Ring Opening *versus* Phenyl–Phosphorus Bond Cleavage in incorporating a Phosphole into Triosmium Clusters†

Antony J. Deeming,[*,a] **Nicholas I. Powell,**[a] **Alejandro J. Arce,**[*,b] **Ysaura De Sanctis**[b] **and Jorge Manzur**[b]

[a] *Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK*
[b] *Chemistry Centre, Instituto Venezolano de Investigaciones Cientificas (IVIC), Apartado 21827, Caracas 1020-A, Venezuela*

The five-membered heterocyclic compound 3,4-dimethyl-1-phenylphosphole (PhPCH=CMeCMe=CH) reacts with [$Os_3(CO)_{11}(MeCN)$] or [$Os_3(CO)_{10}(MeCN)_2$] to give the simple substitution products [$Os_3(CO)_{12-x}(PhPC_4H_2Me_2)_x$] ($x = 1$ or 2) in which the phospholes are co-ordinated as tertiary phosphines through the phosphorus atoms. Thermolysis of these compounds gives decarbonylation compounds containing modified phosphole ligands. Phosphorus–carbon bonds either to the phenyl group or within the five-membered ring have been cleaved. The X-ray structure of the main product [$Os_3(CO)_9(\mu_3$-PhPCHCMeCMeCH)] **1** shows that the organic μ_3 ligand is a six-electron donor which is co-ordinated differently from the corresponding eight-electron donating ligand derived from 1-phenylphosphole in the cluster [$Os_3(CO)_9(\mu_3$-PhPCHCHCHCH)]. There is evidence for the reversible generation of this alternative form, **3**, of the methylated compound **1** by photolysis. A minor product of the thermolysis is the hydrido cluster [$Os_3(\mu$-H)(μ-PCH=CMeCMe=CH)(μ_3-C_6H_4)$(CO)_9$] **2** which contains a five-membered phospholyl ring and an *o*-phenylene (benzyne) ligand which originated from the phenyl group. The X-ray structure shows that the phospholyl ligand bridges two osmium atoms as a phosphido ligand through the phosphorus atom. The major and minor products, **1** and **2**, are both derived by C–P bond cleavage, either in the phosphole ring or to the phenyl substituent respectively.

1-Phenylphosphole ($PhPC_4H_4$) reacts with [$Os_3(CO)_{11}$-(MeCN)] to give [$Os_3(CO)_{11}(PhPC_4H_4)$] which thermally decarbonylates to the nonacarbonyl [$Os_3(CO)_9(PhPC_4H_4)$] and octacarbonyl [$Os_3(CO)_8(PhPC_4H_4)$] which were shown spectroscopically and by X-ray diffraction to contain ring-opened ligands.[1] This chemistry is summarised in Scheme 1; a decarbonyl intermediate was not observed but is believed to have the structure shown in Scheme 1 on the basis of the known structure of the related compound formed by ring opening of selenophene.[2] In each decarbonylated product which we isolated the $PhPC_4H_4$ ligand behaves as an eight-electron donor but the modes of bonding in the two compounds are very different. In this paper we describe the corresponding work with the compound 3,4-dimethyl-1-phenylphosphole. Although there is some evidence for the formation of the analogue of [$Os_3(CO)_9(PhPC_4H_4)$] shown in Scheme 1, much of the chemistry is different. This work is part of an overall study of the heterocyclic compounds thiophene, selenophene, tellurophene[2] and pyrrole[3] with triosmium clusters.

Results and Discussion

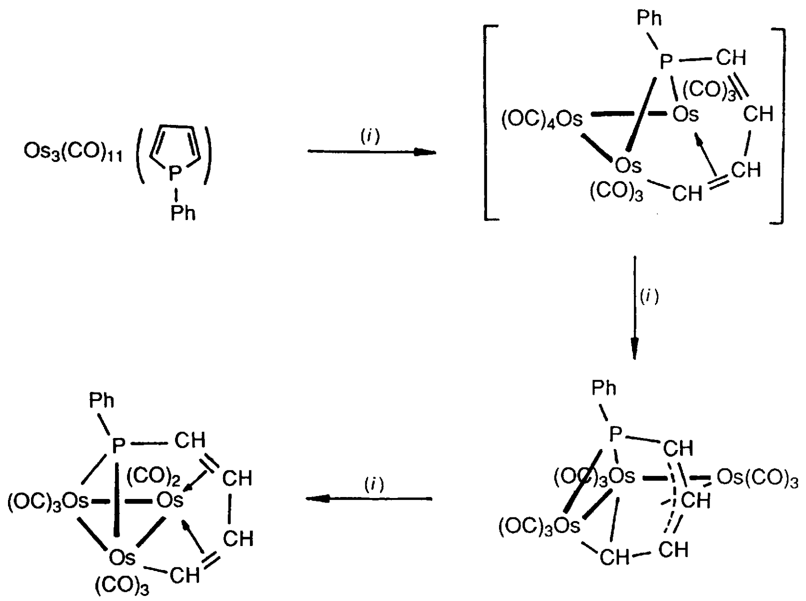
Syntheses.—Both acetonitrile complexes [$Os_3(CO)_{12-x}$-$(MeCN)_x$] ($x = 1$ or 2) react with 3,4-dimethyl-1-phenylphosphole ($PhPC_4H_2Me_2$) to give in different amounts the two complexes [$Os_3(CO)_{12-x}(PhPC_4H_2Me_2)_x$] ($x = 1$ or 2) which are easily separated on silica. These compounds are closely related spectroscopically to known tertiary phosphine analogues[4,5] and so we believe that the phosphole ligands are co-ordinated simply through the phosphorus atoms. As with other tertiary phosphine analogues, two isomers of the 1,2-decacarbonyl cluster are in equilibrium in solution.[6] The ^{31}P-{^1H} NMR spectrum of 1,2-[$Os_3(CO)_{10}(PhPC_4H_2Me_2)_2$] in $CDCl_3$ consists of a singlet for the symmetrical isomer with equivalent phosphole ligands (δ −16.34) and two equal-intensity singlets for the unsymmetrical isomer with non-equivalent phospholes (δ −19.67 and −15.59). This directly corresponds to what has been observed for related compounds with simple tertiary phosphines.[6] In other cases it has been shown that the rate of exchange of the non-equivalent phosphines in the unsymmetrical isomer is greater than the rate of isomer exchange, but we did not measure exchange rates in the phosphole system quantitatively. No evidence for the 1,1 isomer was obtained. See Experimental section for IR and NMR data for these phosphole complexes.

