Reactivity of $[Os_3H(CO)_{10}(MeCN)\{Si(OR)_3\}]$ (R = Me or Et) towards Diphosphines. *X*-Ray Crystal Structures of $[Os_3H(CO)_{10}\{Si(OEt)_3\}(dppe)]$, $[\{Os_3H(CO)_{10}[Si(OMe)_3]\}_2(\mu\text{-dppe})]$ and $[Os_3(CO)_{10}(dppe)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$)†

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The reactivity of $[Os_3H(CO)_{10}(MeCN)\{Si(OR)_3\}]$ (R = Me or Et) towards diphosphines has been studied. The compounds $[Os_3H(CO)_{10}\{Si(OR)_3\}(dppm)]$ are formed in high yield from the reaction with bis(diphenylphosphino)methane (dppm). Formation of three different products $[Os_3H(CO)_{10}\{Si(OR)_3\}(dppe\text{-}P)]$, $[\{Os_3H(CO)_{10}[Si(OR)_3]\}_2(\mu\text{-dppe})]$, and $[Os_3(CO)_{10}(dppe\text{-}PP')]$, has been observed from the reaction with 1,2-bis(diphenylphosphino)ethane (dppe). The product distribution is strictly dependent on the reaction stoicheiometry. The structure of $[Os_3H(CO)_{10}\{Si(OEt)_3\}(dppe\text{-}P)]$ has been determined by *X*-ray diffraction [monoclinic, space group $P2_1/c$, a = 18.092(4), b = 11.924(1), c = 23.210(5) Å, β = 108.29(2)°, Z = 4] unambiguously establishing monodentate co-ordination of the dppe ligand. The dimeric nature of $[\{Os_3H(CO)_{10}[Si(OMe)_3]\}_2(\mu\text{-dppe})]$ has been crystallographically determined [monoclinic, space group $C2/c$, a = 18.07(2), b = 14.134(3), c = 26.60(1) Å, β = 111.72(5)°, Z = 8]. An *X*-ray crystallographic characterization of $[Os_3(CO)_{10}(dppe\text{-}PP')]$ shows the chelating mode of the dppe ligand [monoclinic, space group $P2_1/c$, a = 15.527(2), b = 10.405(5), c = 22.519(3) Å, β = 94.01(1)°, Z = 4]. The compounds $[\{Os_3H(CO)_{10}[Si(OR)_3]\}_2(\mu\text{-dppe})]$ can be prepared alternatively from $[\{Os_3(CO)_{10}(MeCN)\}_2(\mu\text{-dppe})]$ and the appropriate silane $SiH(OR)_3$ (R = Me or Et).

The reactivity of polydentate phosphines towards transition-metal carbonyl clusters has been extensively studied in recent years.[1] It has been shown that multidentate phosphine ligands play a role in maintaining the metal-cluster framework intact under a variety of conditions in which the unsubstituted clusters undergo fragmentation. An example of this stabilization is offered by a triruthenium cluster capped with a tripod silaphosphine ligand $[Ru_3(CO)_9\{MeSi(PBu_2)_3\}]$ which is resistant to fragmentation under the conditions of the Fischer–Tropsch reaction.[2] The bidentate phosphine ligand $Ph_2PCH_2PPh_2$ (dppm) is known for its tendency to form bridged binuclear complexes but stabilization of cluster complexes has also been reported.[3] The greater ability of $Ph_2PCH_2CH_2PPh_2$ (dppe) as a chelating ligand has been recognized but examples are known in which it acts as a monodentate[4] or bridging bidentate ligand.[5]

An exhaustive study of the reactivity of diphosphines $Ph_2P(CH_2)_nPPh_2$ (n = 1—4) towards triosmium clusters containing slightly stabilizing ligands has been reported very recently.[6] Since we have synthesized a new series of triosmium cluster compounds containing Group 4B elements[7] our attention has been drawn by the study of the reactivity of $[Os_3H(CO)_{10}(MeCN)\{Si(OR)_3\}]$ (R = Me or Et) towards the diphosphines dppm and dppe. To our knowledge, in the chemistry of Group 8 metals, the only precedent for a study on the reactivity of hydrido silyl-substituted metal complexes towards diphosphines is represented by the reaction of the mononuclear hydrido silyl iron complex $[FeH(CO)_4(SiR_3)]$ with dppe.[8,9] This leads to the formation of the mononuclear complex $[FeH(CO)_2(dppe)(SiR_3)]$ in which the dppe ligand adopts a chelate mode. The presence in $[Os_3H(CO)_{10}(MeCN)\{Si(OR)_3\}]$ (R = Me or Et) of the weakly co-ordinated MeCN ligand prompted us to investigate its nucleophilic substitution in order to prepare clusters containing diphosphine ligands either bridging or chelating the triosmium unit or linking cluster units. In addition such a reactivity study might give useful information about the stability of the osmium–silicon bond in cluster compounds. Here we report the synthesis and crystal structures of the products obtained by treating $[Os_3H(CO)_{10}(MeCN)\{Si(OR)_3\}]$ with dppe and dppm, respectively as well as an alternative route to the synthesis of silyl-substituted linked clusters from $[\{Os_3(CO)_{10}(MeCN)\}_2(\mu\text{-dppe})]$ and $SiH(OR)_3$ (R = Me or Et).

