

Systematic synthesis of substituted hexanuclear phosphide- and phosphinidene-bridged osmium clusters ‡

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The labilised clusters $[\text{Os}_3(\text{CO})_{11-n}\text{L}_n(\text{NCMe})]$ [$n = 1$, $\text{L} = \text{PMe}_3$ or CNBu^t ; $n = 2$, $\text{L} = \text{P}(\text{OMe})_3$] have been prepared. The reaction of $[\text{Os}_3(\text{CO})_{11-n}\text{L}_n(\text{NCMe})]$ or $[\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}(\text{NCMe})]$ with either $[\text{Os}_3(\text{CO})_{11}(\text{PH}_3)]$ or $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-PH}_2)]$ led to the formation of the phosphide-bridged clusters $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}\{\text{P}(\text{OMe})_3\}(\mu\text{-PH}_2)]$, $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}(\text{PMe}_3)(\mu\text{-PH}_2)]$, $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}(\text{CNBu}^t)(\mu\text{-PH}_2)]$, $[\text{Os}_6(\mu\text{-H})(\text{CO})_{20}\{\text{P}(\text{OMe})_3\}_2(\mu\text{-PH}_2)]$ and the corresponding phosphinidene-bridged clusters $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{21-n}\text{L}_n(\mu_3\text{-PH})]$ [$n = 1$, $\text{L} = \text{CNBu}^t$; $n = 2$, $\text{L} = \text{P}(\text{OMe})_3$] in good yield. The Os_6 clusters have been fully characterised on the basis of their spectroscopic data and the molecular structures of three have been established by single-crystal X-ray analysis. The structures of $[\text{Os}_6(\mu\text{-H})(\text{CO})_{20}\{\text{P}(\text{OMe})_3\}_2(\mu\text{-PH}_2)]$ and $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{19}\{\text{P}(\text{OMe})_3\}_2(\mu_3\text{-PH})]$ differ from those of previously studied hexanuclear phosphide- and phosphinidene-bridged clusters; this difference is attributed to the steric influence of the relatively bulky phosphite ligands. Proton and phosphorus NMR spectroscopy indicate that both these clusters exist in two isomeric forms in solution.

The systematic construction of transition-metal carbonyl clusters containing linking and/or interstitial p-block atoms is an area of continuing interest. The main-group elements often stabilise the cluster bonding network and their reactivity may be used for build-up of metal clusters of high nuclearity.¹ It is known that dinuclear complexes with a bridging $\mu\text{-PRH}$ phosphido moiety will add oxidatively to sources of unsaturated metal fragments to give $\mu_3\text{-PR}$ bridged clusters.² We have shown that co-ordinated phosphine (PH_3) may be utilised to link clusters *via* oxidative addition of a P–H bond.^{3–5} The clusters $[\text{Os}_3(\text{CO})_{11}(\text{PH}_3)]$ **1** and $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-PH}_2)]$ **2** are useful starting materials for such linking reactions and several phosphide- and phosphinidene-bridged clusters, *e.g.* $[\text{Os}_6(\mu\text{-H})(\text{CO})_{22-n}(\text{NCMe})_n(\mu\text{-PH}_2)]$ ($n = 0$ **3** or **14**)⁶ and $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{21-n}(\text{NCMe})_n(\mu_3\text{-PH})]$ ($n = 0$ **5** or **16**)⁵ have been synthesised by the reaction of **1** or **2** with suitable labilised clusters. Linkage of three osmium triangles *via* two phosphide-bridges through the reaction of $[\text{Os}_3(\text{CO})_{10}(\text{PH}_3)_2]$ with 2 equivalents of $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$ has also been attempted. An intra- rather than inter-molecular reaction takes place; $[\text{Os}_3(\text{CO})_{10}(\text{PH}_3)_2]$ forms $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-PH}_2)]$ **2**³ which reacts with $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$ to form $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{21}(\mu_3\text{-PH})]$ **5**.

Thermolysis of the bridged clusters **3**, **5** and **6** leads to encapsulation of the phosphorus atom within a metal framework to form the interstitial phosphide clusters $[\text{Os}_6(\mu\text{-H})(\mu_6\text{-P})(\text{CO})_{18}]$ **7** and $[\text{Os}_6(\mu_6\text{-P})(\text{CO})_{18}]$ **8**.^{5–7} In order to functionalise and explore the reactivity of **7** and **8** attempts at substitution of these clusters have been undertaken. In general, direct substitution through thermolysis or decarbonylation *via* the addition of trimethylamine *N*-oxide leads to extensive decomposition of **7** and **8**.⁸ Similar results are obtained when the same type of reaction is carried out on the phosphinidene-bridged precursors **5** and **6**. Addition of trimethylamine *N*-oxide to **5** in the presence of PPh_3 or $\text{P}(\text{OMe})_3$ leads primarily to the formation of $[\text{Os}_3(\text{CO})_{12-n}(\text{PR}_3)_n]$ ($n = 1$ or 2 ; $\text{R} = \text{Ph}$ or OMe) but $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{21-n}(\text{PR}_3)_n(\mu_3\text{-PH})]$ ($n = 1$ or 2 ;

$\text{R} = \text{Ph}$ or OMe) is also formed in very low yields.⁹ Several isomeric forms of the latter clusters are formed; the isomers have been found to be very hard to separate by TLC. Unlike many other acetonitrile derivatives of osmium clusters, the acetonitrile ligands of **4** and **6** are not substitution labile, and these clusters are therefore not viable starting materials for the synthesis of other substituted derivatives. However, an indirect route to the synthesis of substituted derivatives of **3–6** is the coupling of **1** or **2** with trinuclear osmium clusters containing the desired ligand.¹⁰ Here, we report the synthesis of the new labilised clusters $[\text{Os}_3(\text{CO})_{11-n}\text{L}_n(\text{NCMe})]$ [$n = 1$, $\text{L} = \text{PMe}_3$ **9c** or CNBu^t **9d**; $n = 2$, $\text{L} = \text{P}(\text{OMe})_3$ **10**] and the subsequent coupling of these starting materials with **1** to form $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{21-n}\text{L}_n(\mu_3\text{-PH})]$ or **2** to form $[\text{Os}_6(\mu\text{-H})(\text{CO})_{22-n}\text{L}_n(\mu\text{-PH}_2)]$ ($n = 1$ or 2).

Results and Discussion

The labilised clusters $[\text{Os}_3(\text{CO})_{10}\text{L}(\text{NCMe})]$ are useful 'synthons' for cluster synthesis. The preparation of $[\text{Os}_3(\text{CO})_{10}(\text{PMe}_2\text{Ph})(\text{NCMe})]$ is mentioned in the literature¹¹ and we have previously reported the syntheses of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2(\mu\text{-dppe})]$ ($\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$)¹² and $[\text{Os}_3(\text{CO})_{10}(\text{PR}_3)(\text{NCMe})]$ ($\text{R} = \text{Ph}$ **9a** or OMe **9b**).¹⁰ This series of clusters has been extended to include $[\text{Os}_3(\text{CO})_{11-n}\text{L}_n(\text{NCMe})]$ [$n = 1$, $\text{L} = \text{PMe}_3$ **9c** or CNBu^t **9d**; $n = 2$, $\text{L} = \text{P}(\text{OMe})_3$ **10**]. Clusters **9c**, **9d** and **10** are readily synthesised by reaction of the appropriate cluster $[\text{Os}_3(\text{CO})_{12-n}\text{L}_n]$ ($n = 1$ or 2) with trimethylamine *N*-oxide in the presence of acetonitrile. Infrared spectroscopy indicates clean and complete conversion into the desired products and the spectroscopic data (Table 1) are entirely consistent with the proposed formulations. In addition to the resonances of the relevant phosphine/isocyanide, singlets at typical shifts found for co-ordinated acetonitrile ligands ($\delta \approx 2.57\text{--}2.67$) were found in the proton NMR spectra of **9c**, **9d** and **10**. Purification of **9c** by thin-layer chromatography resulted in relatively extensive cluster breakdown and this product was therefore usually not purified before being used in ensuing synthetic steps.

