New Modes of Attachment of C_5 Rings in Organometallic Compounds: X-Ray Crystal Structures of the Clusters $[Os_3H(Ph_3PC_5H_3)(CO)_x]$ (x = 9 or 10) derived from Cyclopentadienylidenetriphenylphosphorane†

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The cluster $[Os_3(CO)_{10}(MeCN)_2]$ reacts rapidly at room temperature with cyclopentadienylidenetriphenylphosphorane ($Ph_3PC_5H_4$) to give the oxidative-addition compound $[Os_3(\mu\text{-H})(\mu\text{-}Ph_3PC_5H_3)(CO)_{10}]$ **1** which was shown by X-ray structure determination to contain the C_5 ring bonded through a single carbon atom to two osmium atoms. We consider the compound to be zwitterionic with a phosphonium substituent at the five-membered organic ring which is co-ordinated as a μ-alkylidene to the metal atoms which carry a formal negative charge. In solution the compound exists as two slowly interconverting isomers, **1a** and **1b**, which were separated by TLC and which differ only in the substitution position of the phosphonium group. Decarbonylation gives the compound $[Os_3(\mu\text{-H})(\mu_3\text{-}Ph_3PC_5H_3)(CO)_9]$ **2**, which also exists as isomers. The X-ray structure of the major isomer shows it to contain the C_5 ring co-ordinated to the three osmium atoms through two σ Os–C bonds and an η^2 bond. A zwitterionic description is likewise appropriate. The bonding in these compounds suggests new types of cyclopentadienylidene (C_5H_4) co-ordination.

The cyclopentadienyl (C_5H_5) ligand has been central to the development of organometallic chemistry. Apart from its normal η^5-co-ordination mode, it can co-ordinate as a σ or η^3 ligand depending upon the requirements of the metal atom. It can also bridge in various ways. The derived ligand, cyclopentadienylidene (C_5H_4) also appears in a number of co-ordination types. We have been looking at the chemistry of the phosphorus ylide, cyclopentadienylidenetriphenylphosphorane [(triphenylphosphonio)cyclopentadienide, $Ph_3PC_5H_4$] with the triosmium cluster, $[Os_3(CO)_{10}(MeCN)_2]$, and have found that it readily adds oxidatively with C–H bond cleavage and MeCN displacement to give products with C_5 rings bonded to the Os_3 cluster in interesting ways and which suggest new ways that the C_5H_4 ligand might co-ordinate.

Results and Discussion

Cyclopentadienylidenetriphenylphosphorane[1] is expected to contain a nucleophilic C_5 ring as a result of a major contribution from form **B** in addition to a minor contribution from form **A** (Fig. 1). The zwitterionic representation **B** could be regarded as a cyclopentadienyl anion substituted with the phosphonium group and the five-membered ring would therefore be expected to have enhanced nucleophilicity over neutral alkenes even though it is apparently too weakly nucleophilic to undergo normal Wittig chemistry. One might expect that the formation of η^5-$C_5H_4PPh_3$ would dominate the chemistry with mononuclear systems and there are many examples of this (see ref. 2 for some examples). However, clusters frequently have very different chemistry from that of mononuclear compounds. In particular $[Os_3(CO)_{12}]$, or the more reactive species $[Os_3(CO)_{10}(MeCN)_2]$, usually undergoes oxidative addition with C–H bond cleavage in its reactions with unsaturated hydrocarbons rather than forming π complexes. For example, indene (C_9H_8) commonly gives mononuclear η^5-indenyl (C_9H_7) compounds by deprotonation at the acidic CH_2 group. However, with triosmium clusters indene undergoes oxidative addition with C–H bond cleavage at the vinylic sites to give the μ_3-indyne cluster $[Os_3H_2(\mu_3,\eta^2\text{-}C_9H_6)(CO)_9]$ rather than an η^5 complex.[3,4] In a related way, $Ph_3PC_5H_4$ reacts with $[Os_3(CO)_{10}(MeCN)_2]$ by an oxidative addition reaction to give a σ complex and not an η^5 complex. Reaction of the bis(acetonitrile) complex with an equimolar quantity of $Ph_3PC_5H_4$ at room temperature in dichloromethane is complete within seconds resulting in a fairly good yield of the oxidative addition product $[Os_3(\mu\text{-H})(\mu\text{-}Ph_3PC_5H_3)(CO)_{10}]$ **1**, which can be isolated as ruby-red crystals by TLC on silica. Reaction with this phosphorane is very much more rapid than with alkenes which is consistent with the considerable negative charge associated with the five-membered ring; the rates of carbon–hydrogen bond activations of this kind seem to be

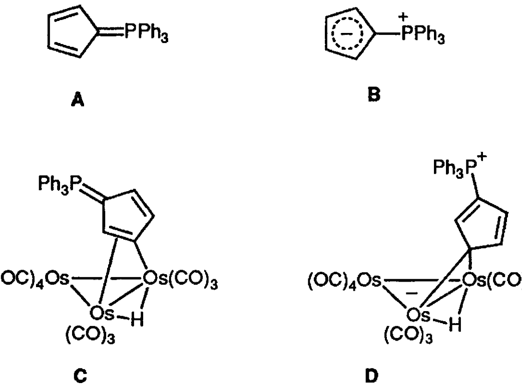

Fig. 1 Resonance forms of cyclopentadienylidenetriphenylphosphorane **A** and **B** and possible alternative structures for the oxidative-addition product $[Os_3(\mu\text{-H})(\mu\text{-}Ph_3PC_5H_3)(CO)_{10}]$ **1**