Treatment of [$Os_3(CO)_{11}(PhPC_4H_2Me_2)$] in refluxing heptane for 10 h led to a mixture containing approximately half of the original starting material. Chromatography on silica gave, as well as starting material, one main band which gave purple crystals of the nonacarbonyl [$Os_3(CO)_9(PhPC_4H_2Me_2)$] **1** (44% conversion). Two other yellow bands were obtained in extremely low yield (<2%). One was characterised, mainly by X-ray diffraction (see below), as [$Os_3(\mu$-H)(μ-$PC_4H_2Me_2$)(μ_3-C_6H_4)$(CO)_9$] **2**, an isomer of **1**. The other minor yellow product, **3**, is also an isomer of **1** but unlike isomer **2**, it is converted readily into **1** on standing. Because of this it could only be characterised spectroscopically. We have found that the purple isomer **1** is converted into this other yellow isomer **3** on irradiation with white light from a fluorescent tube. Essentially complete conversion was possible within 10 min under the conditions we used. Isomer **3** is converted into a mixture containing predominantly isomer **1** over several hours at room temperature in the dark or under low light conditions. No evidence was found for the conversion of isomer **2** into either of the other isomers, **1** and **3**, at room temperature.

Characterisation of the Isomers **1**–**3**.—The cluster [Os_3-$(CO)_9(PhPC_4H_2Me_2)$] **1** is not a hydride (^1H NMR evidence)

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.



Scheme 1 (*i*) Refluxing octane

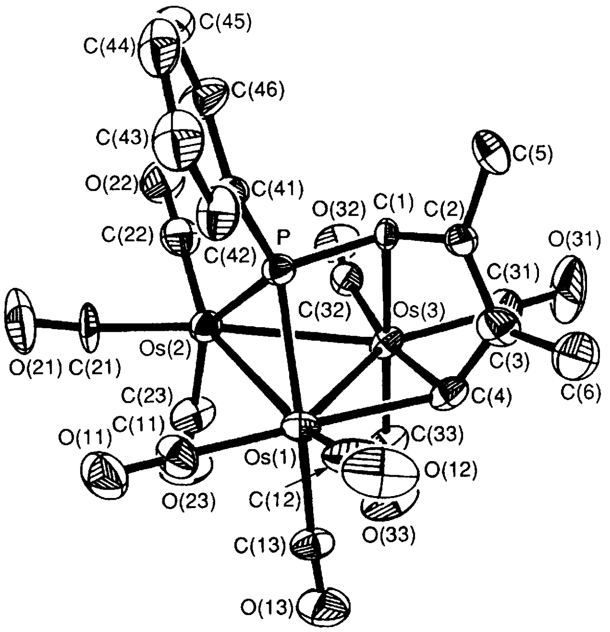


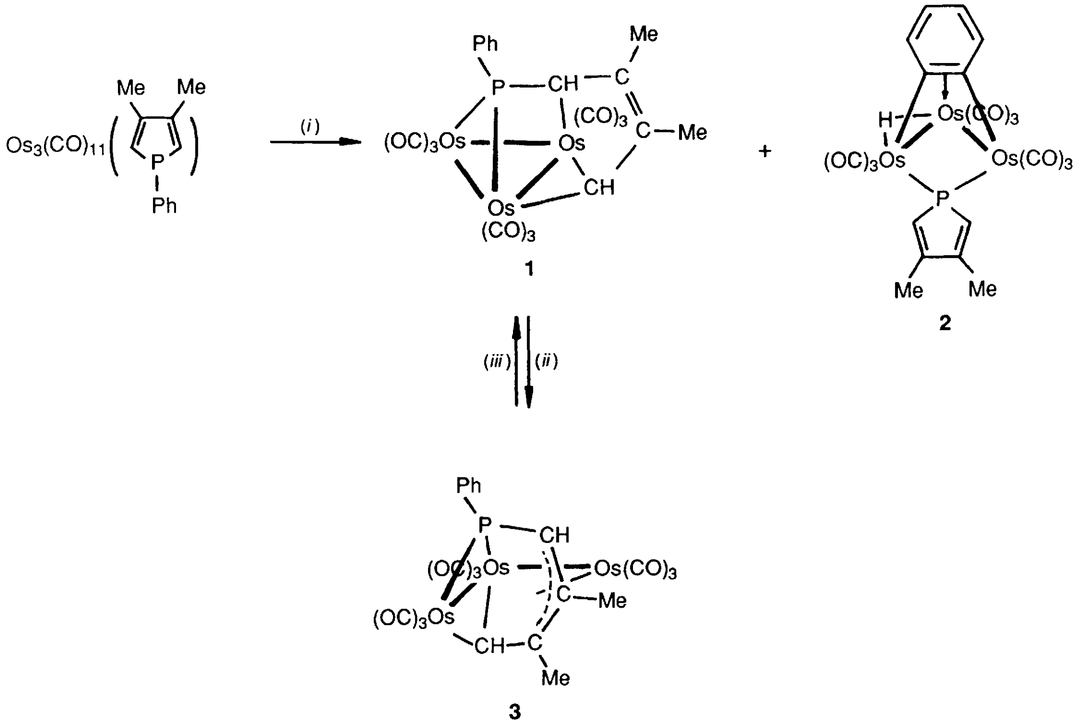
Fig. 1 Molecular structure of the cluster $[Os_3(CO)_9(\mu_3\text{-}PhPC_4H_2Me_2)]$ **1**

