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Synthesis and characterisation of diphenylvinylphosphine-substituted osmium and ruthenium carbonyl clusters; crystal and molecular structures of $[Os_3(CO)_{11}(Ph_2PCH{=}CH_2)]$ and $[Os_3(\mu\text{-}H)(CO)_9(\mu\text{-}Ph_2PCH{=}CH)]$

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Reaction of the activated clusters $[Os_3(CO)_{12-n}(NCMe)_n]$ (n = 1 or 2) with diphenylvinylphosphine ($Ph_2PCH{=}CH_2$) afforded $[Os_3(CO)_{12-n}(Ph_2PCH{=}CH_2)_n]$ (n = 1 **1** or 2 **2**) in good yield. Addition of $Ph_2PCH{=}CH_2$ to $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ resulted in the formation of $[Os_3(\mu\text{-}H)H(CO)_{10}(Ph_2PCH{=}CH_2)]$ **3**. The ruthenium clusters $[Ru_3(CO)_{12-n}(Ph_2PCH{=}CH_2)_n]$ (n = 1 **4** or 2 **5**) have been synthesised by the reaction of $[Ru_3(CO)_{12}]$ with an excess of diphenylvinylphosphine in the presence of a catalytic amount of Na–Ph_2CO. Thermolysis of **1** led to the formation of $[Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}Ph_2PCH{=}CH)]$ **6** in which the vinyl moiety has undergone β elimination. Similarly, **4** and **5** are converted into $[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}Ph_2PCH{=}CH)]$ **7** and the known complex $[Ru_3(\mu\text{-}H)(CO)_8(Ph_2PCH{=}CH_2)(\mu_3\text{-}Ph_2PCH{=}CH)]$ **8** under mild conditions (thermolysis or photolysis). No intermediate species could be detected during the formation of **6**–**8**. All of the new clusters **2**–**7** have been fully characterised on the basis of their spectroscopic data and the molecular structures of **1** and **6** have been established by single-crystal X-ray analysis.

The chemistry of metal complexes containing multifunctional (polydentate) ligands is of interest since such ligands may be used to modify reactivity. This is especially the case for clusters with several possible co-ordination sites. Diphenylvinylphosphine has proven to be such a versatile ligand. It can co-ordinate in a terminal, phosphorus-bonded mode[1] as well as μ-[2] and μ_3-[3] bridging modes which involve π-co-ordination of the vinyl moiety. Dimetallic manganese,[4] iron,[5] molybdenum,[6] palladium,[7] and molybdenum–manganese[8] compounds involving bridging diphenylvinylphosphine ligands have been prepared. In some of these compounds the phosphine ligand has been synthesised *in situ* through the insertion of a diphenylphosphido moiety into the σ bond of a σ:π-co-ordinated vinyl group;[4] such chemical formation of a bridging diphenylvinylphosphine is relatively facile. It has been shown that in the case of $[Mn_2(CO)_8(\mu\text{-}Ph_2PCH{=}CH_2)]$ the co-ordinated vinyl moiety may be displaced by the addition of CO.[4]

Gobetto *et al.*[3] have reported the synthesis of $[Os_3(CO)_{11}(Ph_2PCH{=}CH)]$ **1** in moderate yield (≈20%) from the thermolysis of the parent carbonyl in refluxing octane in the presence of diphenylvinylphosphine. Even though $[Os_3(CO)_{12}]$ was treated with an excess of phosphine only monosubstitution was observed. The similar reaction of $[Ru_3(CO)_{12}]$ in refluxing heptane afforded only one product, proposed to be the bis-substituted cluster $[Ru_3(CO)_{10}(Ph_2PCH{=}CH_2)_2]$ (see below), which when subjected to TLC underwent conversion into the cluster $[Ru_3(\mu\text{-}H)(CO)_8(Ph_2PCH{=}CH_2)(\mu_3\text{-}Ph_2PCH{=}CH)]$.[3,9] The overall yield of the latter compound was approximately 80%.

In our efforts to obtain thermodynamically stable, yet chemically reactive, clusters, we have studied the reactivity of diphenylvinylphosphine towards trinuclear osmium and ruthenium compounds. We were interested in obtaining clusters in which the ligand adopts a $\sigma{:}\eta^2$ bridging mode and thus renders the cluster susceptible to possible nucleophilic attack. Here we report the improved synthesis of **1** and the preparation and characterisation of the new diphenylvinylphosphine clusters $[Os_3(CO)_{10}(Ph_2PCH{=}CH_2)_2]$ **2**, $[Os_3(\mu\text{-}H)H(CO)_{10}(Ph_2PCH{=}CH_2)]$ **3**, $[Ru_3(CO)_{12-n}(Ph_2PCH{=}CH_2)_n]$ (n = 1 **4** or 2 **5**), $[Os_3(\mu\text{-}H)(CO)_9(\mu\text{-}Ph_2PCH{=}CH)]$ **6** and $[Ru_3(\mu\text{-}H)(CO)_9(\mu\text{-}Ph_2PCH{=}CH)]$ **7** as well as the crystal structures of **1** and **6**.

Results and Discussion

Reaction of the moderately labile monoacetonitrile derivative $[Os_3(CO)_{11}(NCMe)]$ with an excess of diphenylvinylphosphine in dichloromethane at ambient temperature yields cluster **1** in substantially higher yield {85%; 75% with respect to $[Os_3(CO)_{12}]$} than that previously reported.[3] Reaction of 2 equivalents of the phosphine with $[Os_3(CO)_{10}(NCMe)_2]$ yields the orange bis-substituted cluster $[Os_3(CO)_{10}(Ph_2PCH{=}CH_2)_2]$ **2**. No evidence was found for a ligand-bridged product. Diphenylvinylphosphine also adds readily to $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ to form the bright yellow cluster $[Os_3(\mu\text{-}H)H(CO)_{10}(Ph_2PCH{=}CH_2)]$ **3** in good yield. The analogous orange mono- and dark orange bis-substituted diphenylvinylphosphine derivatives of $[Ru_3(CO)_{12}]$, *i.e.* $[Ru_3(CO)_{12-n}(Ph_2PCH{=}CH_2)_n]$ (n = 1 **4** or 2 **5**) were prepared in a 'one-pot' synthesis using the method of Bruce *et al.*,[10] *i.e.* reduction of triruthenium dodecacarbonyl by sodium diphenylketyl in tetrahydrofuran (thf) in the presence of the phosphine. This reaction also produced a red compound which may be the tris-substituted cluster $[Ru_3(CO)_9(Ph_2PCH{=}CH_2)_3]$ but this product remains to be fully characterised.