It is known that relatively bulky phosphines/phosphites prefer equatorial positions,¹³ while the linear acetonitrile easily co-ordinates in an axial position on trinuclear osmium

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Table 1 Spectroscopic data for new compounds

Complex	IR, $\nu(\text{C-O})(\text{CH}_2\text{Cl}_2)$	$^1\text{H NMR}$ (δ , J/Hz) ^a	$^{31}\text{P NMR}$ (δ , J/Hz) ^b	Mass (m/z) ^c
9c $[\text{Os}_3(\text{CO})_{10}(\text{PMe}_3)_3(\text{NCMe})]$	2080m, 2026vs, 2012s, 1992s, 1960ms	2.69 (s, NCMe ₃), 1.90 (d, $^2J_{\text{PH}} \approx 10.0$, PMe ₃)	–156.3 (s, PMe ₃)	Obs. 973 Calc. 932 [$^3\text{Os}_3(\text{CO})_{10}(\text{PMe}_3)^+$]
9d $[\text{Os}_3(\text{CO})_{10}(\text{CNBu}^t)(\text{NCMe})]$	2077m, 2056m, 2023vs, 1997vs, 1964s	2.65 (s, NCMe), 1.45 (s, NCBu ^t)		980 939 [$^3\text{Os}_3(\text{CO})_{10}(\text{CNBu}^t)^+$]
10 $[\text{Os}_3(\text{CO})_6(\text{P}(\text{OMe})_3)_2(\text{NCMe})]$	2063m, 2012s, 2000s (sh), 1975vs	3.62 [d, $^3J_{\text{PH}} \approx 8$, P(OMe) ₃], 2.64 (s, NCMe)	–34.4 [br s, P(OMe) ₃]	1117 1117
11a $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}(\text{P}(\text{OMe})_3)_3(\mu\text{-PH}_2)]$	2118w, 2093m, 2076m, 2050vs, 2040s, 2034s, 2012s, 1969m	4.16 [ddd, $^1J_{\text{PH}} \approx 325$, $^3J(\text{H}_\alpha\text{-H}_\beta) \approx 2$, $^2J(\text{H}_\alpha\text{-H}_\beta)$ not resolved, $\mu\text{-PH}_2$], 3.75 [d, $^3J_{\text{PH}} \approx 10$, P(OMe) ₃], –19.92 [dd 't', $^2J(\text{P-H}_\beta) \approx 14$, $J(\text{P-H}_\beta) \approx 8$, $^3J(\text{H}_\alpha\text{-H}_\beta) \approx 3J(\text{H}_\alpha\text{-H}_\beta) \approx 2$, OsH]	–366.0 (t, $^1J_{\text{PH}} \approx 325$, $^2J_{\text{PH}}$ not resolved, $\mu\text{-PH}_2$), –52.0 [s, P(OMe) ₃]	1898 1870 (= 15)
11b $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}(\text{PMe}_3)_3(\mu\text{-PH}_2)]$	2115mw, 2099m, 2071m, 2048s, 2028vs, 2010s, 1980m (sh)	3.94 [ddd, $^1J_{\text{PH}} \approx 320$, $^3J(\text{H}_\alpha\text{-H}_\beta) \approx 2$, $^2J(\text{H}_\alpha\text{-H}_\beta)$ not resolved, $\mu\text{-PH}_2$], 2.08 (d, $^2J_{\text{PH}} \approx 8.8$, PMe ₃), –20.09 [dd 't', $^2J(\text{P-H}_\beta) \approx 14$, $^2J(\text{P-H}_\beta) \approx 8$, $^3J(\text{H}_\alpha\text{-H}_\beta) \approx 3J(\text{H}_\alpha\text{-H}_\beta) \approx 2$, OsH]	–414.8 (t of d, $^1J_{\text{PH}} \approx 321$, $^2J_{\text{PH}} \approx 8.6$, $\mu\text{-PH}_2$), –190.5 (d, $^2J_{\text{PH}} \approx 18.5$, PMe ₃)	1850 1850
11c $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}(\text{CNBu}^t)_3(\mu\text{-PH}_2)]$	2112m, 2099ms, 2079s, 2060s, 2048s, 2028vs, 2010s, 1980m (sh)	4.04 (dd, AB pattern), 1.47 (s, CNBu ^t), –18.60 (d, $^2J_{\text{PH}} \approx 12.9$, OsH)	–409.2 (t of d, $^1J_{\text{PH}} \approx 331$)	1857 1857
12 $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{20}(\text{P}(\text{OMe})_3)_2(\mu\text{-PH}_2)]$	2097m, 2067m, 2047s, 2024vs (br), 2010s (sh), 1985m (sh), 1975 (sh)	3.89 (d of m, $^1J_{\text{PH}} \approx 320$, $\mu\text{-PH}_2$), 3.75 [d, $^3J_{\text{PH}} \approx 12$, P(OMe) ₃], 3.72 [d, $^3J_{\text{PH}} \approx 12$, P(OMe) ₃], –19.72, (m, OsH, major isomer), –19.89 (m, OsH, minor isomer, ratio between isomers ca. 2:1)	–417.5 (t, $^1J_{\text{PH}} \approx 320$, $^2J_{\text{PH}}$ not resolved, $\mu\text{-PH}_2$), –46.6 and –48.5 [s, P(OMe) ₃ , major isomer], –44.3 and –51.6 [s, P(OMe) ₃ , minor isomer]	1994 1994
13 $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{20}(\text{CNBu}^t)(\mu\text{-}_3\text{-PH})]$	2110w, 2092m, 2077ms, 2052m (sh), 2049vs, 2041ms, 2011s, 1968w	6.15 [dd, $^1J(\text{P-H}_\alpha) \approx 336$, $^3J(\text{H}_\alpha\text{-H}_\beta) \approx 4$, PH], 1.45 (s, CNBu ^t), –17.92 [dd, $^2J(\text{P-H}_\beta) \approx 14$, OsH _b], –18.66 [d, $^2J(\text{P-H}_\alpha) \approx 11$, OsH _c], $^3J(\text{H-H}_\alpha)$ not observed	–325.5 [d of 't', $^1J(\text{P-H}_\alpha) = 336$, $^2J(\text{P-H}_\alpha) \approx 2J(\text{P-H}_\alpha) = 12$, $\mu\text{-}_3\text{-PH}$]	1829 1829
14 $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{19}(\text{P}(\text{OMe})_3)_2(\mu\text{-}_3\text{-PH})]$	2090m, 2063m, 2047vs, 2040ms (sh), 2000s (sh), 1972ms	6.05 [d't' (ddd), $^1J(\text{P-H}_\alpha) \approx 328$, $^3J(\text{H}_\alpha\text{-H}_\beta) \approx 3J(\text{H}_\alpha\text{-H}_\beta) \approx 4$, PH], 3.74 [d, $^3J(\text{P-H}) \approx 10$, P(OCH ₃) ₃], 3.69 [d, $^3J(\text{P-H}) \approx 10$, P(OCH ₃) ₃], –17.87 [dd, $^2J(\text{P-H}_\beta) \approx 12$, OsH _b], –19.57 (m, OsH _c)	Isomer a (major): –45.6 [d, $J(\text{PH}) \approx 10$, P(OMe) ₃], –47.0 [d, P(OMe) ₃], –329.0 [d, $J(\text{P-H}_\alpha) \approx 326$, $\mu\text{-}_3\text{-PH}$] Isomer b (minor): –43.8 [d, $J(\text{PH}) \approx 15$, P(OMe) ₃], –50.1 [d, P(OMe) ₃], –330.0 [d, $^1J(\text{P-H}_\alpha) \approx 326$, $\mu\text{-}_3\text{-PH}$]	1966 1966

^a In CDCl₃, reference SiMe₄ (δ 0); ^c In CDCl₃, reference P(OMe)₃ (δ 0), downfield positive. ^b Based on ^{192}Os .

clusters.¹⁴ Based on these facts, it is presumed that in $[\text{Os}_3(\text{CO})_{10}\text{L}(\text{NCMe})]$ (L = phosphine or phosphite) L occupies an equatorial position while the acetonitrile ligand is axially co-ordinated. This combination of an equatorial and an axial ligand on a trinuclear osmium cluster allows a total of four isomers (two pairs of enantiomers) with two magnetically inequivalent positions for the phosphorus ligands (Fig. 1). Only one signal was observed for the phosphorus ligand in **9c**; this is probably due to rapid interconversion between the two types of enantiomers on the NMR time-scale, but it is also possible that the solution equilibrium between different isomers is dominated by one pair of enantiomers. Unlike phosphines and phosphites, it is known from crystallographic and NMR studies^{15,16} that the *tert*-butyl isocyanide ligand can co-ordinate in both axial and equatorial positions on trinuclear osmium clusters. The $\nu(\text{C}-\text{O})$ region of the IR spectrum of **9d**, which is very similar to that of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$, indicates that both ligands occupy axial positions in $[\text{Os}_3(\text{CO})_{10}(\text{CNBu}^t)(\text{NCMe})]$. It is known that isomeric forms of $[\text{Os}_3(\text{CO})_{10}(\text{PR}_3)_2]$ exist^{17,18} and plausible isomeric forms of $[\text{Os}_3(\text{CO})_9\{\text{P}(\text{OMe})_3\}_2(\text{NCMe})]$ are shown in Fig. 1. Considering the structure of $[\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]$, which has been determined by X-ray crystallography,¹⁹ it is likely that the structure of $[\text{Os}_3(\text{CO})_9\{\text{P}(\text{OMe})_3\}_2(\text{NCMe})]$ is that depicted in Fig. 1(i), where the steric interaction between the bulky phosphite ligands is minimised.

