Trinuclear clusters of osmium containing monodentate, chelating and orthometallated forms of 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP)

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The trinuclear cluster [Os$_3$(CO)$_{11}${(R)-BINAP}] **1** containing monodentate (R)-BINAP is formed by thermal treatment of [Os$_3$(CO)$_{12}$] with 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, (R)-BINAP. This complex decarbonylates thermally to give the cluster [Os$_3$(CO)$_{10}${(R)-BINAP}] **2**, which was shown spectroscopically to contain chelating BINAP. On further thermal decarbonylation orthometallation at a phenyl group takes place to give [Os$_3$(μ-H)(CO)$_8${μ$_3$-(R)-BINAP − H}] **3**. There is no evidence for restricted rotation about the P–Ph bonds within the PPh$_2$ groups as we have previously observed for [Ru$_3$(μ-OH)$_2$(CO)$_8${μ-(R)-BINAP}]. This restricted rotation is an effect of crowding and appears to be a distinct property of μ-coordination rather than chelation of BINAP. However, both clusters **1** and **2** are fluxional, but as a result of different processes. Cluster **1** exists as two interconverting isomers **1A** and **1B** (^{31}P NMR evidence) which we believe have different conformations within the monodentate (R)-BINAP ligand. Our observations are consistent with restricted rotations about the Ph$_2$P–naphthyl bonds. The decacarbonyl cluster **2** has C_2 symmetry and shows ^{13}C NMR coalescences consistent with a dynamic merry-go-round motion at the two Os(CO)$_4$ units but not at the Os(CO)$_2$(BINAP) unit. Single-crystal structures of clusters **1** and **3** confirm these two new modes of BINAP coordination.

Chiral diphosphines as chelating ligands have been extensively used in transition-metal-catalysed asymmetric reactions of organic substrates.[1] A notable example is the application of 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP)[2] with ruthenium(II) and rhodium(I) to enantioselective catalysis, giving high enantiomeric excesses in many cases.[3] Structural studies have been carried out for a number of complexes in which BINAP is chelating.[4] Even in the cluster [Ru$_4$(μ-H)$_4$-(CO)$_{10}${(S)-BINAP}], formed by direct reaction of [Ru$_4$(μ-H)$_4$-(CO)$_{12}$] with (S)-BINAP, the ligand is chelating.[5] We have recently characterized the first example of a bridging BINAP ligand in the cluster [Ru$_3$(μ-OH)$_2$(CO)$_8${μ-(R)-BINAP}], which interestingly is crowded to the extent of having restricted rotation about two of the four P–Ph bonds.[6] We now report our results on introducing (R)-BINAP into triosmium clusters to give products with three different modes of coordination. Monodentate BINAP is found in [Os$_3$(CO)$_{11}${(R)-BINAP}] **1**, chelating BINAP in [Os$_3$(CO)$_{10}${(R)-BINAP}] **2**, and ortho-metallated BINAP in the cluster [Os$_3$(μ-H)(CO)$_{11}${(R)-BINAP − H}] **3**. The modes of coordination in **1** and **3** are unprecedented and were confirmed by crystal structure determination. Interestingly we were unable to identify an isomer of **2** containing bridging BINAP. This is surprising in view of the bridging nature of BINAP in [Ru$_3$(μ-OH)$_2$(CO)$_8${μ-(R)-BINAP}][6] and in [Os$_3$(μ-H)$_2$(CO)$_8${μ-(R)-TolBINAP}],[7] where TolBINAP is the 4-tolyl analogue of BINAP.

One of the objectives of this work, still to be realised, is the incorporation of a chelating chiral diphosphine at one metal centre or a bridging chiral diphosphine at two metal centres in clusters and the examination of the reactivity at the remaining metal atoms to establish whether chiral selectivity can be transmitted across a cluster and between metal atoms. In this paper we report our initial characterization of some BINAP derivatives of triosmium clusters and are able to report two new modes of BINAP coordination in addition to chelation and bridging.