Results and Discussion

Preparation of $[Os_3H(CO)_{10}\{Si(OR)_3\}(dppm\text{-}P)]$ (**2**).—The triosmium clusters $[Os_3H(CO)_{10}(MeCN)\{Si(OR)_3\}]$ [R = Me, (**1a**); or Et, (**1b**)] react with 1 equivalent of dppm in toluene solution at 40 °C affording after 20 h $[Os_3H(CO)_{10}\{Si(OR)_3\}(dppm\text{-}P)]$ [R = Me, (**2a**); or Et, (**2b**)] in high yields. A large amount of decomposition together with a small amount of cluster (**2**) and a mixture of uncharacterized by-products was obtained using a 2:1 ratio of cluster to phosphine ligand. Interestingly, formation of $[\{Os_3H(CO)_{10}[Si(OR)_3]\}_2(\mu\text{-dppm})]$ has not been observed. This behaviour is analogous to that observed for the reaction of $[Os_3(CO)_{11}(MeCN)]$ with dppm[6] whereas quantitative formation of $[\{Ru_3(CO)_{11}\}_2(\mu\text{-dppm})]$ has been obtained by the radical ion-initiated reaction of

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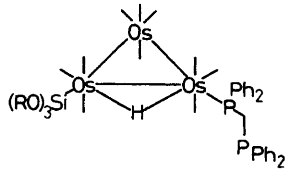
† [1,2-Bis(diphenylphosphino)ethane-1κ*P*]decacarbonyl-$1\kappa^3C$, $2\kappa^3C$, $3\kappa^4C$-μ-hydrido-1:$2\kappa^2$-triethoxysilyl-2κ*Si*-*triangulo*-triosmium, μ-[1,2-bis(diphenylphosphino)ethane-1κ*P*:2κ*P′*]-bis[decacarbonyl-$1\kappa^3C$, $2\kappa^3C$, $3\kappa^4C$-μ-hydrido-1:$2\kappa^2$-trimethoxysilyl-2κ*Si*-*triangulo*-triosmium], and [1,2-bis(diphenylphosphino)ethane-$1\kappa^2PP'$]decacarbonyl-$1\kappa^2C$, $2\kappa^4C$, $3\kappa^4C$-*triangulo*-triosmium.

Supplementary data available: see Instructions for Authors. *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. N.m.r. spectral data for the complexes: ^1H in CD_2Cl_2, ^{31}P-{^1H} in $CDCl_3$ [standard $P(OMe)_3$]; *J* in Hz

(**2a**) $[Os_3H(CO)_{10}\{Si(OMe)_3\}(dppm\text{-}P)]$	δ_H	7.31 (m, Ph), 3.74 (dd, J_{PH} 8.9, 1.3, PCH_2P), 3.52 (s, Me),[a] 3.44 (s, Me), −18.37 (d, J_{PH} 12.5, OsHOs),[a] −19.12 (dd, J_{PH} 12.0, 0.7, OsHOs)
	δ_P	−153.2 (d, J_{PP} 80),[a] −154.2 (d, J_{PP} 74), −166.6 (d, J_{PP} 80),[a] −167.3 (d, J_{PP} 74)
(**2b**) $[Os_3H(CO)_{10}\{Si(OEt)_3\}(dppm\text{-}P)]$	δ_H	7.26 (m, Ph), 3.81 [q, $Si(OCH_2CH_3)_3$],[a] 3.73 [q, $Si(OCH_2CH_3)_3$], 1.19 [t, $Si(OCH_2CH_3)_3$],[a] 1.12 [t, $Si(OCH_2CH_3)_3$], −18.34 (d, J_{PH} 12.3, OsHOs),[a] −19.01 (d, J_{PH} 11.1, OsHOs)
	δ_P	−153.1 (d, J_{PP} 86),[a] −154.0 (d, J_{PP} 82), −165.3 (d, J_{PP} 86),[a] −166.6 (d, J_{PP} 82)
(**3a**) $[Os_3H(CO)_{10}\{Si(OMe)_3\}(dppe\text{-}P)]$	δ_H	7.35 (m, Ph), 3.66 (s, Me),[a] 3.61 (s, Me), 2.99 (m, $-PCH_2CH_2P$), 1.90 (m, $-PCH_2CH_2P$), −19.32 (d, J_{PH} 11.1)
	δ_P	−152.3 (d, J_{PP} 43), −155.5 (d, J_{PP} 43)
(**3b**) $[Os_3H(CO)_{10}\{Si(OEt)_3\}(dppe\text{-}P)]$	δ_H	7.31 (m, Ph), 3.92 [q, $Si(OCH_2CH_3)_3$], 3.81 [q, $Si(OCH_2CH_3)_3$],[a] 3.01 (m, $-PCH_2CH_2P$), 1.91 (m, $-PCH_2CH_2P$), 1.21 [t, $Si(OCH_2CH_3)_3$], 1.20 [t, $Si(OCH_2CH_3)_3$],[a] −18.62 (d, J_{PH} 12.2),[a] −19.22 (d, J_{PH} 11.5)
	δ_P	−149.9 (d, J_{PP} 41),[a] −150.4 (d, J_{PP} 42), −154.0 (d, J_{PP} 41),[a] −154.2 (d, J_{PP} 42)
(**4a**) $[\{Os_3H(CO)_{10}[Si(OMe)_3]\}_2(\mu\text{-}dppe)]$	δ_H	7.46 (m, Ph), 3.53 (s, Me),[a] 3.42 (s, Me), 2.67 [s(br), $P(CH_2)_2P$], −18.68 (d, J_{PH} 12.3),[a] −19.18 (d, J_{PH} 11.1)
	δ_P	−152.5 (s)
(**4b**) $[\{Os_3H(CO)_{10}[Si(OEt)_3]\}_2(\mu\text{-}dppe)]$	δ_H[b]	7.42 (m, Ph), 3.82 [q, $Si(OCH_2CH_3)_3$], 3.70 [q, $Si(OCH_2CH_3)$)],[c] 3.68 [q, $Si(OCH_2CH_3)_3$],[c] 2.59 [m, $P(CH_2)_2P$], 1.20 [t, $Si(OCH_2CH_3)_3$], 1.10 [t, $Si(OCH_2CH_3)_3$],[c] 1.09 [t, $Si(OCH_2CH_3)_3$],[c] −18.62 (d, J_{PH} 12.5), −19.05 (d, J_{PH} 10.7)
	δ_P	−154.4 (d, J_{PP} 40), −155.1 (s), −156.6 (s), −156.7 (d, J_{PP} 40)
(**5**) $[Os_3(CO)_{10}(dppe\text{-}PP')]$	δ_H	7.43 (m, Ph), 2.63 [d, $P(CH_2)_2P$]
(**6**) $[\{Os_3(CO)_{10}(MeCN)\}_2(\mu\text{-}dppe)]$	δ_H	7.37 (m, Ph), 2.58 (s, Me), 2.42 [s(br), $P(CH_2)_2P$]
	δ_P	−149.6 (s)