Products **2**–**5** have been characterised by IR, NMR and mass spectrometry and, in the case of **1**, X-ray crystallography. The IR spectra of these clusters are entirely consistent with those reported for similar phosphine-substituted clusters and their proposed structures are therefore those depicted in Fig. 1. An upfield change in the chemical shift of the vinyl protons by 3–4 ppm is observed when the vinyl group of the phosphine ligand is π-co-ordinated.[4,8] The lack of such an upfield shift in the ^1H NMR spectra of compounds **2**–**5** (*cf.* Table 1) confirms that the vinyl moiety of the ligand is not co-ordinated in these clusters.

Nuclear magnetic resonance spectroscopy reveals that the hydrides of compound **3** are fluxional at room temperature.

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Cooling freezes out this fluxionality, as shown in Fig. 2. The low-temperature NMR spectrum shows that two isomers are present. We propose that the major isomer is that depicted in Fig. 2(*a*); this structure is found in crystal structures of related complexes.[11,12] The size of the $^2J_{PH}$ coupling constant for the major isomer (10.8 Hz) is consistent with the phosphine being located *cis* to the bridging hydride. Coupling between the phosphorus and the terminal hydride, which is expected to be in an axial position[12] is not observed for either of the two isomers. For the minor isomer, the $^2J_{PH}$ coupling between the bridging hydride and the phosphorus atom of the ligand is not significantly different from that of the main isomer. A possible structure for the minor isomer consistent with the observed P–H coupling is one in which the phosphine is co-ordinated in an axial position; most likely in *cis* orientation to the terminal hydride, as this is the sterically less encumbered axial position. However, the cone angle of diphenylvinylphosphine is relatively large and co-ordination of the phosphine in an equatorial position should therefore be favoured; another possible structure for the minor isomer would thus be one where the phosphine is co-ordinated *trans* to the bridging hydride [Fig. 2(*b*)]. Integration of the proton NMR spectrum shows that the ratio of the two isomers is approximately 20 : 1 in CD_2Cl_2.

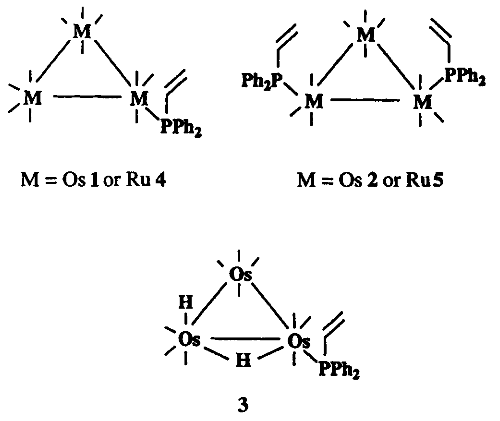


Fig. 1 Proposed structures of $[M_3(CO)_{11}(Ph_2PCH{=}CH_2)]$ (M = Os **1** or Ru **4**), $[M_3(CO)_{10}(Ph_2PCH{=}CH_2)_2]$ (M = Os **2** or Ru **5**) and $[Os_3(\mu\text{-}H)H(CO)_{10}(Ph_2PCH{=}CH_2)]$ **3**

It was possible to grow transparent, yellow crystals of $[Os_3(CO)_{11}(Ph_2PCH{=}CH_2)]$ **1** by slow evaporation of a dichloromethane solution at 4 °C. In order to confirm its proposed structure an X-ray analysis was undertaken. The molecular structure is shown in Fig. 3 and selected bond parameters are listed in Table 2. As expected, the phosphine is co-ordinated in an equatorial position. The cluster consists of a scalene triangle of osmium atoms, the Os(1)–Os(3) edge being somewhat longer than the other two. This is presumably due to the steric interaction of the vinyl (and phenyl) group(s) of the phosphine ligand with the carbonyls of Os(3). Another result of this crowding in the equatorial plane is the slight bending of the equatorial carbonyls away from this edge. Thus, the equatorial carbonyls adjacent to those of the Os(1)–Os(3) edge are pushed towards the other edges; the angles Os(1)–Os(2)–C(24) and Os(2)–Os(3)–C(34) are 89.7(6) and 90.4(6)°, respectively, while all other corresponding angles are greater than 100°. The molecular structure indicates that π-co-ordination may not be achieved without considerable bending of the Os–P bond towards Os(3), as is found in bimetallic complexes containing the μ-σ : π-co-ordinated ligand, where the M–M–P angle is less than 90°.[4,7,8]

In order to remove a carbonyl ligand from cluster **1** and co-ordinate the vinyl moiety of the phosphine ligand, **1** was treated with a slight excess of trimethylamine oxide in dichloromethane at ambient temperature. The IR spectrum of the initial product is very similar to those of clusters of general formula $[Os_3(CO)_{10}(PR_3)(NCMe)]$[13] and is therefore proposed to be $[Os_3(CO)_{10}(Ph_2PCH{=}CH_2)(NMe_3)]$. The co-ordination of trimethylamine in this type of reaction is not unprecedented.[14–16] This cluster proved to be quite unstable and was not isolated. A new, pale yellow, compound **6** was obtained when