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

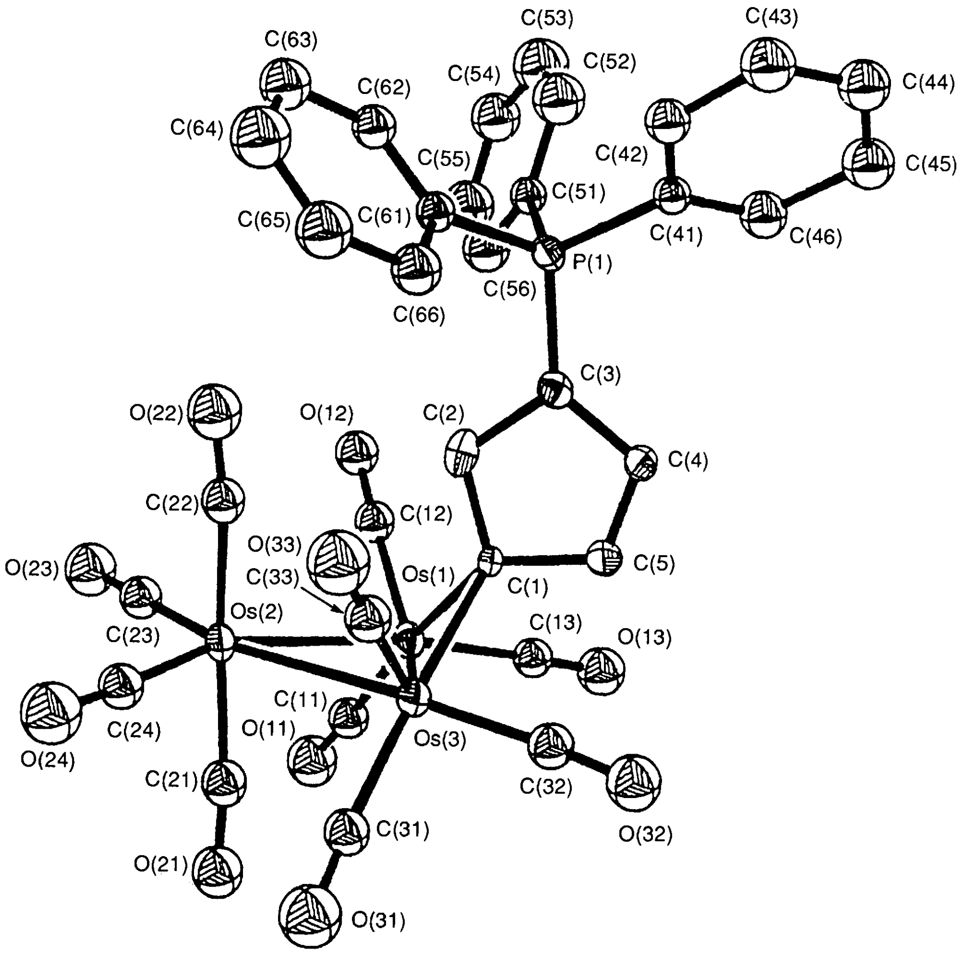


Fig. 2 Molecular structure of [Os(μ-H)(μ-$Ph_3PC_5H_3$)$(CO)_{10}$] **1**

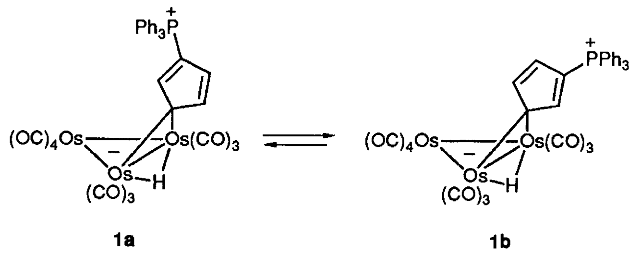
Table 1 Selected bond lengths (Å) and angles (°) for [Os_3(μ-H)(μ-$Ph_3PC_5H_3$)$(CO)_{10}$] **1**

Os(1)–Os(2)	2.882(2)	C(3)–C(4)	1.45(3)
Os(1)–Os(3)	2.782(1)	C(4)–C(5)	1.30(3)
Os(2)–Os(3)	2.863(1)	C(5)–C(1)	1.45(3)
Os(1)–C(1)	2.20(2)	P(1)–C(3)	1.74(2)
Os(3)–C(1)	2.25(2)	P(1)–C(41)	1.81(2)
C(1)–C(2)	1.44(2)	P(1)–C(51)	1.80(2)
C(2)–C(3)	1.43(3)	P(1)–C(61)	1.80(2)
Os(2)–Os(1)–Os(3)	60.7(1)	Os(3)–Os(1)–C(1)	52.1(5)
Os(1)–Os(2)–Os(3)	57.9(1)	Os(3)–C(1)–C(2)	118(1)
Os(1)–Os(3)–Os(2)	61.4(1)	Os(3)–C(1)–C(5)	118(1)
Os(2)–Os(3)–C(1)	91.3(4)	Os(1)–C(1)–Os(3)	77.3(5)
Os(2)–Os(1)–C(1)	91.7(5)	Os(1)–C(1)–C(2)	121(1)
Os(1)–Os(3)–C(1)	50.6(4)	Os(1)–C(1)–C(5)	120(1)