Table 1 Selected bond lengths (Å) and angles (°) for the cluster $[Os_3(CO)_9(PhPC_4H_2Me_2)]$ **1**

Os(1)–Os(2)	2.840(1)	Os(3)–C(1)	2.18(1)
Os(1)–Os(3)	2.791(1)	P–C(41)	1.81(1)
Os(2)–Os(3)	2.844(1)	P–C(1)	1.82(1)
Os(1)–P	2.347(3)	C(1)–C(2)	1.50(2)
Os(2)–P	2.320(4)	C(2)–C(3)	1.37(2)
Os(3)···P	2.848(3)	C(3)–C(4)	1.49(2)
Os(1)–C(4)	2.28(2)	C(2)–C(5)	1.50(3)
Os(3)–C(4)	2.08(1)	C(3)–C(6)	1.45(3)
Os(1)–Os(2)–Os(3)	58.8(1)	Os(2)–P–C(41)	126.9(5)
Os(1)–Os(3)–Os(2)	60.5(1)	C(1)–P–C(41)	112.5(6)
Os(2)–Os(1)–Os(3)	60.7(1)	P–C(1)–C(2)	109.7(9)
Os(1)–P–Os(2)	75.0(1)	C(1)–C(2)–C(3)	116(1)
Os(1)–P–Os(3)	64.1(1)	C(2)–C(3)–C(4)	112(1)
Os(2)–P–Os(3)	65.9(1)	Os(1)–C(4)–C(3)	118(1)
Os(1)–P–C(1)	101.4(4)	Os(3)–C(4)–C(3)	116(1)
Os(2)–P–C(1)	106.6(4)	Os(1)–C(4)–Os(3)	79.4(5)
Os(1)–P–C(41)	127.5(4)		

and, as well as phenyl resonances in the ^1H NMR spectrum, four other ^1H NMR signals were observed (Me signals at δ 1.07 and 2.30; CH signals at δ 2.82 and 11.70). Decarbonylation has led to major changes in the bonding of the phosphole ligand but the product does not correspond spectroscopically at all to the unsubstituted phosphole derivative $[Os_3(CO)_9(PhPC_4H_4)]$, the structure of which we have already described (Scheme 1).[1] The clusters must have corresponding stoichiometries but different structures. A single-crystal X-ray structure determination was performed to sort out differences between the two compounds. The molecular structure of **1** is shown in Fig. 1 and selected bond lengths and angles are in Table 1. Whereas the ligand $PhPC_4H_4$ in $[Os_3(CO)_9(PhPC_4H_4)]$ is an eight-electron donor (Scheme 1) and hence there are only two Os–Os bonds, the corresponding methyl-substituted compound **1** has three Os–Os bonds [2.840(1), 2.791(2) and 2.844(1) Å]. This is because the $PhPC_4H_2Me_2$ ligand is a six-electron donor. Both compounds have ring-opened phosphole ligands formed by P–C bond cleavage. The phosphorus atom in each compound is part of a phosphido bridge and donates three electrons. However, in **1** there is an unco-ordinated C=C bond [C(2)–C(3) 1.37(2) Å]; all the other C–C bonds are longer than 1.49 Å and can be regarded as single. There is an alkylidene bridge through C(4) associated with the shortest Os–Os bond and a σ-Os–C bond between C(1) and Os(3). One way of looking at the differences between the two compounds is that the η^3-allyl interaction in the $PhPC_4H_4$ compound has become a σ-allyl in cluster **1** and to compensate for this an extra Os–Os bond has been formed. Certainly one would expect methyl substitution to destabilise an η^3-allyl with respect to a σ-allyl. Another difference between the compounds is that the phosphido and alkylidene components bridge different Os–Os edges in **1** but the same pair of metal atoms in $[Os_3(CO)_9(PhPC_4H_4)]$. The alkylidene presumably cannot easily bridge a non-bonded pair of Os atoms.

