Synthesis and Characterisation of the Tetranuclear Phosphinidene Clusters $[Os_3MH_2(CO)_{12}(PR)]$ (M = Os, R = Ph or cyclo-C_6H_{11}; M = Ru, R = cyclo-C_6H_{11}) and the Crystal and Molecular Structure of $[Os_4(\mu\text{-}H)_2(CO)_{12}(\mu_3\text{-}PC_6H_{11})]$†

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Reaction of the phosphinidene-capped cluster $[Os_3H_2(CO)_9(PR)]$ (R = Ph or cyclo-C_6H_{11}) with the binary carbonyl $[M_3(CO)_{12}]$ (M = Ru or Os), under reflux in nonane, affords the tetranuclear clusters $[Os_3MH_2(CO)_{12}(PR)]$ [(**1**) M = Os, R = Ph; (**2**) M = Os, R = cyclo-C_6H_{11}; (**3**) M = Ru, R = cyclo-C_6H_{11}] together with the previously reported penta- and hexa-nuclear clusters $[Os_3M_2(CO)_{15}(PR)]$ and $[Os_3M_3(CO)_{17}(PR)]$. The structure of (**2**) has been established by an *X*-ray analysis which shows that there are two independent but structurally similar tetranuclear clusters per asymmetric unit. Within each molecule the four Os atoms adopt a 'butterfly' arrangement, consistent with the 62-electron count, and the phosphinidene ligand bridges an open triangular face defined by one 'bridge' and two 'wingtip' Os atoms. The 12 carbonyl ligands are terminal, and the two hydrides bridge the two remaining 'hinge' to 'wingtip' Os–Os edges. Solution ^1H and ^{31}P n.m.r. spectra for clusters (**1**)—(**3**) are consistent with this ground-state structure, and the positions of the hydrides are confirmed by the observation of ^{187}Os satellites in the ^1H n.m.r. spectra of (**1**) and (**2**). The cluster (**3**) exists as a mixture of three inseparable isomers which arise from the juxtaposition of the Ru atom around the three inequivalent positions of the metal 'butterfly'. The existence of these isomers is confirmed by a detailed analysis of the ^1H and ^{31}P n.m.r. spectra of this complex.

Bridging alkyl- and aryl-phosphinidene groups (μ-PR) have attracted considerable attention recently in transition metal cluster chemistry as ligands capable of stabilising a metal framework during chemical transformation.[1] We have reported that the phosphinidene-capped triosmium clusters $[Os_3H_2(CO)_9(PR)]$ (R = Ph or cyclo-C_6H_{11}) undergo condensation reactions with the binary carbonyl clusters $[M_3(CO)_{12}]$ (M = Os or Ru) at elevated temperatures, to give mixtures of the respective higher nuclearity phosphinidene-capped clusters $[Os_3MH_2(CO)_{12}(PR)]$, $[Os_3M_2(CO)_{15}(PR)]$, and $[Os_3M_3(CO)_{17}(PR)]$ in high overall yield.[2] At the time of this previous report we had structural evidence for the pentanuclear derivatives $[Os_3M_2(CO)_{15}(PR)]$ only, which were shown to have square-based pyramidal metal frameworks. Structural information for the hexanuclear products $[Os_3M_3(CO)_{17}(PR)]$ has not been obtained. In this paper we discuss the relationship between spectroscopic data and structure in the tetranuclear products $[Os_3MH_2(CO)_{12}(PR)]$ and present the *X*-ray crystal and molecular structure of $[Os_4H_2(CO)_{12}(PC_6H_{11})]$. Full experimental details of the condensation reactions to give all three nuclearities of product phosphinidene cluster are given for the first time.

Results and Discussion

We have isolated three tetranuclear clusters $[Os_3MH_2(CO)_{12}(PR)]$ [(**1**) M = Os, R = Ph; (**2**) M = Os, R = cyclo-C_6H_{11}; (**3**) M = Ru, R = cyclo-C_6H_{11}] from the reactions of the appropriate phosphinidene-capped cluster $[Os_3H_2(CO)_9(PR)]$ with the appropriate binary carbonyl cluster $[M_3(CO)_{12}]$. The i.r., ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r., and mass spectroscopic data for the new clusters (**1**)—(**3**) are given in Table 1.

These clusters (**1**)—(**3**) are formally 62-electron species, an electron count for which a 'butterfly' arrangement of the four metal atoms is normally found.[3] To confirm this an *X*-ray crystal structure of the homonuclear cluster (**2**) has been completed. The crystal structure is built up from discrete molecules of $[Os_4(\mu\text{-}H)_2(CO)_{12}(\mu_3\text{-}C_6H_{11})]$ (**2**) separated by normal van der Waals distances. There are two crystallographically independent but essentially identical molecules in each asymmetric unit. The molecular structure of one of these is shown in Figure 1 and the structural parameters are listed in Table 2.

In the molecular structure of (**2**) the four osmium atoms adopt the butterfly arrangement. Three terminal carbonyl ligands are co-ordinated to each metal and the phosphinidene ligand caps an open Os_3 triangle made up of the two 'wingtip' metals, Os(1) and Os(3), and the 'hinge' metal, Os(2). The two hydride ligands were not located directly, but potential energy calculations[4] indicate that they bridge the two long Os(1)–Os(4) and Os(3)–Os(4) edges.