1

2

3
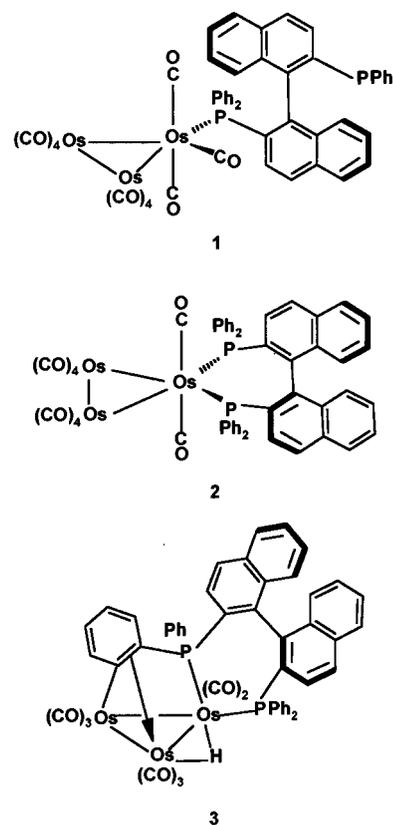
Results and discussion

Treatment of [Os$_3$(CO)$_{12}$] with (R)-BINAP in refluxing hydrocarbon solvent (heptane or octane) gave three isolable products which are air and thermally stable and can be separated on silica. Similar products but in different yields were obtained
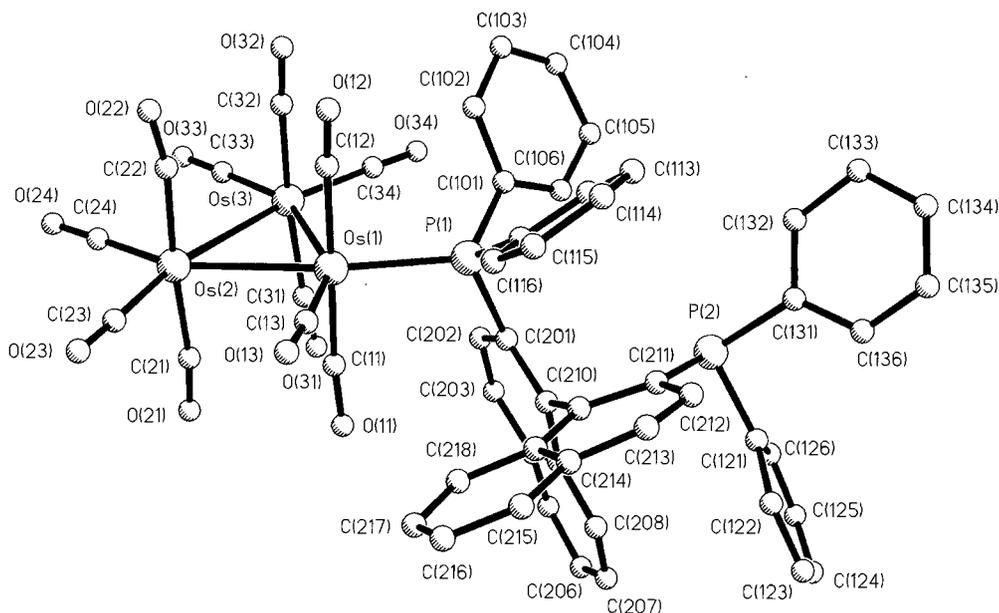
Fig. 1 Molecular structure of $[Os_3(CO)_{11}\{(R)\text{-BINAP}\}]$ **1**.

Table 1 Selected bond lengths (Å) and angles (°) for the cluster $[Os_3(CO)_{11}\{(R)\text{-BINAP}\}]$ **1**

Os(1)–Os(2)	2.989(2)	P(1)–C(111)	1.83(3)
Os(2)–Os(3)	2.880(2)	P(1)–C(201)	1.88(2)
Os(1)–Os(3)	2.915(2)	P(2)–C(121)	1.83(2)
Os(1)–P(1)	2.405(6)	P(2)–C(131)	1.84(2)
P(1)–C(101)	1.80(3)	P(2)–C(211)	1.80(2)
Os(1)–Os(3)–Os(2)	60.00(4)	Os(1)–P(1)–C(201)	110.8(7)
Os(2)–Os(1)–Os(3)	59.40(4)	C(101)–P(1)–C(111)	99.4(12)
Os(1)–Os(2)–Os(3)	60.60(4)	C(101)–P(1)–C(201)	100.0(12)
Os(3)–Os(1)–P(1)	102.8(2)	C(111)–P(1)–C(201)	113.3(12)
Os(2)–Os(1)–P(1)	161.9(2)	C(121)–P(2)–C(131)	100.7(12)
Os(1)–P(1)–C(101)	117.2(8)	C(121)–P(2)–C(211)	102.2(14)
Os(1)–P(1)–C(111)	114.9(8)	C(131)–P(2)–C(211)	102.7(11)

when the mixture is saturated with CO gas during the reaction or when (R)-BINAP is treated with $[Os_3(CO)_{10}(MeCN)_2]$ in THF. The FAB mass spectra of the products in a 3-nitrobenzyl alcohol matrix are consistent with the apparent formulae $[Os_3(CO)_x\{(R)\text{-BINAP}\}]$ **1** (x = 11), **2** (x = 10) and **3** (x = 8).