A very minor yellow product **3** from the preparation has not been fully characterised (IR and ^1H NMR spectra only) but, since this interconverts reversibly with cluster **1**, we believe that they are isomers and probably **3** has the structure shown in Scheme 2 corresponding with the known structure of $[Os_3(CO)_9(PhPC_4H_4)]$.[1] The IR ν(CO) spectra are closely similar and the observed δ values for the two CH groups in **3** {δ 3.39



Scheme 2 (*i*) Refluxing heptane; (*ii*) visible *h*ν; (*iii*) 20 °C, dark

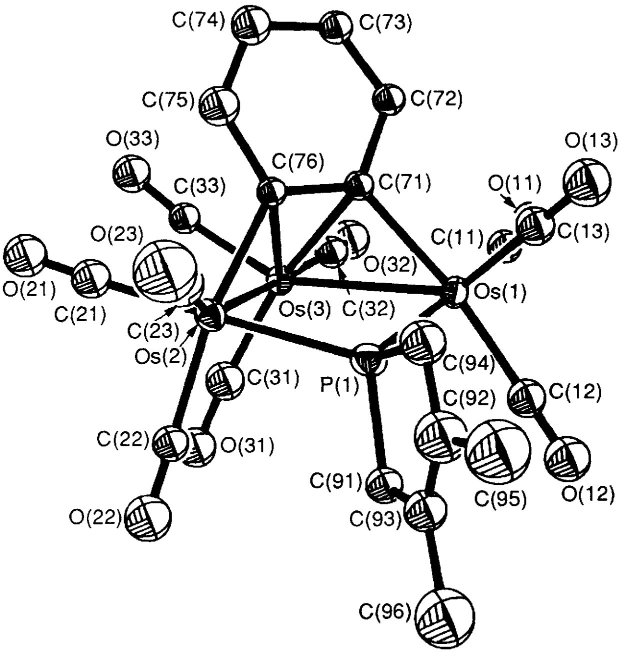


Fig. 2 Molecular structure of molecule A of the cluster [$Os_3(\mu\text{-}H)(\mu\text{-}PC_4H_2Me_2)(\mu_3\text{-}C_6H_4)(CO)_9$] **2**

[d, *J*(PH) 7.0 Hz] and 5.82 [d, *J*(PH) 14.0 Hz]} correspond satisfactorily with the corresponding pair for [$Os_3(CO)_9(PhPC_4H_4)$] [δ 3.40 [dd, *J*(PH) 7.6 Hz] and 4.84 [ddd, *J*(PH) 20.7 Hz]}.

The photochemical rearrangement has not been studied further. Probably electronic excitation leading to the cleavage of an Os–Os bond and a reorganisation of the co-ordination of the μ_3 ligand in response to this has occurred. The unco-ordinated C=C bond in cluster **1** co-ordinates and the alkylidene bridge migrates. The thermal isomerisation back to cluster **1** indicates that **3** is the less-stable isomer.

Another isomer formed in very low yield is cluster **2**. The ^1H NMR spectrum shows that a hydride ligand is present (δ −17.10). The remaining signals are consistent with an unsymmetrical C_6H_4 ligand, becoming symmetrical by exchange at high temperatures, and an unsymmetrical phospholyl ligand, $PC_4H_2Me_2$. The ^1H NMR chemical shifts and coupling constants for the phospholyl ligand in **2** are very similar to those for [$Os_3(CO)_{11}(PhPC_4H_2Me_2)$] and indicate that the ring is only marginally disturbed. A crystal structure determination shows that there are two very similar but independent molecules in the unit cell (A and B) and the structure of molecule A is shown in Fig. 2, the following discussion relating to that molecule. Selected bond lengths and angles are in Table 2. The structure confirms conclusions from the ^1H NMR spectra and is found to be closely related to that of [$Os_3(\mu\text{-}H)(\mu_3\text{-}C_6H_4)(\mu\text{-}AsMe_2)(CO)_9$] formed by thermal decarbonylation of [$Os_3(CO)_{11}(AsMe_2Ph)$][7] and that of the corresponding μ-SPr^i cluster.[8] The hydride ligand was not located but structural details indicate that it lies along the Os(1)–Os(3) edge, which is the longer of the two Os–Os bonds [Os(1)–Os(3) 2.922(2) and Os(2)–Os(3) 2.820(2) Å]. The phospholyl ligand bridges as a three-electron donor through an approximately tetrahedral P atom and is essentially as one might expect. Likewise the C_6H_4 ligand is structurally similar to those in related molecules.[7,8] The plane of the C_6 ring is 69° to the Os_3 plane as is required for the η^2 interaction between C(71) and C(76) to Os(3).

The initial decarbonylation of the cluster [$Os_3(CO)_{11}(PhPC_4H_2Me_2)$] would lead to an unsaturated species which either undergoes P–C bond cleavage in the phosphole ring, possibly *via* initial π complexation, to give clusters **1** and **3** or undergoes orthometallation at the phenyl group to give cluster **2**. Unlike furan,[9] thiophene[2] and pyrrole[3] the decarbonylation is not accompanied by C–H cleavage at the five-membered ring. In its reactions phosphole is behaving more like selenophene and tellurophene.[2,10]

Thermolysis of the clusters [$Os_3(CO)_{10}(PhPC_4H_2Me_2)_2$] was not very straightforward. Some phosphole ligand dissociation must occur because some of cluster **1** is obtained (24%). Presumably clusters **2** and **3** are also obtained but in undetectable quantities. Other more complex products were also obtained in fairly low yield but none of these has yet been characterised.