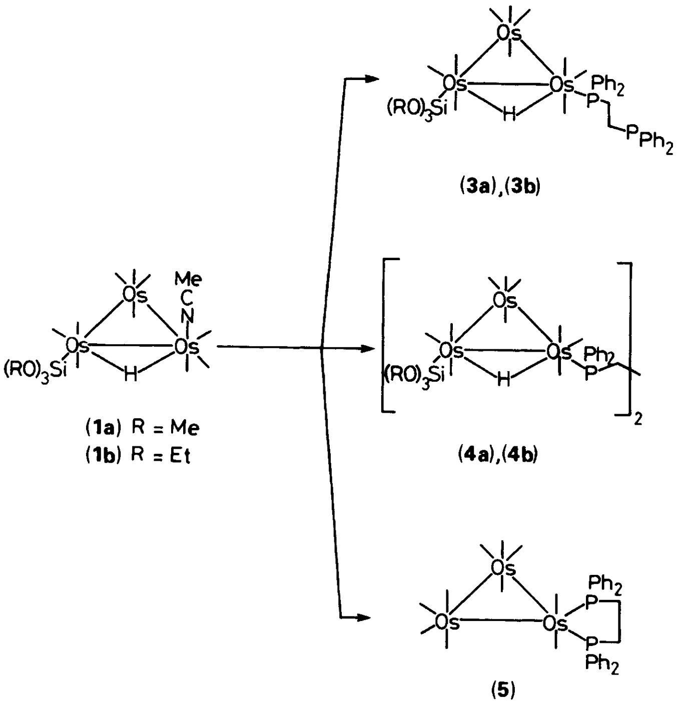
[a] Minor isomer. [b] In $CDCl_3$ solution. [c] Minor isomers in intensity ratio 1:1.



(**A**)

$[Ru_3(CO)_{12}]$ (2:1 molar ratio) with dppm.[10] The co-ordination mode of the dppm ligand in the cluster $[Os_3H(CO)_{10}\{Si(OMe)_3\}(dppm\text{-}P)]$ (**2a**) has been determined on the basis of its ^1H, ^{31}P-{^1H} n.m.r. (see Table 1) and mass spectrometry [*m/z* 1 362 (^{192}Os)]. In the ^1H n.m.r. spectrum the presence of a doublet of doublets at δ 3.74 attributed to the methylene protons of the dppm ligand is indicative of the inequivalence of the two P atoms. The coupling constants of 8.9 and 1.3 Hz are in agreement with the values reported for the monodentate dppm ligand in $[Os_3(CO)_9(\mu\text{-}dppm)(dppm\text{-}P)]$.[1] In addition, the high-field region of the ^1H n.m.r. spectrum shows a doublet of doublets at δ −19.12 (J_{PH} 12.0 and 0.7 Hz) for the hydride signal. The proton-decoupled ^{31}P n.m.r. spectrum recorded in $CDCl_3$ exhibits two doublets centred at −154.2 and −167.3 p.p.m. (J_{PP} 74 Hz) [relative to $P(OMe)_3$], respectively. On the basis of a proton-coupled experiment we assign the resonance at lower field to the co-ordinated P atom and the higher-field resonance to the unco-ordinated phosphorus. The complex $[Os_3H(CO)_{10}\{Si(OEt)_3\}(dppm\text{-}P)]$ (**2b**) has been characterized analogously on the basis of its spectroscopic data. In the ^1H n.m.r. spectrum the signals due to the methylene and methyl groups in the $Si(OEt)_3$ unit are centred at δ 3.73 and 1.12, respectively (see Table 1) with the methylene signals partially superimposed on the resonances of the methylene PCH_2P protons. In the hydride region a doublet centred at δ −19.01 (J_{PH} 11.1 Hz) is present. The ^{31}P-{^1H} n.m.r. spectrum consists of two doublets centred at −154.0 and −166.6 p.p.m., respectively. In view of the fact that bulky ligands tend to adopt equatorial sites in trinuclear clusters[11] and on the basis of the spectroscopic data we assign to compounds (**2**) the structure (A) with the diphosphine acting as a monodentate ligand and in *cis* position with respect to the hydride. The reaction is not stereoselective and minor isomers can be detected both in the ^1H and ^{31}P n.m.r. spectra (see Table 1). The extremely low yields of these isomers have prevented any attempt at interpretation of their geometries.