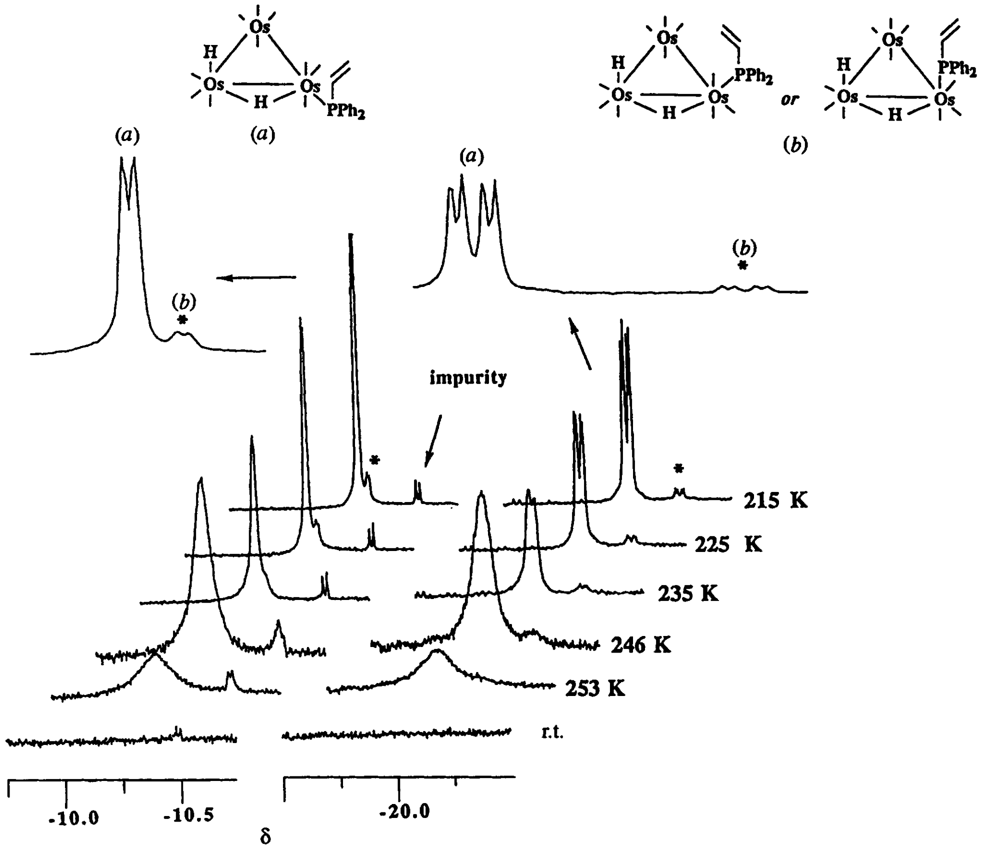


Fig. 2 Variable-temperature NMR spectra of $[Os_3(\mu\text{-}H)H(CO)_{10}(Ph_2PCH{=}CH_2)]$ **3**; r.t. = room temperature

Table 1 Spectroscopic data for compounds **1**–**8**

Complex	IR (ν_{CO}, CH_2Cl_2)	^1H NMR (δ, J/Hz)[a]	^{31}P NMR (δ, J/Hz)[b]	Mass (m/z)[c] obs.	Mass (m/z)[c] calc.	Ref.
1 $[Os_3(CO)_{11}(Ph_2PCH{=}CH_2)]$	2104w, 2064m, 2050s, 2026vs, 2016vs, 2000m[d]	7.71–7.42 (m, Ph), 7.04 [ddd, $^3J(H_a-H_c) = 17.7$, $^3J(H_a-H_b) = 11.3$, $^2J(P-H_a) \approx 25.8$, H_a], 6.05 [ddd, $^3J(P-H_b) = 40.6$, $^2J(H_b-H_c) = 0.8$, H_b], 5.00 [ddd, $^3J(P-H_c) = 21.0$, H_c]	−150.88 (s, br)			3
2 $[Os_3(CO)_{10}(Ph_2PCH{=}CH_2)_2]$	2084m, 2058s, 1999vs, 1965ms(br), 1986ms	7.70–7.15 (m, Ph), 6.64 [ddd, $^3J(H_a-H_c) \approx 20$, $^3J(H_a-H_b) \approx 12$, $^2J(P-H_a) \approx 28.0$, H_a], 5.75 [dd, $^3J(P-H_b) \approx 40$, H_b], 5.00 [dd, $^3J(P-H_c) \approx 15$, H_c]	−156.7 (s, br)	1280	1280	This work
3 $[Os_3(\mu\text{-}H)H(CO)_{10}(Ph_2PCH{=}CH_2)]$	2105m, 2065s, 2048s, 2021s(sh), 1979m(sh)	7.6–7.3 (m, Ph), 6.84 [ddd, $^3J(H_a-H_c) \approx 17.7$, $^3J(H_a-H_b) \approx 11.9$, $^2J(P-H_a) \approx 25.0$, H_a], 6.09 [dd, $^3J(P-H_b) \approx 42.3$, H_b], 5.40 [dd, $^3J(P-H_c) \approx 25.5$, H_c], −10.32 [d, $^2J(H_a-H_b) \approx 3.9$, OsH],[e] −10.36 [d, $^2J(H_a-H_b) \approx 3.4$, OsH],[f] −20.05 [dd, $^2J(P-H_b) \approx 10.8$, OsH],[e] −20.27 [dd, $^2J(P-H_b) \approx 11.0$, OsH][f]	−153.5 (s)	1070	1070	This work
4 $[Ru_3(CO)_{11}(Ph_2PCH{=}CH_2)]$	2095w, 2043ms, 2025s(sh), 2010vs(br)	7.70–7.15 (m, Ph), 6.65 [ddd, $^3J(H_a-H_c) \approx 19$, $^3J(H_a-H_b) \approx 12$, $^2J(P-H_a) \approx 26$, H_a], 5.88 [dd, $^3J(P-H_b) \approx 34.0$, H_b], 4.97 ['t' (dd), $^3J(P-H_c) \approx 19$, H_c]	−115.0 (s, br)	823	823	This work
5 $[Ru_3(CO)_{10}(Ph_2PCH{=}CH_2)_2]$	2069m, 2020s, 1994vs(br)	7.70–7.15 (m, Ph), 6.64 [ddd, $^3J(H_a-H_c) \approx 20$, $^3J(H_a-H_b) \approx 12$, $^2J(P-H_a) \approx 28.0$, H_a], 5.82 [dd, $^3J(P-H_b) \approx 36.0$, H_b], 5.07 ['t' (dd), $^3J(P-H_c) \approx 18.8$, H_c]	−115.0 (s)	1007	1007	This work
6 $[Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}Ph_2PCH{=}CH)]$	2089ms, 2061vs, 2032vs, 2013s, 1990s, 1975m(sh)	8.29 [dd, $^3J(H_a-H_b) \approx 9.4$, $^3J(P-H_b) \approx 9.4$, $^3J(H_a-H_c)$, n.r., CH=C*H*], 7.70–7.15 (m, Ph), 6.55 [dd, $^2J(P-H_a) \approx 12.2$, $^4J(H_b-H_c)$, n.r., C*H*=CH], −19.03 [dd, $^2J(P-H_a) \approx 20.8$, OsH]	−150.1 (m)	1040	1040	This work
7 $[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}Ph_2PCH{=}CH)]$	2088m, 2060s, 2032vs, 2018ms, 1998m, 1975w	8.39 [dd, $^3J(H_a-H_b) \approx 8.8$, $^3J(P-H_b) \approx 40$, $^3J(H_a-H_c)$, n.r., CH=C*H*], 7.72–7.22 (m, Ph), 5.39 [dd, $^2J(P-H_a) \approx 9.6$, $^4J(H_b-H_c)$, n.r., C*H*=CH], −18.62 [dd, $^2J(P-H_a) \approx 17.5$, $^3J(P-H_c) \approx 1$, RuH]	−113.0 (s)	767	767	This work
8 $[Ru_3(\mu\text{-}H)(CO)_8(Ph_2PCH{=}CH_2)(\mu_3\text{-}Ph_2PCH{=}CH)]$	2070vs, 2032vs, 2017vs, 1998m(br), 1970m(br)	8.27 (dd, CH=C*H*), 7.93–7.07 (m, Ph), 6.80 (ddd, H_a), 6.04 (ddd, H_b) 5.74 (ddd, C*H*=CH), 5.40 (dd, H_c), −17.82 (ddd, RuH)[g]	−103.4, −114.3 (m, $Ph_2PCH{=}CH$ and $Ph_2PCH{=}CH_2$)			3

