_{11}$}$_2${μ-1,3-η^2-$C_6H_4(PPh)_3$}] **2** (R_f = 0.50, 55 mg, 30%) were eluted and collected (Found for **1**: C, 32.34; H, 1.51; P, 6.53. Calc. for $C_{35}H_{19}O_{11}Os_3P_3$: C, 32.84; H, 1.49; P, 7.27. Found for **2**: C, 25.04; H, 0.95; P, 3.51. Calc. for $C_{46}H_{19}O_{22}Os_6P_3$: C, 25.58; H, 0.88; P, 4.31%).

(b) At 100 °C. [$Os_3(CO)_{11}$(NCMe)] (175 mg, 0.19 mmol) and **I** (76 mg, 0.19 mmol) were placed in the inner tube of a double-tube reaction vessel and degassed *in vacuo*. Freshly distilled CH_2Cl_2 (10 ml) was placed in the other tube and degassed over three freeze–pump–thaw cycles. The solvent was then transferred to the inner tube. The tube and its contents were heated in a 100 °C oil bath and stirred for 5 h. The reaction mixture changed to red from yellow after 0.5 h. Excess of solvent was then removed under reduced pressure, yielding a red residue. This was then dissolved in the minimum volume of CH_2Cl_2 and subjected to preparative TLC using CH_2Cl_2–hexane (3 : 7 v/v) as eluent. Two major bands of yellow cluster **2** (R_f = 0.59, 60 mg, 30%), and light red cluster [$Os_3(CO)_{10}${μ-1,3-η^2-C_6H_4-$(PPh)_3$}] **3** (R_f = 0.42, 45 mg, 20%) were then eluted and collected (Found for **3**: C, 33.01; H, 1.28; P, 6.66. Calc. for $C_{34}H_{19}O_{10}Os_3P_3$: C, 32.61; H, 1.52 ; P, 7.43%).

(c) At 140 °C. [$Os_3(CO)_{11}$(NCMe)] (189 mg, 0.20 mmol) and **I** (82 mg, 0.20 mmol) were placed in the inner tube of a double-tube reaction vessel, and degassed *in vacuo*. Freshly distilled toluene (10 cm^3) was placed in the other tube and degassed over three freeze–pump–thaw cycles. The solvent was then transferred to the inner tube with reactants. The tube was placed in a 140 °C oil bath and stirred for 4 h. The reaction mixture changed from yellow to dark red after several minutes. The resulting dark red reaction solution was evaporated to dryness under reduced pressure. Three main complexes were obtained from this residue after TLC separation using CH_2Cl_2–hexane (1 : 4 v/v) as eluent. They were yellow cluster [$Os_2(CO)_6${μ$_3$-η^3-$PPhC_6H_4(PPh)_2$}$Os_3(CO)_{11}$] **4** (R_f = 0.50, 15 mg, 6.8%), red cluster [$Os_3(CO)_9${μ$_3$-η^3-$PPhC_6H_4(PPh)_2$}] **5** (R_f = 0.32, 20 mg, 8.2%) and light red cluster **3** (R_f = 0.28, 12 mg, 4.8%) (Found for **4**: C, 26.98; H, 1.41; P, 5.20. Calc. for $C_{41}H_{19}O_{17}Os_5P_3$: C, 26.93; H, 1.04; P, 5.09. Found for **5**: C, 32.23; H, 1.26; P, 6.93. Calc. for $C_{33}H_{19}O_9Os_3P_3$: C, 32.38; H, 1.55; P, 7.60%).

Reaction of [$Os_3(CO)_{10}(NCMe)_2$] with I

This reaction was similar to (**a**) above except that [$Os_3(CO)_{10}(NCMe)_2$] was used instead of [$Os_3(CO)_{10}(NCMe)_2$] (160 mg, 0.17 mmol) was treated with **I** (69 mg, 0.17 mmol). Cluster **3** (R_f = 0.40; 115 mg, 55%) was obtained after TLC using CH_2Cl_2–hexane (3 : 7) as eluent.

Reaction of complex 1 with [$Os_3(CO)_{11}$(NCMe)]

The reaction was similar to (**a**) above. The [$Os_3(CO)_{11}$(NCMe)] (36 mg, 0.039 mmol) was treated with complex **1** (50 mg, 0.039 mmol). Cluster **2** (R_f = 0.48; 43 mg, 52%) was obtained after TLC using CH_2Cl_2–hexane (1 : 3) as eluent.

Conversion of cluster 1 into 3

A single reaction vessel was charged with cluster **1** (40 mg, 0.031 mol) in toluene (10 ml). The solution was degassed over three freeze–pump–thaw cycles. The tube and its contents were heated overnight in a 100 °C oil bath. One major band was eluted [CH_2Cl_2–hexane (1 : 3 v/v)] which was identified by ^{31}P NMR as cluster **3** (R_f = 0.40, 30 mg, 80%).

Acknowledgements

We thank the National University of Singapore for financial support and for a Research Scholarship (to X. Z.).