Reactions of $[Os_3H(CO)_{10}(MeCN)\{Si(OR)_3\}]$ *with dppe.*—The reaction between the hydrido silyl-substituted compounds (**1**) and dppe carried out in toluene at 40 °C in cluster : phosphine molar ratios ranging from 1:1 to 2:1 affords a mixture of products (see Scheme). The nature of the products obtained is not affected by the molar ratio of the starting materials which influences only the product distribution. After thin-layer chromatography on silica eluting with a hexane–diethyl ether mixture, three yellow products were isolated which are, in order of elution, $[Os_3H(CO)_{10}\{Si(OR)_3\}(dppe\text{-}P)]$ (**3**), $[\{Os_3H(CO)_{10}[Si(OR)_3]\}_2(\mu\text{-}dppe)]$ (**4**) and $[Os_3(CO)_{10}(dppe)]$ (**5**). The solution i.r. spectra of compounds (**3**) (see Table 2) exhibit the same band pattern observed for the clusters (**2**), thus supporting the hypothesis that the cluster geometry is retained by changing a dppm for a dppe ligand. The ^1H n.m.r. spectrum of (**3a**) shows in addition to the singlet resonance of the methyl groups in the $Si(OMe)_3$ unit the presence of two multiplets at δ 2.99 and 1.90, respectively attributed to the two non-equivalent pairs of methylene protons of the dppe ligand and a doublet for the hydride in the high-field region. In the ^{31}P-{^1H} n.m.r. spectrum the appearance of two doublets at −152.3 and −155.5 p.p.m., respectively accounts for a monodentate co-ordination of the dppe ligand. The ^1H n.m.r. spectrum of compound (**3b**) in CD_2Cl_2 (see Table 1) reveals in addition to the signals of the $Si(OEt)_3$ unit the presence of two multiplets centred at δ 3.01 and 1.91 assigned to the two non-equivalent methylene groups of the diphosphine ligand. In the high-field region the ^1H n.m.r spectrum shows a doublet at δ −19.22 attributed to the hydride (J_{PH} 11.5 Hz). A minor isomer of (**3b**) could also be detected in solution. This exhibits a doublet for the hydride at δ −18.62 (J_{PH} 12.2 Hz) in addition to the quartet and triplet signals of the $Si(OEt)_3$ protons centred at δ 3.81 and 1.20, respectively. We tentatively assign to this isomer the structure in



Scheme. The reaction of $[Os_3H(CO)_{10}(MeCN)\{Si(OR)_3\}]$[R = Me, (**1a**); or Et, (**1b**)] with dppe in toluene at 40 °C

which the $Si(OEt)_3$ ligand is in *trans* position with respect to the hydride. In the $^{31}P-\{^1H\}$ n.m.r. spectrum the presence of doublets centred at −150.4 and −154.2 p.p.m. confirms the presence of a pendant mode for the dppe ligand with the unco-ordinated phosphorus almost unshifted from the signal of the free phosphine (−154.0 p.p.m.). In order fully to characterize the geometry of the clusters (**3**) and the co-ordination mode of the dppe ligand an *X*-ray single-crystal study has been undertaken on compound (**3b**) (see below).

The dimeric clusters $[\{Os_3H(CO)_{10}[Si(OR)_3]\}_2(\mu\text{-dppe})]$ (**4**) have been characterized by i.r., mass, ^1H and ^{31}P n.m.r. spectroscopy (see Tables 1, and 2) and by a crystal-structure determination for (**4a**). The mass spectrum unambiguously shows a parent-ion peak at *m*/*z* 2 355 and 2 439 (^{192}Os) for (**4a**) and (**4b**), respectively which is consistent with their proposed formulation. In addition, the i.r. spectra of (**4**) in the carbonyl region (see Table 2) closely resemble those of (**3**) and the only way for compounds (**4**) to maintain the same carbonyl geometry is by having the dppe ligand linking two cluster units. In the ^1H n.m.r. spectrum in addition to the resonance of the methyl hydrogens in the $Si(OMe)_3$ unit at δ 3.42, a broad singlet observed at δ 2.67 for the $P(CH_2)_2P$ protons is again in agreement with the equivalence of the two P atoms. In the high-field region a doublet is observed for the hydride (J_{PH} 11.1 Hz). The $^{31}P-\{^1H\}$ n.m.r. spectrum shows a singlet at −152.5 p.p.m. as expected for this class of linked clusters.[12] Minor isomers have been observed which might be generated during the reaction or might arise by rearrangement of the cluster in solution. The room-temperature ^1H n.m.r. spectrum of compound (**4b**) shows the presence in solution of three quartets and three triplets for the $Si(OEt)_3$ methylene and methyl protons respectively, which are approximately in the intensity ratio 2:1:1, suggesting the presence in solution of at least three inseparable isomers. The quartets and triplets of the two minor isomers are closely overlapping. In the ^1H n.m.r. high-field region only two doublets centred at δ −18.62 and −19.05 (J_{PH} 12.5 and 10.7 Hz), respectively in a 1:1 ratio can be detected for the hydrides. This is probably due to accidental coincidence of the hydride signals of the two minor isomers. The $^{31}P-\{^1H\}$ n.m.r. spectrum of (**4b**) confirms the existence of isomers in solution because a complex multiplet is observed instead of the singlet resonance expected for two equivalent P nuclei. A possible interpretation of this spectrum could be to consider the resonances due to two doublets at −154.4 and −156.7 p.p.m., respectively as originated by two P atoms experiencing different environments and the remaining signals as two singlets arising from two isomers containing equivalent P atoms. The nature of the isomers present in solution is not completely clear but of the possible isomers arising by equatorial site exchange of the diphosphine P atoms and/or of the $Si(OEt)_3$ groups the former can be ruled out on the basis of the phosphorus–hydrogen coupling constants which are in the range expected for a phosphorus atom in *cis* position with respect to the hydride. An equatorial–axial site exchange of the diphosphine ligand seems unlikely because of steric hindrance. The $Si(OEt)_3$ groups are presumably involved in an equatorial site-exchange process which generates different isomers.