Spectroscopy and structure of $[Os_3(CO)_{11}\{(R)\text{-BINAP}\}]$ **1**

As expected, cluster **1** contains monodentate BINAP. The ^{1}H NMR spectrum is complex, consistent with an unsymmetrical BINAP ligand, and the ^{31}P-{^{1}H} NMR spectrum shows two moderately broad singlets at δ −14.1 and 8.2 at room temperature which sharpen at 40 °C. Free BINAP gives a signal at δ −14.5 and therefore it is reasonable to suppose that the two signals for **1** correspond to coordinated (δ 8.2) and free (δ −14.1) phosphorus atoms. Monodentate BINAP has not previously been observed so we have determined the single-crystal structure of cluster **1**, obtained as yellow crystals of the dichloromethane solvate, **1**·0.5CH$_2$Cl$_2$, by evaporation of a dichloromethane-hexane mixture. Generally we have found that clusters containing BINAP are difficult to crystallize in a suitable form for single-crystal studies and the two structures reported in this paper are for crystals that are not of ideal quality. In addition there was the problem that **1**·0.5CH$_2$Cl$_2$ formed thin plates. The molecular structure is shown in Fig. 1 and selected bond lengths and angles are in Table 1. The structure has the monodentate BINAP ligand in an equatorial site as we predicted from NMR data. There is no evidence in the many crystal structures determined for clusters of the type $[M_3(CO)_{11}L]$ (M = Ru or Os, L = tertiary phosphine or arsine)

for coordination in any but an equatorial position.[8] Axial sites are crowded as a result of interactions between axial ligands and, although axial substitution is probably favoured electronically, it is only observed with small or rod-shaped ligands.[9] Relative to the structure of (R)-BINAP in the crystal,[6] there has been a rotation about one naphthyl–PPh$_2$ bond to allow coordination to Os(1). In free (R)-BINAP the two lone-pairs are directed inwards and the uncoordinated PPh$_2$ group in **1** has a similar conformation to that of the PPh$_2$ groups in the crystal structure of the free ligand.

Variable-temperature NMR spectra of **1** were recorded to explore possible nonrigidity. Indeed, there are clear changes in the ^{31}P-{^{1}H} NMR spectrum in CDCl$_3$ with changes in temperature (Fig. 2). The two sharp singlets for free and coordinated ^{31}P nuclei at 27 °C broaden considerably at −20 °C and resolve at −55 °C into four sharp singlets at δ −10.8 and 5.4 (major isomer **A**) and at δ −17.9 and 8.7 (minor isomer **B**). The mol ratio **A**:**B** = 1.65:1. We considered initially that these isomers might have different sites of attachment of BINAP at the Os$_3$(CO)$_{11}$ unit, but the IR spectrum of the isomeric mixture in solution is closely similar to those of other tertiary phosphine compounds of the type $[Os_3(CO)_{11}L]$ in which the ligand L is known to be equatorial.[8] The simplicity of the spectrum is only consistent with equatorial coordination for both isomers **1A** and **1B** present in solution. Hence we conclude that the isomers both have equatorial coordination but with different conformational arrangements within the η[1]-BINAP ligand which do not affect the ν(CO) IR spectrum. Note that the largest chemical shift difference between the isomers is for the free PPh$_2$ group (Fig. 2). Rotation about the Ph$_2$P–naphthalene bonds leads to the lone-pair pointing inwards or outwards from the centre of the ligand. In free BINAP in the solid both lone-pairs point inwards in parallel directions, while one of those in cluster **1** points inwards as in free BINAP but the coordinated one, of necessity, points outwards. We believe therefore that isomers **1A** and **1B** may have the conformations in–out and out–out (approximate lone-pair directions) respectively and that rotation about the Ph$_2$P–naphthalene bond for the uncoordinated PPh$_2$ group is rapid at room temperature. At −55 °C this rotation is slow leading to the observed spectra (Fig. 2). Fig. 3 represents our proposed structures for isomers **1A** and **1B**. When the lone-pair is pointing outwards, one phenyl group has a close parallel alignment with the distant naphthyl group. We are attempting to synthesize $[\{Os_3(CO)_{11}\}_2\{(R)\text{-BINAP}\}]$ in which the out–out arrangement
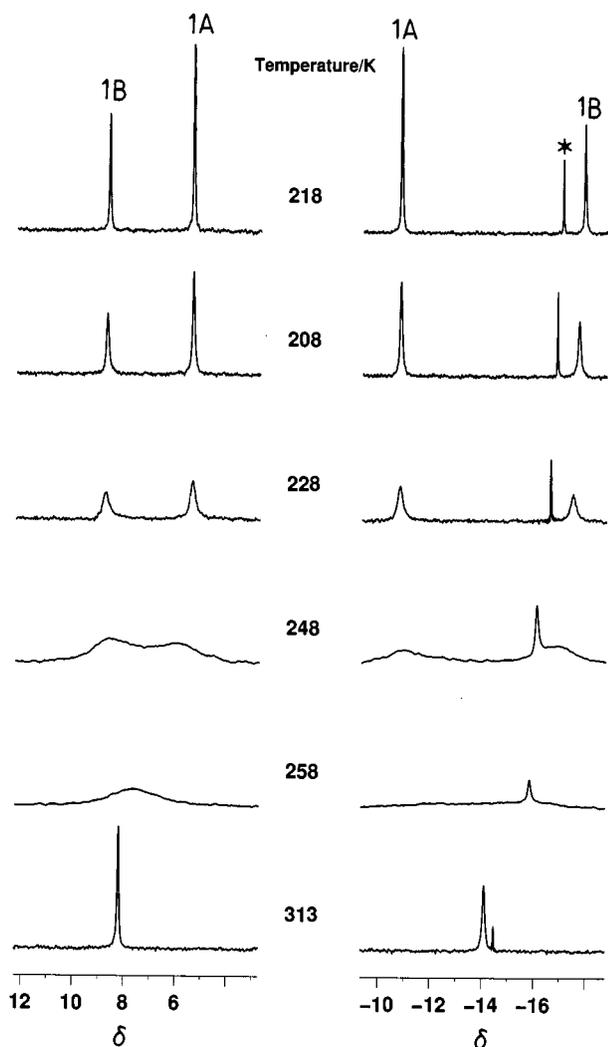
Fig. 2 ^{31}P-{^{1}H} NMR spectra of [Os$_3$(CO)$_{11}${(R)-BINAP}] **1** in CDCl$_3$. The coordinated PPh$_2$ group gives the signals to the left and the free PPh$_2$ group those to the right. The peak marked with * corresponds to free (R)-BINAP.
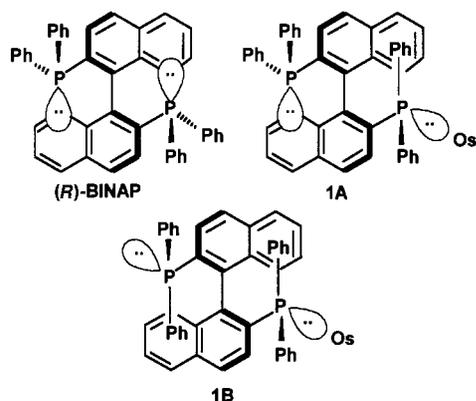

