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Systematic synthesis of hexanuclear phosphido-bridged osmium clusters; crystal and molecular structure of $[Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH_2)]$

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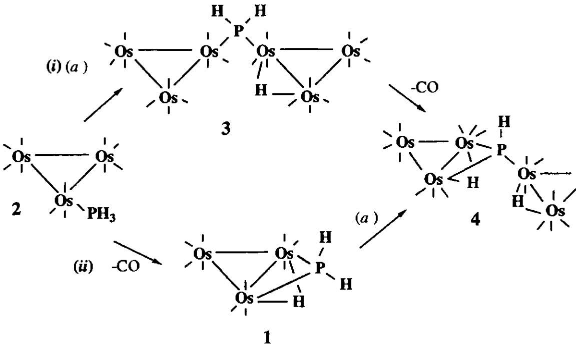
The phosphido-bridged cluster $[Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH_2)]$ and the corresponding phosphinidene-bridged cluster $[Os_6(\mu\text{-}H)_2(CO)_{21}(\mu\text{-}PH)]$ have been prepared from the reaction of $[Os_3(CO)_{11}(PH_3)]$ with $[Os_3(CO)_{11}(NCMe)]$ in toluene. In a similar reaction, $[Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\mu\text{-}PH_2)]$ has been prepared from the reaction of $[Os_3(CO)_{11}(PH_3)]$ with $[Os_3(CO)_{10}(NCMe)_2]$. The two Os_6 clusters have been fully characterized on the basis of their spectroscopic data and, in the case of $[Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH_2)]$, by single-crystal X-ray analysis. In both compounds, two Os_3 triangles are linked by a PH_2 group which is terminally bound to each triangle. Thermolysis of $[Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH_2)]$ and $[Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\mu\text{-}PH_2)]$ leads to the formation of $[Os_6(\mu_6\text{-}P)(CO)_{18}]^-$ and $[Os_6(\mu\text{-}H)(\mu_6\text{-}P)(CO)_{18}]$, respectively.

In the chemistry of bimetallic compounds bridging phosphido groups are often used as inert metal-binding groups to prevent complex fragmentation. There are several examples of complexes in which two mononuclear transition-metal complexes are linked solely *via* a phosphido-bridge. These include secondary (μ-PRH),[1] tertiary (μ-PR_2)[2] and halogeno (μ-PX_2)[3] phosphido-bridges. There are also numerous examples of binuclear transition-metal complexes in which the metals are linked by a single μ-PH_2 bridge without any supporting M–M bond. Schäfer[4–7] has synthesized several PH_2-bridged complexes by hydrogen–silyl exchange of $P(SiMe_3)_2$ bridges through reaction with either methanol, acetic acid or water. Deprotonation of co-ordinated PH_3 to generate terminal PH_2 ligands is facile[8] and has been used to form several hetero- and homo-metallic binuclear phosphido-bridged complexes.[8,9] Similarly, phosphine complexes have been lithiated to generate terminal phosphido anions which have been used to form μ-PH_2 bridges *via* ionic coupling.[10] Other synthetic methods include the direct reaction of metal carbonyls with PH_3[11] and abstraction of the trimethylsilyl moiety of $P(SiMe_3)H_2$ to generate dimeric phosphido-bridged compounds.[12] The crystal structures of $[\{Os(\mu\text{-}PH_2)Cl(CO)(PPh_3)_2\}_2]$,[9] $[(OC)_2(\eta\text{-}C_5H_5)Fe(\mu\text{-}PH_2)Fe(CO)_4]$,[13] $[(OC)_2(\eta\text{-}C_5H_5)Fe(\mu\text{-}PH_2)Mn(\eta\text{-}C_5H_4Me)(CO)_2]$,[13] $[\{Mn(CO)_4(\mu\text{-}PH_2)\}_2]$,[14] $[\{Mn(CO)_4(\mu\text{-}PH_2)\}_3]$[14] and $[\{Ni(\eta\text{-}C_5H_5)(\mu\text{-}PH_2)\}_3]$[14] have been reported.

The prevalence of phosphido-bridges between two mononuclear complexes is thus well documented. An example of a secondary phosphido-unit linking two clusters has recently been published[15] but, to our knowledge, there have been no reports of PH_2 units linking clusters. Oxidative addition of both co-ordinated and unco-ordinated PH_2 to iridium has been demonstrated by Ebsworth and co-workers[16] and we have shown that the cluster $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$ **1**[17] may be used to add one P–H bond oxidatively to an unsaturated metal centre and thus achieve linking of two clusters.[18] A phosphido (μ-PH_2) bridge linking two clusters may result in properties which are similar to those of **1**; new phosphido-clusters are therefore potential starting materials for further cluster build-up. In this paper we report an exploration into the possibility of using the triosmium cluster $[Os_3(CO)_{11}(PH_3)]$ **2**[18] to form PH_2-bridged clusters and an investigation into the thermolysis of such phosphido-linked clusters as a route to clusters containing an interstitial phosphorus atom.