n.r. = Not resolved. [a] In $CDCl_3$, ($SiMe_4$, δ 0). Labelling of vinyl proton resonances: H_a = α-hydrogen, H_b = β-hydrogen *trans* to phosphorus atom, H_c = β-hydrogen *cis* to phosphorus atom. [b] In $CDCl_3$ [$P(OMe)_3$, δ 0], downfield positive. [c] Based on ^{192}Os. [d] In hexane–$CHCl_3$ (60:40), *cf.* ref. 3. [e] Major isomer. [f] Minor isomer. [g] *cf.* Ref. 3 for coupling constants.

'$[Os_3(CO)_{10}(Ph_2PCH{=}CH_2)(NMe_3)]$' was heated in dichloromethane under reflux. This compound has also been synthesised, in higher yield, by thermolysis of **1** in either toluene or dibutyl ether. The presence of a hydride in the ^1H NMR spectrum of **6** indicates that β elimination of a C–H bond has taken place, and the mass spectrum is entirely consistent with the formulation $[Os_3(\mu\text{-}H)(CO)_9(\mu\text{-}Ph_2PCH{=}CH)]$.

Crystals of compound **6** were grown from a dichloromethane–cyclohexane–hexane solution at 4 °C and a single-crystal structure determination was carried out. The structure is shown in Fig. 4; selected bond parameters are listed in Table 3. The molecular structure determination confirms that the vinyl moiety is co-ordinated in the same fashion as that observed for $[Ru_3(\mu\text{-}H)(CO)_8(Ph_2PCH{=}CH_2)(\mu_3\text{-}Ph_2PCH{=}CH)]$ **8**.[3] The three osmium–osmium distances vary between 2.781(1) and 3.023(1) Å and are all significantly different. The long Os(1)–Os(3) distance suggests that the edge is bridged by the hydride. This is supported by the observation that in **8** the hydride has been found in the corresponding position, and that in **6** the carbonyl ligands adjacent to

Table 2 Selected bond parameters (distances in Å, angles in °) for $[Os_3(CO)_{11}(Ph_2PCHCH_2)]$ **1**

Os(1)–Os(2)	2.874(1)	Os(1)–P	2.345(4)
Os(1)–Os(3)	2.903(1)	P–C(1)	1.813(12)
Os(2)–Os(3)	2.885(1)	C(1)–C(2)	1.290(25)
Os(2)–Os(1)–Os(3)	59.9(1)	Os(1)–Os(3)–Os(2)	59.5(1)
Os(2)–Os(1)–P	162.1(1)	Os(1)–P–C(1)	114.2(6)
Os(3)–Os(1)–P	102.8(1)	P–C(1)–C(2)	126.2(13)
Os(1)–Os(2)–Os(3)	60.5(1)		