Fig. 3 Conformation of (R)-BINAP in the solid state[6] (left) with proposed conformations leading to isomers **1A** and **1B** for [Os$_3$(CO)$_{11}$-{(R)-BINAP}].

would be required for the BINAP bridge. This would then give two parallel alignments between phenyl and naphthyl groups.

We have also examined the ^{31}P-{^{1}H} NMR spectra of free BINAP over a range of temperatures to see whether similar conformers to those in cluster **1** are present. There is no evidence for this because the ^{31}P-{^{1}H} 600 MHz NMR spectrum of free BINAP in a 1:1 CD$_2$Cl$_2$–C$_2$Cl$_4$F$_2$ mixture is a sharp singlet down to −100 °C. Either there is only one conformer
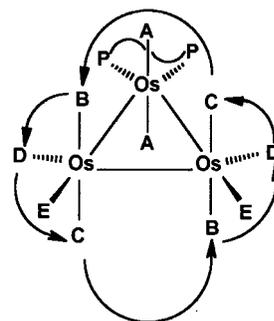

Fig. 4 Representation of cluster 1,1-[Os$_3$(CO)$_{10}${(R)-BINAP}] **2** showing the five non-equivalent CO ligands, A to E, and a mechanism leading to the exchange of carbonyl B, C and D without exchange with A and E.

present in solution or two or more conformations are in rapid exchange even at −100 °C.