Table 2 Selected bond lengths (Å) and angles (°) for the cluster $[Os_3(\mu\text{-}H)(\mu\text{-}PC_4H_2Me_2)(\mu_3\text{-}C_6H_4)(CO)_9]$ **2**

	Molecule A	Molecule B
Os(1)–Os(3)	2.922(2)	2.930(2)
Os(2)–Os(3)	2.820(2)	2.819(2)
Os(1) ••• Os(2)	3.835(2)	3.837(2)
Os(1)–P(1)	2.398(7)	2.396(6)
Os(2)–P(1)	2.383(6)	2.388(7)
Os(1)–C(71)	2.15(2)	2.16(3)
Os(2)–C(76)	2.12(2)	2.11(2)
Os(3)–C(71)	2.29(3)	2.34(2)
Os(3)–C(76)	2.37(3)	2.40(3)
P(1)–C(91)	1.78(3)	1.80(3)
P(1)–C(94)	1.78(4)	1.85(4)
C(91)–C(93)	1.31(4)	1.37(5)
C(92)–C(93)	1.38(6)	1.37(6)
C(93)–C(96)	1.54(3)	1.53(4)
C(92)–C(94)	1.32(3)	1.37(6)
C(92)–C(95)	1.58(6)	1.53(4)
Os(1)–Os(3)–Os(2)	83.8(1)	83.7(1)
Os(1)–C(71)–C(76)	122(1)	121(2)
Os(2)–C(76)–C(71)	125(2)	126(2)
Os(1)–C(71)–Os(3)	82(1)	81(1)
Os(2)–C(76)–Os(3)	77.7(9)	77(1)
C(71)–Os(3)–C(76)	36.1(8)	36.4(7)
Os(1)–P(1)–Os(2)	106.7(2)	106.7(2)
Os(2)–P(1)–C(91)	113.9(8)	112.8(9)
Os(2)–P(1)–C(94)	118(1)	117(1)
Os(1)–P(1)–C(91)	114(1)	113(1)
Os(1)–P(1)–C(94)	114(1)	114(1)
C(91)–P(1)–C(94)	90(1)	94(1)

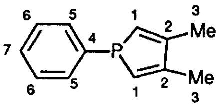
Table 3 Fractional atomic coordinates (× 10^4) for the cluster $[Os_3(CO)_9(PhPC_4H_2Me_2)]$ **1**

Atom	*x*	*y*	*z*
Os(1)	2293(1)	1678(1)	6371(1)
Os(2)	525(1)	3255(1)	6516(1)
Os(3)	616(1)	2513(1)	5134(1)
P	2786(3)	3297(2)	6260(2)
C(1)	2511(14)	3419(9)	5288(7)
C(2)	3708(14)	2940(10)	5035(8)
C(3)	3590(17)	1975(11)	4942(10)
C(4)	2322(14)	1577(10)	5178(8)
C(5)	4926(21)	3534(14)	4899(12)
C(6)	4579(22)	1337(15)	4698(13)
C(41)	4330(13)	3954(9)	6742(8)
C(42)	5547(16)	3538(14)	7124(10)
C(43)	6756(18)	4068(18)	7481(11)
C(44)	6674(17)	5023(18)	7395(10)
C(45)	5381(23)	5519(14)	7014(11)
C(46)	4231(19)	4984(12)	6693(10)
O(32)	−1522(11)	4131(8)	4794(7)
O(22)	−678(17)	5243(9)	6263(9)
O(33)	−1763(12)	1022(9)	5004(10)
O(31)	770(23)	2529(13)	3556(8)
O(13)	402(15)	−98(10)	6258(8)
O(11)	2724(17)	1692(10)	8003(8)
O(12)	5150(12)	705(10)	6498(9)
O(21)	1456(20)	3708(15)	8102(8)
O(23)	−2161(14)	2098(10)	6546(10)
C(32)	−737(16)	3559(11)	4979(8)
C(22)	−232(18)	4473(13)	6354(10)
C(33)	−855(14)	1557(11)	5080(11)
C(31)	680(19)	2509(12)	4108(10)
C(11)	2509(18)	1708(13)	7395(10)
C(21)	1063(20)	3517(14)	7521(9)
C(13)	1112(14)	549(11)	6320(10)
C(23)	−1183(17)	2549(11)	6526(12)
C(12)	4058(18)	1034(11)	6426(12)

Experimental

3,4-Dimethyl-1-phenylphosphole,[11] $[Os_3(CO)_{11}(MeCN)]$, and $[Os_3(CO)_{10}(MeCN)_2]$[12] were synthesised as previously described. The light petroleum used as TLC eluent had the boiling range 30–40 °C.