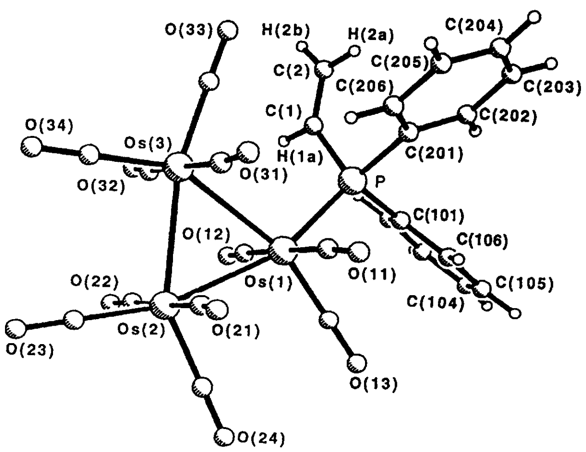


Fig. 3 Molecular structure of $[Os_3(CO)_{11}(Ph_2PCH{=}CH_2)]$ **1**

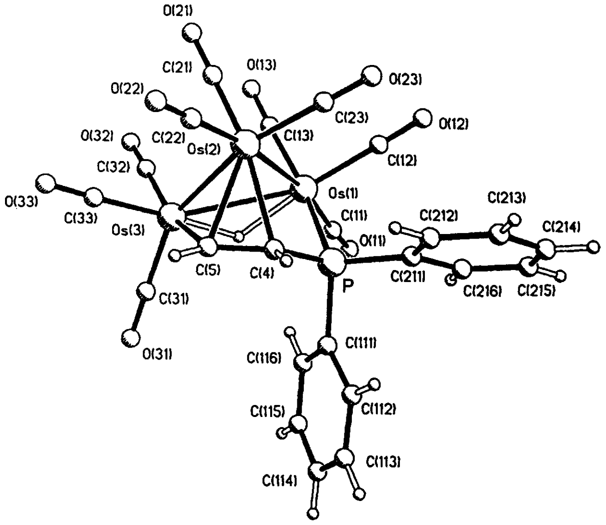


Fig. 4 Molecular structure of $[Os_3(\mu\text{-H})(CO)_9(\mu_3\text{-}Ph_2PCH{=}CH)]$ **6**

Table 3 Selected bond parameters (distances in Å, angles in °) for $[Os_3(\mu\text{-H})(CO)_9(\mu_3\text{-}Ph_2PCHCH)]$ **6**

Os(1)–Os(2)	2.868(1)	C(4)–C(5)	1.401(26)
Os(1)–Os(3)	3.023(1)	Os(2)–C(4)	2.294(14)
Os(2)–Os(3)	2.781(1)	Os(2)–C(5)	2.266(14)
Os(1)–P	2.361(4)	Os(3)–C(5)	2.116(18)
P–C(4)	1.789(16)		
Os(2)–Os(1)–Os(3)	56.3(1)	Os(1)–Os(3)–C(5)	84.5(5)
Os(1)–Os(3)–Os(2)	59.1(1)	Os(2)–Os(3)–C(5)	53.0(4)
Os(1)–Os(2)–Os(3)	64.7(1)	Os(1)–P–C(4)	103.5(5)
Os(2)–Os(1)–P	73.0(1)	Os(2)–C(4)–P	99.6(7)
Os(3)–Os(1)–P	84.6(1)	Os(2)–C(4)–C(5)	71.0(8)
Os(1)–Os(2)–C(4)	78.0(4)	P–C(4)–C(5)	119.3(13)
Os(3)–Os(2)–C(4)	76.6(4)	Os(2)–C(5)–Os(3)	78.7(5)
Os(1)–Os(2)–C(5)	85.7(4)	Os(2)–C(5)–C(4)	73.2(9)
Os(3)–Os(2)–C(5)	48.2(5)	Os(3)–C(5)–C(4)	127.3(12)
C(4)–Os(2)–C(5)	35.8(6)		

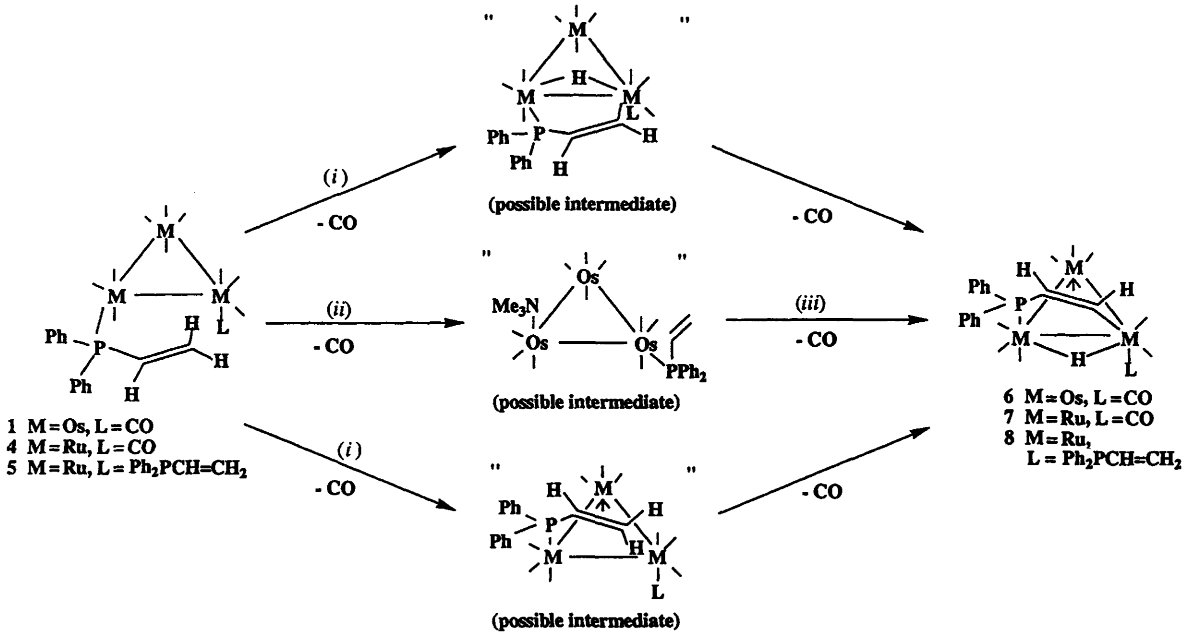
the Os(1)–Os(3) edge are significantly bent away from it. A potential-minimisation calculation using the program HYDEX[17] confirmed that the hydride is indeed bridging the Os(1)–Os(3) edge. In order that Os(3) will have a pseudo-octahedral co-ordination, the carbonyl ligands of this metal atom are slightly skewed with respect to the triangular plane of metal atoms. This reorientation of the carbonyl ligands also reduces the steric interaction between carbonyls C(13)–O(13), C(32)–O(32) and the hydride.