The compound $[Os_3(CO)_{10}(dppe)]$ can exist in two isomeric forms *i.e.* with the diphosphine acting as chelating or bridging ligand, and both isomers have been reported.[6] In our reaction only $[Os_3(CO)_{10}(dppe\text{-}PP')]$ has been isolated and in order further to confirm the co-ordination mode of the dppe ligand a single-crystal *X*-ray study has been undertaken (see below).

Thermolysis of $[Os_3H(CO)_{10}\{Si(OEt)_3\}(dppe\text{-}P)]$ (**3b**).—Compound (**3b**) could be regarded as a suitable precursor of the chelate $[Os_3(CO)_{10}(dppe\text{-}PP')]$ (**5**) obtainable by an intramolecular process of reductive elimination of $SiH(OEt)_3$ and carbonyl migration. In order to verify this, thermolysis of (**3b**) has been studied in toluene at different temperatures. At 40 °C for 4 d compound (**3b**) was unchanged, whereas by refluxing at 60 °C for 2 d or at 75 °C for 20 h complete conversion was observed. Unexpectedly the main product isolated (75% yield) after t.l.c. was an orange compound characterized on the basis of its ^1H and $^{31}P-\{^1H\}$ n.m.r. and mass spectral data as dimeric $\{Os_3H(CO)_{10}[Si(OEt)_3]\}\{Os_3(CO)_9(dppe)\}(\mu\text{-dppe})]$. Formation of this product could be explained through the following two-step reaction mechanism: (1) the monodentate dppe ligand in one molecule of (**3b**) promotes reductive elimination of $SiH(OEt)_3$ in a second molecule of (**3b**) linking together two triosmium units; (2) the second monodentate dppe ligand in the triosmium cluster which has lost the silane bridges through the unco-ordinated P atom the Os–Os edge opposite to the Os–P(dppe-*PP′*) thus forming a six-membered ring. The $^{31}P-\{^1H\}$ n.m.r. spectrum of $[\{Os_3H(CO)_{10}[Si(OEt)_3]\}\{Os_3(CO)_9(dppe)\}(\mu\text{-dppe})]$ shows two broad singlets at −139.4 and −142.5 p.p.m., attributable to a bridging dppe and very close to the value reported for $[Os_3(CO)_{10}(dppe)]$(dppe bridging Os^1 and Os^2) (−138.6 p.p.m.).[6] An alternative structure containing a chelate dppe ligand can be proposed but the formation of a five-membered ring would cause a significant deshielding in the ^{31}P n.m.r. resonances.[13] The appearance of four doublets in the region between −150.3 and −154.1 p.p.m. is consistent with the presence of two isomers in solution. No coupling between the P atoms bridging one Os–Os edge and the P atom of the dppe linking the two trinuclear cluster units has been observed. Since conversion of compound (**3b**) into the chelate complex (**5**) has not taken place, it seems likely that the latter is generated through a complicated intermolecular process.

Structural Characterization of Compounds (**3b**), (**4a**), *and* (**5**).—The molecular structures of compounds (**3b**) and (**4a**) are shown in Figures 1 and 2, respectively, together with the atomic labelling. The two species are closely related and their structural

Table 2. I.r. data (cm^{-1}) for the complexes (carbonyl region) recorded in n-hexane unless otherwise specified

(2a)	2 106w, 2 063m, 2 042s, 2 020vs, 2 009m(sh), 2 001s, 1 987w
(2b)	2 106mw, 2 063m, 2 041s, 2 024s(sh), 2 020vs, 2 000s, 1 985m, 1 973w, 1 967w
(3a)	2 106w, 2 063m, 2 042s, 2 021vs, 2 010m(sh), 2 001s, 1 987w, 1 983w
(3b)	2 106mw, 2 063m, 2 042ms, 2 021vs, 2 010m(sh), 2 000ms,1 986mw, 1 982w(sh), 1 973w
(4a)*	2 107mw, 2 063m, 2 041s, 2 021vs, 2 001m
(4b)	2 107m, 2 063ms, 2 050m(sh), 2 043s, 2 022vs, 2 003ms, 1 988m
(5)	2 094m, 2 044s, 2 016s(sh), 2 009vs, 1 989m, 1 976m, 1 963ms, 1 930m
(6)*	2 082m, 2 031vs, 2 018s, 1 994vs, 1 968s

* In CH_2Cl_2.