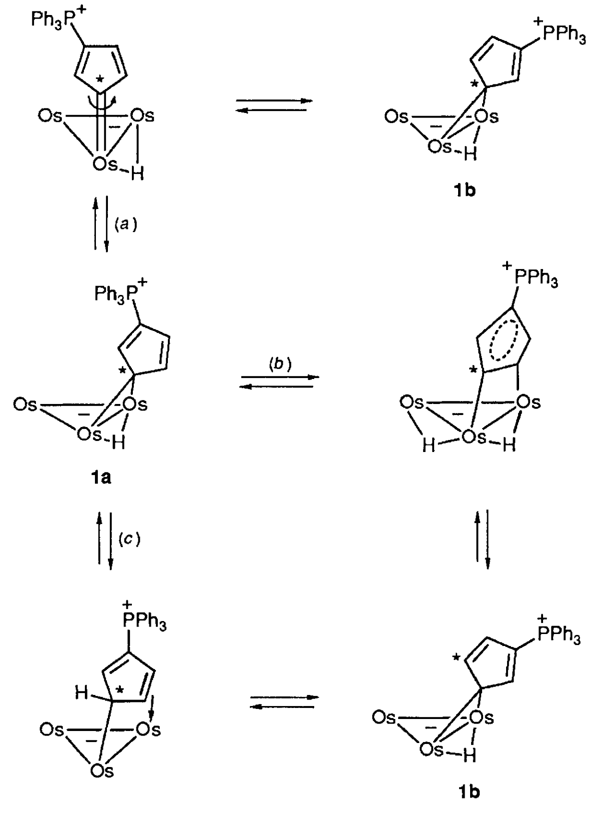
controlled by the rate of initial co-ordination rather than that of the bond-cleavage step. Better donors seem to undergo more facile C–H bond cleavage and C–H cleavage does not seem to be rate determining.

The ^1H NMR spectrum of the newly synthesised compound **1** in $CDCl_3$ indicates that it is a single isomer (see discussion below and data in the Experimental section) resulting from hydride formation (δ −15.34) with cleavage of a C–H bond in the C_5 ring remote from phosphorus. The three remaining H atoms in the ring give multiplets at δ 8.17, 6.95 and 6.26, with coupling between them and with the ^{31}P nucleus consistent with this position of oxidative addition. We believed, on the basis of this spectrum, that compound **1** had either structure **C** or **D** (Fig. 1), corresponding with the two representations **A** and **B** of the starting ylide, or some resonance hybrid of **C** and **D**. The infrared spectrum around 2000 cm^{-1} was characteristic of a species of the general type [Os_3(μ-H)(μ-X)$(CO)_{10}$] but with wavenumbers for ν(CO) which were rather lower than for [Os_3(μ-H)(μ-CH=CH_2)$(CO)_{10}$],[5,6] a good model for form **C**. A similar situation was encountered in the chemistry of furan and of *N*-methylpyrrole with triosmium clusters. Whereas the fur-2-yl complex [Os_3(μ-H)(μ,η^2-C_4H_6O)$(CO)_{10}$] adopts μ,η^2-vinyl type co-ordination corresponding to **C**,[7] the *N*-methylpyrrol-2-yl analogue [Os_3(μ-H)(μ,σ-C_4H_3NMe)$(CO)_{10}$] is found to have the C_4N ring close to perpendicular to the Os_3 plane and the cluster adopts a zwitterionic form closely corresponding to the bonding type **D**.[8] The wavenumbers for CO stretch are lower for the zwitterionic form.

A crystal-structure determination for compound **1** established the vertical zwitterionic form **D**. The molecular structure is shown in Fig. 2 and selected bond lengths and angles are in Table 1. The $Ph_3PC_5H_3$ ligand is co-ordinated through atom C(1) alone; C(2) and C(5) are not considered to be bonding to Os(1) or Os(3) since the distances are too long [Os(1) ··· C(2) 3.19, Os(3) ··· C(2) 3.18, Os(1) ··· C(5) 3.18 and Os(3) ··· C(5) 3.19 Å]. The C(1)C(2)C(3)C(4)C(5) plane is at 88.9° to the Os_3 plane and essentially perpendicular. Thus the best description is that C(1) is involved as a normal μ-alkylidene bridge as in Fig. 1(**D**). In essence it is symmetrically bridged [Os(1)–C(1) 2.20(2), Os(3)–C(1) 2.25(2) Å], which would not be expected for a bridging vinyl. The C–C bonds shown as single in Fig. 1(**D**) are the longest ones in the C_5 ring but when judged in the light of the estimated standard deviations these bonds are not significantly longer than those that are formally double bonds in the same description. As is common for heavy-metal clusters,



Scheme 1



Scheme 2

C–C bond lengths in ligands are not determined accurately enough for comparison purposes. The distance P(1)–C(3) [1.74(2) Å] is rather shorter, but only just significantly so, than the other P–C bonds [1.80(2), 1.80(2) and 1.81(2) Å]. Perhaps there is some minor contribution from form **C** to shorten bond P(1)–C(3), but clearly **D** is overwhelmingly supported by the structural data. The site of PPh_3 substitution is consistent with the ^1H NMR data but we could also have analysed these data satisfactorily for the isomer with the PPh_3 substituent at C(4).