Spectroscopy and structure of [Os$_3$(CO)$_{10}${(R)-BINAP}] 2

Unfortunately we were unable to obtain suitable single crystals for XRD to establish whether BINAP is chelating or bridging in **2**. We have compared the ν(CO) IR spectra of **2** with those of related complexes of the type [Os$_3$(CO)$_{10}$(diphosphine)] which are known to contain either chelating or bridging diphosphines.[10] Isomers are formed in some cases. For example 1,1- and 1,2-isomers of [Os$_3$(CO)$_{10}$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)] have been characterized.[11] We also compared IR spectra of **2** with those of the 1,1- and 1,2-isomers of [Os$_3$(CO)$_{10}$(PMe$_2$Ph)$_2$].[12] Unfortunately the IR spectrum of **2** did not correspond unambiguously with either spectrum of these isomeric forms, although the match was closer for the 1,1-isomers. However, the ^{13}C-{^{1}H} NMR spectra clearly indicate that BINAP is chelating and the cluster is without doubt the 1,1-isomer. It is predicted that there will be five different CO ligand environments in ratio 2:2:2:2:2 for both 1,1- and 1,2-isomers of **2** (Fig. 4 shows the 1,1-isomer). Five signals are indeed observed at −65 °C at δ 203.0, 187.2, 186.1, 174.4 and 169.9 (Fig. 5). The observation of a 1:2:1 triplet for the signal at δ 203.0 (J_{PC} = 7.9 Hz) (more clearly resolved at intermediate temperatures) can only be reconciled with the 1,1-structure with this signal assigned to the carbonyl ligands **A** (Fig. 4). For comparison, the 1,1-isomer of [Os$_3$(CO)$_{10}$(PMe$_2$Ph)$_2$] gives a 1:2:1 triplet at δ 202.1 (J_{PC} = 9.5 Hz) for the corresponding axial carbonyl ligands of the Os(CO)$_2$(PMe$_2$Ph)$_2$ group. This assignment of structure for **2** is confirmed by the pattern of NMR coalescences at higher temperatures. Three of the five CO signals (those at δ 186.1, 174.4 and 169.9) broaden on raising the temperature to −5 °C and are close to coalescence at 40 °C. The signals at δ 203.0 and 187.2 remain sharp over this temperature range. A process involving a merry-go-round exchange at the Os$_2$(CO)$_8$ unit with intermediates containing bridging CO will exchange the CO ligands **B**, **C** and **D** while leaving the CO ligands **A** and **E** unaffected as observed. Fig. 4 shows this process for cluster **2** which we believe is the only one to fit the observed behaviour simply. We did not measure the spectrum above 40 °C because of thermal decarbonylation to give cluster **3** at higher temperatures. We believe there is no way to interpret this NMR behaviour for the alternative structure of **2**, that is 1,2-[Os$_3$(CO)$_{10}${(R)-BINAP}].

Spectroscopy and structure of [Os$_3$(μ-H)(CO)$_8$(μ-(R)-BINAP − H}] 3

The cluster **3** was assigned the apparent stoichiometry [Os$_3$(CO)$_8${(R)-BINAP}] from its mass spectrum but it is not surprising that this apparently unsaturated cluster has undergone internal oxidative addition. The ^{1}H and ^{13}C-{^{1}H} NMR spectra are extremely complex but the double doublet signal in the hydride region of the ^{1}H NMR spectrum at δ −16.86
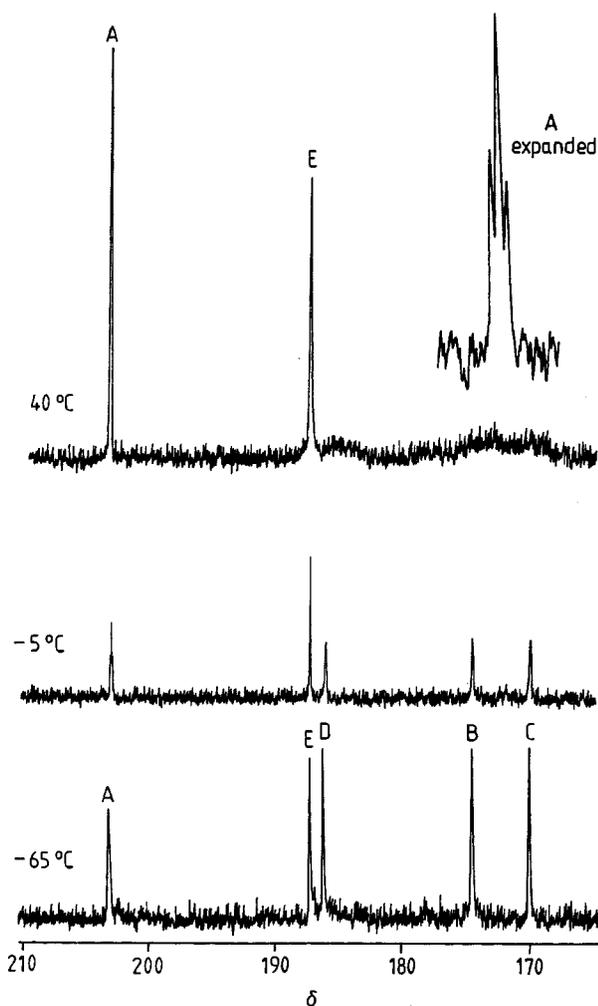
Fig. 5 $^{13}C\text{-}\{^1H\}$ NMR spectra of 1,1-[Os$_3$(CO)$_{10}$\{(*R*)-BINAP\}] **2** showing assignment of signals with reference to Fig. 4, the coalescence of signals B, C and D, and the triplet pattern for signal A.

(J_{PH} = 8.4 and 17.3 Hz) is consistent with an orthometallation product. An examination of the aromatic region seems to indicate metallation at a phenyl group. The $^{31}P\text{-}\{^1H\}$ NMR spectrum (^1H-decoupled in the aromatic but not the hydride region) shows a double doublet for each of the non-equivalent phosphorus nuclei as expected.