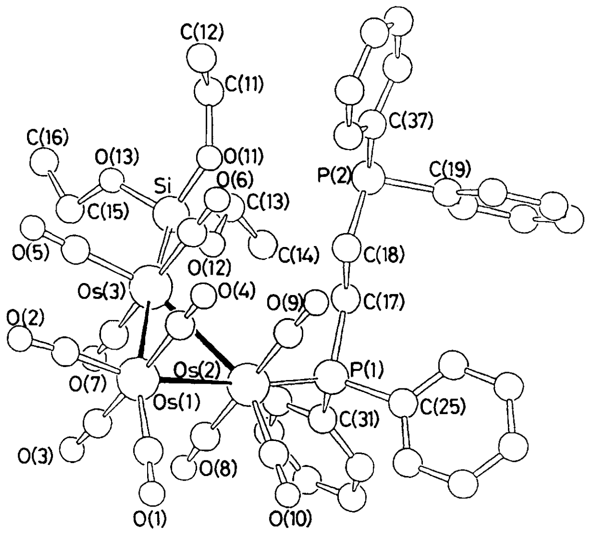


Figure 1. The molecular structure of compound **(3b)** showing the atom labelling; H atoms are omitted for clarity

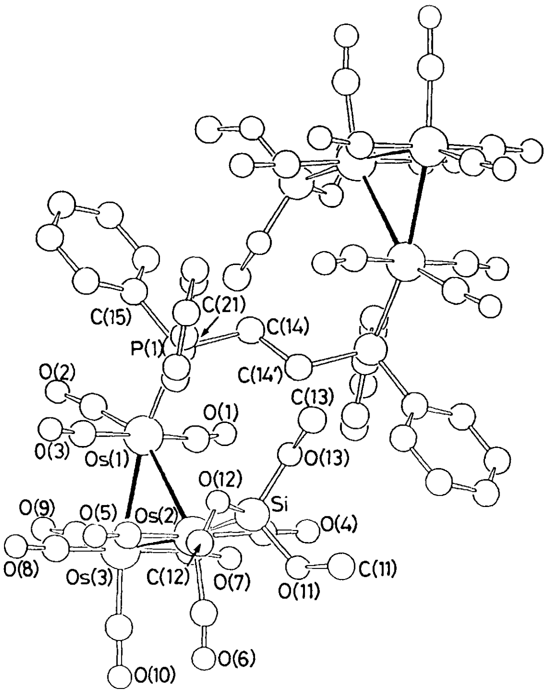


Figure 2. The molecular structure of compound **(4a)** showing the atom labelling. The C atoms of the CO groups bear the same numbering as the corresponding O atoms. The crystallographic centre of symmetry relating the two moieties is placed midway along the C(14)–C(14′) bond

Table 3. Relevant bond distances (Å) and angles (°) for [$Os_3H(CO)_{10}\{Si(OEt)_3\}$(dppe-*P*)] **(3b)**

Os(1)–Os(2)	2.924(1)	Os(2)–Os(3)–Si	115.9(1)
Os(1)–Os(3)	2.890(1)	Os(3)–Os(2)–P(1)	114.2(1)
Os(2)–Os(3)	3.030(1)	Os(2)–P(1)–C(17)	114.9(4)
Os(2)–P(1)	2.362(3)	Os(2)–P(1)–C(25)	115.6(3)
Os(3)–Si	2.400(4)	Os(2)–P(1)–C(31)	114.2(3)
Si–O(11)	1.65(1)	P(1)–C(17)–C(18)	117.1(8)
Si–O(12)	1.63(1)	C(17)–C(18)–P(2)	108.6(8)
Si–O(13)	1.64(1)	C(18)–P(2)–C(19)	100.5(5)
P(1)–C(17)	1.86(1)	C(18)–P(2)–C(37)	101.8(5)
C(17)–C(18)	1.50(2)	C(19)–P(2)–C(37)	102.9(5)
P(2)–C(18)	1.86(1)	Os(3)–Si–O(13)	116.1(4)
P(1)–C(25)	1.83(1)	Os(3)–Si–O(11)	110.2(4)
P(1)–C(31)	1.84(1)	Os(3)–Si–O(12)	110.8(4)
P(2)–C(19)	1.81(1)	Si–O(11)–C(11)	128(1)
P(2)–C(37)	1.83(1)	Si–O(12)–C(13)	121(1)
		Si–O(13)–C(15)	125(1)
mean Os–C(CO)	1.92	O(11)–C(11)–C(12)	109(2)
mean C–O(CO)	1.14	O(12)–C(13)–C(14)	114(2)
mean O–C(Et)	1.44	O(13)–C(15)–C(16)	111(2)
mean C–C(Et)	1.42		

Table 4. Relevant bond distances (Å) and angles (°) for [$\{Os_3H(CO)_{10}[Si(OMe)_3]\}_2(\mu\text{-dppe})$] **(4a)**