The crystal of compound **1** used for structure determination was obtained from a sample of the cluster as first formed by oxidative addition. However, solutions of **1** in $CDCl_3$, when allowed to stand at room temperature for several hours, develop ^1H NMR signals of another species. After several days, the new signals correspond to around 40% of the material and equilibrium appears to have been reached. TLC gave two species with indistinguishable IR spectra around 2000 cm^{-1}. The ^1H NMR spectra indicate that these are isomers: **1a** (major, crystal structure) and **1b** (minor). Similar signals with similar couplings are observed for each species but the chemical shifts differ (see Experimental section). We propose structures for **1a** and **1b** as shown in Scheme 1. The ^1H NMR spectra of pure samples of these isomers in $CDCl_3$ soon show signals of the other isomer and the same equilibrium mixture is obtained from each eventually. We have not determined the mechanism of interconversion. To our knowledge the intramolecular rotation of a μ alkylidene has not been demonstrated previously except by a mechanism involving σ-alkylidene intermediates.[9–11] Transformation of **D** into **C** (Fig. 1) does not suggest an obvious route for the transformation. μ,η^2-Vinyl ligands are known to rapidly exchange σ bonds between the bridged metal atoms, but *exo–endo* interconversion has not been established except in the case of the η^2-thien-2-yl ligand in $[Os_3(\mu\text{-}H)(\mu,\eta^2\text{-}C_4H_3S)H_3(CO)_9]$.[12] In this case *exo–endo* conversion probably occurs *via* an S-bonded species which is a special case and not appropriate to this present situation. It is possible that the mechanism is not a μ-alkylidene rotation but rather a H-atom-transfer process with the intermediate $[Os_3(Ph_3PC_5H_4)(CO)_{10}]$ or $[Os_3H_2(Ph_3PC_5H_2)(CO)_{10}]$, in which case atom C(1) does not remain bonded to the metal atoms throughout but after the transformation C(5) becomes Os bonded. Scheme 2 illustrates two possible ways the isomerisation could occur with H-atom migrations [routes (*b*) and (*c*)] as well as the σ-alkylidene route (*a*). We attempted to carry out deuteriation studies by synthesising $[Os_3(\mu\text{-}D)(Ph_3PC_5H_3)(CO)_{10}]$ to show whether or not the isomerisation led to H-atom transfer from Os to C atoms but were unsuccessful in getting this material. Protonation with deuteriated acid followed by deprotonation did not lead to this compound.

Table 2 Selected bond lengths (Å) and angles (°) for $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PC_5H_3)(CO)_9]$ **2**

Os(1)–Os(2)	2.838(1)	C(1)–C(2)	1.42(2)
Os(1)–Os(3)	2.957(1)	C(2)–C(3)	1.48(2)
Os(2)–Os(3)	2.782(1)	C(3)–C(4)	1.37(2)
Os(1)–C(5)	2.27(1)	C(4)–C(5)	1.42(2)
Os(1)···C(1)	2.63(1)	C(1)–C(5)	1.44(2)
Os(2)–C(1)	2.45(1)	P(1)–C(3)	1.75(1)
Os(2)–C(2)	2.36(1)	P(1)–C(41)	1.79(1)
Os(3)–C(1)	2.11(1)	P(1)–C(51)	1.79(1)
		P(1)–C(61)	1.82(1)
Os(2)–Os(1)–Os(3)	57.3(1)	Os(3)–Os(2)–C(1)	47.0(2)
Os(1)–Os(2)–Os(3)	63.5(1)	Os(3)–Os(2)–C(2)	75.7(3)
Os(1)–Os(3)–Os(2)	59.2(1)	Os(2)–C(1)–Os(3)	74.9(3)
Os(1)–Os(2)–C(1)	59.0(3)	Os(2)–C(1)–C(2)	69.2(6)
Os(1)–Os(2)–C(2)	86.5(3)	Os(2)–C(1)–C(5)	115.2(7)
Os(1)–Os(3)–C(1)	59.6(3)	Os(3)–C(1)–C(2)	126.7(9)
Os(2)–Os(1)–C(5)	80.4(3)	Os(3)–C(1)–C(5)	122.4(8)
Os(2)–Os(3)–C(1)	58.1(3)	Os(1)–C(5)–C(1)	86.9(7)
Os(3)–Os(1)–C(5)	72.1(3)	Os(1)–C(5)–C(4)	121.5(7)

Thermolysis of isomer **1a** or a **1a**–**1b** mixture in refluxing toluene led to the decarbonylation product $[Os(\mu\text{-}H)(\mu_3\text{-}Ph_3PC_5H_3)(CO)_9]$ **2**. We had expected that decarbonylation would lead to the dihydride $[Os_3(\mu\text{-}H)_2(Ph_3PC_5H_2)(CO)_9]$, a reaction with precedents with other alkenes,[13] but the ^1H NMR spectrum shows that **2** is a monohydride. As with compound **1**, there is a major and a minor isomer of **2** in solution but, unlike **1**, these could not be separated by chromatography. The IR spectrum of compound **2** is simple, indicating that the isomers have essentially the same spectrum. The wavenumbers, ν(CO), are low which suggests a zwitterionic form with an exocyclic phosphonium group in an overall neutral cluster. The ^1H NMR spectrum was not easy to analyse in terms of structure (phenyl resonances partially obscure the C_5 ring resonances) so a single-crystal X-ray structure determination was carried out.