The C_α–C_β distance of the vinyl moiety is 1.40(3) Å. This is significantly longer than found for the terminal diphenylvinylphosphine ligands of compounds **1** [1.29(3) Å] and **8** [1.35(4) Å], yet shorter than a 'typical' single carbon–carbon bond ($\approx$1.54 Å). The corresponding bond in **8** is similarly elongated, 1.45(3) Å. Carbon–carbon distances comparable to that in **6** are observed for $[Mn_2(CO)_8(\mu\text{-}Ph_2PCH{=}CH_2)]$ [1.372(4) Å] and $[Mn_2(CO)_7(PEt_3)(\mu\text{-}Ph_2PCH{=}CH_2)]$ [1.42(2) Å].[4] A co-ordination mode resembling that observed in **6** and **8** is found for the bridging phosphine ligand in $[Mo_2Cl_2(\mu\text{-}PPh_2)(\mu\text{-}Ph_2PCH{=}CH)(cp)_2]$[6] (cp = η^5-C_5H_5) in which the carbon atoms of the vinyl moiety are essentially sp^3 hybridised, as evidenced by the C–C bond length [1.46(1) Å] and relevant bond angles. The fact that the osmium–phosphorus distances are not significantly different in **1** and **6** [2.345(4) and 2.361(4) Å] implies that a bonding scheme in which the double bond of the vinyl moiety is delocalised over the P–C–C backbone may not be invoked.

The formation of the μ_3-bridging mode may take place *via* an intermediate involving either π-co-ordination of the vinyl group or oxidative addition of a β-C–H bond (Scheme 1). Although we have found no evidence of a σ-co-ordinated intermediate of the type '$[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-}Ph_2PCH{=}CH)]$' or a π-co-ordinated complex, '$[Os_3(CO)_{10}(\mu\text{-}\sigma{:}\eta\text{-}Ph_2PCH{=}CH_2)]$', in the formation of compound **6** their existence cannot be excluded.

The monosubstituted ruthenium diphenylvinylphosphine cluster **4** is more reactive than the corresponding osmium cluster. In fact it is difficult to isolate **4** as it is photosensitive in solution and rapidly (and cleanly) converted into the yellow product **7** in sunlight. The IR spectrum of compound **7** is similar to that of **6** and both the ^1H NMR and mass spectra support the formulation $[Ru_3(\mu\text{-H})(CO)_9(\mu_3\text{-}Ph_2PCH{=}CH)]$. Infrared spectroscopy indicates that the photoconversion is complete in approximately 2 h. The reaction gives a quantitative yield of **7** but, as in the case of the osmium derivative, there is no evidence of an intermediate. It has been observed that photolysis of $[Ru_3(CO)_{12}]$[18] or reaction of $[Ru_3(CO)_{12}]$ with phosphines under photolytic conditions[19] can generate mononuclear ruthenium species. Kinetic studies[20] have indicated the presence of a trinuclear intermediate which subsequently fragments. If photofragmentation of **4** were to take place, mononuclear fragments should be generated and bis- and possibly tris-substituted trinuclear diphenylvinylphosphine clusters should be formed as a result of recombination of such fragments. We have observed no side-products in the formation of **7** and the reaction sequence is therefore proposed to correspond to that outlined in Scheme 1. Conversion of **4** into **7** can also be brought about by relatively mild heating (60 °C in hexane) in which case the reaction is complete in a couple of hours. Similarly, **5** is also photosensitive and is rapidly converted into the known cluster $[Ru_3(\mu\text{-H})(CO)_8(Ph_2PCH{=}CH_2)(\mu_3\text{-}Ph_2PCH{=}CH)]$ **8**[3] when exposed to sunlight. The TLC purification of **4** and **5** was carried out in the dark in order to prevent conversion into **7** and **8**.

Attempts at further nucleophilic substitution of compound **6** by the addition of PPh_3 or $P(OMe)_3$ have proven unsuccessful



Scheme 1 Possible reaction pathways for the formation of $[Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}Ph_2PCH{=}CH)]$ **6**, $[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}Ph_2PCH{=}CH)]$ **7** and $[Ru_3(\mu\text{-}H)(CO)_8(Ph_2PCH{=}CH_2)(\mu_3\text{-}Ph_2PCH{=}CH)]$ **8**. Reaction conditions: (*i*) M = Os, reflux in dibutyl ether; M = Ru, L = CO or $Ph_2PCH{=}CH_2$, reflux in hexane or *hν*; (*ii*) M = Os, Me_3NO, CH_2Cl_2; (*iii*) M = Os, reflux in CH_2Cl_2

and no reaction was observed even when **6** was subjected to prolonged thermolysis at elevated temperatures in the presence of a nucleophile. One yellow and one red product were isolated from the reaction of **7** with triphenylphosphine at 60 °C in toluene. Proton NMR spectroscopy revealed that the co-ordination of the diphenylvinylphosphine ligand was unchanged in the products which are presumed to be simple substitution products of **7**, possibly $[Ru_3(\mu\text{-}H)(CO)_8(PPh_3)(\mu_3\text{-}Ph_2PCH{=}CH)]$ and $[Ru_3(\mu\text{-}H)(CO)_7(PPh_3)_2(\mu_3\text{-}Ph_2PCH{=}CH)]$. These clusters were not further characterised.

The crystal structure of compound **1** indicates that a diphenylvinylphosphine ligand may not be able to span an Os–Os bond in $[M_3(CO)_{12}]$ without considerable strain on the ligand and/or cluster. The results outlined above, and those of Gobetto *et al.*,[3] suggest that it may not be possible to prepare the putative clusters $[M_3(CO)_{10}(\mu\text{-}\sigma{:}\eta^2\text{-}Ph_2PCH{=}CH_2)]$ (M = Ru or Os). On the other hand, the conversion into the β-eliminated μ_3-bridging mode of the ligand is relatively facile, especially for derivatives of $[Ru_3(CO)_{12}]$; this co-ordination mode appears to have great thermodynamic (and kinetic) stability in trinuclear osmium and ruthenium clusters.