Reaction of $[Os_3(CO)_{11}(MeCN)]$ *with* 3,4-*Dimethyl*-1-*phenylphosphole*.—A solution of the acetonitrile cluster (0.100 g) and the phosphole (0.060 g) in dichloromethane (30 cm^3) was stored under nitrogen at room temperature for 3 d. Most of the solvent was removed under reduced pressure and the solution chromatographed (TLC) [SiO_2; eluent, light petroleum initially and then light petroleum–dichloromethane (5:1 v/v)] to give two clearly resolved bands. The upper band gave $[Os_3(CO)_{11}(PhPC_4H_2Me_2)]$ as yellow crystals (0.084 g, 81%) formed by slow evaporation of a dichloromethane solution (Found: C, 25.9; H, 1.15. $C_{23}H_{13}O_{11}Os_3P$ requires C, 25.9; H, 1.25%). IR (cyclohexane), ν(CO)/cm^{-1}: 2107m, 2053s, 2033s, 2018s, 2001m, 1990m, 1977m and 1960w. NMR ($CDCl_3$): ^1H (400 MHz), δ 2.16 [dd, Me, *J*(PH) *ca.* 1, *J*(HH) *ca.* 1], 6.53 [dd, CH, *J*(PH) 35.8, *J*(HH) *ca.* 1] and 7.47 (m, Ph); ^{13}C (*J* are couplings to ^{31}P), δ 17.20 (d, C^3, *J* 13.2), 127.31 (d, C^1, *J* 56), 128.91 (d, C^5, *J* 11.2), 130.24 (d, C^6, *J* 10.8), 130.61 (d, C^7, *J* 2.5), 133.5 (d, C^4, *J* 50), 150.96 (d, C^2, *J* 11 Hz) and *ca.* 172 (s, CO); ^{31}P-{^1H} (162 MHz), δ −16.40 (s). The lower band gave $[Os_3(CO)_{10}(PhPC_4H_2Me_2)_2]$ as orange crystals (0.012 g, 16%) also from dichloromethane (Found: C, 33.4; H, 2.1. $C_{34}H_{26}O_{10}Os_3P_2$ requires C, 33.3, H, 2.15%). IR (cyclohexane), ν(CO)/cm^{-1}: 2083w, 2026m, 2010w, 2002s, 1968m and 1954m. NMR ($CDCl_3$): ^1H (400 MHz), δ 2.15 [dd, Me, *J*(PH) *ca.* 1, *J*(HH) *ca.* 1], 6.5 [dd, CH, *J*(PH) 34, *J*(HH) *ca.* 1] and 7.4 (m, Ph); ^{31}P-{^1H} (162 MHz), δ −16.34 (s, sym. isomer), −19.67 and −15.59 (s, unsym. isomer).



Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ *with* 3,4-*Dimethyl*-1-*phenylphosphole*.—A solution of the bis(acetonitrile) compound (0.085 g) and the phosphole (0.060 g) in dichloromethane (20 cm^3) was kept at room temperature under nitrogen for 2 h and the solvent removed under reduced pressure. The residue was dissolved in a minimum of dichloromethane and chromatographed as above. The same two compounds were obtained as in the above experiment: $[Os_3(CO)_{11}(PhPC_4H_2Me_2)]$ as yellow crystals (0.034 g, 34%) and $[Os_3(CO)_{10}(PhPC_4H_2Me_2)_2]$ as orange crystals (0.074 g, 65%).

Thermal Treatment of $[Os_3(CO)_{11}(PhPC_4H_2Me_2)]$.—A solution of the cluster (0.247 g) in heptane (30 cm^3) was refluxed under nitrogen for 10 h. The solvent was removed under reduced pressure and the residue dissolved in a minimum of dichloromethane. Chromatography (PLC) [SiO_2; eluent, light petroleum–dichloromethane (10:1 v/v)] gave five bands. The top band yielded $[Os_3(CO)_9(PhPC_4H_2Me_2)]$ **1** as purple crystals (0.052 g, 44% based on starting material consumed) from a cyclohexane–dichloromethane mixture (Found: C, 24.75; H, 1.15. $C_{21}H_{13}O_9Os_3P$ requires C, 24.95; H, 1.3%). IR (cyclohexane), ν(CO)/cm^{-1}: 2088m, 2056s, 2043s, 2017m, 2002m, 1991w, 1987(sh) and 1974w. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.07 [d, Me, *J*(PH) 6.0], 2.30 [d, Me, *J*(PH) 12.3], 2.82 [d, CH, *J*(PH) 9.8], 7.40 (m, Ph) and 11.70 [d, CH, *J*(PH) *ca.* 1 Hz]. The next band gave $[Os_3(\mu\text{-}H)(\mu\text{-}\overline{PCHCMeCMeCH})(\mu_3\text{-}C_6H_4)(CO)_9]$ **2** as yellow crystals (0.002 g, 1.7%) from a cyclohexane–dichloromethane mixture. Too little was obtained for elemental analysis and it was characterised spectroscopically and by X-ray diffraction. IR (cyclohexane), ν(CO)/cm^{-1}: 2095w, 2072s, 2045s,

Table 4 Fractional atomic coordinates (× 10^4) for the cluster $[Os_3(\mu\text{-}H)(\mu\text{-}PC_4H_2Me_2)(\mu_3\text{-}C_6H_4)(CO)_9]$ **2**