Scheme 1 (*a*) $[Os_3(CO)_{11}(NCMe)]$

Results and Discussion

Gentle heating (55 °C) of a toluene solution of $[Os_3(CO)_{11}(PH_3)]$ **2** and $[Os_3(CO)_{11}(NCMe)]$ for 16–24 h results in the formation of the new cluster $[Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH_2)]$ **3** in good, *albeit* never quantitative, yield; the corresponding phosphinidene-bridged cluster $[Os_6(\mu\text{-}H)_2(CO)_{21}(\mu\text{-}PH)]$ **4**[18] is formed as a side product. Two possible side reactions (Scheme 1) may explain the formation of **4**. (*i*) The ejection of a carbonyl ligand from **2** and subsequent intramolecular oxidative addition to form $[Os_3(\mu\text{-}H)(CO)_{11}(\mu\text{-}PH_2)]$ competes with the oxidative addition of a P–H bond of $[Os_3(CO)_{11}(PH_3)]$ to an '$Os_3(CO)_{11}$' fragment. Subsequent reaction of the phosphido cluster **2** with $[Os_3(CO)_{11}(NCMe)]$ forms the phosphinidene-bridged cluster.[18] (*ii*) Conversion of **3** into **4** *via* the ejection of a carbonyl ligand with concomitant oxidative addition of a P–H bond. We have found that it is possible to form **4** in relatively low yield through gentle thermolysis of **3** and it is likely that both of the above-mentioned side reactions take place in the synthesis of **3**. Cluster **3** is also obtained in moderate yield when $[Os_3(CO)_{11}(PH_3)]$ is heated at 45–50 °C in toluene. Phosphane is a relatively weak ligand,[8] as demonstrated by the thermolysis of $[Os_3(CO)_{10}(PH_3)_2]$ to form **2**.[19] The above-mentioned reaction is another example of this relative lability, as the most likely mechanism for the formation of the phosphido bridge is dissociation of PH_3, followed by the oxidative addition of a P–H bond of a second molecule of $[Os_3(CO)_{11}(PH_3)]$.

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Table 1 Infrared spectral data for the new compounds (CH_2Cl_2)

Complex		ν(C–O)/cm^{-1}
3	$[Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH_2)]$	2144w, 2104m, 2095s, 2070 (sh), 2063vs, 2050s, 2025s (sh), 2017vs, 1982m, 1945mw (sh)
5	$[Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\mu\text{-}PH_2)]$	2113w, 2098m, 2078ms, 2057s, 2047s, 2025s (sh), 2016vs, 1981m (sh)
7/8	$[Os_6(\mu\text{-}H)(CO)_{21}(\mu_3\text{-}PH)]^-/[Os_6(CO)_{22}(\mu\text{-}PH_2)]^-$	2091mw, 2068w, 2044s, 2011vs, 1974m

Table 2 Proton and proton-coupled ^{31}P NMR data for new compounds

Compound	δ(^1H),[a] J/Hz	δ(^{31}P),[b] J/Hz
3	4.07 (d, $^1J_{PH} \approx 332.5$, $^2J_{HH}$, $^3J_{HH}$ not observed, μ-PH_2), −18.82 (d, $^2J_{PH} \approx 12.0$, OsH)	−409.2 (t of d, $^1J_{PH} \approx 333$, $^2J_{PH} \approx 12$, μ-PH_2)
5	4.06 [dd(d), AB pattern, $^1J_{PH} \approx 331.3$, μ-PH_2], 2.67 (s, $NCCH_3$), −15.99 (d, $^2J_{PH} \approx 12.2$, $^3J_{HH}$, not resolved, OsH)	−409.5 (t of d, $^1J_{PH} \approx 330.5$, $^2J_{PH} \approx 12.2$, μ-PH_2)
7/8[c]	7.7–7.3 [m, $N(PPh_3)_2^+$], 3.88 (d, $^1J_{PH} \approx 322.5$)	−119.9 [s, $N(PPh_3)_2^+$], −417.0 (t, $^1J_{PH} \approx 320$, μ-PH_2)

[a] In $CDCl_3$, $SiMe_4$ (δ 0). [b] In $CDCl_3$, $P(OMe)_3$ (δ 0), downfield positive. [c] See ref. 18 for data for complex **7**.