The dihedral angle between the two 'wings' of the butterfly, Os(1)Os(2)Os(4) and Os(2)Os(3)Os(4), in (**2**) is 103.6° (in the second molecule the dihedral angle is also 103.6°) and the Os(1)···Os(3) separation is 4.045(2) Å [4.037(2) Å in the second molecule]. This dihedral angle is intermediate between the values of 97.7° found in $[Os_4H_4(CO)_{12}(OH)]^+$,[5] where the OH group bridges the wingtip metals, and 112.2(1)° in $[Os_4H_3(CO)_{12}(NCMe)_2]^+$,[6] where the butterfly remains unbridged, and is significantly lower than the range of values observed in a variety of alkyne-capped butterfly structures (112.7—144.1°).[7] In the case of (**2**) the observed dihedral angle is probably a consequence of the preferred bite of the co-ordinatively flexible capping phosphine ligand rather than an electronic requirement of the bonding within the cluster core. A μ_3-phosphinidene ligand capping an open metal triangle has been reported previously in $[Ru_4(CO)_{13}(\mu_3\text{-}PPh)]$[8] and in a number of mixed-metal clusters.[9]

The trend in Os–P distances in (**2**) is for the hinge Os–P

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† 1,1,1,2,2,2,3,3,3,4,4,4-Dodecacarbonyl-di-μ-hydrido-1,2,3-μ_3-cyclohexylphosphido-*tetrahedro*-tetraosmium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Spectroscopic data for new compounds[a]

(**1**) $[Os_4H_2(CO)_{12}(PPh)]$	ν(CO) (hexane)	2 106mw, 2 078vs, 2 031vs, 2 008s, 1 963w
	^1H, N.m.r.	7.7—7.3 (m, PPh), −19.12 [d, *J*(PH) 6.8, 2 OsH *and* ^{187}Os satellites: ddd, *J*($H^{187}Os$) 36.1, *J*(HP) 6.8, *J*(HH′) 2.3; dd, *J*($H^{187}Os$) 19.4, *J*(HP) 6.8]
	^{31}P-{^1H} N.m.r.	61.57 (s, PPh)
	M^+	*m/z* 1 214 (−12 CO)
(**2**) $[Os_4H_2(CO)_{12}(PC_6H_{11})]$	ν(CO) (hexane)	2 105mw, 2 074vs, 2 028vs, 2 004s, 1 960w
	^1H N.m.r.	1.9—1.3 (m, PC_6H_{11}), −19.09 [d, *J*(PH) 6.8, 2 OsH *and* ^{187}Os satellites: ddd, *J*($H^{187}Os$) 36.6, *J*(HP) 6.8, *J*(HH′) 2.5; dd, *J*($H^{187}Os$) 29.6, *J*(HP) 6.8]
	^{31}P-{^1H} N.m.r.	97.52 (s, PC_6H_{11})
	M^+	*m/z* 1 220 (−12 CO)
(**3**) $[Os_3RuH_2(CO)_{12}(PC_6H_{11})]$	ν(CO) (hexane)	2 104mw, 2 073vs, 2 028vs, 2 002s, 1 960w
	^1H N.m.r.[b]	2.2—1.3 [m, PC_6H_{11}, isomers (**A**)—(**C**)], −18.49 [d, *J*(PH) 9.5, RuH, isomer (**A**)], −19.12 [d, *J*(PH) 7.0, OsH *and* ^{187}Os satellites: ddd, *J*(H-^{187}Os) 37, *J*(HP) 7, *J*(HH′) 3; dd, *J*($H^{187}Os$) 30, *J*(HP) 7; isomer (**C**)], −19.30 [dd, *J*(PH) 7.3, *J*(HH′) 2.6, RuH, isomer (**B**)], −19.35 [dd, *J*(PH) 10.4, *J*(HH′) 2.6, RuH, isomer (**B**)]. Hydride multiplets (**A**):(**B**):(**C**) integrate 1.0:2.6:2.0
	^{31}P-{^1H} N.m.r.[b]	169.29 [s, PC_6H_{11}, isomer (**B**)], 157.89 [s, PC_6H_{11}, isomer (**C**)], 108.35 [s, PC_6H_{11}, isomer (**A**)]. Peaks (**A**):(**B**):(**C**) integrate 1.0:2.3:2.0
	M^+	*m/z* 1 130(−12 CO)

[a] N.m.r.: δ values in p.p.m., coupling constants (*J*) in Hz. I.r.: ν(CO) in cm^{-1}. [b] Analysed as a mixture of three inseparable isomers, (**A**)—(**C**).

