Structural and nuclear magnetic resonance studies of triosmium and triruthenium carbonyl cluster derivatives containing pentaphenylcyclopentaphosphane

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The reaction of pentaphenylcyclopentaphosphane $(PPh)_5$ with $[Os_3(CO)_{10}(NCMe)_2]$ in 1 : 1 molar ratio afforded a pair of inversion isomers, **1** and **2**, with the molecular formula $[Os_3(CO)_{10}\{(PPh)_5\}]$. A similar reaction in 3 : 1 molar ratio gave a different cluster $[Os_3(CO)_{10}\{(PPh)_5\}_2]$ **3**. The clusters $[Os_3(CO)_{11}\{(PPh)_5\}]$ **4** and $[\{Os_3(CO)_{11}\}_2\{(PPh)_5\}]$ **5** were obtained from reaction of $(PPh)_5$ with $[Os_3(CO)_{11}(NCMe)]$. Compound **4** reacted with $[Ru_3(CO)_{11}(NCMe)]$ to generate the cluster $[(OC)_{11}Os_3\{(PPh)_5\}Ru_3(CO)_{11}]$ **6**. Compounds **4** and **5** were converted into **1** and **2** when heated in sealed tubes at 80 °C. In clusters **1** and **2** the triosmium unit is chelated by the cyclophosphane ligand through the 1,3-phosphorus atoms of the ring, and their main difference lies in the orientations adopted by the aromatic rings attached to the unco-ordinated phosphorus. Variable-temperature NMR studies showed that the two inversion isomers can undergo interconversion. In **4** one osmium atom of the triosmium unit is co-ordinated to one phosphorus atom of the cyclophosphorus ligand, while in **5** the two triosmium units are each linked *via* co-ordination of one Os atom to a phosphorus atom of the cyclophosphane ring. With the help of two-dimensional ^{31}P NMR spectroscopy, the correlations between phosphorus atoms for clusters **1**, **2**, **4** and **5** were established.

Cyclophosphanes which exhibit an interesting and diversified reactivity with transition-metal carbonyls have been the subject of many articles.[1–5] Recently increasing attention has been paid to the chemistry of cyclophosphanes with transition-metal carbonyl clusters. Reactions of the tetrameric cyclophosphorus compound, $(Bu^tP)_4$, with ruthenium carbonyl clusters, resulted in several cluster derivatives where the cyclophosphanes, being rich phosphinidene sources, had been completely disrupted to yield phosphido group(s)[6,7] We have reported that reactions of cyclophosphanes with ruthenium or osmium carbonyl clusters generate not only phosphinidene groups but also diphosphene segments from partial disruption of the cyclic phosphorus rings.[8,9] We now report (*i*) the reactions between triosmium carbonyl clusters and pentameric $(PPh)_5$, which afford several cluster derivatives where the phosphorus ring structure remains intact and (*ii*) two-dimensional phosphorus-31 nuclear magnetic resonance studies of some of these derivatives. A preliminary communication of some of this work has been published.[8]

Results and Discussion

The reactions of the various substituted triosmium or ruthenium carbonyl clusters with pentaphenylcyclopentaphosphane were carried out *in vacuo*. All the new clusters have been characterised by elemental analysis and spectroscopic methods. The IR data are given in Table 1 and the NMR chemical shifts and coupling constants are in Table 2. The structures for **1**, **2**, **4** and **5**, as shown in Fig. 1, have been established by single-crystal X-ray analysis.[8] The phosphorus atom correlations for the four clusters have been deduced by two-dimensional correlation (COSY-90 and -45) ^{31}P NMR experiments.

Reactions of $(PPh)_5$ with $[Os_3(CO)_{10}(NCMe)_2]$ in 1 : 1 molar ratio

The cyclophosphane, $(PPh)_5$, reacted with 1 equivalent of the activated trinuclear cluster $[Os_3(CO)_{10}(NCMe)_2]$ in dichloromethane at room temperature overnight to give an orange

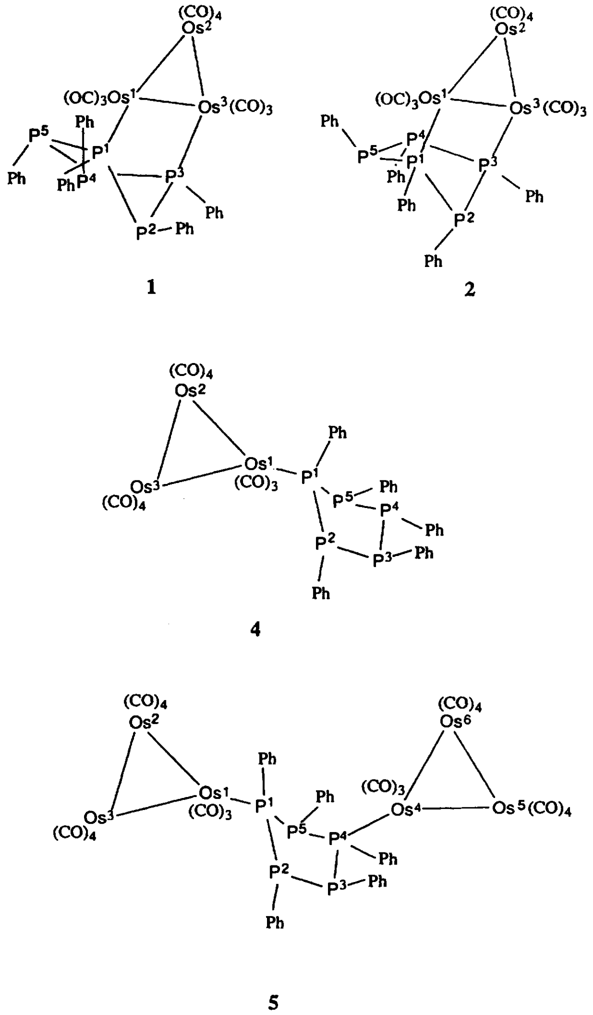


Fig. 1 Structures of compounds **1**, **2**, **4** and **5**

mixture which afforded an orange compound **1** in quite good yield (33%) and a yellow compound **2** in very low yield (2%), as well as a trace amount of cluster **4** after separation by thin-layer chromatography (TLC) using CH_2Cl_2–hexane (3:7) as eluent. A similar reaction at 80 °C in dichloromethane in a sealed tube gave only clusters **1** and **2** in almost equal yields (15 and 17% respectively). Cluster **4** was not found under these conditions.

The solid cluster $[Os_3(CO)_{10}\{1,3\text{-}(PPh)_5\}]$ **1** is much more stable than $(PPh)_5$. No sign of decomposition was detected when a solid sample was exposed to air at 20 °C for a few days. It converts slowly into cluster **2** in solution at room temperature. Recrystallisation of pure cluster **1** always generates orange crystals of **1** and yellow crystals of **2** even at −25 °C. Therefore the crystals of **1** for X-ray analysis were obtained by rapidly diffusing hexane into a dichloromethane solution of it in appropriate concentration. Cluster **2** was also far more stable than $(PPh)_5$. The crystalline **2** could be kept for 1 year under nitrogen at room temperature with no change. The yellow crystals of **2** for single-crystal X-ray analysis were obtained upon standing of a solution of the appropriate amount of product dissolved in dichloromethane–hexane (1:4 v/v) for a few days at room temperature. A trace amount of **4** was formed due to a small amount of cluster $[Os_3(CO)_{11}(NCMe)]$ being present in $[Os_3(CO)_{10}(NCMe)_2]$. Cluster **4** was not obtained at 80 °C because $[Os_3(CO)_{11}\{(PPh)_5\}]$ **4** was easily converted into **1** and **2** at that temperature.