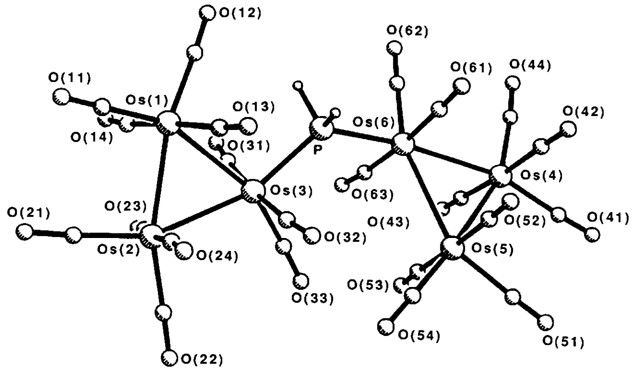


Fig. 1 Molecular structure of $[Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH_2)]$ **3** showing the atom numbering scheme. The hydrogen atoms of the phosphido moiety are placed in idealized positions

Reaction of $[Os_3(CO)_{11}(PH_3)]$ **2** with the bis(acetonitrile) complex $[Os_3(CO)_{10}(NCMe)_2]$ under the conditions used for the synthesis of **3** resulted in the formation of $[Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\mu\text{-}PH_2)]$ **5**. As in the case of **3**, the yield of **5** was good, although the phosphinidene cluster **4** was always present as a side product. The phosphinidene-bridged cluster is presumably formed *via* the ejection of the acetonitrile ligand from **5**; this suggests that side reaction (*i*) is the more likely source of the phosphinidene-bridged side product.

Clusters **3** and **5** have been characterized by IR, ^1H and ^{31}P NMR spectroscopy as well as mass spectrometry (*cf.* Tables 1 and 2). The proton NMR spectra confirm the existence of phosphorus-co-ordinated protons, as these resonances show a large P–H coupling ($^1J_{PH} \approx 333$ **3** and ≈331 Hz **5**). Furthermore, the resonances are shifted approximately two ppm upfield (to around δ 4) with respect to the resonances of the corresponding phosphinidene-bridged clusters.[18] This change in shift in conjunction with integration of the proton spectra (PH_2; 2 H; OsH; 1 H) indicates that phosphido-bridges have been formed. The ^1H NMR spectra of **3** and **5** both show a hydride resonance at a shift which is common for bridging hydrides. The phosphorus–hydride coupling ($^2J_{PH} \approx 12.0$ **3** or ≈12.2 Hz **5**) is of the same order as those reported for the corresponding phosphinidene-bridged clusters **4** and $[Os_6(\mu\text{-}H)_2(CO)_{20}(NCMe)(\mu\text{-}PH)]$ **6**. This indicates that in both **4** and **6** the hydride is located on an edge adjacent to the phosphorus atom and that they are *cis* to each other.

In the case of cluster **3**, the two phosphido-hydrogens, the hydride and the phosphorus atom should be observed as an A_2MX spin system if there is free rotation around one, or both, of the Os–P bonds. The crystal structure of **3** (see below) indicates that the two osmium triangles are brought into such close proximity that such rotation could be hindered by interlocking carbonyl ligands; an ABMX pattern might therefore be expected but only a doublet is observed for the phosphido-protons (*cf.* Table 2). While the most likely explanation for this spectrum is conformational flexibility about the Os–P bonds, rapid intramolecular exchange of the phosphido-hydrogens or a very small shift difference between these protons cannot be ruled out. To investigate possible fluxionality, the low-temperature ^1H NMR spectrum of **3** was recorded but no change was observed at 180 K. Coupling between the phosphide protons and the hydride of **3** could not be resolved. The ^1H NMR spectrum of **5** reveals two overlapping AB-type doublets of doublets for the phosphido protons.

The proton-coupled phosphorus spectra of these clusters are in both cases triplets of doublets. This provides incontrovertible evidence for the existence of PH_2 bridges, the phosphorus resonance being split into a triplet by the two (approximately equivalent) protons which are attached to it. The additional splitting is due to coupling to the hydride. As was observed for the resonances of the protons of the phosphido bridge, the phosphorus resonance of this moiety is significantly shifted towards higher field, by approximately 90 ppm, as compared to the resonances of the μ-PH moiety of **4** and **6** (δ ≈ −409.2 **3** or −409.5 **5**, *cf.* Table 2). Although ^{31}P NMR shifts are difficult to predict by electronic theories,[20] one may conclude that this shift is due to greater electron density around the phosphorus atom, reflecting the fact that it is acting as a three-electron donor, whereas the μ-PH ligand donates four electrons to the cluster.