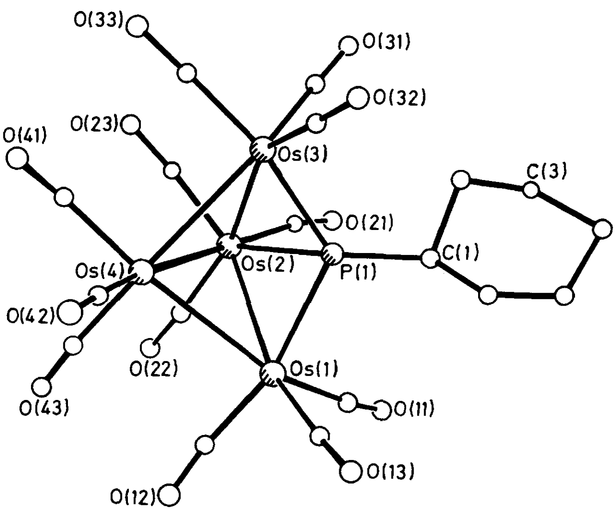


Figure 1. Molecular structure of one of the independent molecules of $[Os_4(\mu\text{-}H)_2(CO)_{12}(\mu_3\text{-}PC_6H_{11})]$ (**2**), showing the atom labelling scheme

Table 2. Selected bond lengths (Å) and angles (°) for $[Os_4(\mu\text{-}H)_2(CO)_{12}(\mu_3\text{-}PC_6H_{11})]$ (**2**)

	Molecule 1	Molecule 2
Os(2)–Os(1)	2.871(2)	2.875(2)
Os(4)–Os(1)	3.013(2)	3.010(2)
Os(3)–Os(2)	2.876(2)	2.866(2)
Os(4)–Os(2)	2.846(2)	2.853(2)
Os(4)–Os(3)	3.013(2)	3.008(2)
P(1)–Os(1)	2.31(1)	2.36(1)
P(1)–Os(2)	2.35(1)	2.41(1)
P(1)–Os(3)	2.33(1)	2.34(1)
C(1)–P(1)	1.88(4)	1.89(5)
Os(4)–Os(1)–Os(2)	57.8(1)	57.9(1)
P(1)–Os(1)–Os(2)	52.7(3)	53.8(3)
P(1)–Os(1)–Os(4)	77.2(3)	78.4(3)
Os(3)–Os(2)–Os(1)	89.5(1)	89.3(1)
Os(4)–Os(2)–Os(1)	63.6(1)	63.4(1)
Os(4)–Os(2)–Os(3)	63.6(1)	63.5(1)
P(1)–Os(2)–Os(1)	51.3(3)	52.2(2)
P(1)–Os(2)–Os(3)	51.7(3)	51.7(2)
P(1)–Os(2)–Os(4)	80.1(3)	80.9(2)
Os(4)–Os(3)–Os(2)	57.7(1)	58.1(1)
P(1)–Os(3)–Os(2)	52.5(3)	54.1(3)
P(1)–Os(3)–Os(4)	76.9(3)	78.8(3)
Os(2)–Os(4)–Os(1)	58.6(1)	58.7(1)
Os(3)–Os(4)–Os(1)	84.3(1)	84.3(1)
Os(3)–Os(4)–Os(2)	58.7(1)	58.5(1)
Os(2)–P(1)–Os(1)	76.0(3)	74.1(3)
Os(3)–P(1)–Os(1)	121.3(5)	118.5(4)
Os(3)–P(1)–Os(2)	75.8(3)	74.3(3)

distance [average 2.38(2) Å for the two molecules] to be longer than the wingtip Os–P distance [average 2.34(2) Å]. While this trend is not significant in terms of the estimated standard deviations on the bond parameters it is similar to the significant differences in Ru–P lengths in $[Ru_4(CO)_{13}(\mu_3\text{-}PPh)]$.[8] The Os–P–Os angles in (**2**) are also similar to the Ru–P–Ru angles of 74.3(1), 121.0(1), and 72.6(1)° in $[Ru_4(CO)_{13}(\mu_3\text{-}PPh)]$,[8] consistent with a similar bonding contribution from the phosphorus atom in the two clusters. The Os–P distances in (**2**) lie within the range of Ru–P distances found in ruthenium clusters where a phosphinidene ligand caps an open Ru_3 triangular face [2.302(2)—2.395(1) Å][8,10] but are slightly longer than in complexes where a phosphinidene caps a closed Ru_3 triangular face [2.282(1)—2.310(2) Å].[11,12]

The metal–metal bond lengths within the butterfly core of (**2**) follow the trends observed in other Os_4 butterfly clusters where the Os–Os hinge bond is not bridged by a hydride. The Os(2)–Os(4) length is similar to the distance of 2.831(2) Å found for the hinge edge in $[Os_4H_4(CO)_{12}(OH)]^+$.[5] The hydride-bridged hinge–wingtip edge lengths are marginally shorter than the range of distances [3.025(2)—3.130(2) Å] found in other hydride-bridged butterly systems.[4,5,13] The phosphinidene-capped hinge–wingtip edges are not significantly different from the Os–Os unbridged edges of length 2.877(1) Å in $[Os_4H_3(CO)_{12}I]$.[13]

The bond parameters within the phosphinidene ligand do not deviate significantly from the expected values.