The molecular structure of what is probably the major isomer in solution is shown in Fig. 3 and selected bond lengths and angles are in Table 2. The carbon atoms, C(1), C(2) and C(5), are all involved in the bonding of the ligand to the metal atoms with the ligand in a μ_3 mode. Hydrogen atoms were not located but we believe these are correctly positioned at C(2), C(4) and C(5) as in the decacarbonyl **1**. The hydride ligand bridges Os(1) and Os(3) on the basis of Os–Os bond lengths [Os(1)–Os(3) 2.957(1) Å compared with Os(1)–Os(2) 2.838(1)

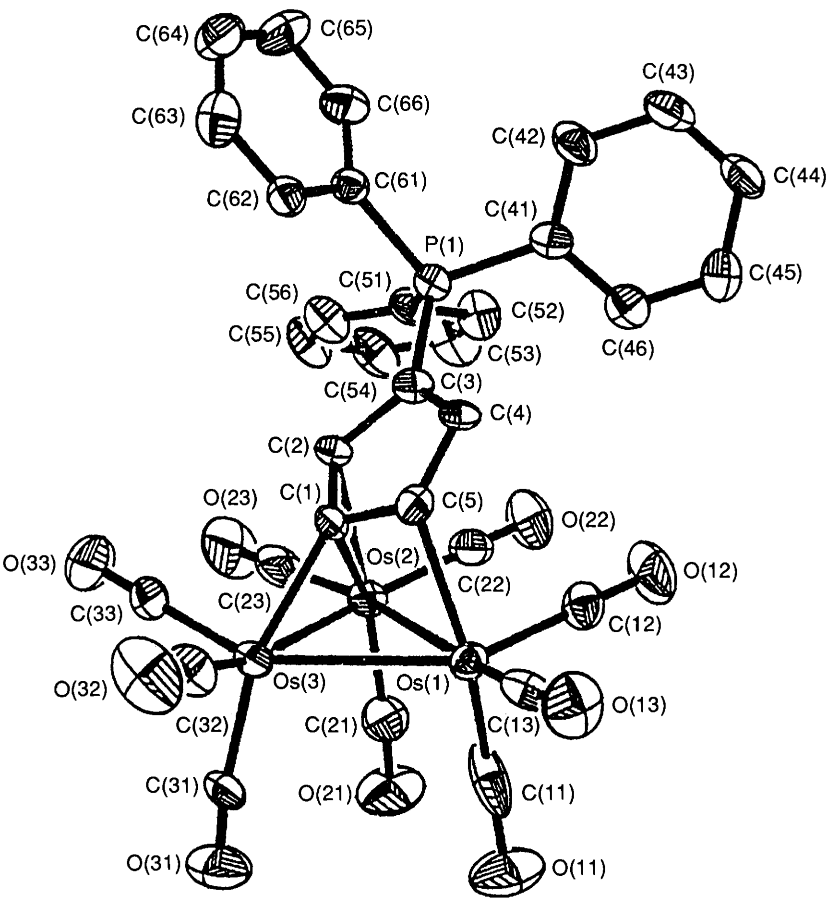


Fig. 3 Molecular structure of $[Os_3(\mu-H)(\mu_3-Ph_3PC_5H_3)(CO)_9]$ **2**

2a **2b**

Scheme 3

and Os(2)–Os(3) 2.782(1) Å] and CO ligand positions. The $C_5H_3PPh_3$ ligand could be thought to donate four electrons through two Os–C σ bonds [Os(1)–C(5) 2.27(1) and Os(3)–C(1) 2.11(1) Å] and through an η^2 interaction through C(1) and C(2) to Os(2) [Os(2)–C(1) 2.45(1) and Os(2)–C(2) 2.36(1) Å]. As with cluster **1**, we formally locate a negative charge at the metal atoms and the cluster is electron-precise. However, the C_5 ring is not too far from symmetrical with respect to atoms Os(1) and Os(2). For instance, the bond length Os(2)–C(1) of 2.45(1) Å might be compared with the corresponding (non-bonding) distance Os(1) ··· C(1) of 2.63(1) Å. Breaking bond Os(2)–C(1) and making Os(1)–C(1) would shift the η^2 interaction to the other side, that is to Os(1). The hydride ligand would need to shift from the Os(3)–Os(1) to the Os(2)–Os(3) edge. The net effect of this would be to generate an isomer with PPh_3 at the other carbon atom not bonded to osmium (Scheme 3). We believe that the other isomer detected in the ^1H NMR spectrum is this species but we have not confirmed this.