Os(1)–Os(2)	3.049(1)	Os(2)–Os(1)–P(1)	114.7(1)
Os(1)–Os(3)	2.903(1)	Os(1)–Os(2)–Si	115.1(2)
Os(2)–Os(3)	2.896(1)	Os(1)–P(1)–C(14)	113.0(1)
Os(1)–P(1)	2.357(5)	Os(1)–P(1)–C(15)	112.6(6)
Os(2)–Si	2.404(6)	Os(1)–P(1)–C(21)	117.9(4)
Si–O(11)	1.68(2)	P(1)–C(14)–C(14′)	112(2)
Si–O(12)	1.64(2)	Os(2)–Si–O(11)	109(1)
Si–O(13)	1.64(2)	Os(2)–Si–O(12)	116(1)
P(1)–C(14)	1.88(1)	Os(2)–Si–O(13)	106(1)
C(14)–C(14′)	1.49(1)	Si–O(11)–C(11)	122(2)
P(1)–C(15)	1.79(1)	Si–O(12)–C(12)	128(2)
P(1)–C(21)	1.83(1)	Si–O(13)–C(13)	124(2)
mean Os–C(CO)	1.91(3)		
mean C–O(CO)	1.14(3)		
mean O–C(Me)	1.41(4)		

features can be discussed together. Relevant bond distances and angles are reported in Tables 3 and 4, for **(3b)** and **(4a)** respectively. The main difference arises from the co-ordination mode of the dppe ligand: while in **(3b)** the diphosphine acts as a monodentate ligand with the other P free (Figure 1) in **(4a)** the diphosphine bridges two $HOs_3(CO)_{10}\{Si(OMe)_3\}$ cluster units related by a crystallographic centre of symmetry placed midway along the C–C(dppe) bond. Metal–metal distances within the Os_3 triangle range from 2.890(1) to 3.030(1) Å [average 2.948(1) Å] and from 2.896(1) to 3.049(1) Å [average 2.949(1) Å] in **(3b)** and **(4a)** respectively, the long bonds being between the two Os atoms which have undergone CO substitution. Three rather different ligand environments can be recognized around the

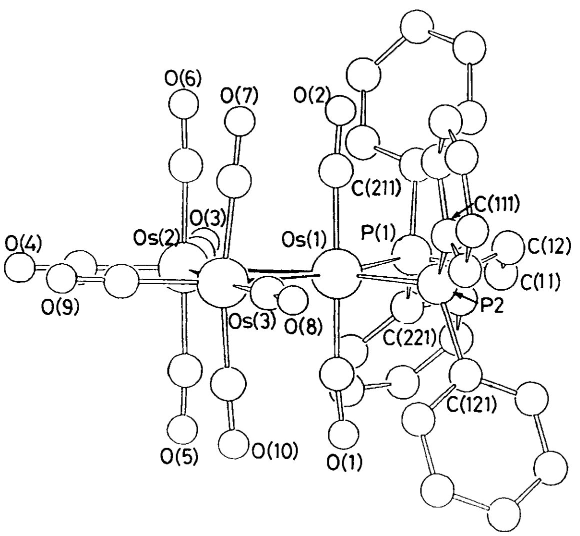


Figure 3. The molecular structure of compound (**5**); H atoms are omitted for clarity

Table 5. Relevant bond distances (Å) and angles (°) for [$Os_3(CO)_{10}(dppe)$] (**5**)

Os(1)–Os(2)	2.913(1)	C(4)–O(4)	1.122(9)
Os(2)–Os(3)	2.889(1)	C(5)–O(5)	1.124(8)
Os(1)–Os(3)	2.914(1)	C(6)–O(6)	1.120(8)
Os(1)–P(1)	2.307(2)	C(7)–O(7)	1.138(8)
Os(1)–P(2)	2.302(2)	C(8)–O(8)	1.137(8)
Os(1)–C(1)	1.913(6)	C(9)–O(9)	1.132(9)
Os(1)–C(2)	1.930(6)	C(10)–O(10)	1.138(8)
Os(2)–C(3)	1.903(7)	P(1)–C(11)	1.845(6)
Os(2)–C(4)	1.923(8)	P(2)–C(12)	1.834(6)
Os(2)–C(5)	1.952(8)	C(11)–C(12)	1.537(9)
Os(2)–C(6)	1.947(7)	P(1)–C(211)	1.831(6)
Os(3)–C(7)	1.939(8)	P(1)–C(221)	1.821(6)
Os(3)–C(8)	1.895(7)	P(2)–C(111)	1.826(6)

in the C–P–C values [average 101.7(5)°], although they are comparable with the C–P–C angles at the metal-co-ordinated P atom (103.5°). The angles Os–P–C and Os–Si–O are also strictly comparable [average 114.9(3) and 112.4(4)°, respectively]. A similarly bound monodentate diphosphine ligand can be seen in the pentanuclear species [$Os_5C(CO)_{15}(dppe)$].[4]