Crystal and molecular structure of $[Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH_2)]$ 3

Based on the spectroscopic data, the structures of $[Os_6(\mu\text{-}H)(CO)_{22-n}(NCMe)_n(\mu\text{-}PH_2)]$ (n = 0 **3** or 1 **5**) were formulated as depicted in Scheme 1. Orange, brick-shaped crystals of cluster **3**, suitable for X-ray analysis, were grown from a dichloromethane–hexane solution at 4 °C and the crystal structure was determined in order to establish the full molecular geometry. The molecular structure is depicted in Fig. 1. Table 3 contains selected bond parameters and fractional coordinates in Table 4. The structure is similar to that of $[Os_6(\mu\text{-}H)(CO)_{22}\{\mu\text{-}P(CF_3)H\}]$.[15] The Os–Os bond distances vary from 2.85–2.90 Å {*cf.* $[Os_3(CO)_{12}]$: 2.88 Å[21]} with the exception of the Os(5)–Os(6) edge, which has a bond length of 3.05 Å. This observation, in conjunction with the fact that the equatorial carbonyl *cis* to the Os(5)–Os(6) edge is significantly bent away from the edge [C(54)–Os(5)–Os(6) 117.0°], indicates that the hydride is located on this edge. The dihedral angle between the planes of the two osmium triangles is 35.0° which may be compared to that of $[\mathrm{Os_6(\mu\text{-}H)(CO)_{22}\{\mu\text{-}P(CF_3)H\}}]$ (88.8°).[14] Whether this difference is due to steric effects or possibly a crystal-packing phenomenon is not entirely clear. Examination of the crystal packing of **3** reveals that there are no unusually short intermolecular distances. We have found that the dihedral angles between the metal planes, as well as their relative orientation with respect to each other, vary considerably in the compounds $[\mathrm{Os_6(\mu\text{-}H)(CO)_{22-\mathit{n}}L_\mathit{n}(\mu\text{-}PH_2)}]$ ($n = 0$ or 1; L = CO, phosphine, nitrile or isocyanide);[22] these variations are probably attributable to subtle steric interactions between the ligands of the two metal triangles. As found for the phosphido-bridged complexes $[\mathrm{(OC)_2(\eta\text{-}C_5H_5)Fe(\mu\text{-}PH_2)Fe(CO)_4}]$[13] and $[\mathrm{(OC)_2(\eta\text{-}C_5H_5)Fe(\mu\text{-}PH_2)Mn(\eta\text{-}C_5H_4Me)(CO)_2}]$,[13] the angles around the phosphorus atom are distorted in **3**. The Os(3)–P–Os(6) angle is 124.3°. The Os–P distances are also clearly different, Os(3)–P 2.37 and Os(6)–P 2.41 Å. Schäfer *et al.*[13] have pointed out that if a localized bonding scheme is invoked for μ-$\mathrm{PH_2}$ bridges one may expect a shorter bond distance for the σ-donor bond to the 17(47)-electron fragment than for the σ-donor/π-acceptor bond to the 16(46)-electron fragment. This is contrary to what is observed for **3** and $[\mathrm{(OC)_2(\eta\text{-}C_5H_5)Fe(\mu\text{-}PH_2)Mn(\eta\text{-}C_5H_4Me)(CO)_2}]$. Metal–phosphorus bond distances may vary by more than 0.1 Å and it is therefore impossible to draw any definite conclusions from the observed bond lengths in **3**.

Table 3 Selected bond lengths (Å) and angles (°) for $[\mathrm{Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH_2)}]$ **3**

Os(1)–Os(2)	2.890(1)	Os(4)–Os(6)	2.884(1)
Os(1)–Os(3)	2.889(1)	Os(5)–Os(6)	3.047(1)
Os(2)–Os(3)	2.849(1)	Os(3)–P	2.373(5)
Os(4)–Os(5)	2.903(1)	Os(6)–P	2.407(4)
Os(3)–Os(2)–Os(1)	60.5(1)	Os(2)–Os(2)–Os(1)	60.5(1)
P–Os(3)–Os(1)	97.2(1)	P–Os(3)–Os(2)	156.8(1)
C(31)–Os(3)–P	86.6(7)	C(32)–Os(3)–P	88.2(6)
Os(6)–Os(4)–Os(5)	63.5(1)	C(33)–Os(3)–P	103.0(6)
Os(5)–Os(6)–Os(4)	58.5(1)	C(54)–Os(5)–Os(4)	174.8(5)
P–Os(6)–Os(5)	110.5(1)	C(54)–Os(5)–C(51)	96.5(8)
C(62)–Os(6)–P	92.7(5)	P–Os(6)–Os(4)	168.2(1)
C(63)–Os(6)–P	89.2(6)	C(61)–Os(6)–P	86.5(5)
Os(3)–Os(1)–Os(2)	59.1(1)		