Atom	*x*	*y*	*z*
Os(1)	1 355(1)	5 324(1)	2 104(1)
Os(2)	1 433(1)	9 194(1)	2 609(1)
Os(3)	1 895(1)	7 566(1)	2 483(1)
P(1)	1 012(1)	7 333(7)	2 048(3)
C(71)	1 766(5)	6 055(22)	2 959(10)
C(72)	2 024(5)	5 027(24)	3 375(10)
C(73)	2 262(5)	5 357(24)	3 927(11)
C(74)	2 256(6)	6 749(26)	4 137(12)
C(75)	2 018(6)	7 716(28)	3 767(12)
C(76)	1 762(5)	7 480(22)	3 150(10)
C(91)	659(5)	7 855(24)	1 336(11)
C(92)	360(7)	7 214(34)	1 704(16)
C(93)	349(6)	7 687(28)	1 245(14)
C(94)	687(6)	6 897(28)	2 164(13)
C(95)	12(8)	6 908(37)	1 668(16)
C(96)	−9(7)	8 156(36)	686(14)
C(11)	1 662(6)	3 871(26)	2 153(11)
O(11)	1 849(4)	3 039(19)	2 166(8)
C(12)	999(6)	4 890(26)	1 287(12)
O(12)	777(5)	4 669(20)	844(9)
C(13)	1 184(6)	4 111(27)	2 408(12)
O(13)	1 076(4)	3 367(20)	2 598(9)
C(21)	1 811(6)	10 585(27)	3 052(12)
O(21)	2 042(4)	11 362(19)	3 316(8)
C(22)	1 168(6)	10 513(25)	1 961(12)
O(22)	1 018(4)	11 269(20)	1 587(9)
C(23)	1 211(7)	9 656(32)	2 960(15)
O(23)	1 065(6)	9 951(28)	3 151(12)
C(31)	1 779(6)	9 015(28)	1 950(13)
O(31)	1 703(4)	9 827(20)	1 587(9)
C(32)	2 193(6)	6 277(26)	2 417(12)
O(32)	2 391(4)	5 673(20)	2 387(9)
C(33)	2 307(5)	8 571(23)	3 071(11)
O(33)	2 585(4)	9 018(17)	3 450(8)
Os(4)	1 227(1)	635(1)	4 957(1)
Os(5)	1 153(1)	4 458(1)	4 411(1)
Os(6)	1 718(1)	3 096(1)	5 425(1)
P(2)	806(1)	2 485(7)	4 361(3)
C(81)	1 485(5)	2 854(22)	4 439(10)
C(82)	1 707(5)	3 182(26)	4 229(11)
C(83)	1 945(6)	2 267(28)	4 298(12)
C(84)	2 010(6)	972(27)	4 578(12)
C(85)	1 826(5)	543(22)	4 778(10)
C(86)	1 555(4)	1 424(21)	4 709(10)
C(101)	448(6)	1 851(28)	3 658(12)
C(102)	132(7)	2 067(34)	3 590(16)
C(103)	152(7)	2 650(32)	4 039(15)
C(104)	500(6)	2 995(28)	4 541(13)
C(105)	−228(9)	1 629(41)	3 036(16)
C(106)	−167(9)	2 957(41)	4 055(16)
C(41)	987(6)	−681(26)	4 318(12)
O(41)	856(4)	−1 423(19)	3 949(8)
C(42)	1 587(6)	−700(28)	5 491(12)
O(42)	1 815(5)	−1 537(22)	5 790(9)
C(43)	949(7)	136(29)	5 208(13)
O(43)	783(5)	−179(20)	5 377(9)
C(51)	1 451(7)	5 985(33)	4 485(14)
O(51)	1 646(6)	6 904(25)	4 532(10)
C(52)	943(5)	5 722(26)	4 661(11)
O(52)	841(5)	6 498(22)	4 843(9)
C(53)	829(7)	4 682(29)	3 608(13)
O(53)	605(5)	4 876(23)	3 132(10)
C(61)	2 091(6)	2 060(27)	6 095(12)
O(61)	2 309(5)	1 488(20)	6 504(9)
C(62)	2 057(7)	4 188(29)	5 444(13)
O(62)	2 283(4)	4 866(21)	5 472(9)
C(63)	1 637(6)	4 444(30)	5 783(13)
O(63)	1 580(4)	5 321(20)	6 020(8)

2019s, 2017(sh), 2003m, 1990w and 1974w. ^1H NMR ($CDCl_3$, 400 MHz, −50 °C): δ −17.10 (s, OsH), 2.07 (s, Me), 2.23 (s, Me), 5.95 [d, CH, *J*(PH) 40.0], 6.50 [d, CH, *J*(PH) 38.0 Hz], 6.78, 7.04, 8.52 and 8.97 (m, C_6H_4). The third yellow band was readily converted into the purple compound **1** and was only characterised spectroscopically as cluster **3**; it is believed to be an isomer of **1** (see Results and Discussion). IR (cyclohexane), ν(CO)/cm^{-1}: 2080m, 2056s, 2028s, 2009s, 1988m, 1982(sh), 1977s and 1955w. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.56 (s, Me), 2.64 (s, Me), 3.39 [d, CH, *J*(PH) 7.0], 5.82 [d, CH, *J*(PH) 14.0 Hz] and 7.50 (m, Ph). The fourth band gave starting material (0.123 g) and the fifth a trace of orange powder (0.003 g) which was not characterised.

Photolysis of $[Os_3(CO)_9(PhPC_4H_2Me_2)]$ **1**.—A solution of cluster **1** in cyclohexane (5 cm^3) was irradiated with white light from a fluorescent tube and the colour changed from purple through to orange and then yellow over 10 min. The IR spectrum showed a complete conversion but slow evaporation over hours resulted in the regeneration of cluster **1**.

Thermal Treatment of $[Os_3(CO)_{10}(PhPC_4H_2Me_2)_2]$.—A solution of the cluster (0.124 g) in octane (25 cm^3) was refluxed under nitrogen for 4 h. The solvent was removed and TLC work-up on SiO_2 eluting with light petroleum and then with a light petroleum–dichloromethane mixture (10:1 v/v) gave three bands. The first was the cluster **1** (0.022 g, 24%) while the other two orange products (0.002 and 0.012 g) were uncharacterised.