The basic manner in which the organic ligands are bonded to the metal atoms in compounds **1** or **2** does not seem to depend upon the presence of the triphenylphosphonium substituent at the C_5 ring and we can confidently predict that there should be directly related systems without this substituent. For example, the complex $[Os_3(\mu-H)_2(\mu-C_5H_4)(CO)_{10}]$ related both to **1** and to $[Os_3(\mu-H)_2(\mu-CH_2)(CO)_{10}]$[14] should be accessible and likewise $[Os_3(\mu-H)_2(\mu_3-C_5H_4)(CO)_9]$ which would be analogous to **2**. An extra hydride ligand is needed in each case for the compound to be neutral.

We have also carried out reactions of $Ph_3AsC_5H_4$, analogous to the phosphorus compound, with $[Os_3(CO)_{10}(MeCN)_2]$ with the idea that As–C cleavage would be easier than P–C cleavage so that there was the possibility of products with the C_5 ring but without the $AsPh_3$ unit. To some extent these expectations were justified but the consequences were different. Rapid reaction between $[Os_3(CO)_{10}(MeCN)_2]$ and $Ph_3AsC_5H_4$ at room temperature or below gave $[Os_3(CO)_{10}(AsPh_3)_2]$ as the major product and we were unable to isolate any compounds containing the C_5 ring or to establish the fate of this group.

Experimental

Cyclopentadienylidenetriphenylphosphorane ($Ph_3PC_5H_4$) was used as obtained from Aldrich and $[Os_3(CO)_{10}(MeCN)_2]$ was synthesised in a way similar to that reported.[15] TLC eluents were distilled before use.

Reaction of $Ph_3PC_5H_4$ *with* $[Os_3(CO)_{10}(MeCN)_2]$.—Brown $Ph_3PC_5H_4$ (0.0350 g, 0.107 mmol) in dichloromethane solution (2 cm^3) was added to a yellow solution of the bis(acetonitrile) cluster (0.100 g, 0.107 mmol) in dichloromethane (15 cm^3) at room temperature. There was an immediate colour change to dark red and after 5 min the solution was evaporated to dryness under reduced pressure. Chromatography of the residue [TLC, SiO_2, eluent dichloromethane–light petroleum (b.p. < 40 °C)–

diethylether (12:83:5 v/v/v)] gave one main orange-red band which was extracted with dichloromethane. Addition of heptane to the extract and evaporation of most of the dichloromethane gave ruby-red crystals of [$Os_3(\mu$-H)(μ-$Ph_3PC_5H_3)(CO)_{10}$], isomer **1a** (0.0805 g, 61%) (Found: 33.3; H, 1.45. $C_{33}H_{19}O_{10}Os_3P$ requires C, 33.65; H, 1.65%). IR (CH_2Cl_2) ν(CO)/cm^{-1}: 2083m, 2067w, 2039vs, 2031s, 1994vs and 1965s; ^{1}H NMR ($CDCl_3$, 27 °C): δ 8.17 (dt, H^A), 7.75–7.55 (m, Ph), 6.95 (dt, H^B), 6.26 (dt, H^C) and −15.34 (s, OsH) [$J(PH^A)$ 6.8, $J(PH^B)$ 4.3, $J(PH^C)$ 1.6, $J(H^AH^B)$ 1.7, $J(H^BH^C)$ 4.3 and $J(H^AH^C)$ 1.7 Hz]. The crystal selected for the single-crystal structure determination was from this batch so we believe that the above spectroscopic data correspond with the isomer **1a** found in the crystal.

Table 3 Crystallographic data for [$Os_3(\mu$-H)(μ-$Ph_3PC_5H_3)(CO)_{10}$] **1** and [$Os_3(\mu$-H)(μ_3-$Ph_3PC_5H_3)(CO)_9$] **2** *

	1	**2**
Formula	$C_{33}H_{19}O_{10}Os_3P$	$C_{32}H_{19}O_9Os_3P$
M	1177.08	1149.08
Colour	Dark red	Yellow
Crystal size/mm	0.30 × 0.08 × 0.16	0.13 × 0.36 × 0.40
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_1cn$	$P2_1/n$
a/Å	9.358(3)	13.016(4)
b/Å	15.420(5)	12.279(2)
c/Å	23.033(4)	20.250(3)
β/°	90	91.65(2)
U/Å	3324(1)	3235(2)
Z	4	4
D_c/g cm^{-3}	2.35	2.36
μ(Mo-Kα)/cm^{-1}	115.6	118.7
F(000)	2160	2104
No. orientation reflections	28	30
2θ range/°	8–26	13–26
Total data	3320	6283
Unique data	3112	5712
Data with $I_o > 1.5\sigma(I_o)$	2761	4645
Parameters refined	233	406
R	0.0420	0.0497
R'	0.0403	0.0514
g in weighting scheme	0.000 383	0.001 073
Max. shift/esd in final refinement	0.002	0.001
Largest residual peak (close to Os)/e Å^{-3}	1.0	2.7

* Data in common: $R = \Sigma[|F_o| - |F_c|]/\Sigma F_o$; $R' = [\Sigma w(|F_o| - F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w = [\sigma^2(F_o) + g(F_o{}^2)]^{-1}$; Mo-Kα radiation, λ = 0.710 73 Å; 2θ collection range 5–50°.