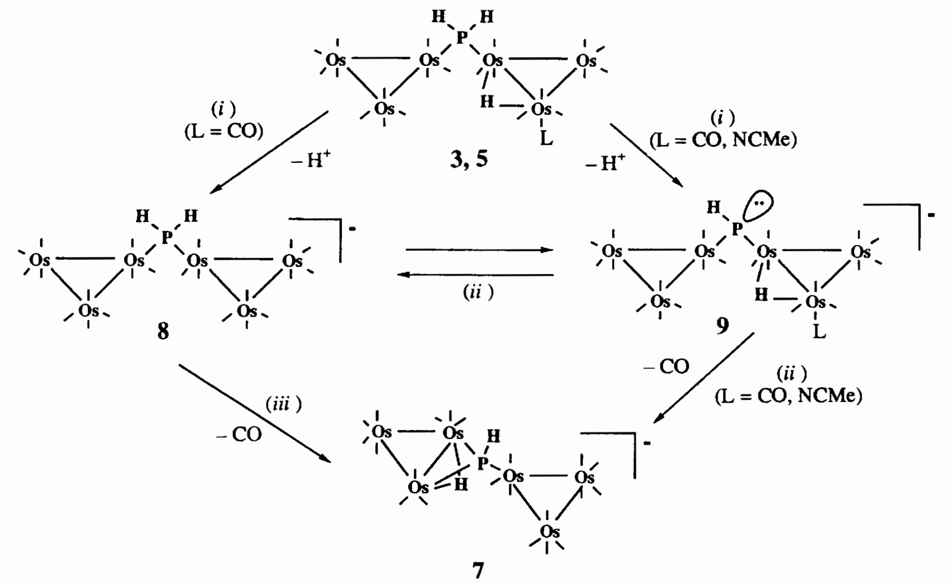
Reactivity studies

Reaction of $[\mathrm{Os_6(\mu\text{-}H)(CO)_{22-\mathit{n}}(NCMe)_\mathit{n}(\mu\text{-}PH_2)}]$ (n = 0 3 or 1 5) with base. Reaction of $[\mathrm{Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH_2)}]$ **3** with an excess of $[\mathrm{N(PPh_3)_2}]\mathrm{Cl}$ or $[\mathrm{PPh_3Me}]\mathrm{Br}$ in dichloromethane for approximately 12 h led to the formation of a mixture of anions. A doublet at δ 3.88 and a doublet of doublets at δ 4.49 in the ^{1}H NMR spectrum indicated not only the presence of a phosphido but also a phosphinidene moiety. The shifts of these two types of protons are slightly upfield when compared to the neutral clusters **3** and $[\mathrm{Os_6(\mu\text{-}H)_2(CO)_{21}(\mu_3\text{-}PH)}]$ **4**. Proton-coupled phosphorus NMR spectroscopy also indicated the presence of both moieties, a phosphide resonance (triplet) at δ ≈ −417.0 and a phosphinidene resonance (doublet) at δ ≈ −317.8. The latter resonance is indicative of the previously characterized $[\mathrm{Os_6(\mu\text{-}H)(CO)_{21}(\mu_3\text{-}PH)}]^-$ **7**[18] and the hydride resonance found in the proton NMR spectrum (Table 2) confirms that this ion is indeed present. Attempted separation of the two anions by repeated TLC was not successful. Reprotonation of the anionic mixture by addition of trifluoroacetic acid yielded both $[\mathrm{Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH_2)}]$ and $[\mathrm{Os_6(\mu\text{-}H)_2(CO)_{21}(\mu\text{-}PH)}]$ in approximately 3 : 1 ratio.

Possible explanations for the formation of both a phosphido- and a phosphinidene-bridged anion are outlined in Scheme 2. The acidities of the phosphorus protons and the hydride may be comparable. Abstraction of the hydride leads to the formation of an isomer which we formulate as $[\mathrm{N(PPh_3)_2}][\mathrm{Os_6(CO)_{22}(\mu\text{-}PH_2)}]$ **8**. The phosphido-resonances in the ^{1}H and ^{31}P NMR spectra are attributed to this compound. If a proton is abstracted from the phosphido-moiety we postulate that the short-lived intermediate $[\mathrm{N(PPh_3)_2}][\mathrm{Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH)}]$ **9** is formed. This cluster is bridged by a μ-PH bridge which possesses a lone electron pair and a negative charge resides (formally) on the phosphorus atom. The lone pair is expected to be very reactive[23] and, in an intramolecular nucleophilic attack by the PH group, a carbonyl ligand is displaced and **7** is formed. When the mixture of the two anions is refluxed in thf **7** is the exclusive product, indicating that **8** is converted into **7** through oxidative addition of one of the P–H bonds of $[\mathrm{Os_6(CO)_{22}(\mu\text{-}}$