The conversion between clusters **1** and **2** is significantly faster at 80 °C. When either pure **1** or **2** is heated at 80 °C in dichloromethane in a sealed tube a mixture of similar amounts of **1** and **2** could always be obtained.

Attempts to prepare the tri- or poly-dentate cluster $[Os_3(CO)_{12-n}\{(PPh)_n\}]$ ($n \geq 3$) were not successful. Reactions of $(PPh)_5$ with 1 equivalent of the activated trinuclear cluster $[Os_3(CO)_{10}(NCMe)_2]$ in a Carius tube in dichloromethane at higher temperatures (100 and 120 °C) overnight resulted in a light yellow solution which could not be separated by TLC. Attempts to grow crystals directly from the light yellow solution were unsuccessful.

Selected bond lengths, angles and non-bonded distances $P(x) \cdots P(y)$ for compounds **1** and **2** are listed in Table 3. The $(PPh)_5$ moiety acts as a bidentate ligand, occupying 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 in the pair of inversion isomers. The structures differ essentially in the orientations adopted by the aromatic rings attached to the unco-ordinated phosphorus atoms. As seen in the representative Newman projections shown in Fig. 2 the group Ph^2 is *cis* to Os atoms in **1** while Ph^2 is *trans* to Os atoms in **2**, viewed either from P^2 to P^3 or from P^2 to P^1. In free $(PPh)_5$ the phosphorus ring can flip freely. On chelating to the two osmium atoms the two

Table 1 Infrared data (cm^{-1}) in the carbonyl region in cyclohexane

Complex	
1 $[Os_3(CO)_{10}\{1,3\text{-}(PPh)_5\}]$	2098m, 2036m, 2023s, 2016vs, 1982m, 1967w, 1949w
2 $[Os_3(CO)_{10}\{1,3\text{-}(PPh)_5\}]$	2095m, 2036m, 2025s, 2012vs, 1980m, 1965w, 1954w
3 $[Os_3(CO)_{10}\{(PPh)_5\}_2]$	2087w, 2034m, 2065w, 2056vw, 2102m (sh), 2005vs, 1999s, 1976w, 1960w
4 $[Os_3(CO)_{11}\{(PPh)_5\}]$	2020vs, 2001w, 1989m, 1977w, 1957vw
5 $[\{Os_3(CO)_{11}\}_2\{1,3\text{-}(PPh)_5\}]$	2106m, 2058s, 2035m, 2024s (sh), 2022vs, 2004m, 1991m, 1981w
6 $[(OC)_{11}Os_3\{1,3\text{-}(PPh)_5\}Ru_3(CO)_{11}]$	2110w, 2073s, 2060s, 2051s, 2039m, 2024vs, 2017m (sh), 2006w, 1993m, 1980w, 1970w, 1959w

Table 2 Proton and ^{31}P NMR data in CD_2Cl_2

Complex	δ_P(J/Hz)	δ_H
1	109.6 [m, P^4, $J(P^4P^5) = 224.1$, $J(P^4P^3) = 224.0$, $J(P^4P^2) = 160.1$, $J(P^4P^1) = 7.2$], 4.0 [m, P^1, $J(P^1P^2) = 224.5$, $J(P^1P^5) = 273.5$, $J(P^1P^3) = 19.9$], −3.7 [m, P^2, $J(P^2P^3) = 224.0$, $J(P^2P^5) = 22.5$], −62.6 [m, P^5, $J(P^5P^3) = 81.7$], −63.4 (m, P^3)	7.37 (m)
2	62.5 [m, P^4, $J(P^4P^3) = 301.8$, $J(P^4P^5) = 242.7$, $J(P^4P^1) = 9.0$, $J(P^4P^2) = 5.0$], 15.3 [m, P^1, P^2, $J(P^1P^2) = 241.0$], −15.6 [m, P^3, $J(P^3P^1)$ or $J(P^3P^2) = 370.8$, $J(P^3P^5) = 51.9$], −41.5 [m, P^5, $J(P^5P^1)$ or $J(P^5P^2) = 254.2$]	7.35 (m)
3	17.2 (m, 1P), −2.2 (m, 1P), −12.8 (m, 1P), −28.7 (m, 1P), −37.8 (m, 1P)	7.29 (m)
4	15.4 (m, P), −0.50 (m, 1P), −16.8 (m, P), −30.90 (m, 1P), −301.54 (m, 1P)	7.43 (m)
5	36.9 [dd, P^3, $J(P^3P^2) = 322.5$, $J(P^3P^4) = 299.7$], 20.5 [m, P^5, $J(P^5P^4) = 403.1$, $J(P^5P^1) = 184.2$, $J(P^5P^2) = 54.6$], −0.2 [dd, P^1, $J(P^1P^2) = 308.7$], −19.9 [m, P^2, $J(P^2P^4) = 22.1$], −35.6 (m, P^4)	7.35 (m)
6	78.7 (m, 1P), 71.0 (m, 1P), 36.9 (m, 1P), 3.1 (m, 1P), −36.1 (m, 1P)	7.33 (m)

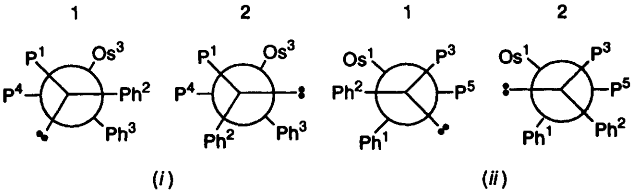


Fig. 2 Representative Newman projections: (*i*) viewed from P^2 to P^3, (*ii*) viewed from P^2 to P^1

Table 3 Selected bond lengths (Å), angles (°) and non-bonded distances (Å) of $P(x) \cdots P(y)$ for compounds **1** and **2**

	1	**2**
Os(1)–Os(2)	2.866(2)	2.890(1)
Os(1)–Os(3)	2.876(2)	2.901(1)
Os(2)–Os(3)	2.878(2)	2.874(1)
P(1)–P(2)	2.221(5)	2.227(3)
P(1)–P(5)	2.249(4)	2.224(4)
P(2)–P(3)	2.260(4)	2.219(3)
P(3)–P(4)	2.230(4)	2.259(3)
P(4)–P(5)	2.219(5)	2.214(3)
P–P (mean)	2.236	2.229
Os(1)–P(1)	2.336(4)	2.324(3)
Os(3)–P(3)	2.325(4)	2.339(3)
Os–P (mean)	2.331	2.332
P–C (mean)	1.843	1.832
Os–C (mean)	1.902	1.925
C–O (mean)	1.155	1.146
P(2) ··· P(4)	3.036	3.696
P(1) ··· P(3)	3.093	3.073
P(2) ··· P(5)	3.325	3.392
P(1) ··· P(4)	3.440	3.352
P(3) ··· P(5)	3.350	3.377
Os(2)–Os(1)–Os(3)	60.2(1)	59.5(1)
Os(1)–Os(2)–Os(3)	60.1(1)	60.4(1)
Os(1)–Os(3)–Os(2)	59.7(1)	60.1(1)
P(2)–P(1)–P(5)	96.1(2)	99.3(1)
P(1)–P(2)–P(3)	87.3(2)	87.4(1)
P(2)–P(3)–P(4)	85.0(1)	111.3(1)
P(3)–P(4)–P(5)	97.7(2)	98.1(1)
P(1)–P(5)–P(4)	100.7(2)	98.1(1)
P–P–P (mean)	93.4	98.4

phosphorus atoms in the 1,3 positions of the phosphorus rings are held firmly by the two adjacent osmium atoms in the triosmium cluster. However, the two structures can still interconvert by inverting the lone pairs of electrons on the unco-ordinated phosphorus atoms so that the phenyl groups on these phosphorus atoms are in different relative orientations in the isomers.