Single-crystal X-Ray Structure Determinations for Clusters **1** *and* **2**.—*General conditions.* A single crystal of each compound was fixed to a glass fibre mounted on a goniometer on a Nicolet R3v/m diffractometer operating with Mo-Kα radiation (λ = 0.710 73 Å). Unit cells were determined by auto-indexing 25 orientation reflections in the range 18 ⩽ 2θ ⩽ 31° for **1** and 29 reflections in the range 11 ⩽ 2θ ⩽ 30° for **2**. Intensity data measured at room temperature were corrected for Lorentz and polarisation effects and for decay (minimal in each case) using the intensities of three reflections measured throughout the data collection as standards. Empirical absorption corrections were applied by the azimuthal scan method.

Cluster **1**: *crystal data.* $C_{21}H_{13}O_9Os_3P$, *M* = 1010.9, size 0.70 × 0.50 × 0.40mm, monoclinic, space group $P2_1/n$, *a* = 9.561(3), *b* = 14.080(3), *c* = 18.995(6) Å, β = 102.94(3)°, *U* = 2492(1) Å^3, *Z* = 4, *F*(000) = 1816, D_c = 2.69 g cm^{-3}, μ(Mo-Kα) = 153.9 cm^{-1}.

Data collection. 4891 Data, of which 4402 are unique, were collected in the range 5 ⩽ 2θ ⩽ 50° in the ω–2θ mode.

Structure solution and refinement. Direct methods, 3711 data with $F_o > 3\sigma(F_o)$ used in refining 307 parameters, all atoms anisotropic, H-atoms excluded, final *R* = 0.0567, *R′* = 0.0627, where $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ and $w = 1/[\sigma^2(F_o) + 0.001\,66(F_o)^2]$; largest shift/e.s.d. in final cycle = 0.007, largest peak in final Fourier difference map = 3.3 e Å^{-3}, close to Os atoms.

Cluster **2**: *crystal data.* $C_{21}H_{13}O_9Os_3P$, *M* = 1010.9, size 0.10 × 0.30 × 0.10 mm, monoclinic, space group *C*2/*c*, *a* = 46.313(15), *b* = 9.333(2), *c* = 29.180(11) Å, β = 126.81(2)°, *U* = 10 098(1) Å^3, *Z* = 16, *F*(000) = 7264, D_c = 2.66 g cm^{-3}, μ(Mo-Kα) = 151.9 cm^{-1}.

Data collection. 5289 Unique intensity data were collected in the range 5 ⩽ 2θ ⩽ 50° in the ω mode.

Structure solution and refinement. Direct methods, 3875 data with $F_o > 3\sigma(F_o)$ used in refining 313 parameters, Os and P atoms anisotropic, all others isotropic, H atoms are included in idealised positions riding on respective carbon atoms with C–H 0.96 Å and isotropic thermal parameters 0.08 Å^2. Final $R = 0.0542$, $R' = 0.0467$, where $w = 1/[\sigma^2(F_o) + 0.000\,08(F_o)^2]$; largest shift/e.s.d. in final cycle = 0.001, largest peak in final Fourier difference map = 1.1 e Å^{-3}, close to Os atoms.

Fractional atomic coordinates for clusters **1** and **2** are in Tables 3 and 4 respectively. Structures were solved and refined using SHELXTL PLUS[13] on a MicroVax II computer.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the SERC for a grant for the Nicolet diffractometer and for a research studentship (for N. I. P.).

References

1 A. J. Arce, Y. De Sanctis, J. Manzur, A. J. Deeming and N. I. Powell, *J. Organomet. Chem.*, 1991, **408**, C18.

2 A. J. Arce, A. J. Deeming, Y. De Sanctis, R. Machado, J. Manzur and C. Rivas, *J. Chem. Soc., Chem. Commun.*, 1990, 1568.

3 A. J. Deeming, A. J. Arce, Y. De Sanctis, M. Day and K. I. Hardcastle, *Organometallics*, 1989, **8**, 1408; 1990, **9**, 6.

4 A. J. Deeming, *Adv. Organomet. Chem.*, 1986, **26**, 1.

5 A. J. Deeming, B. F. G. Johnson and J. Lewis, *J. Chem. Soc. A*, 1970, 897.

6 A. J. Deeming, S. Donovan-Mtunzi, S. E. Kabir and P. J. Manning, *J. Chem. Soc., Dalton Trans.*, 1985, 1037.

7 A. J. Deeming, I. P. Rothwell, M. B. Hursthouse and J. D. J. Backer-Dirks, *J. Chem. Soc., Dalton Trans.*, 1981, 1879.

8 R. D. Adams, D. A. Katahira and L.-W. Yang, *Organometallics*, 1982, **1**, 235.

9 D. Himmelreich and G. Müller, *J. Organomet. Chem.*, 1985, **297**, 341.

10 A. J. Deeming, R. Machado, C. Rivas, Y. De Sanctis and A. J. Deeming, *J. Organomet. Chem.*, in the press.

11 A. Breque, F. Mathey and P. Savignai, *Syntheses*, 1981, 983.

12 B. F. G. Johnson, J. Lewis and D. A. Pippard, *J. Chem. Soc., Dalton Trans.*, 1981, 407; *J. Organomet. Chem.*, 1978, **145**, C4; J. N. Nicholls and M. D. Vargas, *Inorg. Synth.*, 1989, **26**, 289.

13 G. M. Sheldrick, SHELXTL PLUS, Package for crystal structure determination, University of Göttingen, 1986.

Received 27*th June* 1991; *Paper* 1/03209G