Experimental

All manipulations involving air- or moisture-sensitive reagents were carried out under inert atmospheres of nitrogen or argon using standard Schlenk and vacuum-line techniques. Although the new compounds reported are not particularly air- or moisture-sensitive, reactions were regularly carried out under a nitrogen atmosphere. All solvents were dried by distillation over the appropriate drying agents. The starting materials $[Os_3(CO)_{12-n}(NCMe)_n]$ (n = 1 or 2)[21] and $[Os(\mu\text{-}H)_2(CO)_{10}]$)[22] were prepared by literature methods. Diphenylvinylphosphine (Strem Chemicals) was used as received.

All chromatographic separations and ensuing work-up were carried out in open air. Thin-layer chromatography was carried out on either Merck 60 F-254 0.25 mm precoated silica gel plates or 2 mm thick plates prepared in the University of Cambridge Chemical Laboratory. Columns were packed with Merck 60 (70–230 mesh ASTM) silica gel. Infrared spectra were recorded on a Perkin-Elmer 983 grating or 1710 Fourier-transform spectrometer, proton NMR spectra using Bruker WM 250 and AM 400 Fourier-transform spectrometers, ^{31}P and ^{13}C spectra on a Bruker AM 400 spectrometer and fast atom bombardment mass spectra using a Kratos MS902 spectrometer with a matrix of dithioglycerol or 2-nitrobenzyl alcohol.

Preparations

$[Os_3(CO)_{11}(Ph_2PCH{=}CH_2)]$ 1. In a typical reaction, $[Os_3(CO)_{11}(NCMe)]$ (84 mg, 0.090 mmol) was dissolved in dichloromethane (15 cm^3). A dilute (*ca.* 2 mol dm^{-3}) dichloromethane–1,2-dichloroethane solution of $Ph_2PCH{=}CH_2$ was added by pipette, one drop at a time at intervals of approximately 5 min. The reaction was monitored by IR spectroscopy and stopped after approximately 30 min when only ν_{CO} resonances due to the product (*cf.* Table 1) could be observed. The solution was filtered through a silica plug (approximately 1.5 × 5 cm), concentrated to less than 5 cm^3 and subjected to TLC using dichloromethane–hexane (1 : 1) as eluent. Two bands were found; in order of decreasing R_f, $[Os_3(CO)_{12}]$, yellow (trace) and $[Os_3(CO)_{11}(Ph_2PCH{=}CH_2)]$ **1**, bright yellow. Recrystallisation from a dichloromethane–hexane solution gave 84 mg (0.076 mmol) of yellow microcrystals (yield 85%).

$[Os_3(CO)_{10}(Ph_2PCH{=}CH_2)_2]$ 2. The synthetic method and work-up procedure were analogous to that for compound **1**. In a typical reaction $[Os_3(CO)_{10}(NCMe)_2]$ (74 mg) was used as starting material. Recrystallisation from dichloromethane–hexane afforded 87.5 mg (0.068 mmol, 86%) of light orange-yellow microcrystals of $[Os_3(CO)_{10}(Ph_2PCH{=}CH_2)_2]$ **2**.

$[Os_3(\mu\text{-}H)H(CO)_{10}(Ph_2PCH{=}CH_2)]$ 3. One drop of a 23 mol dm^{-3} 1,2-dichloroethane solution of diphenylvinylphosphine (1.15 mmol, excess) was added to a solution of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ (25 mg, 0.029 mmol) in dichloromethane (20 cm^3). The solution turned from purple to yellow within 5 min, and IR spectroscopy indicated complete conversion into $[Os_3(\mu\text{-}H)H(CO)_{10}(Ph_2PCH{=}CH_2)]$ within 15 min. The solution was concentrated under a stream of nitrogen and subjected to TLC using dichloromethane–hexane (1 : 1) as

Table 4 Crystal data and data-collection parameters * for the structures of $[Os_3(CO)_{11}(Ph_2PCH{=}CH_2)]$ **1** and $[Os_3(\mu\text{-}H)(CO)_9(\mu\text{-}Ph_2PCH{=}CH)]$ **6**

	1	**6**
Formula	$C_{25}H_{13}O_{11}Os_3P$	$C_{23}H_{13}O_9Os_3P$
M	1086.0	1034.95
Crystal colour, habit	Yellow block	Orange-yellow block
Crystal size/mm	0.30 × 0.50 × 0.50	0.22 × 0.24 × 0.35
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a/Å	11.223(3)	10.607(7)
b/Å	11.570(3)	10.797(4)
c/Å	12.320(3)	23.366(14)
α/°	88.080(2)	
β/°	75.320(2)	101.82(5)
γ/°	67.340(2)	
Z	2	4
U/Å^3	1424.3(6)	2619(3)
D_c/g cm^{-3}	2.544	2.624
$F(000)$	988	1864
2θ Range/°	5.0–50.0	5.0–45.0
μ/mm^{-1}	13.48	14.66
Maximum, minimum transmission	0.0244, 0.0789	0.0852, 0.3199
Reflections measured	5424 ($\pm h$, $\pm k$, $-l$)	5326 ($\pm h$, $+k$, $-l$)
Unique reflections	5148	3418
R_{int}	0.013	0.018
Observed reflections (criterion)	4203 [$F > 4\sigma(F)$]	4501 [$F > 6\sigma(F)$]
Weighting scheme, w	$[\sigma^2(F) + 0.0015F^2]^{-1}$	$[\sigma^2(F) + 0.0015F]^{-1}$
R	0.049	0.050
R'	0.063	0.062
Maximum, minimum in final difference map/e Å^{-3}	1.43, −1.90	2.78, −3.48

* Details in common: background measurement, stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time; three standard reflections measured every 97.

eluent. One yellow band was found. Recrystallisation from dichloromethane–hexane gave 21 mg (0.021 mmol) of yellow microcrystals of $[Os_3(\mu\text{-}H)H(CO)_{10}(Ph_2PCH{=}CH_2)]$ **3**, yield ≈73%.