Table 4 Fractional atomic coordinates (× 10^4) for $[\mathrm{Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH_2)}]$ **3**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	2 520(1)	3 569(1)	314(1)	O(32)	4 441(13)	5 595(8)	1 685(12)
Os(2)	1 799(1)	4 443(1)	1 650(1)	C(33)	4 092(14)	4 150(11)	3 309(13)
Os(3)	3 743(1)	3 906(1)	2 073(1)	O(33)	4 291(10)	4 323(7)	4 070(8)
Os(4)	8 468(1)	3 586(1)	4 240(1)	C(41)	9 453(15)	4 025(12)	5 223(14)
Os(5)	7 063(1)	4 872(1)	4 012(1)	O(41)	10 050(10)	4 238(9)	5 794(10)
Os(6)	6 697(1)	3 335(1)	2 899(1)	C(42)	9 061(14)	4 101(11)	3 326(14)
P	5 198(3)	3 422(3)	1 783(3)	O(42)	9 448(10)	4 366(9)	2 871(11)
C(11)	1 485(16)	3 824(12)	−716(15)	C(43)	7 856(15)	3 011(12)	5 079(14)
O(11)	886(11)	3 975(12)	−1 326(10)	O(43)	7 575(11)	2 659(9)	5 583(10)
C(12)	3 241(15)	2 796(12)	−182(14)	C(44)	9 055(16)	2 591(13)	4 019(15)
O(12)	3 626(14)	2 320(10)	−472(12)	O(44)	9 335(13)	2 003(9)	3 849(16)
C(13)	3 335(14)	4 414(11)	17(13)	C(51)	7 967(14)	5 480(11)	4 964(13)
O(13)	3 770(12)	4 874(10)	−234(10)	O(51)	8 468(11)	5 816(8)	5 462(9)
C(14)	1 781(15)	2 756(13)	744(14)	C(52)	7 598(13)	5 356(10)	3 068(13)
O(14)	1 396(15)	2 200(10)	947(12)	O(52)	7 879(12)	5 644(9)	2 513(11)
C(21)	476(16)	4 420(12)	1 007(15)	C(53)	6 527(17)	4 333(9)	4 926(12)
O(21)	−315(10)	4 327(11)	645(11)	O(53)	6 257(10)	4 042(8)	5 473(9)
C(22)	1 705(13)	5 129(11)	2 614(13)	C(54)	6 069(14)	5 643(11)	3 802(13)
O(22)	1 633(14)	5 526(9)	3 208(10)	O(54)	5 434(10)	6 108(8)	3 685(11)
C(23)	1 657(16)	3 533(13)	2 373(15)	C(61)	7 290(13)	3 768(10)	1 994(13)
O(23)	1 513(11)	3 010(9)	2 826(10)	O(61)	7 637(11)	4 012(9)	1 444(9)
C(24)	2 130(14)	5 349(12)	966(13)	C(62)	6 939(14)	2 283(11)	2 545(13)
O(24)	2 303(11)	5 916(8)	633(9)	O(62)	7 100(14)	1 653(7)	2 339(10)
O(31)	3 462(15)	2 799(13)	2 307(14)	C(63)	6 015(15)	2 844(12)	3 735(14)
C(31)	3 350(11)	2 143(7)	2 444(10)	O(63)	5 605(11)	2 509(9)	4 180(10)
C(32)	4 135(13)	4 987(11)	1 817(12)				



Scheme 2 (*i*) Excess of $[N(PPh_3)_2]Cl$, CH_2Cl_2, room temperature (r.t.); (*ii*) CH_2Cl_2, r.t.; (*iii*) tetrahydrofuran (thf), heat

$PH_2)]^-$, with concomitant carbonyl ejection. On the other hand, reaction of $[Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\mu\text{-}PH_2)]$ **5** with an excess of $[N(PPh_3)_2]Cl$ led to the exclusive formation of $[N(PPh_3)_2][Os_6(\mu\text{-}H)(CO)_{21}(\mu_3\text{-}PH)]$ **7**. In earlier studies[18] we have found that the hydrides of $[Os_6(\mu\text{-}H)_2(CO)_{20}(NCMe)(\mu_3\text{-}PH)]$ **6** are much less acidic than those of $[Os_6(\mu\text{-}H)_2(CO)_{21}(\mu_3\text{-}PH)]$ and attempts to deprotonate **6** were unsuccessful. It may be that the hydride of **5** is of a similar basicity. Therefore, we believe that the phosphido moiety is exclusively deprotonated to yield $[Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\mu_3\text{-}PH)]^-$. This is immediately followed by displacement of the labile acetonitrile ligand by the nucleophilic phosphorus atom (Scheme 2).