Reaction of $[\text{Os}_3(\text{CO})_{11}(\text{PH}_3)]$ **1** with either **9a**, **9c**, **9d** or **10** under mild conditions in toluene leads to the formation of the bright yellow mono- and bis-substituted clusters $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}\{\text{P}(\text{OMe})_3\}(\mu\text{-PH}_2)]$ **11a**, $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}(\text{PMe}_3)(\mu\text{-PH}_2)]$ **11b**, $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}(\text{CNBu}^t)(\mu\text{-PH}_2)]$ **11c** and $[\text{Os}_6(\mu\text{-H})(\text{CO})_{20}\{\text{P}(\text{OMe})_3\}_2(\mu\text{-PH}_2)]$ **12** in relatively good yield (50–60%). Similarly, reaction of $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-PH}_2)]$ **2** with **9d** or **10** affords the corresponding substituted hexanuclear clusters $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{21-n}\text{L}_n(\mu_3\text{-PH})]$ [$n = 1$, L = CNBu^t **13**; $n = 2$, L = P(OMe)₃ **14**] in good yield (>70%). Comparison of the ¹H and ³¹P NMR spectra of **11a–11c** and **12–14** to those of previously synthesised phosphido- and phosphinidene-linked clusters^{5,6,10} permitted a tentative assignment of the structure of the products.

In the proton NMR spectra of compounds **11a** and **11b** doublets of doublets centred around δ 4 with large P–H coupling constants are indicative of a phosphido moiety⁶ (Table 1). The hydride resonances (Fig. 2) show the co-ordination of the phosphine/phosphite adjacent to the hydride; there is coupling to the phosphine/phosphite as well as coupling to the phosphorus and protons of the phosphido bridge. In addition to the resonances attributable to the ligands, the proton NMR of **11c** reveals a set of AB-type, overlapping doublets of doublets at approximately δ 4. The resolution-enhanced spectrum reveals additional coupling to the hydride. The spectrum is very similar to that of $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}(\text{NCMe})(\mu\text{-PH}_2)]$ **4**,⁶ suggesting that the solution structures of **4** and **11c** are similar. Triplets of doublets, at shifts varying from δ ca. –354 to –415 are found in the ³¹P NMR spectra of **11a–11c**. These spectra are entirely consistent with those found for similar $\mu\text{-PH}_2$ bridges in **3** and **4**. In the light of the spectroscopic data and earlier results, the proposed structures of **11a–11c** are those depicted in Fig. 3.

The ¹H NMR spectrum of compound **12** indicates that there are two isomers. In the 'phosphido region' (ca. δ 3–5) a doublet of relatively broad multiplets with a large P–H coupling (ca. 320 Hz) is found at δ 3.89. There are two hydride resonances which are present in an approximate 2:1 ratio in CDCl₃. The ³¹P NMR spectrum of this cluster also shows the existence of two isomers: while there is only one resonance for the phosphido moiety (presumably due to accidental overlap) there are four resonances for two sets of two (inequivalent) phosphites between δ –44 and –52 (cf. Table 1). Based on the structural evidence from the crystal structure determination of **12** (see below), the two isomers are proposed to have the structures depicted in Fig. 3.

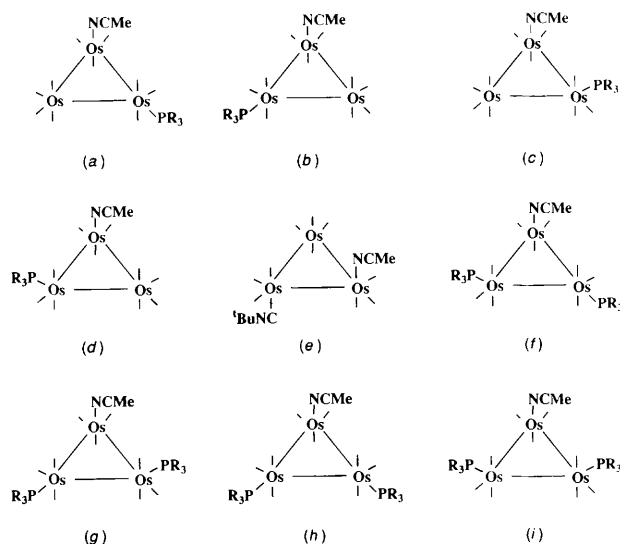


Fig. 1 Possible isomeric structures of $[\text{Os}_3(\text{CO})_{10}(\text{PR}_3)(\text{NCMe})]$ (R = Ph **9a**, OMe **9b** or Me **9c**) [(a)–(d)], proposed structure of $[\text{Os}_3(\text{CO})_{10}(\text{CNBu}^t)(\text{NCMe})]$ **9d** [(e)] and possible isomeric structures of $[\text{Os}_3(\text{CO})_9\{\text{P}(\text{OMe})_3\}_2(\text{NCMe})]$ **10** [(f)–(i)]

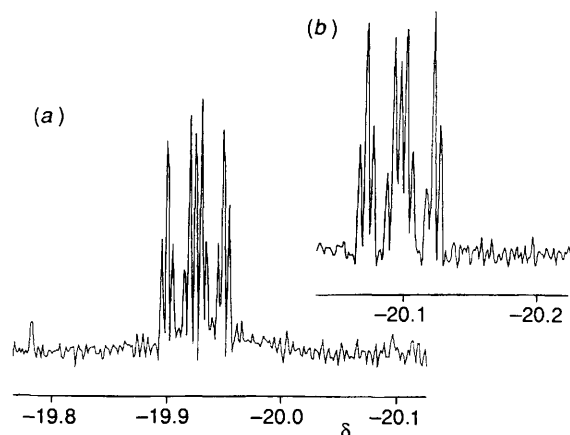


Fig. 2 Resolution-enhanced ¹H NMR hydride resonances (400 MHz) of (a) $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}\{\text{P}(\text{OMe})_3\}(\mu\text{-PH}_2)]$ **11a** and (b) $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}(\text{PMe}_3)(\mu\text{-PH}_2)]$ **11b**

Orange-yellow, cuboidal crystals of $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}(\text{CNBu}^t)(\mu\text{-PH}_2)]$ **11c** and yellow crystals of the bis-substituted compound $[\text{Os}_6(\mu\text{-H})(\text{CO})_{20}\{\text{P}(\text{OMe})_3\}_2(\mu\text{-PH}_2)]$ **12**, suitable for X-ray diffraction, were grown by slow evaporation of a dichloromethane–hexane solution at 4 °C. In order to confirm the proposed structures their crystal structures were determined by X-ray crystallography. The molecular structure of **11c** is shown in Fig. 4. Selected bond distances and angles are summarised in Table 2. The structure of $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}(\text{CNBu}^t)(\mu\text{-PH}_2)]$ is very similar to those of $[\text{Os}_6(\mu\text{-H})(\text{CO})_{22-n}(\text{NCMe})_n(\text{PH}_2)]$ ($n = 0$ **3** or **1** **4**).⁶ The isocyanide ligand is co-ordinated in an axial position, suggesting that the proposed structure (Fig. 1) of $[\text{Os}_3(\text{CO})_{10}(\text{CNBu}^t)(\text{NCMe})]$ **9d** is correct; it is located in the position *trans* to that of the acetonitrile ligand in the molecular structure of **4**.⁵ The dihedral angle between the two osmium triangles is 49.3° and the Os–P–Os angle is 125.4(3)°. The non-bonding distance between Os(1) and Os(4) is ca. 4.21 Å. The hydride appears to be bridging the bis-substituted edge, *i.e.* the Os–Os edge to which the phosphite and isocyanide ligands are linked; the distance between Os(4) and Os(5) is 3.046(2) Å as compared to the average of ca. 2.88 Å for the other metal–metal bonds. The carbonyl ligand C(53)–O(53) is significantly bent away from the Os(4)–Os(5) edge, the Os(4)–Os(5)–C(53) angle being 115.4(9)°. The *tert*-butyl moiety of the isocyanide ligand is disordered; the orientation represented by