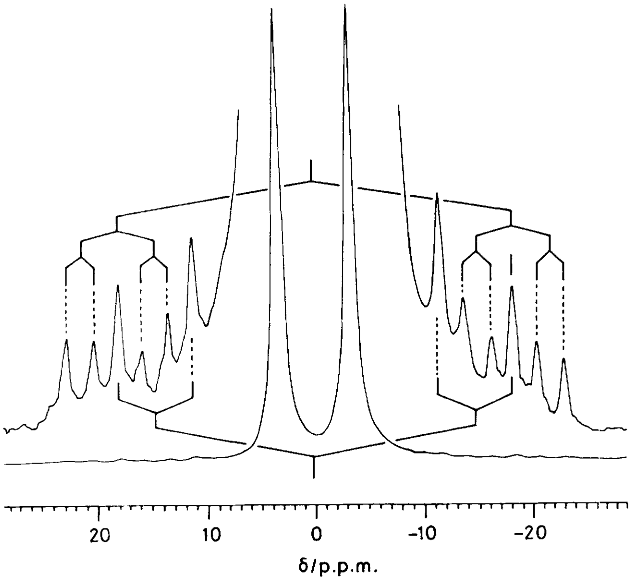
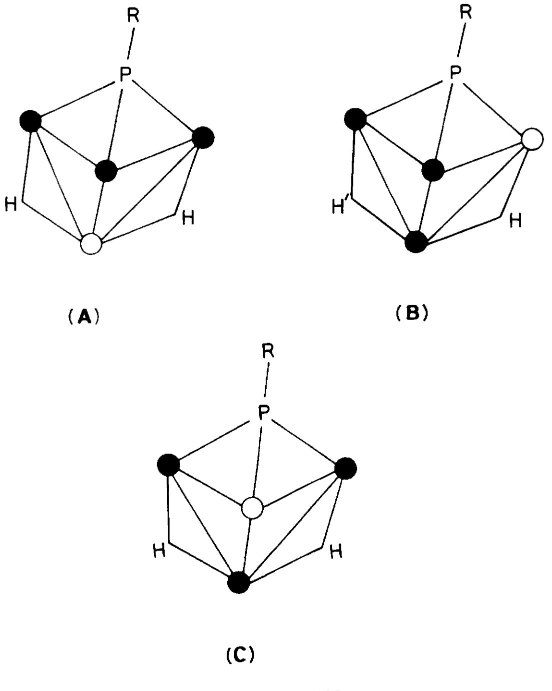


Figure 2. Expansion about the hydride signal at δ −19.09 p.p.m. in the ^1H n.m.r. spectrum (in CD_2Cl_2, spin rate 35 Hz) of $[Os_4(\mu\text{-}H)_2(CO)_{12}(\mu_3\text{-}PC_6H_{11})]$ showing the satellites arising from coupling to ^{187}Os ($I = \frac{1}{2}$, abundance 1.6%)



(A) (B)

(C)

Figure 3. Possible isotopomers ($M = {}^{187}Os$) and isomers ($M = Ru$) for the clusters $[Os_3MH_2(CO)_{12}(PR)]$ (R = Ph or cyclo-C_6H_{11})

Spectroscopic data for all the clusters $[Os_3MH_2(CO)_{12}(PR)]$ are consistent with the butterfly structure found for (**2**) being maintained by (**1**)—(**3**) in solution and confirm our positioning of the hydride atoms. Hydrogen-1 and ^{31}P n.m.r. spectra of the homonuclear clusters (**1**) and (**2**) show the resonances expected for the capping phosphinidene group (Table 1). Also observed in the ^1H n.m.r. spectra is a high-field doublet due to the two equivalent hydride ligands coupling with the phosphorus atom [at −19.12 for (**1**) and −19.09 p.p.m. for (**2**)]. A complex set of ^{187}Os satellites (^{187}Os, $I = \frac{1}{2}$, abundance 1.6%) are observed about each of these hydride signals [illustrated for (**2**) in Figure 2]. These spectral features are readily explained by considering the possible isotopomers containing only a single ^{187}Os nucleus (with the natural abundance of ^{187}Os being 1.6% other isotopomers will not be observed):* there are three (Figure 3).

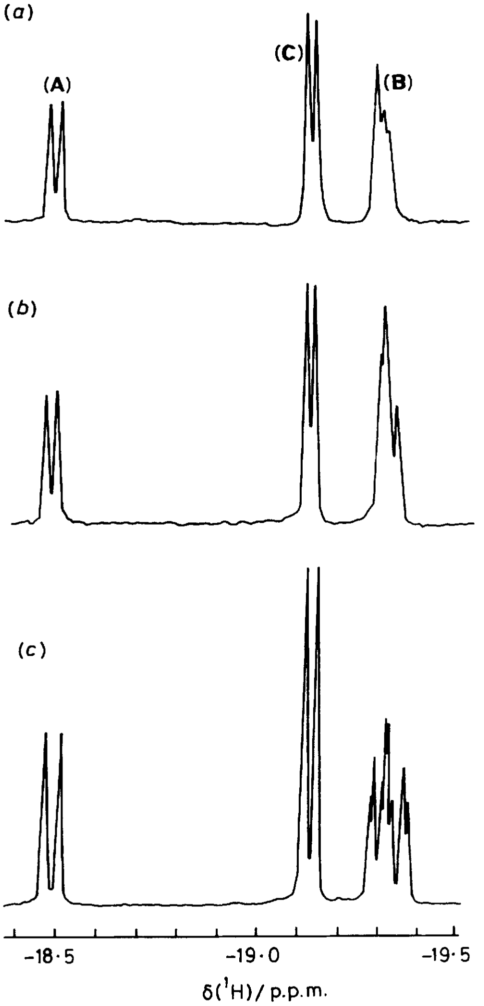


Figure 4. Variation of the high-field hydride signals in the ^1H n.m.r. spectrum ($[^2H_8]$toluene) of $[Os_3RuH_2(CO)_{12}(PC_6H_{11})]$ with temperature: (*a*) 370, (*b*) 340, (*c*), 293 K