Besides the different orientations of the phenyl groups the following aspects of the two structures are also noteworthy. (*a*) As shown in Table 4 [which lists the P–P–P–P torsion angles for clusters **1**, **2**, **4**, **5** and free $(PPh)_5$], the whole phosphorus atom frameworks in both clusters are heavily distorted with respect to the geometry of free $(PPh)_5$. The average P–P distances for both clusters (2.260 for **1** and 2.259 Å for **2**) are longer than that (2.220 Å) of free $(PPh)_5$.[10] The average P–P–P angle (93.4°) in the phosphorus ring in **1** is much smaller than that (98.8°) in **2** which is much closer to that in free $(PPh)_5$ (100.0°). This reflects a smaller torsional strain of the ring in **2** than that in **1**.

(*b*) The angle P(1)–P(2)–P(3) 87.3° in compound **1** is almost equal to that (87.4°) in **2**. These two angles are much smaller than the average P–P–P angle of free $(PPh)_5$ because the two phosphorus atoms in the 1,3 positions in the rings must move closer to fit the short Os–Os distance formation of the co-ordination compound, resulting in more puckering in the rings. Another small P–P–P angle (85.1°) observed in **1**, which is also the smallest such angle found in cyclopentaphosphanes and their complexes or clusters, is attributed to steric crowding between the carbonyls and the phenyl groups Ph^2 and Ph^4, as shown in the space-filling representations of **1** and **2** in Fig. 3.

(*c*) The structures of compounds **1** and **2** are derived from that of the parent carbonyl $[Os_3(CO)_{12}]$ by replacement of an equatorial carbonyl group on each of two Os atoms by a P atom of the cyclophosphane. In $[Os_3(CO)_{12}]$ the average M–M distance is 2.877 Å, one of the three bonds being slightly longer than the other two.[11] The average M–M distance in **2** (2.888 Å) is longer than that of **1** (2.873 Å) which is similar to that of the parent cluster $[Os_3(CO)_{12}]$. The bridged Os–Os distance in **1** is similar to that of the non-bridged Os–Os distances. This is in contrast with observations in diphosphine triosmium clusters $[Os_3(CO)_{10}(\text{diphosphine})]$ [diphosphine = $Ph_2P(CH_2)_nPPh_2$, *i.e.* dppe (n = 2), dppp (n = 3) or dppb (n = 4)] where the bridged are significantly longer than the non-bridged Os–Os distances.[12,13] However, the bridged Os(1)–Os(3) distance of **2** (2.901 Å) is longer than that of **1** (2.876 Å).

NMR spectroscopy

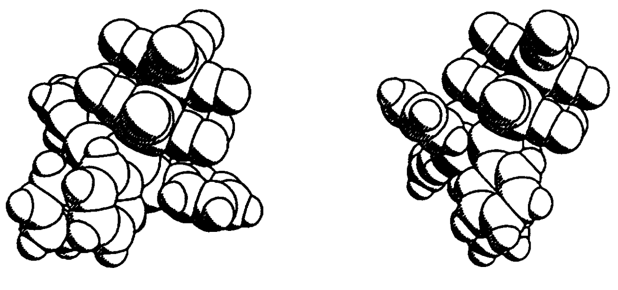
The ^1H NMR spectra show multiplets at δ_H 7.37 and 7.35 for clusters **1** and **2**, respectively, due to phenyl groups. No bridging hydride is found in the negative range of the ^1H NMR spectra. All ^1J coupling constants for both **1** and **2** fall within the normal range of direct P–P coupling constants for cyclophosphanes.[14] Among the long-range coupling constants, a very large $^2J(P^2P^4)$ = 160.1 Hz was observed which is similar to some direct P–P coupling constants. This is attributed to steric crowding between Ph^2, Ph^4 and carbonyl groups which causes the free electron pairs at P^2 and P^4 of **1** to become directed towards each other therefore generating a large long-range coupling constant. Analysis of the distances of non-bonded phosphorus atoms shows that the distance between P^2 and P^4 of **1** is the shortest (3.036 Å) amongst the unco-ordinated phosphorus atoms. This small separation (0.66 Å less than that in **2**) is a possible reason for a strong interaction between Ph^2 and Ph^4).

The two-dimensional COSY-90 ^{31}P NMR spectrum of compound **1** is shown in Fig. 4. The signals are marked A, B, C, D_1 and D_2 from the low-field end. All the cross-peaks appear invariably as complete squares. Two cross-peaks A–C and A–D_1 or D_2 are correlated with signal A, two B–C and B–D_1 or D_2 with signal B and three A–C, B–C and C–D_1 or D_2 with C. Signal D is correlated with A and B. The two-dimensional COSY-45 ^{31}P NMR spectrum is shown in Fig. 5. Amongst all the cross-peaks found in the COSY-90 spectrum, only A–C is an obvious long-range coupling. Since A–D_1, A–D_2, B–C and B–D are direct couplings, the connectivity of the phosphorus ring of cluster **1** can be deduced as in Fig. 6(*a*).

The two-dimensional COSY-90 ^{31}P NMR spectrum of compound **2** is shown in Fig. 7. The signals are marked A, B_1, B_2, C and D from the low-field end. Cross-peaks are found

Table 4 Torsion angles (°) P–P–P–P for compounds **1**, **2**, **4**, **5** and free $(PPh)_5$

	1	2	4	5	$(PPh)_5$
P(5)–P(1)–P(2)–P(3)	64.4	62.3	−32.7	2.2	2.2
P(1)–P(2)–P(3)–P(4)	−79.8	−43.6	−6.6	−39.9	33.3
P(2)–P(3)–P(4)–P(5)	−23.8	9.0	43.5	65.5	−58.1
P(3)–P(4)–P(5)–P(1)	64.0	30.4	−63.7	−64.1	60.6
P(4)–P(5)–P(1)–P(2)	−25.9	−63.1	60.8	36.9	−36.5



1 **2**

Fig. 3 Space-filling representations of the structures of compounds **1** and **2**