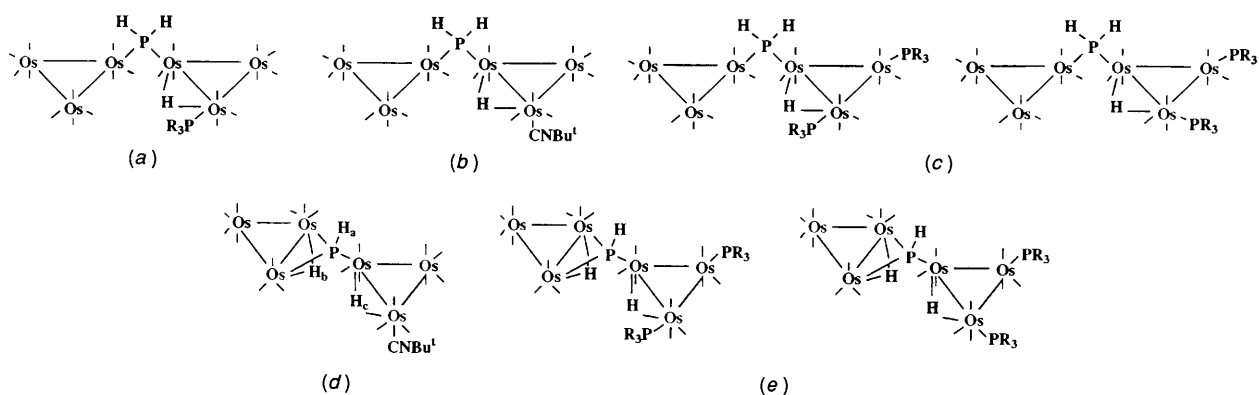


Fig. 3 Proposed molecular structures of $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}\{\text{P}(\text{OMe})_3\}(\mu\text{-PH}_2)]$ **11a** [(a)] and $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}(\text{CNBu}^t)(\mu\text{-PH}_2)]$ **11c** [(b)], possible isomeric structures of $[\text{Os}_6(\mu\text{-H})(\text{CO})_{20}\{\text{P}(\text{OMe})_3\}_2(\mu\text{-PH}_2)]$ **12** [(c)], proposed molecular structure of **13** [(d)] and possible isomeric structures of $[\text{Os}_6(\mu\text{-H})(\text{CO})_{19}\{\text{P}(\text{OMe})_3\}_2(\mu_3\text{-PH})]$ **14** [(e)]

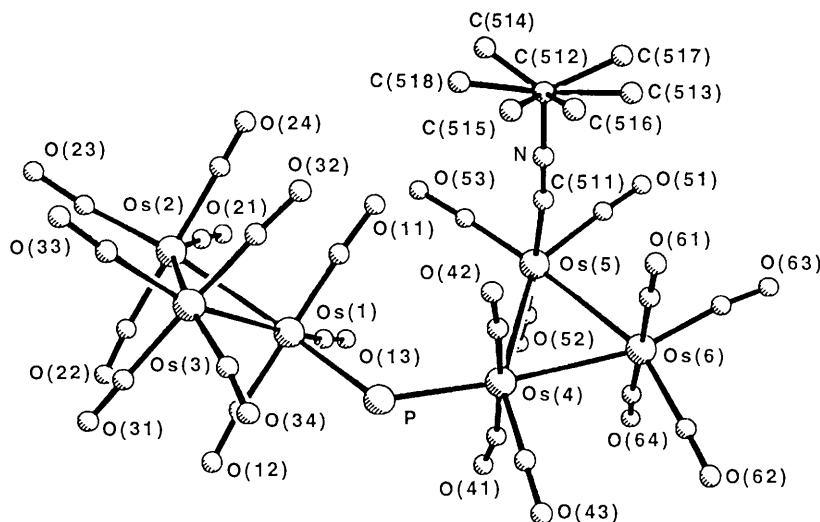


Fig. 4 The molecular structure of $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}(\text{CNBu}^t)(\mu\text{-PH}_2)]$ **11c**

Table 2 Selected bond lengths (Å) and angles (°) for $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}(\text{CNBu}^t)(\mu\text{-PH}_2)]$ **11c**

Os(1)–Os(2)	2.855(1)	Os(1)–P	2.356(6)
Os(1)–Os(3)	2.889(2)	Os(4)–P	2.405(7)
Os(2)–Os(3)	2.890(2)	Os(5)–C(511)	2.042(32)
Os(4)–Os(5)	3.046(2)	N–C(511)	1.146(41)
Os(4)–Os(6)	2.885(2)	N–C(512)	1.445(40)
Os(5)–Os(6)	2.889(1)		
Os(2)–Os(1)–Os(3)	60.4(1)	Os(6)–Os(4)–P	175.0(2)
Os(2)–Os(1)–P	164.3(2)	Os(4)–Os(5)–C(511)	91.5(7)
Os(3)–Os(1)–P	104.0(2)	Os(6)–Os(5)–C(511)	90.2(6)
Os(1)–Os(2)–Os(3)	60.4(1)	Os(4)–Os(6)–Os(5)	63.7(1)
Os(1)–Os(3)–Os(2)	59.2(1)	Os(1)–P–Os(4)	125.4(3)
Os(5)–Os(4)–Os(6)	58.2(1)	C(511)–N–C(512)	171.9(21)
Os(5)–Os(4)–P	117.3(2)	Os(5)–C(511)–N	172.7(18)

C(516), C(517) and C(518) is favoured with an occupancy of *ca.* 60%.

The molecular structure of compound **12** (Fig. 5) resembles those of **5**, **6** and **11c**. Selected bond distances and angles are summarised in Table 3. The structural features of the phosphido bridge are similar to those of other $\mu\text{-PH}_2$ bridged compounds;^{6,20} the Os(1)–P(1)–Os(4) angle is 124.0(4)° and the Os(1)–P(1) and Os(4)–P(1) distances are 2.390(7) and 2.362(8) Å, respectively. The hydride ligand, which bridges the Os(1)–Os(3) edge, has been located using the potential minimisation program HYDEX;²¹ its position is also evident from structural parameters. The length of the Os(1)–Os(3) edge is 3.047(2) Å as compared to the average of *ca.* 2.88 Å for the five other Os–Os edges. Furthermore, the equatorial phosphorus ligands are bent

away to accommodate the hydride. Thus, the Os(1)–Os(3)–P(3) angle is 112.4(2)° and the Os(3)–Os(1)–P(1) angle is 105.0(2)°. The non-bonding distance between Os(1) and Os(4) is *ca.* 4.20 Å. The metal–phosphite bond lengths, Os–P_{av} 2.276(9) Å, are comparable to those observed for $[\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]$ (Os–P_{av} 2.286 Å). There are two relatively bulky phosphorus ligands *cis* to the hydride if the $\text{Os}_3(\text{CO})_{11}(\mu\text{-PH}_2)$ fragment is viewed as a phosphorus ligand. This appears to be unfavourable from a steric point of view but is similar to the situation observed for the cluster $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\text{PMe}_2\text{-Ph})_2]^+$ ²² which exists in two isomeric forms; the isomer in which both phosphines are *cis* to the hydride predominates. It is proposed that the two isomeric forms of **12** (Fig. 3) correspond to those observed for $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\text{PMe}_2\text{Ph})_2]^+$ and that