Isotopomer (**A**) has an ^{187}Os atom in the hinge position to which both hydrides but not the phosphorus atom bind. Coupling of the ^{187}Os atom with the two equivalent hydrides splits the doublet of unlabelled (**1**) and (**2**) into the observed doublet of doublets [(**1**), $^1J(H^{187}Os)$ 19.4, $^2J(HP)$ 6.8; (**2**), $^1J(H^{187}Os)$ 29.6, $^2J(HP)$ 6.8 Hz].

Isotopomer (**B**) has a wingtip ^{187}Os atom. Thus the symmetry of the cluster has been lowered so that couplings between the now inequivalent hydride ligands can be observed. The satellite pattern arises as follows: the hydride bonded to the labelled Os atom is split into a doublet by this atom and further couples with the phosphorus atom and the other inequivalent hydrogen atom to give a doublet of doublets [(**1**), $^1J(H^{187}Os)$ 36.1, $^2J(HP)$ 6.8, $^2J(HH')$ 2.3; (**2**), $^1J(H^{187}Os)$ 36.6, $^2J(HP)$ 6.8, $^2J(HH')$ 2.5 Hz]. In the final isotopomer (**C**), neither hydride is

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* The use of ^{187}Os satellites in the ^1H n.m.r. spectra of osmium cluster compounds in making structural assignments is discussed in ref. 14.

Table 3. Atomic co-ordinates (× 10^4) for [$Os_4(\mu\text{-}H)_2(CO)_{12}(\mu_3\text{-}PC_6H_{11})$] (**2**)

Atom	*x*	*v*	*z*	Atom	*x*	*y*	*z*
Os(1)	1 470(2)	349(1)	8 300(1)	Os(6)	6 471(2)	3 296(1)	4 308(1)
Os(2)	1 563(2)	0	6 752(1)	Os(7)	9 240(2)	2 894(1)	3 921(1)
Os(3)	4 354(2)	405(1)	6 402(1)	Os(8)	9 084(2)	3 435(1)	5 303(1)
Os(4)	4 123(2)	−141(1)	7 776(1)	P(2)	7 135(11)	2 655(3)	4 631(5)
P(1)	2 207(14)	621(3)	7 109(6)	C(10)	5 823(52)	2 245(15)	4 352(28)
C(1)	975(42)	1 026(12)	6 792(21)	C(20)	5 974(41)	2 124(12)	3 436(21)
C(2)	1 418(56)	1 385(17)	7 323(30)	C(30)	4 850(52)	1 772(14)	3 296(24)
C(3)	225(74)	1 708(20)	7 256(35)	C(40)	5 036(81)	1 451(22)	3 784(36)
C(4)	477(68)	1 814(19)	6 338(34)	C(50)	5 022(52)	1 592(13)	4 639(24)
C(5)	191(61)	1 450(16)	5 621(29)	C(60)	6 110(44)	1 917(12)	4 888(22)
C(6)	1 372(59)	1 126(17)	5 906(30)	O(51)	3 251(20)	2 592(10)	5 654(19)
O(11)	2 366(39)	911(9)	9 605(16)	O(52)	5 275(34)	3 547(7)	7 012(14)
O(12)	293(41)	−275(7)	9 413(18)	O(53)	7 473(49)	2 375(10)	7 131(21)
O(13)	−1 916(17)	584(13)	8 093(31)	O(61)	3 848(25)	2 974(10)	3 283(16)
O(21)	−1 046(26)	337(10)	5 737(16)	O(62)	4 458(37)	3 899(8)	5 105(20)
O(22)	2 811(32)	−554(6)	5 506(12)	O(63)	7 681(35)	3 844(7)	3 039(16)
O(23)	−632(30)	−556(9)	7 561(21)	O(71)	8 022(44)	2 653(13)	2 277(11)
O(31)	3 421(34)	663(9)	4 723(11)	O(72)	11 429(39)	2 224(6)	4 106(22)
O(32)	6 771(25)	1 029(6)	6 615(15)	O(73)	11 195(40)	3 447(10)	2 945(21)
O(33)	6 338(34)	−157(9)	5 462(18)	O(81)	10 482(39)	4 065(7)	4 278(18)
O(41)	2 487(39)	−789(7)	8 643(20)	O(82)	11 865(24)	3 372(10)	6 430(14)
O(42)	5 742(30)	−739(7)	6 761(15)	O(83)	7 497(37)	4 062(9)	6 244(20)
O(43)	6 816(30)	−152(14)	8 968(18)	C(51)	4 493(23)	2 707(12)	5 748(14)
C(11)	1 889(52)	716(10)	9 107(21)	C(52)	5 757(46)	3 340(8)	6 537(21)
C(12)	747(44)	−31(9)	9 015(20)	C(53)	7 016(47)	2 595(9)	6 676(17)
C(13)	−656(15)	485(9)	8 202(47)	C(61)	4 863(20)	3 091(8)	3 660(15)
C(21)	−69(42)	212(17)	6 131(21)	C(62)	5 218(39)	3 662(9)	4 838(21)
C(22)	2 442(47)	−342(10)	5 999(20)	C(63)	7 168(38)	3 628(8)	3 485(14)
C(23)	313(45)	−365(10)	7 286(23)	C(71)	8 511(43)	2 725(12)	2 904(11)
C(31)	3 809(67)	542(17)	5 334(13)	C(72)	10 704(35)	2 498(8)	4 070(23)
C(32)	5 868(28)	794(8)	6 498(24)	C(73)	10 514(41)	3 241(10)	3 350(21)
C(33)	5 639(35)	64(11)	5 823(18)	C(81)	9 862(60)	3 832(7)	4 646(34)
C(41)	3 069(39)	−538(7)	8 317(19)	C(82)	10 857(35)	3 392(17)	5 976(24)
C(42)	5 020(32)	−514(6)	7 099(15)	C(83)	8 239(72)	3 844(14)	5 902(36)
C(43)	5 806(37)	−158(24)	8 513(22)				
Os(5)	6 462(2)	2 944(1)	5 856(1)				