Thermolysis of $[Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH_2)]$ 3 and $[Os_6(CO)_{22}(\mu\text{-}PH_2)]^-$ 8. In order to investigate whether it is possible to synthesize interstitial phosphido clusters using $[Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH_2)]$ as a starting material the compound was heated to reflux in xylene for 12 h. The only product isolated was the anion $[Os_6(\mu_6\text{-}P)(CO)_{18}]^-$ **10**.[18] The corresponding thermolysis of $[Os_6(\mu\text{-}H)_2(CO)_{21}(\mu_3\text{-}PH)]$ leads to formation of the hydrido-cluster $[Os_6(\mu\text{-}H)(\mu_6\text{-}P)(CO)_{18}]$ **11**.[18]

Reflux of the salt $[PPh_3Me][Os_6(\mu\text{-}H)(CO)_{21}(\mu\text{-}PH)]/[Os_6(CO)_{22}(\mu\text{-}PH_2)]$ **7/8** in xylene for approximately 12 h resulted in the formation of the $[PPh_3Me]^+$ salt of **10**. It is likely that the initial step in the reaction is the conversion of $[Os_6(CO)_{22}(\mu\text{-}PH_2)]^-$ into $[Os_6(\mu\text{-}H)(CO)_{21}(\mu\text{-}PH)]^-$, although this could not be detected by IR spectroscopy. It is possible that $[Os_6(CO)_{22}(\mu\text{-}PH_2)]^-$ is an intermediate in the formation of **10** from $[Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH_2)]$ **3**.

Experimental

All manipulations involving air- or moisture-sensitive reagents were carried out under inert atmospheres of nitrogen or argon using standard Schlenk and vacuum-line techniques. All reactions involving PH_3 gas (BOC gases) were carried out under an argon atmosphere with rigorous exclusion of air. All solvents were dried by distillation over the appropriate drying agents. The starting materials $[Os_3(CO)_{12-n}(NCMe)_n]$ (n = 1 or 2),[24] $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$ **1**[17,18] and $[Os_3(CO)_{11}(PH_3)]$ **2**[17,18] were prepared by literature methods.

All chromatographic separations and ensuing work-up were carried out in open air. Thin-layer chromatography was carried out on either Merck 60 F-254 0.25 mm precoated silica gel plates or 2 mm thick plates prepared in the University of Cambridge Chemical Laboratory. Columns were packed with Merck 60 (70–230 mesh ASTM) silica gel. Infrared spectra were recorded on a Perkin-Elmer 983 grating or 1710 Fourier-transform spectrometer, ^1H NMR spectra using Bruker WP 80 SY, WM 250 and AM 400 Fourier-transform spectrometers ^{31}P and ^{13}C spectra on a Bruker AM 400 spectrometer and fast atom bombardment mass spectra using a Kratos MS902 spectrometer with a matrix of dithioglycerol or 2-nitrobenzyl alcohol.

Preparations

$[Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH_2)]$ 3. In a typical reaction, $[Os_3(CO)_{11}(PH_3)]$ (99 mg, 0.108 mmol) and $[Os_3(CO)_{11}(NCMe)]$ (107 mg, 0.116 mmol) were stirred at 45 °C in toluene (150 cm^3). The reactants dissolved completely after approximately 2 h. During the course of the reaction the solution changed from yellow to very bright yellow. The reaction was monitored by IR spectroscopy and was adjudged to be complete after *ca.* 12 h, when no ν(C–O) resonances due to the starting materials were detected. The solvent was removed under a stream of nitrogen, after which the solid was redissolved in the minimum volume of dichloromethane and subjected to thin-layer chromatography using dichloromethane–hexane (1 : 1) as eluent. Six bands were detected (in order of decreasing R_f): $[Os_3(CO)_{12}]$, yellow (trace); $[Os_3(CO)_{11}(PH_3)]$, bright yellow (trace); $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$ **1**, 5 mg; $[Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH_2)]$ **3**, bright yellow, 112 mg (0.062 mmol, 57%); $[Os_6(\mu\text{-}H)_2(CO)_{21}(\mu\text{-}PH)]$, yellow, 23 mg (0.013 mmol, 12%) and a sixth yellow band, *ca.* 5 mg, not identified. Yields quoted are after recrystallization from dichloromethane–hexane. Compound **3** [Found (Calc.): C, 14.65 (14.65); H, 0.60 (0.15); P, 1.05 (1.70)%]: mass spectrum *m/z*, 1802 (Calc. 1802).