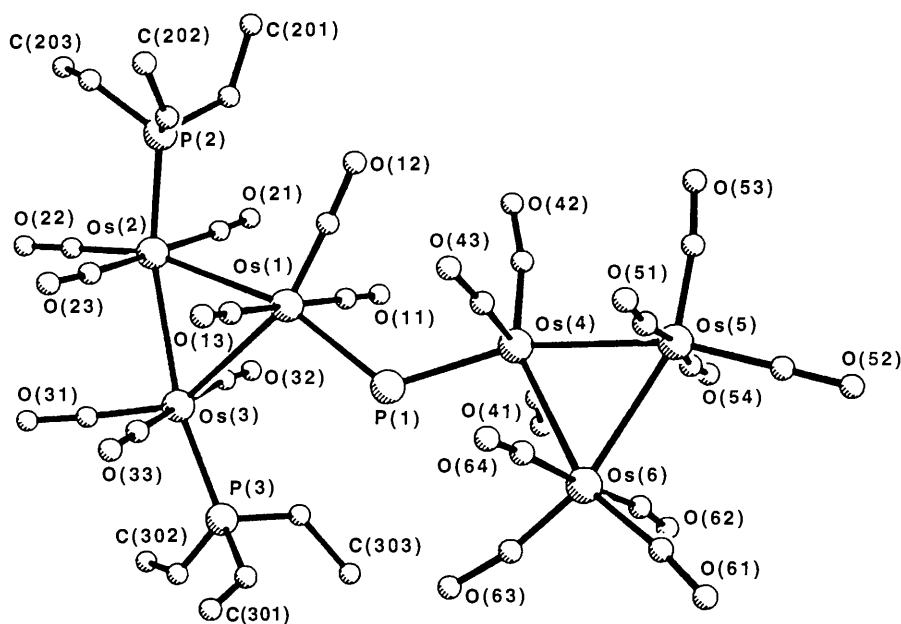


Fig. 5 The molecular structure of $[\text{Os}_6(\mu\text{-H})(\text{CO})_{20}\{\text{P}(\text{OMe})_3\}_2(\mu\text{-PH}_2)]$ **12**

Table 3 Selected bond lengths (Å) and angles (°) for $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}\{\text{P}(\text{OMe})_3\}_2(\mu\text{-PH}_2)]$ **12**

Os(1)–Os(2)	2.882(2)	Os(3)–P(3)	2.287(9)
Os(1)–Os(3)	3.047(2)	Os(4)–Os(5)	2.840(2)
Os(1)–P(1)	2.390(7)	Os(4)–Os(6)	2.879(2)
Os(2)–Os(3)	2.897(2)	Os(4)–P(1)	2.362(8)
Os(2)–P(2)	2.265(9)	Os(5)–Os(6)	2.887(2)
Os(2)–Os(1)–Os(3)	58.4(1)	Os(5)–Os(4)–P(1)	158.9(2)
Os(1)–Os(2)–Os(3)	63.6(1)	Os(6)–Os(4)–P(1)	99.5(2)
Os(1)–Os(3)–Os(2)	57.9(1)	Os(1)–P(1)–Os(4)	124.0(4)
Os(5)–Os(4)–Os(6)	60.6(1)	Os(1)–Os(2)–P(2)	97.6(2)
Os(4)–Os(5)–Os(6)	60.4(1)	Os(3)–Os(2)–P(2)	160.2(2)
Os(4)–Os(6)–Os(5)	59.0(1)	Os(1)–Os(3)–P(3)	112.4(2)
Os(2)–Os(1)–P(1)	163.3(2)	Os(2)–Os(3)–P(3)	167.6(2)
Os(3)–Os(1)–P(1)	105.0(2)		

the predominant isomer is that which corresponds to the crystal structure of **12**. The reason for this predominance is unclear. It is possible that the isomers of **12** arise by formation of a phosphido bridge to different isomers of **10**, but in the phosphinidene analogue of **12**, *i.e.* **14** (see below), it appears that there are two isomers which interconvert in solution and this may also be the case for **12**. It has been observed that the presence of a bridging hydride increases the barrier to isomer interconversion in trinuclear ruthenium and osmium clusters.^{22,23} In the case of the clusters $[\text{Ru}_3(\mu\text{-H})\text{L}(\text{CO})_9]$, where L is a triply co-ordinated alkyne, these barriers are increased upon the co-ordination of phosphines to the metal centre, regardless of whether site exchange takes place *via* pairwise exchange of ligands or ‘turnstile’ rotation of the ligands.²³ It may be that a similar phenomenon is observed in the case of **12**, *i.e.* the molecular structure observed by X-ray diffraction, which is proposed to be the major isomer, is the kinetic product of the reaction of $[\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}(\text{NCMe})]$ with $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-PH}_2)]$. The formation of the second isomer, which appears to be favoured from a steric point of view, is hindered by the increased barrier for migration of the phosphite ligand.

The structure of compound **12** differs from the other structures of phosphido-bridged clusters in the orientation of the two osmium triangles. The phosphite-substituted metal triangle is orientated in such a way that steric interactions with

the carbonyl ligands of the other metal triangle are minimised. This means that the substituted triangle has been turned by roughly 180° in comparison to the axially substituted clusters. Thus, the presence of a relatively bulky equatorial ligand has a profound influence on the cluster geometry. The triangles are approximately coplanar, but not completely so because coplanarity would cause the carbonyl ligands of Os(1) and Os(4) to be eclipsed and thus bring the equatorial carbonyls of these two osmium atoms in such close proximity that there may be steric interference. There is a staggered orientation of the carbonyl ligands of Os(1) and Os(4); the dihedral angle between the planes of the triangles is relatively small (25.5°).

In the phosphido-bridged clusters **11c**, **12**, **5** and **6** there is a slight twist of the ligand arrangement of the osmium atoms comprising the metal triangles which do not possess a hydride. The ‘ $\text{Os}_3(\mu\text{-H})(\text{CO})_{11-n}\text{L}_n(\mu\text{-PH}_2)$ ’ fragments ($n = 1$ or 2) may be viewed as bulky phosphorus ligands co-ordinated to these osmium triangles. Steric interactions between ligands may force a rearrangement of the ligand polyhedron and thus effect a different cluster structure. In the case of mono-, di- and tri-substituted phosphine/phosphite derivatives of $[\text{M}_3(\text{CO})_{12}]$ ($\text{M} = \text{Ru}$ or Os)^{19,24} it has been observed that the overall ligand arrangement shifts from a D_{3h} -like symmetry to D_3 and this appears to be the case for the phosphido-bridged clusters discussed here. The reorientation of the ligands is most pronounced for **5** and **6**.

The phosphinidene-linked clusters **13** and **14** have been characterised by IR, ^1H and ^{31}P NMR spectroscopy, mass spectrometry, microanalysis and, in the case of **14**, X-ray crystallography. The proton NMR spectrum of **13** differs from that of previously synthesised phosphinidene-bridged hexanuclear osmium clusters^{5,10} in that fewer couplings are observed both for the phosphinidene proton and the hydrides. This suggests that the solution structure of **13** is different to those of the other phosphinidene-bridged clusters discussed here. This difference may lie in the relative orientation of the two metal triangles with respect to each other.

As in the case of compound **12**, the ^1H and ^{31}P NMR spectra of **14** reveal that there are two isomers. The hydride signal(s) of **14** are virtually identical to those observed for the upfield hydride signal of **12**. Similarly, the phosphite signals of the two compounds are very similar. The protons of the phosphido moiety are seen as a doublet of relatively broad multiplets at δ 6.05. The assignment of the hydride resonances is based on the

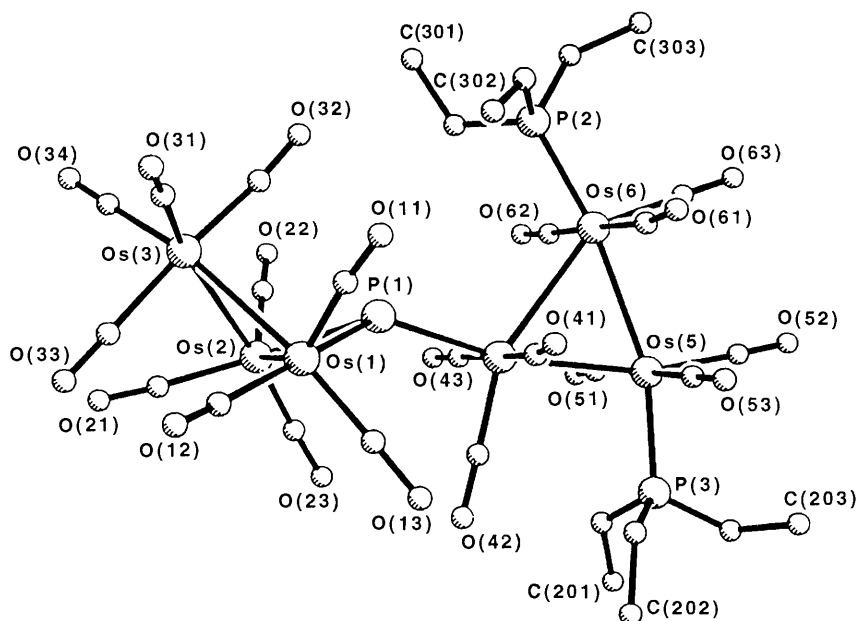


Fig. 6 The molecular structure of $[\text{Os}_6(\mu\text{-H})(\text{CO})_{19}\{\text{P}(\text{OMe})_3\}_2(\mu_3\text{-PH})]$ **14**