bound directly to an ^{187}Os atom and no satellites result. Note that the relative intensities of each of the satellite multiplets (see Figure 2) support these interpretations: isotopomer (**A**) should occur at only half the frequency of isotopomer (**B**) but in (**A**) two hydrides directly couple to ^{187}Os as opposed to a single hydride in (**B**). Thus both sets of multiplets should occur at equal intensity as is observed.

We now turn our attention to the heteronuclear cluster [$Os_3RuH_2(CO)_{12}(PC_6H_{11})$] (**3**). Although the i.r. spectrum, mass spectroscopic and analytical data for this compound are consistent with it being a single cluster, ^{1}H and ^{13}P-{^{1}H} n.m.r. spectra (Table 1) show that it is a mixture of three inseparable isomers. These isomers, (**A**)—(**C**), arise from juxtaposition of the Ru atom around the three inequivalent positions of the metal butterfly as shown in Figure 3. Assignment of the three sets of high-field hydride multiplets in the ^{1}H n.m.r. spectrum (Figure 4) and the three singlets observed in the ^{31}P-{^{1}H} n.m.r. spectrum of (**3**) (Table 1) to each of the three isomers (**A**)—(**C**) is straightforward.

In the ^{1}H n.m.r. spectrum the more complex set of hydride multiplets (two doublets of doublets) must arise from the asymmetrical isomer (**B**). Both of the remaining isomers have approximate $C_s(m)$ symmetry and equivalent hydrides. The doublet at δ −19.12 p.p.m. has approximately the same P–H coupling and approximately the same chemical shift as is found for the homonuclear analogue (**2**) suggesting that the hydrides giving rise to this resonance bridge two Os atoms, *i.e.* isomer (**C**). This is confirmed by closer inspection of this doublet; the same pattern of ^{187}Os satellites is seen about it as found for (**2**) (see above). The remaining doublet at δ −18.49 p.p.m. is assigned by default to isomer A.

In the ^{31}P-{^{1}H} n.m.r. spectrum of (**3**) there are two singlets at lower field (δ 169.29 and 157.89 p.p.m.) from the remaining singlet (δ 108.35 p.p.m.) which shows only a small change in chemical shift from the value found for its homonuclear analogue (**2**) (δ 97 p.p.m.). To assign these peaks we note the prediction of Shafer and Zipfel[15] and the observation of Huttner and co-workers[16] that the paramagnetic contribution of M–M bonding to the ^{31}P chemical shift decreases with increasing M–M bond strength in the order Fe > Ru > Os (*i.e.* the phosphorus resonances for isomers with the P atom directly bonded to the Ru atom should occur at lower field). Thus the high-field singlet in the ^{31}P-{^{1}H} n.m.r. spectrum of (**3**) is attributed to isomer (**A**) in which the phosphorus atom bonds three osmium atoms. Comparison of the integrals of the remaining pair of lower field singlets with those for the hydride multiplets in the corresponding ^{1}H n.m.r. spectrum of (**3**) allows assignment of the lower field peak (δ 169.29 p.p.m.) to isomer (**B**) and the remaining peak to isomer (**C**). That the ^{31}P-{^{1}H} n.m.r. resonance for the PR group of isomer (**B**) should be at lower field than isomer (**C**) is not unreasonable. In the molecular structure of (**2**) the Os(wingtip)–P distance is greater than the Os(hinge)–P distance and consequently contributions of the ruthenium atom to the ^{31}P chemical shift should be greatest in isomer (**B**).

We have looked, and find no evidence, for exchange between isomers (**A**)—(**C**) in the high-temperature ^{1}H n.m.r. spectrum of (**3**). Equilibration between isomers (**A**)—(**C**) requires both movement of the hydride ligands and the phosphinidene group over the cluster surface. In the ^{1}H n.m.r. spectrum the three high-field hydride multiplets from isomers (**A**)—(**C**) (Figure 4) would be expected to collapse simultaneously if such a process was occurring. At the highest temperature studied (370 K) the doublets from the hydrides of the symmetrical isomers (**A**) and (**C**) remain sharp indicating that no exchange is occurring between isomers. However, as the temperature is raised the multiplet from the inequivalent hydrides of isomer (**B**) (which along with the phosphorus atom form an ABX spin system) shows changes typical for these two hydride ligands (AB of the spin system) beginning to exchange (Figure 4). A limiting spectrum was not obtained.