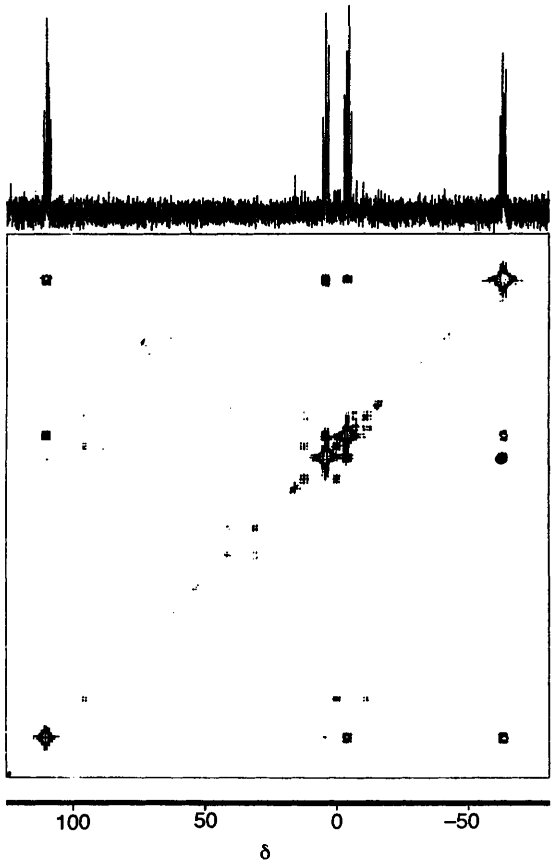


Fig. 4 Two-dimensional COSY-90 ^{31}P NMR spectrum of compound **1**

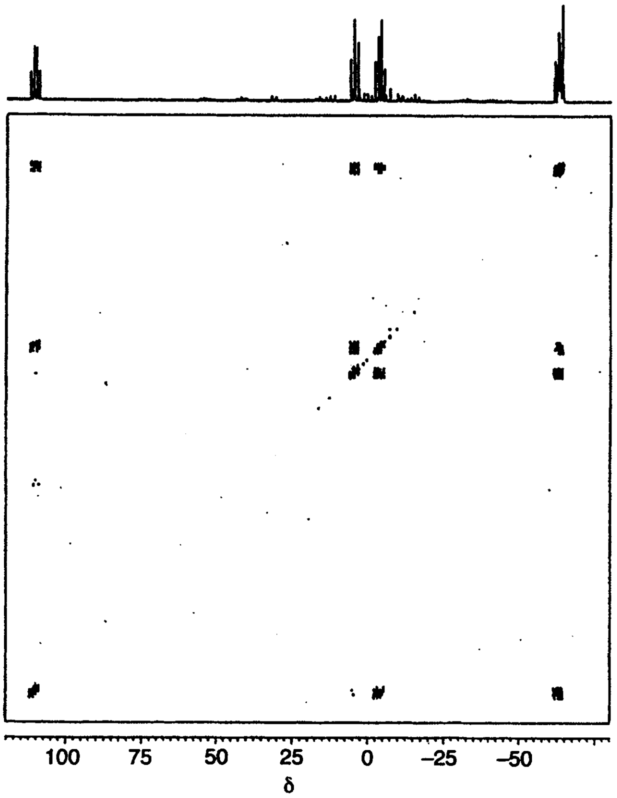


Fig. 5 Two-dimensional COSY-45 ^{31}P NMR spectrum of compound **1**

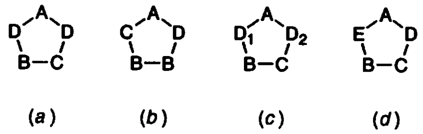


Fig. 6 Connectivity of phosphorus ring: (*a*) for compound **1**, (*b*) for **2**, (*c*) for **4** and (*d*) for **5**

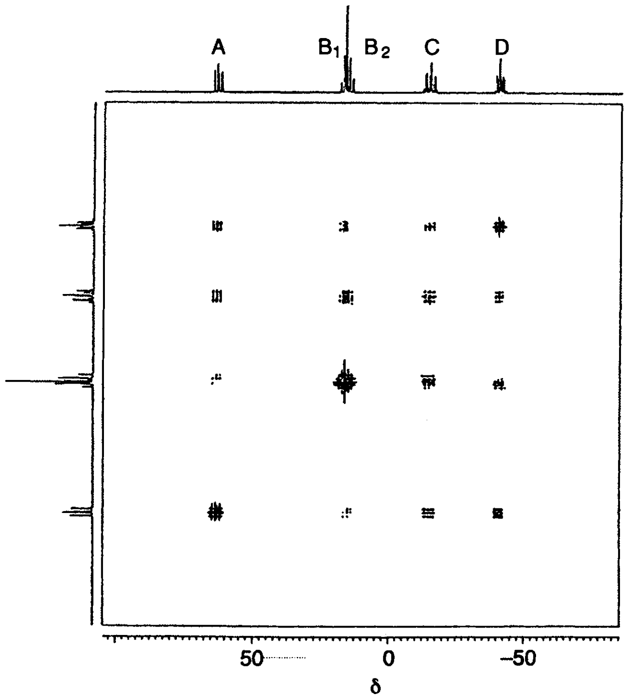


Fig. 7 Two-dimensional COSY-90 ^{31}P NMR spectrum of compound **2**

between every pair of phosphorus nuclei. The two-dimensional COSY-45 spectrum of **2** is shown in Fig. 8. Since A–C, A–D are direct couplings, while C–D, A–B_1 and A–B_2 are long-range couplings, the connectivity of the phosphorus ring of cluster **2** can be deduced [Fig. 6(*b*)].

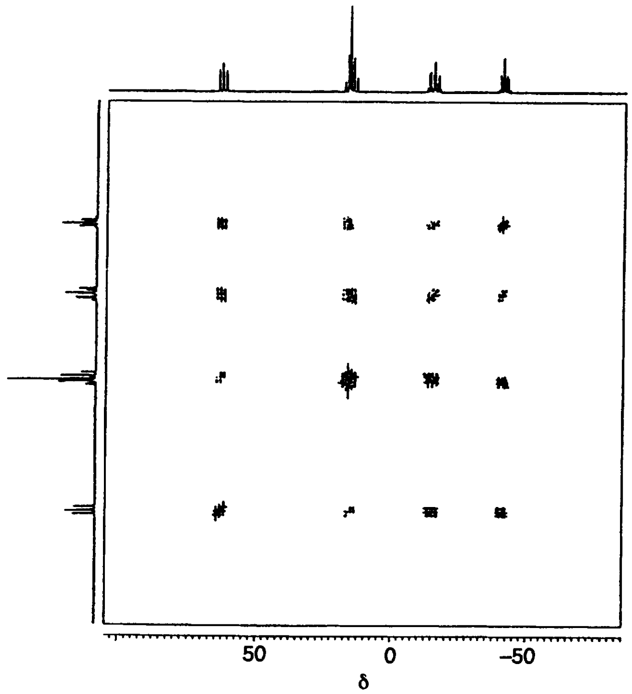


Fig. 8 Two-dimensional COSY-45 ^{31}P NMR spectrum of compound **2**

When variable-temperature studies were performed on a pure sample of compound **1** signals of cluster **2** appeared at 70 °C. From 70 to 100 °C the intensities of the signals from **2** increase rapidly, whereas those of **1** decrease quickly. Finally, an equilibrium is established between **1** and **2**. Although steric crowding between the phenyl and carbonyl groups in **1** is more pronounced than that in **2**, steric crowding among the phenyl groups in **1** is less severe than that in **2**. If a phenyl group directed to one side of the triosmium plane is designated as α and one directed to the opposite side as β, the arrangement of phenyl groups in **1** can be represented as βαβαβ while that in **2** is ββββα. The lone pairs of electrons on the phosphorus atoms alternate in a *trans* manner around the ring of free $(PPh)_5$.[10] This is to be expected in order to minimise lone pair–lone pair and R group–R group interactions, and this is the case for all known crystal structures.[15–23] Therefore, it is obvious that steric crowding among the phenyl groups in **2** is much larger than that in **1**. Another interesting feature is that only two inversion isomers **1** and **2** are found in this system although other isomers, for example, βββαβ or βαβαα, are possible. The implication here is that the lone pairs of electrons on one or two but not all three unco-ordinated phosphorus atoms invert. Another example involving inversion of phosphorus is $P_9Bu^t_3$ which has four possible types of inversion isomers.[24] Though the structure of only one isomer has been characterised by single-crystal X-ray analysis,[25] all four inversion isomers are detected by ^{31}P NMR spectroscopy.[26]

Reaction of $(PPh)_5$ with $[Os_3(CO)_{10}(NCMe)_2]$ at 3:1 molar ratio

The reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with three times the molar amount of $(PPh)_5$ in dichloromethane overnight at room temperature gave an orange mixture. This afforded a major orange product **3** and two minor products when subjected to TLC with dichloromethane–hexane (3:7) as eluent. The two minor products were identified by spectroscopic methods to be compounds **1** and **2**. Crystals of **3** suitable for X-ray study were not obtained since the cluster was unstable in solution and the solid state, even at −20 °C under nitrogen. The IR data in the carbonyl region are similar to those of $[Os_3(CO)_{10}(PPh_3)_2]$ [2085w, 2070vw, 2050w, 2030vs, 2015m, 2000vs, 1998m (br), 1969m and 1951mw cm^{-1} in cyclohexane].[27] The ^{31}P NMR spectrum shows five multiplets at δ_P 17.2 (m, 1 P), −2.2 (m, 1 P), −12.8 (m, 1 P), −28.7 (m, 1 P) and −37.8 (m, 1 P). The cluster is proposed to be $[Os_3(CO)_{10}\{(PPh)_5\}_2]$ **3** on the basis of elemental analysis and spectroscopic data, with the proposed structure in Fig. 9.