Table 4 Selected bond lengths (Å) and bond angles (°) for $[\text{Os}_6(\mu\text{-H})(\text{CO})_{20}\{\text{P}(\text{OMe})_3\}_2(\mu_3\text{-PH})]$ **14**

Os(1)–Os(2)	2.893(2)	Os(4)–Os(6)	3.065(1)
Os(1)–Os(3)	2.884(1)	Os(4)–P(1)	2.398(5)
Os(1)–P(1)	2.412(5)	Os(5)–Os(6)	2.903(1)
Os(2)–Os(3)	2.884(1)	Os(5)–P(2)	2.286(5)
Os(2)–P(1)	2.429(6)	Os(6)–P(3)	2.282(6)
Os(4)–Os(5)	2.895(1)		
Os(2)–Os(1)–Os(3)	59.9(1)	Os(4)–Os(5)–Os(6)	63.8(1)
Os(2)–Os(1)–P(1)	53.6(1)	Os(4)–Os(5)–P(2)	98.4(1)
Os(3)–Os(1)–P(1)	85.9(1)	Os(6)–Os(5)–P(2)	162.2(1)
Os(1)–Os(2)–Os(3)	59.9(1)	Os(4)–Os(6)–Os(5)	58.0(1)
Os(1)–Os(2)–P(1)	53.0(1)	Os(4)–Os(6)–P(3)	112.8(2)
Os(3)–Os(2)–P(1)	85.6(1)	Os(5)–Os(6)–P(3)	170.7(2)
Os(1)–Os(3)–Os(2)	60.2(1)	Os(1)–P(1)–Os(2)	73.4(2)
Os(5)–Os(4)–Os(6)	58.2(1)	Os(1)–P(1)–Os(4)	127.4(2)
Os(5)–Os(4)–P(1)	167.8(1)	Os(2)–P(1)–Os(4)	128.2(2)
Os(6)–Os(4)–P(1)	109.6(1)		

^1H NMR spectrum of $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{21}(\mu_3\text{-PH})]$ **5**.⁵ Integration of the spectrum indicates that the two isomers are present in an approximate 2:1 ratio in CDCl_3 . In the ^{31}P NMR spectrum of this cluster there are two overlapping phosphinidene resonances at $\delta -329$ and -330 ($^1J_{\text{PH}} \approx 320$ Hz) and four resonances for two sets of two (inequivalent) phosphites at $\delta -43$ to -50 . It is proposed that the structures and relative distribution of the two isomers correspond to those proposed for **12**.

It was possible to grow yellow crystals of $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{19}\{\text{P}(\text{OMe})_3\}_2(\mu_3\text{-PH})]$ **14** by slow evaporation of a chloroform–dichloromethane–hexane solution at 4°C . In order to confirm the proposed structure, an X-ray analysis was performed. The molecular structure of **14** is shown in Fig. 6. Selected bond distances and angles are summarised in Table 4. The structure of **14** is very similar to that of $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{20}\{\text{P}(\text{OMe})_3\}_2(\mu_3\text{-PH})]$ **15**¹⁰ both in terms of the osmium–phosphinidene framework and the ligand arrangement, *i.e.* the phosphido moiety is co-ordinated *cis* to one of the phosphite ligands [the ‘ $\text{Os}_3(\text{CO})_{11}(\text{PH}_2)$ ’ fragment being considered a phosphorus ligand]. The hydride ligands in **14** have been located by the use of HYDEX.²¹ As suggested for **15**, one hydride [H(12)] spans the Os–Os edge which is bridged by the phosphinidene moiety while the hydride on the phosphite-substituted osmium triangle [H(46)] is located *cis* to the phosphinidene moiety and one of the trimethyl phosphite

ligands. The dihedral angle between the planes of the two osmium triangles is 90.0° . Steric interactions are, as in **15**, dominated by the phosphite ligand *cis* to the bridging phosphinidene cap. Therefore, the arrangement of the cluster framework is virtually identical to that of **15**, *i.e.* the substituted osmium triangle has been rotated *ca.* 180° with respect to its orientation in the axially substituted analogue $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{20}(\text{NCMe})(\mu_3\text{-PH})]$ **6**. The Os(4)–Os(6) edge which is bridged by a hydride is significantly elongated: its length is $3.065(1)$ Å as compared to the average length of the other Os–Os edges, which is *ca.* 2.89 Å. The metal–phosphite bond lengths, $\text{Os}–\text{P}_{\text{av}}$ $2.284(6)$ Å, are comparable to those observed for $[\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]$ and **12**. The phosphite ligand co-ordinated to Os(5) does not appear to influence the geometry of the cluster; it is not located in a position where its steric requirements influence the ‘other’ cluster triangle. However, this ligand causes a significant expansion of the osmium triangle to which it is co-ordinated. This may be attributed to the expansion of the ligand sphere that is caused by the introduction of a bulky ligand: in order to optimise metal–ligand interactions, the M–M bond distances also expand. All Os–Os edges of **14** are significantly longer (by *ca.* 0.01 – 0.06 Å) than the corresponding edges in **15**;¹⁰ they are also longer than the distances found in **6**.⁵ It is unclear whether the molecular structure in solution is the same as that found in the crystal. Unlike the phosphide-bridged clusters, the carbonyl ligands of

the two metal triangles in the phosphinidene-bridged clusters discussed here (see below) are virtually interlocked and it is therefore unlikely that there is a significant difference in the cluster framework in the solution and solid-state structures of **14**. A ^1H NMR spectrum of dissolved crystals of **14** reveals the resonances due to both isomers. Although it is possible that the crystal picked for the structure determination of **14** is not representative of the batch, *i.e.* that both isomers crystallise, we believe that the observed NMR spectrum suggests that interconversion between the two isomeric structures is relatively facile in solution while the structure observed in the crystal structure is favoured in the solid state.

The molecular structures of compounds **14** and **15** are very similar and may be compared to that of $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{20}(\text{NCMe})(\mu_3\text{-PH})]$ **6**.^{3,4} Due to the different positions of co-ordination of the acetonitrile/phosphite ligands, the osmium triangles do not adopt the same orientation in **14** and **15** as in **6**. As in the case of the hexanuclear phosphide-linked clusters, the substituted osmium triangles of the phosphite clusters are rotated approximately 180° with respect to its orientation in the acetonitrile-substituted cluster; this difference is schematically depicted in Fig. 7. Because the phosphinidene link brings the two metal triangles in close proximity to each other it appears to be impossible for the phosphite-substituted clusters to adopt the same metal-phosphorus framework as that of **6** without causing strong steric interaction between the carbonyl ligands of Os(2) and Os(3) and the relatively bulky phosphite ligand which is co-ordinated *cis* to the hydride.

As it has been found that thermolysis of compounds **3**, **5** or **6** affords interstitial phosphido-clusters, the thermolysis of substituted hexanuclear phosphide- and phosphinidene-bridged clusters was investigated in the hope of obtaining similar (substituted) phosphido-clusters. However, thermolysis of $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}(\text{CNBu}^t)(\mu\text{-PH}_2)]$ **11c**, $[\text{Os}_6(\mu\text{-H})(\text{CO})_{20}\{\text{P}(\text{OMe})_3\}_2(\mu\text{-PH}_2)]$ **12**, $[\text{Os}_6(\mu\text{-H})(\text{CO})_{20}(\text{CNBu}^t)(\mu_3\text{-PH})]$ **13** or $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{20}\{\text{P}(\text{OMe})_3\}(\mu_3\text{-PH})]$ **15** in refluxing toluene or xylene did not result in any discernible products but only slow decomposition of the phosphide- or phosphinidene-bridged clusters to several unidentified compounds in low yields.