$[Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\mu\text{-}PH_2)]$ 5. The synthesis and work-up procedure for this compound were analogous to that described above. In a typical reaction, $[Os_3(CO)_{11}(PH_3)]$ (64.9 mg, 0.070 mmol) was treated with $[Os_3(CO)_{10}(NCMe)_2]$ (61.8 mg, 0.066 mmol). Thin-layer chromatography gave five bands (in order of decreasing R_f): two faint yellow bands (trace) which were ignored; an orange-yellow band (*ca.* 2 mg), not identified; $[Os_6(\mu\text{-}H)_2(CO)_{21}(\mu\text{-}PH)]$, yellow, 12 mg (0.007 mmol, 10%) and $[Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\mu\text{-}PH_2)]$ **5**, bright yellow, 62.3 mg (0.034 mmol, 52%). Yields quoted were after recrystallization from dichloromethane–hexane. Compound **5** [Found (Calc.): C, 15.25 (15.25); H, 0.30 (0.35); P, 1.95 (1.70)%]: mass spectrum m/z, 1815 (Calc. 1815).

Deprotonations

Complex 3. In a typical reaction complex **3** (21.3 mg, 0.012 mmol) was dissolved in dichloromethane (20 cm^3) to which $[N(PPh_3)_2]Cl$ (21.1 mg, 0.012 mmol) was added. The mixture was stirred for 11 h after which more $[N(PPh_3)_2]Cl$ (6.0 mg) was added and the mixture stirred for 12 h. Further addition (12.3 mg) did not result in any change of the IR spectrum of the reaction mixture. The solvent was removed *in vacuo*. The resultant solid was redissolved in the minimum volume of dichloromethane and subjected to thin-layer chromatography (dichloromethane–hexane, 5:1 v/v). Two bands were found: one faint yellow, $R_f \approx 0.8$, not identified; one bright yellow, $R_f \approx 0.3$, $[Os_6(\mu\text{-}H)(CO)_{21}(\mu\text{-}PH)]^-$ **7**/$[Os_6(CO)_{22}(\mu\text{-}PH_2)]^-$ **8**, 15 mg, 0.008 mmol, 67% based on $[Os_6(CO)_{22}(\mu\text{-}PH_2)]$. Mass spectrum: m/z, 1773 (**7**), 1801 (**8**).

Complex 5. In a typical reaction complex **5** (17.9 mg, 0.010 mmol) was treated with $[N(PPh_3)_2]Cl$ (21.1 mg) which was added in three aliquots over a period of 2 d. Thin-layer chromatography (dichloromethane–hexane, 5:1 v/v) yielded $[N(PPh_3)_2][Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\mu\text{-}PH_2)]$ ($R_f \approx 0.3$, 10 mg, 0.004 mmol, 40%) and two minor bands which were not identified.

Crystallography

Crystals of complex **3** were grown by slow evaporation from a CH_2Cl_2–hexane solution, and a suitable crystal was mounted on a glass fibre.

Crystal data. $C_{22}H_3O_{22}Os_6P$, $M = 1791.42$, monoclinic, space group $P2_1/c$ (no. 14), $a = 14.328(3)$, $b = 16.658(5)$, $c = 15.528(7)$ Å, $\beta = 103.79(2)°$, $U = 3537$ Å^3 (by least-squares refinement of diffractometer angles from 50 automatically centred reflections in the range $17 < 2\theta < 25°$, $\lambda = 0.710\,69$ Å), $Z = 4$, $D_c = 3.36$ g cm^{-3}, D_m not measured, $F(000) = 3128$. Yellow rectangular plates. Crystal dimensions (distance to faces from centre): 0.038 (100, $\bar{1}00$) × 0.016 ($0\bar{1}1$, $01\bar{1}$) × 0.167 (011, $0\bar{1}\bar{1}$) mm, μ(Mo-Kα) = 215.90 cm^{-1}.

Data collection and processing. STOE AED diffractometer, 30 step ω–θ scan mode with ω-scan width 0.05°, ω-scan speed ranging from 1.0 to 4.0 s per step, graphite-monochromated Mo-Kα radiation; 5031 reflections measured ($5.0 < 2\theta < 45.0°$, $\pm h$, $+k$, $-l$), 4351 unique [merging $R = 0.028$ after numerical absorption correction (maximum, minimum transmission factors 0.185, 0.026)] giving 3791 with $F > 4\sigma(F)$. Three check reflections showed no significant variations during data collection.

Structure analysis and refinement. 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. Hydrogen atoms attached to phosphorus were placed in idealized positions (P–H 1.44 Å) and were assigned a common isotropic thermal parameter. The hydride was not located directly. The weighting scheme $w = 1.996/[\sigma^2(F) + 0.001F^2]$, with $\sigma(F)$ from counting statistics, gave reasonable agreement analyses. Final R and R' were 0.042 and 0.043. Highest peak in final difference map 3.2 e Å^{-3} close to Os atom position. The structure was solved and refined using SHELX 76[25] installed on the University of Cambridge IBM 3084Q computer. Neutral atom scattering factors were taken from ref. 26.

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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