Reactions of $(PPh)_5$ with $[Os_3(CO)_{11}(NCMe)]$

Treatment of $(PPh)_5$ with a two-fold molar amount of $[Os_3(CO)_{11}(NCMe)]$ in dichloromethane at room temperature overnight yielded a yellow mixture which afforded four bands when subjected to TLC. The trace amount of a yellow solid isolated from band 1 was identified as $[Os_3(CO)_{12}]$ on the basis of infrared data. Another yellow minor compound from band 2 was unstable and as a consequence could not be fully characterised. The third band gave a yellow major compound $[Os_3(CO)_{11}\{(PPh)_5\}]$ **4** (yield 48%) while the last band afforded an orange major linked compound $[\{Os_3(CO)_{11}\}_2\{1,3\text{-}(PPh)_5\}]$ **5** (yield 45%). Orange crystals of **4** suitable for single-crystal X-ray analysis were obtained upon standing of a solution of the appropriate amount of product in dichloromethane–hexane (2:25 v/v) for a few days at 0 °C. Similarly, orange crystals of **5** were obtained upon standing a solution of the product dissolved in dichloromethane–hexane (1:5 v/v) for 1 week at room temperature.

A similar reaction carried out at 80 °C, however, generated quite different products. The reaction in a Carius tube yielded a yellow solution with some yellow powder. Purification of the solution by TLC gave three compounds. One was found to be the cluster $[Os_3(CO)_{12}]$, while the other two were identified as **1** and **2** by IR and ^{31}P NMR methods. To investigate further this reaction, pure **4** and **5** were separately heated in a Carius tube in dichloromethane at 80 °C overnight; **4** was found to transform into **1** and **2**, while **5** gave **1**, **2** and $[Os_3(CO)_{12}]$. As shown in Scheme 1, a lone pair of electrons on P^3 in **4** attacks the neighbouring osmium atom, from which one CO group is displaced to give compound **1**. Inversion of **1** gives rise to **2** and finally an equilibrium between **1** and **2** is established. In Scheme 2, a lone pair of electrons on P^3 in **5** attacks the neighbouring osmium atom in one of the two triosmium moieties with the elimination of one CO group. The Os–P bond of the other triosmium moiety is broken because of steric crowding in the bridging pattern, and the triosmium moiety captures another CO from the solution so that **1** and $[Os_3(CO)_{12}]$ are formed. Rapid inversion of **1** at 80 °C gives rise to **2**. Finally, an equilibrium between **1** and **2** is established.

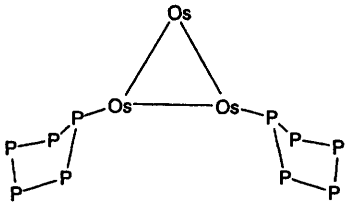
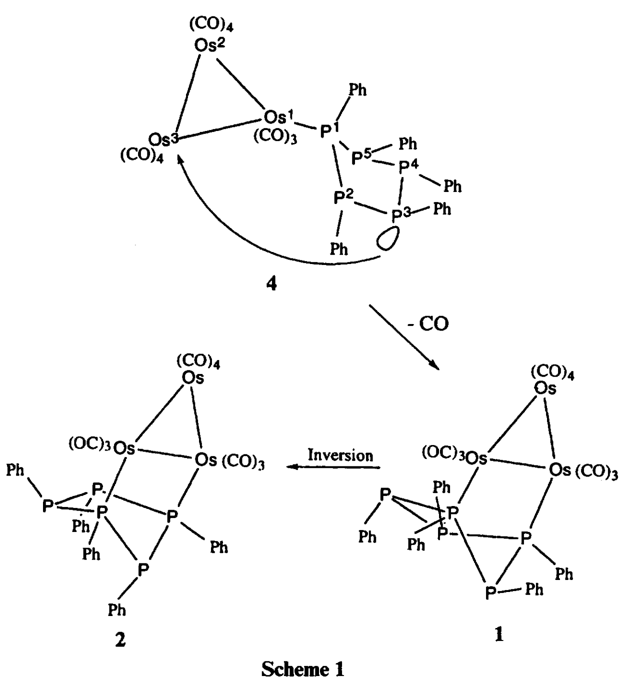


Fig. 9 Proposed structure of $[Os_3(CO)_{10}\{(PPh)_5\}_2]$ **3**

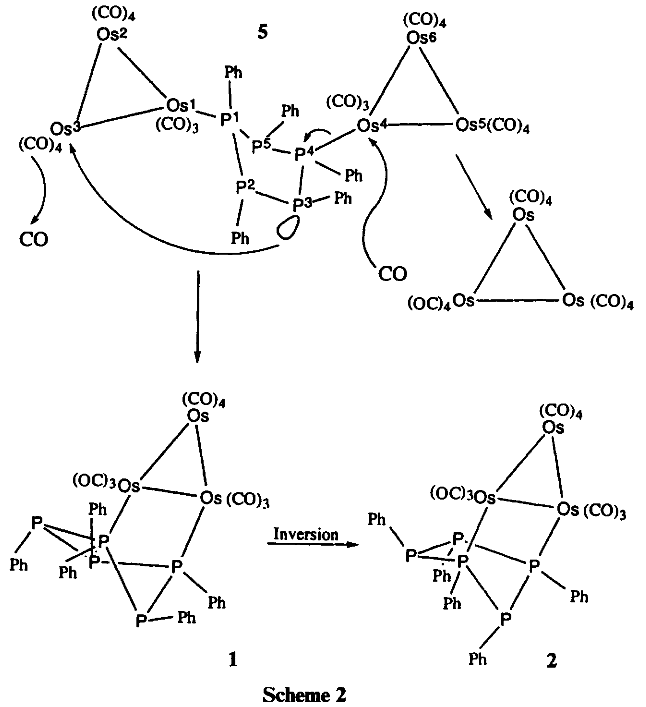
The structure of compound **4** (selected bond lengths and angles in Table 5) comprises an isosceles triangle of osmium atoms with the bulky cyclopolyphosphane ligand bonded to Os(1) *via* an equatorial site. The longest Os–Os bond (2.917 Å) is much longer than the other two (2.881 Å). A comparison with other monosubstituted derivatives $[M_3(CO)_{11}L]$ from $[M_3(CO)_{12}]$ (M = Os or Ru, L = Group 15 ligand) is shown in Table 6. The M–M bond *cis* to the Group 15 ligand is the longest of the three and there is generally little difference between the other two M–M distances. The steric bulk of these Group 15 ligands is responsible for the extra long M–M separation. Changes in the M^1–M^3 separation could be related directly to the cone angles of these Group 15 ligands.[30]

The average P–P distance is 2.228 Å, the longest of the five bonds being 2.234 Å and the shortest being 2.217 Å. These bond distances are slightly longer than those of free (PPh_5). The average P–P–P angle is 98.7° (the largest being 103.8 and the smallest 94.5°), comparable to that of free $(PPh)_5$. The geometry of the phosphorus ring moiety in **4** is less distorted than in **1** and **2**. The orientations of the phenyl groups alternate in a *trans* manner around the ring of the $(PPh)_5$ moiety.