Experimental

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk and vacuum-line techniques. The solvents were distilled over appropriate drying agents prior to use. Infrared spectra were recorded as solutions in 0.5 mm NaCl cells on a Perkin-Elmer 983 grating or 1710 Fourier-transform spectrometer with carbon monoxide as calibrant, fast atom bombardment mass spectra were using a Kratos MS902 spectrometer with a matrix of dithioglycerol or 2-nitrobenzyl alcohol and proton and phosphorus NMR spectra on Bruker WM250 or AM400 spectrometers. Routine separation of products was performed by thin-layer chromatography using commercially prepared glass plates, pre-coated to 0.25 mm thickness with Merck Kieselgel 60F₂₅₄ or 2 mm thick plates prepared in the University of Cambridge Chemical Laboratory. The starting materials $[\text{Os}_3(\text{CO})_{11}(\text{PH}_3)]$ **1** and $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-PH}_2)]$ **2** were synthesised according to literature methods.^{5,25}

Preparations

$[\text{Os}_3(\text{CO})_{10}(\text{PMe}_3)(\text{NCMe})]$ **9c**. In a typical reaction, a dichloromethane-acetonitrile solution (*ca.* 20 cm³) of dry trimethylamine oxide (5 mg, 0.066 mmol) was added to a solution of $[\text{Os}_3(\text{CO})_{11}(\text{PMe}_3)]$ (61.3 mg, 0.064 mmol) in dichloromethane-acetonitrile (85:15, *ca.* 30 cm³) over a period of *ca.* 12 h. Infrared spectroscopy indicated complete conversion to $[\text{Os}_3(\text{CO})_{10}(\text{PMe}_3)(\text{NCMe})]$ **9c**. Thin-layer chromato-

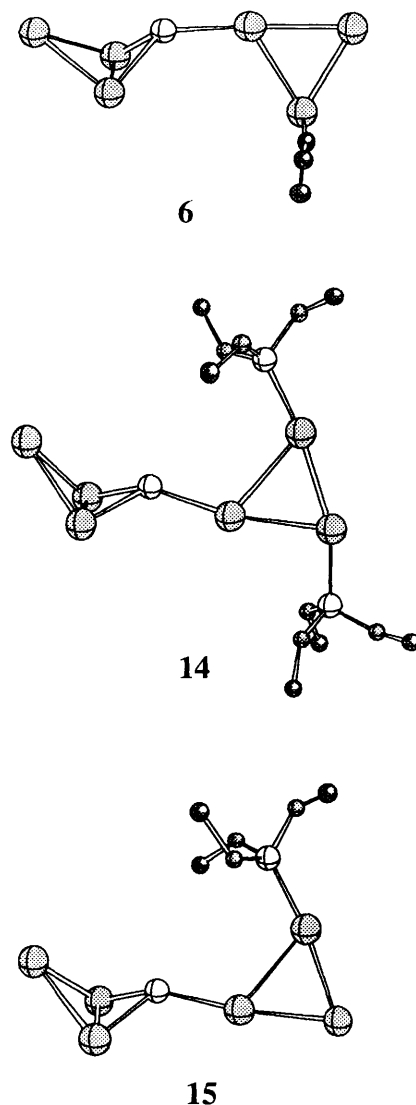


Fig. 7 The osmium-phosphorus ligand frameworks of $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{20}(\text{NCMe})(\mu_3\text{-PH})]$ **6**, $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{19}\{\text{P}(\text{OMe})_3\}_2(\mu_3\text{-PH})]$ **14** and $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{20}\{\text{P}(\text{OMe})_3\}(\mu_3\text{-PH})]$ **15**

graphy using dichloromethane-hexane (1:1) as eluent yielded **9c** in *ca.* 50% yield.

$[\text{Os}_3(\text{CO})_{10}(\text{CNBu}^t)(\text{NCMe})]$ **9d**. The synthesis of this compound is analogous to that of **9c**. In a typical reaction, $[\text{Os}_3(\text{CO})_{11}(\text{CNBu}^t)]$ (51.2 mg, 0.053 mmol) was dissolved in dichloromethane-acetonitrile (85:15, *ca.* 50 cm³). To this solution, a solution of Me_3NO (5 mg, 0.066 mmol, 1.25 equivalents) in dichloromethane-acetonitrile was added dropwise over a period of *ca.* 4 h. The solution was maintained at 0°C until all Me_3NO had been added and then allowed to warm to room temperature over *ca.* 4 h during which all $\nu(\text{C-O})$ resonances due to the starting material disappeared. The reaction was stopped and the solution reduced in volume to less than 5 cm³. Thin-layer chromatography using dichloromethane-hexane (1:1) as eluent gave two yellow bands and a brown baseline. They were, in order of decreasing R_f : $[\text{Os}_3(\text{CO})_{11}(\text{CNBu}^t)]$, yellow, 7 mg and $[\text{Os}_3(\text{CO})_{10}(\text{CNBu}^t)(\text{NCMe})]$ **9d**, yellow, *ca.* 30 mg (0.030 mmol, 58%).

$[\text{Os}_3(\text{CO})_9\{\text{P}(\text{OMe})_3\}_2(\text{NCMe})]$ **10**. The synthesis of this compound was analogous to that of **9c**. In a typical reaction, $[\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]$ (150 mg, 0.139 mmol) was dissolved in dichloromethane-acetonitrile (85:15, *ca.* 50 cm³). A solution of Me_3NO (11.5 mg, 0.152 mmol, ≈ 1.1 equivalent) was added dropwise over a period of approximately 12 h. The

Table 5 Crystal data and data-collection parameters* for the structures of $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}(\text{CNBu}^t)(\mu\text{-PH}_2)]$ **11c**, $[\text{Os}_6(\mu\text{-H})(\text{CO})_{20}\{\text{P}(\text{OMe})_3\}_2(\mu\text{-PH}_2)]$ **12** and $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{19}\{\text{P}(\text{OMe})_3\}_2(\mu_3\text{-PH})]$ **14**

	11c	12	14
Formula	$\text{C}_{26}\text{H}_{12}\text{NO}_{21}\text{Os}_6\text{P}$	$\text{C}_{26}\text{H}_{21}\text{O}_{26}\text{Os}_6\text{P}_3$	$\text{C}_{25}\text{H}_{21}\text{O}_{25}\text{Os}_6\text{P}_3$
<i>M</i>	1846.6	1983.5	1955.5
Crystal colour, habit	Orange-yellow block	Yellow block	Yellow block
Crystal size/mm	0.40 × 0.40 × 0.36	0.50 × 0.50 × 0.50	0.11 × 0.19 × 0.34
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/a$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
<i>a</i> /Å	18.956(5)	9.366(3)	9.559(2)
<i>b</i> /Å	12.347(3)	13.721(3)	13.223(3)
<i>c</i> /Å	19.226(4)	19.380(4)	17.480(5)
α /°	90	69.45(2)	88.24(2)
β /°	118.33(2)	83.74(2)	79.00(2)
γ /°	90	83.16(2)	86.77(3)
<i>Z</i>	4	2	2
<i>U</i> /Å ³	3961.0(16)	2309.4(10)	2165.0(10)
<i>D_c</i> /g cm ⁻³	3.076	2.852	2.999
<i>F</i> (000)	3256	1772	1744
2θ Range/°	5.0–45.0	5.0–50.0	5.0–45.0
Scan mode	96 step ω–2θ	96 step ω–2θ	31 step ω–θ
Scan speed/° min ⁻¹	3.00–29.30	3.00–29.30	0.9–3.6
Scan range (ω)/°	1.40 + <i>K</i> α separation	1.40 + <i>K</i> α separation	0.93 + <i>K</i> α separation
Absorption correction	Semiempirical	Numerical	Numerical
Maximum/minimum transmission	0.0271, 0.2573	0.0852, 0.3199	0.0173, 0.3017
Reflections measured	5804 ($\pm h, \pm k, -l$)	6459 ($\pm h, \pm k, \pm l$)	6063 ($\pm h, \pm k, -l$)
Unique reflections	5148	6017	5655
<i>R</i> _{int}	0.014	0.018	0.036
Observed reflections [<i>F</i> > 4σ(<i>F</i>)]	3933	4501	4583
Weighting scheme, <i>w</i>	$[\sigma^2(F) + 0.0050F^2]^{-1}$	$[\sigma^2(F) + 0.0017F^2]^{-1}$	$[\sigma^2(F) + 0.0018F^2]^{-1}$
<i>R</i>	0.052	0.066	0.058
<i>R</i> '	0.076	0.078	0.070
Maximum, minimum in final difference map/e Å ⁻³	1.43, -1.90	4.77, -2.41	2.94, -4.36

* Details in common: 293 K; monochromated Mo–Kα ($\lambda = 0.71069$ Å) radiation; background measurement, stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time; 3 standard reflections measured every 97.

reaction was monitored by IR spectroscopy and stopped when no ν(C–O) resonances due to the starting material could be detected. Following solvent removal, TLC using dichloromethane–hexane (1 : 1) as eluent allowed the isolation of two yellow bands, in order of decreasing *R_f*: $[\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]$, yellow, 25 mg and $[\text{Os}_3(\text{CO})_9\{\text{P}(\text{OMe})_3\}_2(\text{NCMe})]$ **10**, yellow, ca. 80 mg, (0.072 mmol, 52%). Yields quoted are after recrystallisation from dichloromethane–hexane.