A single-crystal structure determination established the arrangement of the orthometallated BINAP ligand at the triosmium unit. Generally poor crystals were obtained from a methanol–dichloromethane solution but an adequate crystal was found for study. The molecular structure is shown in Fig. 6 and selected bond lengths and angles are in Table 2. Unlike the precursor cluster **2** which has 1,1-diequatorial BINAP coordination, cluster **3** has 1,1-axial-equatorial coordination of the BINAP at Os(2) as well as a bridging coordination of the orthometallated phenyl group at Os(1) and Os(3). Fig. 6 shows that the mode of μ$_3$-bridging in this ligand system requires the BINAP to have axial–equatorial coordination. Thus Os(2) is bonded to P(1) and P(2) and orthometallation has occurred at Os(3) which carries the σ-Os(3)–C(101) bond, while Os(1) has an η^2-contact to C(101) and C(106) of the orthometallated phenyl ring. The geometry of the η^1:η^2-phenyl is unexceptional with the σ-Os(3)–C(101) bond being significantly shorter than the Os–C distances in the η^2-contact. The hydride ligand was not located but CO ligand positions show that it is bridging Os(2) and Os(3), which is the longest Os–Os contact [3.061(2) Å] compared with Os(1)–Os(2) [2.885(2) Å] and Os(1)–Os(3) [2.799(2) Å]. The hydride must lie close to the intersection of the C(22)–Os(2) and C(33)–Os(3) vectors, slightly above the Os$_3$ plane. The orthometallated ligand is a seven-electron donor

Table 2 Selected bond lengths (Å) and angles (°) for the cluster [Os$_3$-(μ-H)(CO)$_8$\{(*R*)-BINAP − H\}] **3**

Os(1)–Os(2)	2.885(2)	Os(1)–C(106)	2.45(3)
Os(2)–Os(3)	3.061(2)	P(1)–C(111)	1.80(5)
Os(1)–Os(3)	2.799(2)	P(1)–C(201)	1.84(4)
Os(2)–P(1)	2.399(9)	P(1)–C(106)	1.86(4)
Os(2)–P(2)	2.380(10)	P(2)–C(121)	1.83(4)
Os(1)–C(101)	2.35(3)	P(2)–C(131)	1.86(4)
Os(3)–C(101)	2.11(3)	P(2)–C(211)	1.87(3)
P(1)–Os(2)–P(2)	93.5(4)	Os(2)–P(2)–C(121)	119.0(14)
Os(1)–Os(2)–P(1)	74.4(30)	Os(2)–P(2)–C(131)	115.0(12)
Os(3)–Os(2)–P(1)	84.5(2)	Os(2)–P(2)–C(211)	107.3(11)
Os(2)–P(1)–C(201)	112.4(4)	P(1)–C(106)–C(101)	119(3)
Os(2)–P(1)–C(111)	124(2)	P(1)–C(106)–C(105)	118(3)
Os(2)–P(1)–C(106)	105.0(12)		

making the cluster a 48-electron species. Although we would expect there to be three Os–Os bonds, the Os(2)···Os(3) distance of 3.061(2) Å would normally be considered too long for a bonding interaction.

We previously reported the cluster [Ru$_3$(μ-H)(CO)$_9$\{μ-(*R*)-BINAP − H\}][6] which has significantly different spectroscopic characteristics from those of cluster **3** but this is not surprising since the Ru cluster has an extra CO ligand. Most likely the η^1:η^2 bridging nature of the orthometallated phenyl in **3** is replaced by an η^1 coordinated phenyl in the Ru compound without any η^2 contact. No suitable crystals for XRD work were formed and therefore this cannot be confirmed.

Experimental

Materials and spectra

The clusters [Os$_3$(CO)$_{12}$] and [Os$_3$(CO)$_{10}$(MeCN)$_2$] were prepared by published methods.[13,14] The (*R*)-BINAP was used as obtained from Aldrich. Octane, heptane, and decane used were dried over sodium wire. Solvents THF and dichloromethane were dried and re-distilled. 300 and 400 MHz spectra were obtained on a Bruker AC300 and Varian VXR400 spectrometers at UCL respectively. 600 MHz spectra were obtained on the University of London Intercollegiate Research Service using a Bruker AMX600 spectrometer at Queen Mary and Westfield College. ^{31}P NMR spectra (ref. H$_3$PO$_4$) were obtained on a Bruker AMX400 spectrometer (University of London Intercollegiate Research Service at King's College London). IR spectra were obtained on a Nicolet 280 FT-IR spectrometer, and FAB MS (3-nitrobenzyl alcohol matrix) on a ZAB mass spectrometer.