The structure of compound **5** consists of two discrete triosmium triangles linked at two equatorial sites by the cyclopolyphosphane through two phosphorus atoms at the 1,3 positions. As in the case of **4**, the M–M bonds *cis* to the phosphorus atoms, Os(1)–Os(3) (2.930 Å) and Os(4)–Os(5) (2.927 Å), are the longest Os–Os distances and significantly



Scheme 1

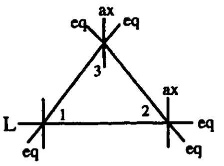


Scheme 2

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

	4	**5**
Os(1)–Os(2)	2.881(1)	2.882(1)
Os(1)–Os(3)	2.917(1)	2.930(1)
Os(2)–Os(3)	2.881(1)	2.876(1)
Os(4)–Os(6)		2.871(1)
Os(4)–Os(5)		2.927(1)
Os(5)–Os(6)		2.873(1)
Os(1)–P(1)	2.345(3)	
Os(1)–P(3)		2.335(4)
Os(4)–P(1)		2.359(6)
P(1)–P(2)	2.222(4)	2.271(6)
P(1)–P(5)	2.234(5)	2.278(9)
P(2)–P(3)	2.234(4)	2.238(9)
P(3)–P(4)	2.231(4)	2.215(7)
P(4)–P(5)	2.217(4)	2.192(7)
P–P (mean)	2.228	2.239
P–C (mean)	1.843	1.831
Os–C (mean)	1.891	1.910
C–O (mean)	1.163	1.146
Os(2)–Os(1)–Os(3)	59.6(1)	59.3(1)
Os(1)–Os(2)–Os(3)	60.8(1)	61.2(1)
Os(1)–Os(3)–Os(2)	59.6(1)	59.5(1)
Os(5)–Os(4)–Os(6)		59.4(1)
Os(4)–Os(5)–Os(6)		59.3(1)
Os(4)–Os(6)–Os(5)		61.3(1)
P(2)–P(1)–P(5)	97.7(2)	102.1(3)
P(1)–P(2)–P(3)	102.9(2)	103.5(3)
P(2)–P(3)–P(4)	103.8(2)	94.3(3)
P(3)–P(4)–P(5)	94.5(2)	96.0(3)
P(1)–P(5)–P(4)	94.7(2)	95.2(3)
P–P–P (mean)	98.7	98.2

Table 6 Distances (Å) M–M in [$M_3(CO)_{11}L$] (M = Os or Ru, L = Group 15 ligand)



M	L	M^1–M^2	M^2–M^3	M^2–M^3	Ref.
Ru	CO	2.852	2.851	2.860	28
Os	CO	2.874	2.857	2.882	11
Os	$(PPh)_5$	2.881	2.881	2.917	
Ru	$P(C_6H_{11})_5$	2.878	2.874	2.920	27
Os	$PBu^t_2(NH_2)$	2.900	2.881	2.953	29
Os	PPh_3	2.891	2.886	2.918	30
Ru	PPh_3	2.876	2.875	2.907	30
Os	$P(OMe)_3$	2.890	2.892	2.908	31

longer than the other four bonds. This is attributed to the steric repulsion between the bulky ligand and the adjacent equatorial carbonyl ligands. A similar situation was previously seen in [$\{Os_3(CO)_{11}\}_2$(dppa)] (dppa = $Ph_2PCCPPh_2$).[32] There is no significant difference among the other four Os–Os distances. The average P–P–P angle in **5** (98.2°) is closer to that (100.0°) of free $(PPh)_5$. Owing to this linkage pattern in which the phosphorus ring is bonded to two 'heavy' triosmium groups, the average P–P distance (2.239 Å) is much longer than that (2.217 Å) of free $(PPh)_5$ and even longer than that (2.228 Å) of **4**. The geometry of the phosphorus ring moiety in **5** is similar to that of free $(PPh)_5$. The torsion angles of **5** are very close to those of free $(PPh)_5$ as shown in Table 4. Another feature is that atoms P(5), P(1), P(2) and P(3) are almost in the same plane since the torsion angle P(5)–P(1)–P(2)–P(3) is only 2.2°, as in free $(PPh)_5$. Therefore the phosphorus ring has an envelope structure where only P(4) is out of the plane. The phenyl groups in **5** also alternate in a *trans* manner around the ring of the $(PPh)_5$ moiety.

NMR spectroscopy. The ^1H NMR spectra for compounds **4** and **5** show multiplets at δ_H 7.43 and 7.35, respectively, which are attributed to the phenyl protons. No bridging hydride is found in the negative range of the ^1H NMR spectra.

The two-dimensional COSY-90 ^{31}P NMR spectrum of [$Os_3(CO)_{11}\{(PPh)_5\}$] **4** with ^{31}P nuclei marked A, B, C, D_1 and D_2 is shown in Fig. 10. Distinct cross-peaks are seen for each pair of phosphorus nuclei except for A and B indicating a weak interaction between these two. The two-dimensional COSY-45 spectrum is shown in Fig. 11. Compared to the COSY-90 spectrum, the corners of some cross-peaks have been clipped off, while others remain as squares. In a COSY-45 spectrum cross-peaks from direct couplings retain the shape of a square, while the corners of cross-peaks from long-range couplings are clipped off. Based on this, we can deduce direct couplings between P_A and P_{D1}, and between P_A and P_{D2}, but indirect couplings for the pairs P_A and P_B and P_A and P_C. Similarly P_B connects P_C directly while both P_B and P_C are indirectly connected to P_A. The cross-peaks between P_C and P_{D1} or P_{D2} embody a square for P_C and P_{D2} and an incomplete square for P_C and P_{D1}. Therefore P_C is connected to P_{D2}, P_B to P_{D1}. This gives the arrangement of the P_5 ring as in Fig. 6(*c*).

The two-dimensional COSY-90 ^{31}P NMR spectrum of compound **5** is shown in Fig. 12 where the signals are marked A, B, C, D and E from the low-field end. All the cross-peaks appear invariably as complete squares. Two, A–D and A–E, are related to signal A, three B–C, B–D and B–E, to B, two B–C and C–D, to C, four A–D, B–D, C–D and D–E, to D and three, A–E, B–E and D–E, to E. Direct and indirect connectivities are not distinguished in a COSY-90 ^{31}P NMR spectrum.

The two-dimensional COSY-45 ^{31}P NMR spectrum is shown in Fig. 13. Cross-peaks are A–D, A–E, B–C, B–D, B–E, C–D and D–E, of which some are distorted (*e.g.* B–C), and some are deficient squares (*e.g.* B–D), compared to those of the COSY-90 spectrum. The tilts of the cross-peaks B–D and D–E are positive, *i.e.* in the same sense as the diagonal. Hence, these cross-peaks B–D and D–E arise from coupling by indirectly connected phosphorus nuclei. The remaining cross-peaks are due to the coupling by directly connected phosphorus nuclei, (A–D and A–E for signal A, B–C and B–E for B, B–C and C–D for C, and A–D and C–D for signal D and A–E and B–E for E). Therefore, the phosphorus-atom connectivity of the cyclophosphane ring can be established to be as in Fig. 6(*d*).