Experimental

All reactions were performed with the exclusion of air in solvents distilled under nitrogen from appropriate drying reagents immediately prior to use. Products were separated in air by column chromatography on silica (Kieselgel 60, 70—230 mesh ASTM).

Proton, ^{13}C, and ^{31}P n.m.r. data were obtained on Bruker WM 250, WH 400, or Varian XL 100 instruments at 20 °C using deuteriated solvents as lock and reference [^{1}H and ^{13}C, $SiMe_4$ ($\delta = 0$); ^{31}P, $P(OMe)_3$ ($\delta = 0$)]. Infrared spectra were recorded on a Perkin-Elmer 983 instrument between 2 200 and 1 600 cm^{-1}. Mass spectra were obtained on a AEI MS12 spectrometer with *ca.* 70 eV (1.12×10^{-17}J) ionizing potential at 90—150 °C. Tris(perfluoroheptyl)-*s*-triazine was used as reference.

All chemicals, except where stated, were purchased from commercial sources and used as supplied. The compounds $[Os_3(CO)_{11}(MeCN)]$ and $[Os_3H(CO)_{10}(PR)]$ (R = Ph or cyclo-C_6H_{11}) were prepared by the literature methods.[17]

Preparations.—(*i*) $[Os_3H(CO)_{10}(\mu\text{-}PHR)]$ (R = Ph *or* cyclo-C_6H_{11}). Both these compounds have been previously reported to be formed in low to moderate yields from thermolysis of $[Os_3(CO)_{12}]$ with the appropriate phosphine PH_2R. We report here full details of our higher yield synthesis of these compounds.

In a typical reaction, to $[Os_3(CO)_{11}(MeCN)]$ (300 mg) dissolved in CH_2Cl_2 (60 cm^3) was added the primary phosphine PH_2R (*ca.* 2 mol equiv.). After 1 h, the i.r. spectrum of the solution shows clean conversion to the corresponding cluster $[Os_3(CO)_{11}(PH_2R)]$. R = Ph: ν(CO), 2 110mw, 2 056s, 2 036s, 2 020vs, 1 988m cm^{-1}. R = cyclo-C_6H_{11}: ν(CO), 2 109mw, 2 055s, 2 034s, 2 018vs, 1 987m cm^{-1}. The solvent was removed *in vacuo* and the residue dissolved in MeOH (50 cm^3). Excess of Na_2CO_3 (500 mg) was added and the reaction mixture stirred until i.r. showed conversion to the anions $[Os_3(CO)_{10}(PHR)]^-$ to be complete (typically 45—90 min). $Na[Os_3(CO)_{10}(\mu\text{-}PHPh)]$: ν(CO) (MeOH), 2 067mw, 2 004s, 1 994vs, 1 982 (sh), 1 966mw, 1 949mw, 1 926m cm^{-1}. $Na[Os_3(CO)_{10}(\mu\text{-}PHC_6H_{11})]$: ν(CO) (MeOH), 2 065mw, 2 002s, 1 991vs, 1 980 (sh), 1 965mw, 1 948mw, 1 924m cm^{-1}. The excess Na_2CO_3 was filtered off under nitrogen and CF_3COOH was added dropwise until the solution reached a pH of 5.5. The solvent was then removed and the residue subjected to column chromatography using hexane as eluant. Removal of the solvent from the single yellow band yields $[Os_3H(CO)_{10}(\mu\text{-}PHR)]$ (280—300 mg, 88—95%). R = Ph: ν(CO) (hexane), 2 106m, 2 064vs, 2 055s, 2 025vs, 2 009s, 1 996s cm^{-1}. R = cyclo-C_6H_{11}: ν(CO) (hexane), 2 105m, 2 062vs, 2 052s, 2 023vs, 2 008, 1 991s, 1 980mw, 1 954w cm^{-1}.

(*ii*) *Homonuclear phosphinidene clusters.* $[Os_6(CO)_{17}(\mu\text{-}PR)]$, $[Os_5(CO)_{15}(\mu\text{-}PR)]$, *and* $[Os_4H_2(CO)_{12}(\mu\text{-}PR)]$ (R = Ph *or* cyclo-C_6H_{11}. Typically $[Os_3H(CO)_{10}(\mu\text{-}PHR)]$ (200 mg) and $[Os_3(CO)_{12}]$ (200 mg) were refluxed together in nonane (30 cm^3) for 20 h. During this time the reaction mixture darkens from pale yellow to deep red (R = Ph) or red-brown (R = cyclo-C_6H_{11}). After cooling, the solvent was removed *in vacuo* and the residue subjected to column chromatography using hexane as eluant. The first faint yellow band removed was found to be a mixture of $[Os_4H_4(CO)_{12}]$ and $[Os_3H_2(CO)_9(\mu\text{-}PR)]$ (*ca.* 30—40 mg) which were identified by comparison of their spectroscopic properties with those of authentic samples. This band was closely followed by a second yellow band from which crystallised pale yellow $[Os_4H_2(CO)_{12}(\mu\text{-}PR)]$ (*ca.* 20—50 mg). The eluant was then changed to 10% CH_2Cl_2–hexane to remove first a deep red band. Recrystallisation of the product from this band gives red-black blocks of $[Os_5(CO)_{15}(\mu\text{-}PR)]$ (*ca.* 260—200 mg). Continued elution of the column with CH_2Cl_2–hexane gave a brown band, which was recrystallised from toluene–hexane to give a black crystals of $[Os_6(CO)_{17}(\mu\text{-}PR)]$ (*ca.* 20—30 mg).