Direct thermal reaction of [Os$_3$(CO)$_{12}$] with BINAP in heptane

A solution of BINAP (0.040 g) and [Os$_3$(CO)$_{12}$] (0.060 g) in heptane (25 cm^3) was refluxed under nitrogen for 3.5 h. The solution became darker after 1.5 h and faint orange after 3.5 h. The solution was cooled to 5 °C for one hour to allow the excess of [Os$_3$(CO)$_{12}$] to crystallize. After filtration through a thin layer of silica, the solvent was removed from the filtrate under reduced pressure. The residual solid was separated by preparative TLC (2 mm, Merck 1045), eluting with a dichloromethane–hexane mixture (3:7 by volume). Three bands yielded yellow **1** (10%), orange **2** (15%) and yellow **3** (14%) respectively. Cluster **1**: IR (cyclohexane), ν(CO)/cm^{-1}: 2066vs, 2030vs, 2009s, 1992vw, 1976vs, 1961s, 1942w. ^1H NMR (CDCl$_3$, 20 °C): δ 6.15 (t), 6.45 (d), 6.5 to 7.8 (overlapping multiplets), 8.40 (dt). ^{31}P-\{^1H\} NMR (CDCl$_3$, 20 °C): δ −14.1 (s) and 8.2 (s) at 40 °C and δ 5.4 (s), −10.8 (s) (isomer **1A**), 8.7 (s), −17.9 (s) (isomer **1B**) at −55 °C. FAB MS: observed centre of isotopic envelope 1504, calculated for parent molecular ion 1500. Cluster **2**: IR (cyclohexane), ν(CO)/cm^{-1}: 2095m, 2049s, 2015s, 2010vs, 1999m, 1988m, 1971w, 1904w. ^1H NMR (CDCl$_3$, 20 °C): δ 6.40 (d), 6.85
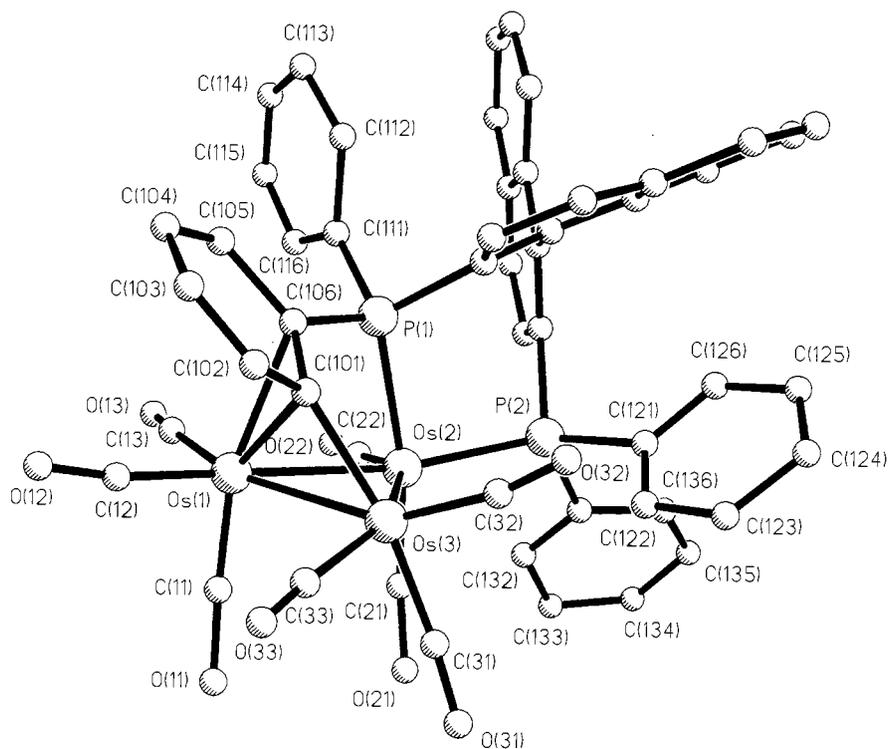
Fig. 6 Molecular structure of [Os₃(μ-H)(CO)₈{(R)-BINAP − H}] **3**.