References

1 G. G. Hlatky and R. H. Crabtree, *Coord. Chem. Rev.*, 1985, **65**, 1.
2 D. S. Moore and S. D. Robinson, *Chem. Soc. Rev.*, 1983, 415.
3 R. G. Hayter, *J. Am. Chem. Soc.*, 1963, **85**, 3120; R. G. Hayter, *Inorg. Chem.*, 1964, **3**, 711.
4 J. Chatt and D. A. Thornton, *J. Chem. Soc.*, 1964, 1005.
5 A. H. Cowley and K. E. Hill, *Inorg. Chem.*, 1973, **12**, 1446.
6 H. G. Ang, K. W. Ang, S. G. Ang and A. L. Rheingold, *J. Chem. Soc., Dalton Trans.*, 1996, 3131.
7 H. G. Ang, L. L. Koh and Q. Zhang, *J. Chem. Soc., Dalton Trans.*, 1995, 2757.
8 H. G. Ang, S. G. Ang, W. L. Kwick and Q. Zhang, *J. Organomet. Chem.*, 1995, **485**, C10.
9 H. G. Ang, S. G. Ang and Q. Zhang, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1996, 3843.
10 H. G. Ang, S. G. Ang and Q. Zhang, *J. Chem. Soc., Dalton Trans.*, 1996, 2773.
11 H. G. Ang, S. G. Ang and Q. Zhang, *J. Chem. Soc., Dalton Trans.*, 1996, **109–110**, 145.
12 B. F. G. Johnson, T. M. Layer, J. Lewis, P. R. Raithby and W. T. Wong, *J. Chem. Soc., Dalton Trans.*, 1993, 973.
13 E. Charalambous, L. Heuer, B. F. G. Johnson, J. Lewis, W. S. Li, M. McPartlin and A. D. Massey, *J. Organomet. Chem.*, 1994, **468**, C9.
14 H. G. Ang, S. G. Ang and X. Wang, *J. Chem. Soc., Dalton Trans.*, 2000, 3429.
15 R. B. King and R. H. Reimann, *Inorg, Chem.*, 1976, **15**, 184.

16 E. P. Kyba, K. L. Hassett, B. Sheikh, J. S. Mckennis, R. B. King and R. E. Davis, *Organometallics*, 1985, **4**, 994.
17 M. Castiglioni, R. Giordano and E. Sappa, *J. Organomet. Chem.*, 1988, **342**, 97.
18 A. J. Deeming and M. Underhill, *J. Chem. Soc.*, *Dalton Trans.*, 1973, 2727.
19 A. J. Deeming, B. F. G. Johnson and J. Lewis, *J. Chem. Soc. A*, 1970, 897.
20 C. J. Jameson, *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis: Theoretical Considerations: Spin–spin Coupling*, eds. J. G. Verkade and L. D. Quinn, VCH Publishers, New York, 1987, ch. 6.
21 M. I. Bruce, M. J. Liddell, C. A. Hughes, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1988, **347**, 157.
22 R. E. Benfield, B. F. G. Johnson, P. R. Raithby and G. M. Sheldrick, *Acta Crystallogr.*, *Sect. B*, 1978, **34**, 666.
23 V. M. Hansen, A. K. Ma, K. Biradha, R. K. Pomeroy and M. J. Zaworotko, *Organometallics*, 1998, **17**, 5267.
24 J. J. Daly, *J. Chem. Soc. A*, 1966, 1020.
25 F. G. Mann and A. J. H. Mercer, *J. Chem. Soc.*, *Perkin Trans. 1*, 1972, 1631.
26 A. J. Amoroso, B. F. G. Johnson, J. Lewis, A. D. Massey, P. R. Raithby and W. T. Wong, *J. Organomet. Chem.*, 1992, **440**, 219.
27 A. J. Deeming, S. Donovan-Mtunzi, K. I. Hardcastle, S. E. Kabir, K. Henrick and M. McPartlin, *J. Chem. Soc.*, *Dalton Trans.*, 1988, 579.
28 S. E. Kabir, A. Miah, L. Nesa, K. Uddin, K. L. Hardcastle, E. Rosenberg and A. J. Deeming, *J. Organomet. Chem.*, 1995, **492**, 41.
29 M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 1977, **16**, 878.
30 A. J. Carty, S. A. MacLaughlin and D. Nucciarone, *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis: Stereochemistry of Metal Complexes*: *Phosphido Bridging Ligands*, eds. J. G. Verkade and L. D. Quinn, VCH Publishers, New York, 1987, ch. 16.
31 P. Leoni, M. Pasquali, G. Pieri and U. Englert, *J. Organomet. Chem.*, 1996, **514**, 243.
32 M. Oki, *Application of Dynamic NMR Spectroscopy to Organic Chemistry*, VCH Publishers, Deerfield Beach, FL, 1985.
33 R. F. Alex and R. K. Pomeroy, *Organometallics*, 1987, **6**, 2437.
34 B. F. G. Johnson, J. Lewis, B. E. Reichert and K. T. J. Schorpp, *J. Chem. Soc.*, *Dalton Trans.*, 1976, 1403.
35 B. F. G. Johnson and J. Lewis, *Inorg. Synth.*, 1972, **13**, 93.
36 J. N. Nicholls and M. D. Vargas, *Inorg. Synth.*, 1989, **26**, 290.
37 SHELXTL, version 5.1, Bruker AXS, Inc., Madison, WI, 1997.
38 W. A. Herderson, Jr., M. Epstein and F. S. Seichter, *J. Am. Chem. Soc.*, 1963, **85**, 2462.