Isomerisation of [$Os_3(\mu$-H)(μ-$Ph_3PC_5H_3)(CO)_{10}$] **1a**.—A solution of the initial product **1** (0.100 g) was dissolved in a mixture of dichloromethane (10 cm^3) and heptane (10 cm^3) and the solution allowed to stand for 24 h at room temperature. The solvent was removed under reduced pressure and the residue redissolved in dichloromethane (3 cm^3) and separated by TLC [SiO_2, eluent dichloromethane–light petroleum (b.p. <40 °C) (3:17 v/v)]. The sample gave one major orange-red band and a pink band which were collected separately. The major band was characterised as the starting isomer **1a** and the minor pink band as isomer **1b**. These isomers gave indistinguishable IR spectra in CH_2Cl_2 (see data above). The ^{1}H NMR spectrum of **1a** was as given above. A $CDCl_3$ solution gave over hours new weak signals for **1b**. The ^{1}H NMR spectrum ($CDCl_3$) of **1b** was assigned by comparison of the patterns of the observed multiplets with those of **1a**: δ 7.95 (dt, H^B), 7.75–7.55 (m, Ph), 7.02 (dt, H^A), 6.39 (dt, H^C) and −15.59 (s, OsH). The J values are similar to those for compound **1a**. Even when it was recorded rapidly after isolation, the ^{1}H NMR spectrum of **1b** showed signals due to impurities of **1a** which grew steadily and gave the most intense signals within a few hours.

Thermolysis of [$Os_3(\mu$-H)(μ-$Ph_3PC_5H_3)(CO)_{10}$] **1**.—Compound **1** as a mixture of isomers (0.138 g, 0.117 mmol) was heated under reflux in toluene (75 cm^3). Over 4 h the colour changed from ruby-red through to yellow. The solvent was removed under reduced pressure and the residue chromatographed [TLC, SiO_2, eluent dichloromethane–light petroleum (b.p. <40 °C) (7:3 v/v)] to give one major yellow band which was extracted with dichloromethane. Addition of heptane and evaporation gave yellow crystals (0.096 g, 70%) of [$Os_3(\mu$-H)(μ_3-$Ph_3PC_5H_3)(CO)_9$] **2** (Found: C, 33.0; H, 1.6; P, 2.85. $C_{32}H_{19}O_9Os_3P$ requires C, 33.45; H, 1.65; P, 2.7%). IR (CH_2Cl_2) ν(CO)/cm^{-1}: 2067s, 2036vs, 2004vs, 1978s, 1958s and 1926m; ^{1}H NMR ($CDCl_3$, 27 °C): δ −16.35 (s, isomer **2a**),

Table 4 Fractional atomic coordinates (× 10^4) for [$Os_2(\mu$-H)(μ-$Ph_3PC_5H_3)(CO)_{10}$] **1**

Atom	x	y	z
Os(1)	1186	1550(1)	2330(1)
Os(2)	−1640(1)	1158(1)	1906(1)
Os(3)	−687(1)	2902(1)	2085(1)
P(1)	3119(6)	2704(3)	90(2)
C(1)	1452(20)	2597(10)	1687(7)
C(2)	1487(20)	2405(11)	1077(8)
C(3)	2622(22)	2881(10)	808(8)
C(4)	3247(22)	3381(12)	1276(8)
C(5)	2587(24)	3224(12)	1761(10)
C(41)	4018(21)	3637(11)	−219(8)
C(42)	3495(29)	3988(12)	−730(9)
C(43)	4259(33)	4663(15)	−998(11)
C(44)	5480(29)	4947(15)	−767(11)
C(45)	6057(35)	4624(15)	−231(10)
C(46)	5248(28)	3913(14)	25(10)
C(51)	4296(25)	1789(11)	−1(8)
C(52)	5172(34)	1757(18)	−471(12)
C(53)	6089(45)	1010(18)	−508(14)
C(54)	6025(36)	369(18)	−139(12)
C(55)	5113(34)	453(18)	302(12)
C(56)	4277(32)	1167(14)	385(11)
C(61)	1548(22)	2476(11)	−334(8)
C(62)	1550(26)	1866(13)	−755(9)
C(63)	369(30)	1729(16)	−1121(11)
C(64)	−775(42)	2197(16)	−1010(13)
C(65)	−869(35)	2858(16)	−593(11)
C(66)	355(30)	2984(15)	−228(11)
O(11)	672(22)	251(12)	3309(8)
C(11)	830(25)	775(14)	2936(9)
O(12)	2581(19)	167(10)	1586(7)
C(12)	2034(25)	686(14)	1858(9)
O(13)	3971(22)	2112(11)	2944(7)
C(13)	2948(25)	1930(13)	2697(9)
O(21)	−2425(23)	1186(11)	3211(8)
C(21)	−2049(29)	1197(15)	2711(10)
O(22)	−1144(22)	1243(11)	592(8)
C(22)	−1240(26)	1233(13)	1100(10)
O(23)	−1402(26)	−816(11)	1836(8)
C(23)	−1456(29)	−60(13)	1875(9)
O(24)	−4769(27)	1444(13)	1696(10)
C(24)	−3539(28)	1337(13)	1792(10)
O(31)	−3373(29)	3221(14)	2796(9)
C(31)	−2367(27)	3067(14)	2531(10)
O(32)	280(22)	4710(11)	2408(7)
C(32)	−20(27)	4021(14)	2278(9)
O(33)	−2148(25)	3356(12)	950(9)
C(33)	−1605(30)	3187(13)	1391(10)