(d), 6.92 (td), 7.0 to 7.3 (overlapping m), 7.35 (td), 7.45 (dd), 7.84 (d), 7.89 (d). ^{13}C-{^{1}H} NMR (100 MHz, CDCl₃, 20 °C): δ 203.0, 187.2, 186.1, 174.4, 169.9 (CO-signals), 141 to 125 (aryl signals, many overlapping). ^{31}P-{^{1}H} NMR (CDCl₃, 20 °C) δ −5.8 (s). FAB MS: observed centre of isotopic envelope 1473, calculated for parent molecular ion 1472. Cluster **3**: IR (cyclohexane) ν(CO)/cm^{-1}: 2108m, 2055s, 2037s, 2020vs, 2000m, 1992s, 1979s, 1963w, 1958w. ^{1}H NMR (CDCl₃, 20 °C): δ 8.46 (d), 7.7 to 7.2 (overlapping m), 7.10 (dt), 6.93 (m), 6.8 to 6.6 (overlapping m), 6.40 (d), 6.19 (dd), −16.86 (dd, J_{PH} = 8.4, 17.3 Hz). ^{13}C-{^{1}H} NMR (CDCl₃, 20 °C,): δ 184.7, 183.8, 178.8, 178.1 (CO-signals), 151 to 122 (complex aryl signals). ^{31}P-{^{1}H} NMR (CDCl₃, 20 °C): δ 4.18 and 2.13. FAB MS: observed centre of isotopic envelope 1417, calculated for parent molecular ion 1417 (Found: C, 45.35; H, 2.7; P, 4.0. C₅₂H₃₂O₈Os₃P₂ requires C, 44.1; H, 2.3; P, 4.35%). A similar reaction in refluxing octane (1.5 h) gave **1** (12%), **2** (24%) and **3** (36%) and a reaction in refluxing decane (45 min) with CO bubbling through the reaction mixture. Thermolysis of [Os₃(CO)₁₁(BINAP)] **1** in toluene-d₈ in a 10 mm NMR tube at 105 °C over 5.5 hours gave conversion to clusters **2** and **3**.

Reaction of [Os₃(CO)₁₀(MeCN)₂] with BINAP

The cluster [Os₃(CO)₁₀(MeCN)₂] (0.10 g) and an equimolar quantity of (R)-BINAP were refluxed in dry THF (25 cm³) for 30 min. The products isolated by TLC on silica were **2** (50%) and minor quantities of **1** and **3** which were only characterized by their IR spectra. Cluster **1** is probably formed from traces of [Os₃(CO)₁₁(MeCN)] in the osmium starting material.

Crystallography

Yellow crystals of **1·0.5CH₂Cl₂** and **3** were grown from hexane–dichloromethane mixtures. X-Ray data were collected at room temperature using a Nicolet R3v/m diffractometer with crystals mounted in air. Details of the crystal structure determinations are given in Table 3. Structures were solved by direct methods using SHELXTL PLUS[15] and refined using SHELXL 93.[16] All non-H atoms of **1·0.5CH₂Cl₂** except for CH₂Cl₂ were refined anisotropically and the dichloromethane

Table 3 Crystal data and structure solution and refinement parameters for clusters **1·0.5CH₂Cl₂** and **3**[a]

	1·0.5CH₂Cl₂	3
Formula	C₅₅.₅H₃₃ClO₁₁Os₃P₂	C₅₂H₃₂O₈Os₃P₂
M	1543.81	1417.32
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$
a/Å	15.610(4)	10.661(4)
b/Å	10.957(2)	21.26(2)
c/Å	16.186(4)	24.21(2)
β/°	108.97(2)	90
U/Å³	2618.0(11)	5489(6)
Z	2	4
μ(Mo-Kα)/cm^{-1}	74.34	70.32
Scan mode	ω-2θ	ω
2θ range/°	5–50	5–50
hkl range	0,0,−18 to 18,13,18	0,0,0 to 12,25,28
Total data	4958	5266
Unique data	4773	5266
Parameters in refinement	571	321
R (all data)[b]	0.0783	0.1131
[$I > 2\sigma(I)$]	0.0595	0.0891
$wR2$ (all data)[c]	0.161	0.273
[$I > 2\sigma(I)$]	0.136	0.241
Goodness of fit	1.068	1.075
Abs. struct. parameter	−0.02(3)	0.02(5)

[a] Both structures: direct methods structure solution, graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å), three standard reflections every 97, no decay, data corrected for absorption empirically by ψ-scan method, maximum and minimum transmission 0.986 and 0.501 for **1** and 0.930 and 0.728 for **3**, full-matrix least-squares refinement of F^2. [b] $R = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. [c] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{\frac{1}{2}}$ where $w = 1/[\sigma^2(F_o)^2 + (0.0578p)^2 + 54.72p]$ for **1** and $w = 1/[\sigma^2(F_o)^2 + (0.0866p)^2 + 478.5p]$ for **3**, where $p = (F_o^2 + 2F_c^2)/3$.

C and Cl atoms were filled into final cycles of refinement. Only the Os, P and O atoms of **3** were refined anisotropically. H-atoms in both crystals were included in idealised positions, riding upon their respective carbon atoms, with C–H distance fixed at 0.96 Å and isotropic thermal parameters at 0.08 Å³.

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See http://www.rsc.org/suppdata/dt/1998/3819/ for crystallographic files in .cif format.

Acknowledgements

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