$[Ru_3(CO)_{12-n}(Ph_2PCH{=}CH_2)_n]$ (n = 1 4 or 2 5). An excess of $Ph_2PCH{=}CH_2$ (2 drops of a 23 mol dm^{-3} 1,2-dichloroethane solution, *ca.* 0.230 mmol) was added to a solution of $[Ru_3(CO)_{12}]$ (120 mg, 0.188 mmol) in thf (20 cm^3). A strong solution of $Na\text{–}PH_2CO^{\bullet}$ in thf was added by pipette, one drop at a time at intervals of approximately 10 min. The reaction was monitored by IR spectroscopy and stopped when the ν_{CO} resonances due to the starting material could no longer be detected. The solvent was removed under a stream of nitrogen. The residue was redissolved in dichloromethane (*ca.* 5 cm^3) and subjected to TLC in the dark [eluent dichloromethane–hexane (1:1)]. Four bands were found: in order of decreasing R_f, $[Ru_3(CO)_{11}(Ph_2PCH{=}CH_2)]$ **4**, orange, 15 mg, 10%; $[Ru_3(\mu\text{-}H)(CO)_8(Ph_2PCH{=}CH_2)(\mu_3\text{-}Ph_2PCH{=}CH)]$ **8**,[3] yellow, 3 mg (0.003 mmol), 2%; $[Ru_3(CO)_{10}(Ph_2PCH{=}CH_2)_2]$ **5**, dark orange-red, 56 mg (0.056 mmol), 30%; '$[Ru_3(CO)_9(Ph_2PCH{=}CH_2)_3]$', dark red, 45 mg (0.056 mmol), 20%. Yields quoted are after recrystallisation from dichloromethane–hexane.

$[Os_3(\mu\text{-}H)(CO)_9(\mu\text{-}Ph_2PCH{=}CH)]$ 6. *Method A.* The compound $[Os_3(CO)_{11}(Ph_2PCH{=}CH_2)]$ **1** (53.1 mg, 0.048 mmol) was dissolved in dichloromethane (50 cm^3). To this solution was added dropwise a solution of NMe_3O (4.8 mg, 0.064 mmol) in dichloromethane (*ca.* 20 cm^3) until IR spectroscopy showed the formation of '$[Os_3(CO)_{10}(Ph_2PCH{=}CH_2)(NMe_3)]$' [$\nu_{CO}$, ($CH_2Cl_2$): 2082mw, 2029vs, 2019s, 1993vs and 1965m cm^{-1}]. The solution was then refluxed for approximately 1 h, after which it was reduced in volume and subjected to thin-layer chromatography. Recrystallisation from a dichloromethane–hexane solution gave 20 mg of pale yellow microcrystals of $[Os_3(\mu\text{-}H)(CO)_9(Ph_2PCH{=}CH)]$ **6** (yield ≈50%).

Method B. In a typical reaction, $[Os_3(CO)_{11}(Ph_2PCH{=}CH_2)]$ **1** (86 mg, 0.074 mmol) was dissolved in the minimum volume of dichloromethane. To this solution, dibutyl ether (*ca.* 50 cm^3) was added, and refluxed for approximately 12 h (further heating leads to extensive decomposition), during which it turned from yellow to very pale yellow. The solvent was removed *in vacuo*. The residue was redissolved in dichloromethane (*ca.* 5 cm^3) and subjected to TLC using dichloromethane as eluent. One pale yellow band and a black baseline due to decomposed material were found. Recrystallisation from a dichloromethane–hexane solution gave 54 mg (0.052 mmol) of pale yellow microcrystals of **6** (yield 68%). Compound **6** may also be synthesised by reflux of **1** in toluene. However, this reaction takes longer to go to completion (approximately 16–18 h) and the yield is lower (*ca.* 50%).

$[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}Ph_2PCH{=}CH)]$ 7. *Method A.* In a typical reaction, a solution of $[Ru_3(CO)_{11}(Ph_2PCH{=}CH_2)]$ **4** (20 mg, 0.018 mmol) in dichloromethane (25 cm^3) was exposed to visible light (sunlight or 100 W lamp) for 1 h, during which it gradually turned from light orange to yellow. The solution was reduced in volume to less than 5 cm^3 and then subjected to thin-layer chromatography [dichloromethane–hexane (1:1)] which yielded one yellow band. Recrystallisation from dichloromethane–hexane gave approximately 15 mg (0.014 mmol) of orange-red $[Ru_3(\mu\text{-}H)(CO)_9(\mu\text{-}Ph_2PCH{=}CH)]$ **7** (yield ≈79%).

Method B. In a typical reaction, $[Ru_3(CO)_{11}(Ph_2PCH{=}CH_2)]$ (50 mg, 0.045 mmol) was dissolved in hexane and heated at 60 °C. The solution turned from orange to yellow within a couple of minutes. The reaction was monitored by IR spectroscopy and adjudged to be complete in *ca.* 2.5 h. The method of purification was the same as in method A; yield *ca.* 35 mg (0.034 mmol, 75%).

Crystallography

Intensity data for compounds **1** and **6** were collected at 293 K on a Nicolet R3m/V diffractometer using monochromated Mo-Kα (λ 0.710 69 Å) radiation and a 96-step ω–2θ scan mode, with a scan speed varying from 3.00 to 29.30° min^{-1} and a scan width of 1.40° + Kα separation. In each case the data were corrected for Lorentz-polarisation effects and for absorption using a semiempirical method based on ψ-scan data. Relevant data are summarised in Table 4. The structures were solved by a combination of centrosymmetric direct methods (Os atom positions) followed by Fourier-difference techniques. Full-matrix least-squares refinement, based on *F*, with Os, P and O atoms anisotropic was carried out on a Digital Micro Vax II computer using the SHELXTL PLUS[23] package of crystallographic programs. For both **1** and **6** the hydrogens of the phenyl and vinyl moieties were generated in their ideal positions and allowed to ride on the relevant carbon atoms. No attempt was made to locate the hydride ligand in **6**.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/138.

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