$[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}\{\text{P}(\text{OMe})_3\}(\mu\text{-PH}_2)]$ **11a**. In a typical reaction, $[\text{Os}_3(\text{CO})_{11}(\text{PH}_3)]$ **1** (35 mg, 0.038 mmol) was treated with $[\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}(\text{NCMe})]$ (40 mg, 0.039 mmol) in toluene (ca. 50 cm³) at 45 °C. Thin-layer chromatography gave six bands, in order of decreasing *R_f*: $[\text{Os}_3(\text{CO})_{12}]$, yellow (trace); $[\text{Os}_3(\text{CO})_{11}(\text{PH}_3)]$, yellow (trace); $[\text{Os}_3(\text{CO})_{11}(\text{PMe}_3)]$, yellow (trace); a yellow compound (trace) not identified; $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}\{\text{P}(\text{OMe})_3\}(\mu\text{-PH}_2)]$ **11a**, bright yellow, 36 mg (0.019 mmol, 50%) and $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{20}\{\text{P}(\text{OMe})_3\}(\mu\text{-PH})]$ **15**, yellow, 10 mg (0.005 mmol, 13%). Yields quoted are after recrystallisation from dichloromethane–hexane.

$[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}(\text{PMe}_3)(\mu\text{-PH}_2)]$ **11b**. In a typical reaction, $[\text{Os}_3(\text{CO})_{11}(\text{PH}_3)]$ (21.6 mg, 0.024 mmol) was treated with $[\text{Os}_3(\text{CO})_{10}(\text{PMe}_3)(\text{NCMe})]$ (25.5 mg, 0.026 mmol) in toluene (ca. 25 cm³). Thin-layer chromatography gave five bands, in order of decreasing *R_f*: $[\text{Os}_3(\text{CO})_{12}]$, yellow (trace); $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-PH}_2)]$, yellow (trace); $[\text{Os}_3(\text{CO})_{11}(\text{PMe}_3)]$, yellow (trace); a yellow compound (trace) not identified and $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}(\text{PMe}_3)(\mu\text{-PH}_2)]$ **11b**, bright yellow, 26 mg (0.014 mmol, 58%). Yield quoted is after recrystallisation from dichloromethane–hexane.

$[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}(\text{CNBu}^t)(\mu\text{-PH}_2)]$ **11c**. The synthesis and work-up procedure for this compound were analogous to those

of **11a**. In a typical reaction, $[\text{Os}_3(\text{CO})_{11}(\text{PH}_3)]$ (35 mg, 0.038 mmol) was treated with $[\text{Os}_3(\text{CO})_{10}(\text{CNBu}^t)(\text{NCMe})]$ (40 mg, 0.041 mmol) in toluene (35 cm³). Thin-layer chromatography gave five bands, in order of decreasing *R_f*: two faint yellow bands (trace) which were not identified; $[\text{Os}_6(\mu\text{-H})(\text{CO})_{21}(\text{CNBu}^t)(\mu\text{-PH}_2)]$ **11c**, very bright yellow, 40.2 mg (0.022 mmol, 58%); $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{20}(\text{CNBu}^t)(\mu_3\text{-PH})]$ **13**, yellow, 17 mg (0.009 mmol, 24%) and a yellow compound, ca. 1 mg, not identified. Yields quoted are after recrystallisation from dichloromethane–hexane.

$[\text{Os}_6(\mu\text{-H})(\text{CO})_{20}\{\text{P}(\text{OMe})_3\}_2(\mu\text{-PH}_2)]$ **12**. The synthesis and work-up procedure for this compound were analogous to those of **11a**. In a typical reaction, $[\text{Os}_3(\text{CO})_{11}(\text{PH}_3)]$ (24 mg, 0.026 mmol) was treated with $[\text{Os}_3(\text{CO})_9\{\text{P}(\text{OMe})_3\}_2(\text{NCMe})]$ (27 mg, 0.024 mmol) in toluene (ca. 50 cm³) at 40 °C. Thin-layer chromatography afforded, in order of decreasing *R_f*: four yellow bands (trace), not isolated; $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{19}\{\text{P}(\text{OMe})_3\}_2(\mu_3\text{-PH})]$ **14**, bright yellow, 5 mg (0.002 mmol, 8%) and $[\text{Os}_6(\mu\text{-H})(\text{CO})_{20}\{\text{P}(\text{OMe})_3\}_2(\mu\text{-PH}_2)]$ **12**, bright yellow, 24 mg (0.012 mmol, 50%). Yields quoted are after recrystallisation from dichloromethane–hexane.

$[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{20}(\text{CNBu}^t)(\mu_3\text{-PH})]$ **13**. In a typical reaction, $[\text{Os}_3(\text{CO})_{10}(\text{CNBu}^t)(\text{NCMe})]$ (ca. 40 mg, 0.041 mmol) and $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-PH}_2)]$ (41.2 mg, 0.046 mmol) were dissolved in the minimum volume of dichloromethane (ca. 5 cm³). Toluene (30 cm³) was added and the resultant solution stirred at 45 °C for 26 h. During the reaction a bright yellow precipitate of $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{20}(\text{CNBu}^t)(\mu_3\text{-PH})]$ **13** was produced. It was filtered off and washed with toluene and hexane. The solvent was removed from the filtrate under a stream of nitrogen. The filtrate was redissolved in dichloromethane and subjected to TLC. Several bands were isolated. The first was identified as $[\text{Os}_3(\text{CO})_{11}(\text{CNBu}^t)]$, yellow, ca. 3 mg, and the

second as $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{20}(\text{CNBu}^t)(\mu_3\text{-PH})]$ **13**, yellow, ca. 3 mg. Minor bands followed, but were not identified. Total yield of $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{20}(\text{CNBu}^t)(\mu_3\text{-PH})]$ **13** after recrystallisation from dichloromethane–hexane: 40.3 mg (0.022 mmol, 54%) (Found: C, 16.40; H, 0.70; P, 1.95. $\text{C}_{25}\text{H}_{12}\text{NO}_{20}\text{Os}_6\text{P}$ requires C, 16.40; H, 0.65; P, 1.70%).

$[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{19}(\text{P}(\text{OMe})_3)_2(\mu_3\text{-PH})]$ **14**. The synthesis of this compound was analogous to that of **13**. In a typical reaction, $[\text{Os}_3(\text{CO})_9\{\text{P}(\text{OMe})_3\}_2(\text{NCMe})]$ **10** (ca. 25 mg, 0.022 mmol) was treated with $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-PH}_2)]$ (ca. 20 mg, 0.022 mmol) in toluene (30 cm³) at 50 °C. The reaction was stopped after approximately 12 h and the solvent was removed under a stream of nitrogen. Thin-layer chromatography using dichloromethane–hexane (1 : 1) as eluent gave two bright yellow bands, in order of decreasing R_f : $[\text{Os}_6(\mu\text{-H})_2(\text{CO})_{19}\{\text{P}(\text{OMe})_3\}_2(\mu_3\text{-PH})]$ **14**, bright yellow, ca. 20 mg (0.010 mmol, 45%) (Found: C, 15.30; H, 1.05; P, 4.75. $\text{C}_{25}\text{H}_{21}\text{O}_{25}\text{Os}_6\text{P}_3$ requires C, 15.25; H, 1.05; P, 4.75%) and $[\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]$, yellow, 10 mg. Yields quoted are after recrystallisation from dichloromethane–hexane.

X-Ray analysis of compounds **11c**, **12** and **14**

For compounds **11c** and **12** intensity data were collected on a Nicolet R3m/V diffractometer and for **14** on a STOE four-circle diffractometer. In each case the data were corrected for Lorentz polarisation effects and for absorption. The relevant data for the crystal structure analyses are summarised in Table 5. The structures were solved by a combination of centrosymmetric direct methods (Os atom positions) followed by Fourier-difference techniques. Full-matrix least-squares refinement on F with Os, P and O atoms anisotropic employed the SHELXTL PLUS program²⁶ [in the case of **11c**, the C(511) and N atoms were also kept anisotropic]. Additional constraints were placed on some of the carbonyl ligands in **11c** and **12**; Os–C 1.900(1), C–O 1.160(1) Å. No attempt was made to locate hydrogen atoms in the structure of **11c**. For **12** and **14** the hydrogens of the phosphite ligands were generated in their ideal positions and allowed to ride on the relevant carbon atoms. The hydride ligands of **12** and **14** were located using the potential-minimisation program HYDEX.²¹ Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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