Reactions of [$Os_3(CO)_{11}\{(PPh)_5\}$] 4 with [$Ru_3(CO)_{11}(NCMe)$]

The reaction of [$Os_3(CO)_{11}\{(PPh)_5\}$] **4** with [$Ru_3(CO)_{11}$(NCMe)] (1 : 1.5 molar ratio) in freshly distilled dichloromethane was started from solid CO_2–acetone temperature and slowly warmed to 5 °C over a period of 3 h. The reaction was then kept at 5 °C for 2 h to yield a dark red mixture which gave a new orange cluster **6** and unreacted **4** when subjected to TLC using dichloromethane–hexane (1 : 4) as eluent. The orange product (yield 43%) was proposed to be [$(OC)_{11}Os_3\{1,3\text{-}(PPh)_5\}Ru_3(CO)_{11}$] **6** on the basis of spectroscopic data and elemental analysis results, Fig. 14. It could not be obtained when the same reaction was carried out at room temperature (about 30 °C). Only the five known products were identified: [$Ru_3(CO)_{12}$], [$Ru_3(CO)_{10}\{1,3\text{-}(PPh)_5\}$], **9**, **4**, **1** and **2**.

Experimental

The reactions described were carried out under nitrogen in evacuated reaction tubes using vacuum-line techniques. All solvents were dried over appropriate drying agents[33] and distilled prior to use. The compounds $(PPh)_5$,[34] [$Os_3(CO)_{11}$(NCMe)],[35] [$Ru_3(CO)_{11}$(NCMe)][36] and [$Os_3(CO)_{10}(NCMe)_2$][37] 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 Merck Kieselgel

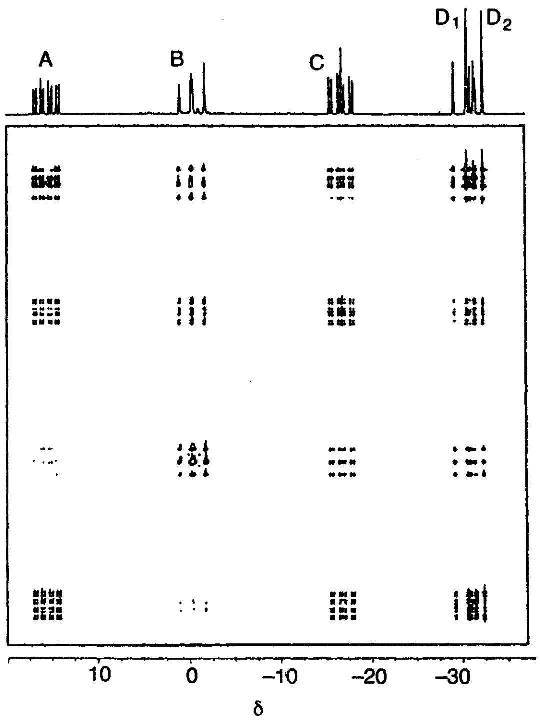


Fig. 10 Two-dimensional COSY-90 ^{31}P NMR spectrum of $[Os_3(CO)_{11}\{(PPh)_5\}]$ **4**

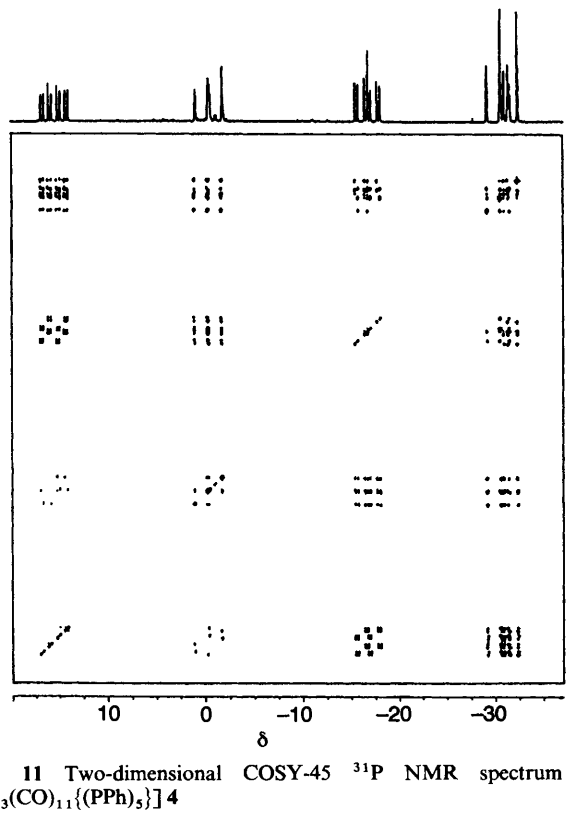


Fig. 11 Two-dimensional COSY-45 ^{31}P NMR spectrum of $[Os_3(CO)_{11}\{(PPh)_5\}]$ **4**

60GF$_{254}$, 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 Perkin-Elmer model 983 G spectrophotometer, ^1H and ^{31}P NMR spectra on Bruker 500 and 600 MHz Fourier-transform spectrometers using $SiMe_4$ (^1H) and H_3PO_4 (^{31}P) as references.

Reactions of $(PPh)_5$

With $[Os_3(CO)_{10}(NCMe)_2]$ at room temperature in 1 : 1 ratio. The compound $[Os_3(CO)_{10}(NCMe)_2]$ (155 mg, 0.165 mmol)

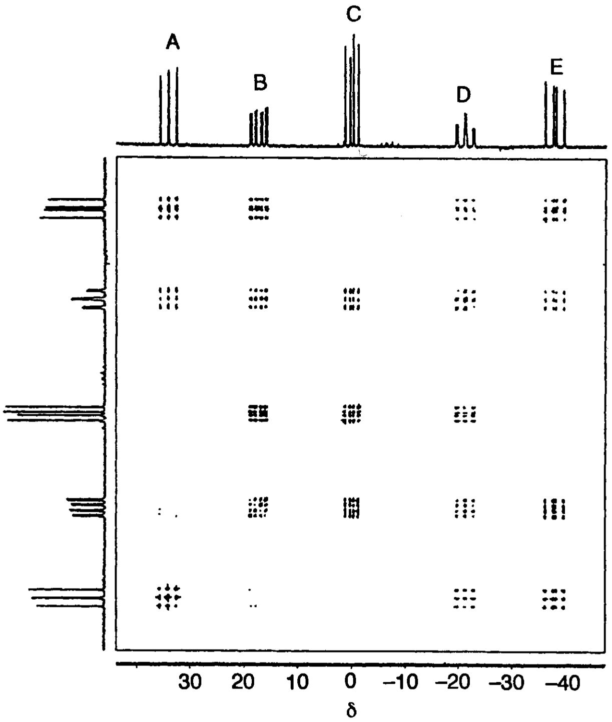


Fig. 12 Two-dimensional COSY-90 ^{31}P NMR spectrum of $[\{Os_3(CO)_{11}\}_2\{(PPh)_5\}]$ **5**

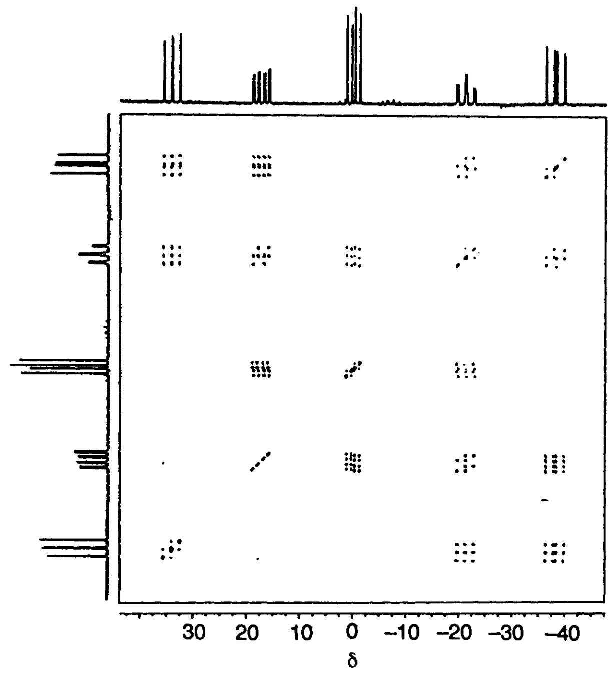


Fig. 13 Two-dimensional COSY-45 ^{31}P NMR spectrum of $[\{Os_3(CO)_{11}\}_2\{(PPh)_5\}]$ **5**