Changing $[Os_3H_2(CO)_{10}]$ for $[Os_3(CO)_{12}]$ and/or $[Os_3H_2(CO)_9(\mu\text{-}PR)]$ for $[Os_3H(CO)_{10}(\mu\text{-}PHR)]$ was found to have little effect on either product distribution or yield of these reactions.

(*iii*) *Heteronuclear phosphinidene clusters.* $[Os_3Ru_3(CO)_{17}(\mu\text{-}PR)]$, $[Os_3Ru_2(CO)_{15}(\mu\text{-}PR)]$, *and* $[Os_3RuH_2(CO)_{12}(\mu\text{-}PR)]$ (R = Ph *or* cyclo-C_6H_{11}). The appropriate cluster $[Os_3H(CO)_{10}(PRH)]$ (150 mg) and $[Ru_3(CO)_{12}]$ (160 mg) were refluxed together in octane (30 cm^3) for 21 h. The reaction mixture slowly darkens from yellow to dark brown. After taking the reaction mixture to dryness *in vacuo*, the residue was chromatographed using either 15% toluene–hexane (R = Ph) or 8% toluene–hexane (R = cyclo-C_6H_{11}) as eluant. A light yellow band containing traces of $[Ru_4H_4(CO)_{12}]$ and $[Os_4H_2(CO)_{12}(\mu\text{-}PR)]$ (*ca.* 20 mg) was crystallised. This was followed by a red-brown band. Recrystallisation of the residue from this band from CH_2Cl_2–hexane gives dark brown-red pyramidal crystals of $[Os_3Ru_2(CO)_{15}(\mu\text{-}PR)]$ (*ca.* 95—105 mg). Next eluted was an orange band which gave a small amount of $[Ru_6C(CO)_{17}]$ (*ca.* 5—15 mg) and finally a brown band from which crystallised black rhombs of $[Os_3Ru_3(CO)_{17}(\mu\text{-}PR)]$ (*ca.* 30—40 mg).

Crystal Structure Determination of $[Os_4(\mu\text{-}H)_2(CO)_{12}(\mu_3\text{-}PC_6H_{11})]$ (**2**).—Suitable single crystals of (**2**) were obtained by slow crystallisation from hexane solution, and a crystal was mounted on a glass fibre with epoxy-resin.

Crystal data. $C_{18}H_{13}O_{12}Os_4P$, M = 1 213.05, orthorhombic, a = 8.666(1), b = 35.523(3), c = 16.723(1) Å, U = 5 148.0 Å^3 (by least-squares refinement on diffractometer angles for 58 automatically centred reflections in the range $15 < 2\theta < 22°$, λ = 0.710 69 Å), space group $Pc2_1b$ (alternative setting $Pca2_1$, no. 29), Z = 8, D_c = 3.13 g cm^{-3}, $F(000)$ = 4 400. Yellow platelet; crystal dimensions (distance to faces from centre): 0.040 $(010, 0\bar{1}0) \times 0.127\ (011, 0\bar{1}\bar{1}) \times 0.174\ (\bar{1}11, 1\bar{1}\bar{1}) \times 0.190\ (212, \bar{2}\bar{1}\bar{2})$ nm; μ(Mo-K_α) = 197.94 cm^{-1}.

Data collection and processing.[18] Stoe-Siemens AED diffractometer, 24-step ω scan mode with scan width of 0.04° for each step, scan time 0.75—3.0 s per step, graphite-monochromated Mo-K_α radiation. 7 499 Reflections measured ($5.0 < 2\theta < 45.0°$, $-h$, $-k$, $\pm l$), 3 432 unique [merging R = 0.080 after numerical absorption correction (max., min. transmission factors 0.233, 0.022)] giving 2 979 with $F > 5\sigma(F)$. Three standard reflections showed no significant variation in intensity.

Structure analysis and refinement. Computer-aided interpretation of Patterson synthesis (Os atoms) followed by Fourier difference techniques. Blocked full-matrix least-squares refinement with Os and P atoms anisotropic. Os–C(carbonyl) and C–O distances constrained at 1.910(1) and 1.160(1) Å, respectively. The weighting scheme $w = 2.724/[\sigma^2(F_o) + 0.001F_o^2]$ with $\sigma(F_o)$ from counting statistics gave satisfactory agreement analyses. Final Fourier difference map showed ripples of *ca.* 7 e Å^{-3} close to Os atom positions but no other areas of significant electron density. Final R and R' values were 0.056 and 0.056. Programs and computers used and sources of scattering factor data are given in ref. 18. Final atomic co-ordinates are presented in Table 3. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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