Table 5 Fractional atomic coordinates (× 10^4) for $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PC_5H_3)(CO)_9]$ **2**

Atom	*x*	*y*	*z*
Os(1)	1165(1)	1663(1)	1920(1)
Os(2)	−989(1)	1530(1)	2084(1)
Os(3)	100(1)	2874(1)	2961(1)
P(1)	−1736(2)	3547(2)	245(2)
C(1)	−137(10)	3292(9)	1958(5)
C(2)	−1084(10)	3267(9)	1593(6)
C(3)	−830(10)	3352(9)	887(6)
C(4)	220(9)	3403(8)	856(6)
C(5)	687(9)	3308(9)	1498(6)
C(41)	−1197(10)	3226(9)	−535(6)
C(42)	−1271(13)	3912(11)	−1073(6)
C(43)	−880(16)	3648(13)	−1678(7)
C(44)	−423(12)	2646(13)	−1749(6)
C(45)	−327(12)	1924(12)	−1218(7)
C(46)	−703(11)	2210(11)	−610(7)
C(51)	−2852(10)	2734(11)	367(6)
C(52)	−3065(11)	1817(11)	−5(7)
C(53)	−3925(14)	1187(14)	155(9)
C(54)	−4516(14)	1449(15)	667(8)
C(55)	−4330(11)	2378(14)	1026(7)
C(56)	−3490(10)	3002(12)	866(7)
C(61)	−2160(10)	4956(9)	245(6)
C(62)	−1707(10)	5706(10)	671(6)
C(63)	−2039(13)	6789(13)	665(8)
C(64)	−2865(17)	7076(14)	225(10)
C(65)	−3321(14)	6330(14)	−182(10)
C(66)	−2965(14)	5295(13)	−166(8)
C(11)	1398(16)	427(13)	2364(7)
O(11)	1720(11)	−395(11)	2698(8)
C(12)	980(11)	951(10)	1087(7)
O(12)	929(11)	572(9)	584(6)
C(13)	2576(12)	2061(11)	1821(6)
O(13)	3407(9)	2241(10)	1713(6)
C(21)	−790(14)	230(14)	2576(8)
O(21)	−678(11)	−521(9)	2906(7)
C(22)	−1290(11)	766(12)	1270(7)
O(22)	−1476(10)	306(9)	804(6)
C(23)	−2348(14)	1709(15)	2372(8)
O(23)	−3175(10)	1783(13)	2539(7)
C(31)	188(12)	1903(13)	3718(6)
O(31)	210(12)	1216(11)	4106(6)
C(32)	981(13)	4004(14)	3289(7)
O(32)	1461(12)	4706(11)	3499(7)
C(33)	−1195(13)	3479(12)	3193(7)
O(33)	−1956(11)	3841(12)	3331(6)

−16.57 (s, isomer **2b**) and 7.0–7.9 (unassigned multiplets with Ph overlapping C_5H_3 resonances).

Crystal Structure Determinations for Clusters **1** *and* **2**.—Essential details of the unit cell parameters, data collections, structure solutions and refinements for **1** and **2** are in Table 3. Crystals of each were grown by evaporation of solutions in hexane–dichloromethane. Crystals were mounted on glass fibres on goniometers on a Nicolet R3v/m diffractometer operating with Mo-Kα radiation (λ = 0.710 73 Å). Unit cells were obtained by auto-indexing and least-squares fitting of 28 orientation reflections with $8 \leqslant 2\theta \leqslant 26°$ for compound **1** and 30 reflections with $13 \leqslant 2\theta \leqslant 26°$ for compound **2**, selected from rotation photographs. The data collections were made at around 20 °C in the ω–2θ scan mode with $5 \leqslant 2\theta \leqslant 50°$. Reflection intensities were corrected for Lorentz and polarisation effects and for a minimal amount of decay based on the intensities of three standard reflections collected periodically throughout the data collections. Empirical absorption corrections were made by the psi-scan method.

The structures were solved by direct methods and were refined by alternating cycles of full-matrix least squares and by Fourier difference syntheses. For compound **1** the Os and P atoms and the C atoms of the five-membered ring were refined anisotropically and the hydrogen atoms were included in idealised positions in the later stages of the refinement. All non-H atoms were refined anisotropically for **2** and the H atoms were introduced in idealised positions. In both structures H atoms were allowed to ride on C atoms with C–H distances of 0.96 Å and *U* of 0.08 Å^2. The hydride ligands were not detected and no attempt was made to include these in the model. Fractional atomic coordinates for compounds **1** and **2** are in Tables 4 and 5 respectively.

All calculations were carried out using a MicroVax II computer using SHELXTL PLUS.[16]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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