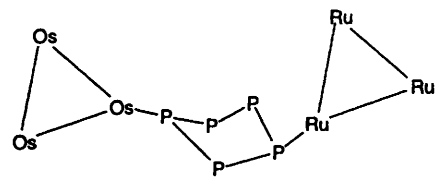


Fig. 14 Proposed structure of $[(OC)_{11}Os_3\{1,3\text{-}(PPh)_5\}Ru_3(CO)_{11}]$ **6**

and $(PPh)_5$ (89 mg, 0.165 mmol) were placed in one tube of a double reaction vessel, and degassed under vacuum. Freshly distilled dichloromethane (15 cm^3) was placed in the other tube of the vessel, and degassed *in vacuo*. The solvent was transferred to the other tube by condensation with a liquid-nitrogen bath.

Upon slowly warming to room temperature the mixture slowly changed from brown-yellow to orange. It was then stirred continuously for 24 h. The excess of solvent was removed under vacuum. The residue gave compounds **1** (63 mg, $R_f = 0.37$), **2** (4 mg, $R_f = 0.29$) and **3** (8 mg, $R_f = 0.46$) when subjected to TLC with dichloromethane–hexane (3:7) as eluent (Found: C, 34.8; H, 1.65; P, 10.8. Calc. for $C_{40}H_{25}O_{10}Os_3P_5$ **1**: C, 34.5; H, 1.80; P, 11.15%).

With $[Os_3(CO)_{10}(NCMe)_2]$ at 80 °C in 1:1 molar ratio. The compounds $[Os_3(CO)_{10}(NCMe)_2]$ (200 mg, 0.213 mmol) and $(PPh)_5$ (115 mg, 0.213 mmol) were placed in a Carius tube. The tube was evacuated on a vacuum line for 10 min. Degassed dichloromethane (10 cm^3) was transferred to the tube through the vacuum line. The reaction mixture was degassed again and sealed in the tube *in vacuo*. The tube was then placed in an iron pipe and heated in an oven overnight at 80 °C. The solution turned from brown-yellow to bright orange. Upon cooling the tube was opened under a nitrogen atmosphere. The resultant orange solution was transferred to a round-bottomed flask (50 cm^3). The excess of solvent was removed under vacuum. The residue yielded compounds **1** (46 mg) and **2** (51.2 mg) when subjected to TLC with dichloromethane–hexane (7:13) as eluent (Found: C, 34.45; H, 1.70; P, 10.45. Calc. for $C_{40}H_{25}O_{10}Os_3P_5$ **2**: C, 34.5; H, 1.80; P, 11.15%).

With $[Os_3(CO)_{10}(NCMe)_2]$ at room temperature in 3:1 molar ratio. The compound $[Os_3(CO)_{10}(MeCN)_2]$ (129 mg, 0.137 mmol) and $(PPh)_5$ (225 mg, 0.417 mmol) were placed in one tube of a double reaction vessel, and degassed under vacuum. Freshly distilled dichloromethane (20 cm^3) was placed in the other tube of the vessel and degassed *in vacuo*. The solvent was transferred to the other tube by condensation with a liquid-nitrogen bath. Upon slowly warming to room temperature the mixture slowly changed from brown-yellow to light orange. It was then stirred continuously for 20 h. The excess of solvent was removed under vacuum. The residue afforded compounds **1** (15 mg), **2** (4 mg) and **3** (65 mg, $R_f = 0.24$) when subjected to TLC with dichloromethane–hexane (3:7) as eluent (Found: C, 44.7; H, 3.00; P, 15.1. Calc. for $C_{70}H_{50}O_{10}Os_3P_{10}$ **3**: C, 43.5; H, 2.60; P, 16.05%).

With $[Os_3(CO)_{11}(NCMe)]$ at room temperature in 1:2 molar ratio. The compounds $(PPh)_5$ (44 mg, 0.081 mmol) and $[Os_3(CO)_{11}(NCMe)]$ 150 mg, (0.163 mmol) were placed in one tube of a double reaction vessel, and degassed under vacuum. Freshly distilled dichloromethane (10 cm^3) was placed in the other tube and degassed *in vacuo*. The solvent was transferred into the other tube by condensation with a liquid-nitrogen bath. After warming to room temperature the mixture was stirred for 17 h. It slowly changed from yellow to orange. The excess of solvent was removed under vacuum. The residue gave compounds **4** (55 mg, $R_f = 0.53$), **5** (84 mg, $R_f = 0.43$) and $[Os_3(CO)_{12}]$ (1 mg, $R_f = 0.90$) when subjected to TLC using dichloromethane–hexane (3:7) as eluent (Found: C, 34.7; H, 1.75; P, 10.95. Calc. for $C_{41}H_{25}O_{11}Os_3P_5$ **4**: C, 34.9; H, 1.75; P, 10.8. Found: C, 27.15; H, 1.10; P, 6.75. Calc. for $C_{52}H_{25}O_{22}Os_6P_5$ **5**: C, 27.2; H, 1.00; P, 6.60%).

With $[Os_3(CO)_{11}(NCMe)]$ at 80 °C in 1:1 molar ratio. The compounds $[Os_3(CO)_{11}(NCMe)]$ (100 mg, 0.109 mmol) and $(PPh)_5$ (59 mg, 0.109 mmol) were added to a Carius tube. The tube was evacuated on a vacuum line for 10 min. Degassed dichloromethane (10 cm^3) was transferred to the tube through the vacuum line. The mixture was degassed again and sealed in the tube *in vacuo*. The tube was then placed in an iron pipe and heated in an oven for 17 h at 80 °C. The solution turned from yellow to bright orange. After cooling the tube was opened under a nitrogen atmosphere. The resultant orange solution with an insoluble fine yellow solid was filtered through a sinter. The filtrate was transferred to a round-bottomed flask (50 cm^3). The excess of solvent was removed under vacuum. The residue generated compounds **1** (12 mg), **2** (15 mg) and $[Os_3(CO)_{12}]$ (3 mg) when subjected to TLC with dichloromethane–hexane (3:7) as eluent.

Reaction of $[Os_3(CO)_{11}\{(PPh)_5\}]$ with $[Ru_3(CO)_{11}(NCMe)]$

The compounds $[Os_3(CO)_{11}\{(PPh)_5\}]$ (71.5 mg, 0.050 mmol) and $[Ru_3(CO)_{11}(NCMe)]$ (49.0 mg, 0.075 mmol) (excess) were placed in one tube of a double reaction vessel and degassed under vacuum. Freshly distilled dichloromethane (10 cm^3) was placed in the other tube and degassed *in vacuo*. The solvent was transferred into the other tube by condensation with a liquid-nitrogen bath. The bath was then replaced by a solid CO_2–acetone bath the temperature of which was allowed to increase slowly to 5 °C in 3 h and then kept at 5 °C for 2 h. The mixture changed from orange to dark red. The excess of solvent was removed under vacuum. The residue afforded compounds **4** (43 mg) and **6** (44 mg, $R_f = 0.35$) when subjected to TLC using dichloromethane–hexane (1:4) as eluent (Found: C, 30.55; H, 1.50; P, 7.25. Calc. for $C_{52}H_{25}O_{22}Os_3P_5Ru_3$ **6**: C, 30.75; H, 1.25; P, 7.65%).

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