The molecular structure of compound (**5**) is shown in Figure 3 together with the atomic labelling scheme. Relevant bond distances and angles are reported in Table 5. Compound (**5**) is constituted of an isosceles osmium triangle having two 'long' [Os(1)–Os(2) 2.913(1), Os(1)–Os(3) 2.914(1) Å] and one 'short' [Os(2)–Os(3) 2.889(1) Å] bonds. The 'short' bond is opposite to the Os atom bearing the chelating dppe ligand. This metal atom also bears two terminal CO ligands, while the remaining two each have four terminal CO groups. The molecular structure is very regular and can be seen as derived from that of [$Os_3(CO)_{12}$][14] by replacing two radial CO groups on the same Os atom with the Os–P interactions. The idealized molecular symmetry is C_2 with the pseudo-two-fold axis bisecting the Os(2)–Os(3) bond and comprising Os(1). Such molecular symmetry is violated mainly by the P-bound phenyl groups whose orientation is almost certainly dictated by the balance of both inter- and intra-molecular interactions. The Os(1)–P bond lengths are almost identical [2.307(2) and 2.302(2) Å] and the two P atoms are nearly coplanar with the Os_3 triangle (angle between Os_3 and OsP_2 plane 5.1°). The two C atoms of the C_2H_4 group are placed one above and one below the OsP_2 plane according to the molecular symmetry. The five-membered ring in (**5**) generates a rather acute P–Os–P angle at the chelation site [85.9(1)°], however this does not seem to lead to abnormally close P···P atoms. The P(1)···P(2) contact [3.14(2) Å] is in fact comparable with that observed in many species containing a M–P–C–P–M five-membered system such as [$Ru_4H_4(CO)_{10}(\mu\text{-dppm})$] [3.14(1) Å].[15] The structural relationships observed between (**5**) and the bridged species can be found again in several other cases of bridge–chelate isomerism such as the pairs [$Ru_4H_4(CO)_{10}(dppe)$][16] and

Experimental

All reactions were carried out under nitrogen although subsequent work-up was carried out without no precaution to exclude air. All the solvents were dried over appropriate drying agents and distilled before use. Infrared spectra were recorded on a Perkin-Elmer PE 983 spectrometer, fast atom bombardment mass spectra on Kratos MS 50 and MS 890 spectrometers, and ^{1}H and ^{31}P n.m.r. spectra on Bruker WM 250 and AM 400 instruments using $CDCl_3$ or CD_2Cl_2 as the internal reference (^{1}H n.m.r.) and $P(OMe)_3$ as external reference (^{31}P). Products were separated in air by t.l.c. on 20 × 20 cm glass plates coated with a 0.25-mm layer of Merck Kieselgel 60 F_{254}, using hexane–diethyl ether (1:1) as eluant. The cluster $[\{Os_3(CO)_{11}\}_2(\mu\text{-dppe})]$ was prepared by literature methods.[6]

Synthesis of $[Os_3H(CO)_{10}\{Si(OMe)_3\}(\text{dppm-}P)]$ **(2a)**.—The compound $[Os_3H(CO)_{10}(MeCN)\{Si(OMe)_3\}]$ **(1a)** (0.058 g, 0.06 mmol), previously prepared by treating $[Os_3(CO)_{10}(MeCN)_2]$ with an excess of $SiH(OMe)_3$ in CH_2Cl_2 solution,[7] and dppm (0.022 g, 0.06 mmol) were heated in toluene (25 cm^3) at 40 °C for 15 h. Removal of the solvent and t.l.c. of the residue separated two yellow fractions yielding $[Os_3H(CO)_{10}\{Si(OMe)_3\}(\text{dppm-}P)]$ **(2a)** (0.060 g, 77.3%) and an uncharacterized by-product.

Synthesis of $[Os_3H(CO)_{10}\{Si(OEt)_3\}(\text{dppm-}P)]$ **(2b)**.—The compound $[Os_3H(CO)_{10}(MeCN)\{Si(OEt)_3\}]$ **(1b)** was synthesized from the reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with an excess of $SiH(OEt)_3$ in CH_2Cl_2 at room temperature.[7] This compound (0.050 g, 0.05 mmol) and an equimolar amount of dppm (0.018 g) were heated in toluene (30 cm^3) at 40 °C for 20 h. Removal of the solvent and separation by t.l.c. of the reaction products, under the same conditions as used for compound **(2a)** led to the isolation of compound **(2b)** (0.026 g, 40%) and of two uncharacterized by-products. Repetition of the reaction with a 2:1 molar ratio of compound **(1b)** (0.050 g) to dppm (0.009 g) and subsequent work-up as above gave only compound **(2b)** in low yield (0.003 g, 5%) and a large amount of decomposition.

Reactions of $[Os_3H(CO)_{10}(MeCN)\{Si(OMe)_3\}]$ **(1a)** *with dppe*.—The diphosphine (0.010 g, 0.02 mmol) was added to a toluene solution (25 cm^3) containing compound **(1a)** (0.050 g, 0.05 mmol) and the reaction mixture was heated at 40 °C for 16 h. Evaporation of the solvent followed by t.l.c. of the residue yielded in order of decreasing R_f: $[Os_3H(CO)_{10}\{Si(OMe)_3\}(\text{dppe-}P)]$ **(3a)** (in trace amount), $[\{Os_3H(CO)_{10}[Si(OMe)_3]\}_2(\mu\text{-dppe})]$ **(4a)** (0.025 g, 43.3%), $[Os_3(CO)_{10}(\text{dppe-}PP')]$ **(5)** (in low yields), and at least two minor uncharacterized products. A similar reaction was carried out using a 1:1 molar ratio of cluster **(1a)** (0.060 g, 0.06 mmol) to dppe (0.024 g). Evaporation of the solvent and chromatographic work-up gave three yellow products: **(3a)** (0.039 g, 48.4%), **(4a)** which was crystallized by slow evaporation of a CH_2Cl_2–hexane mixture to yield orange needles (0.008 g, 12.7%), and finally **(5)** (0.004 g, 5.9%).

Reactions of $[Os_3H(CO)_{10}(MeCN)\{Si(OEt)_3\}]$ **(1b)** *with dppe*.—A solution of compound **(1b)** (0.050 g, 0.05 mmol) and dppe (0.004 g, 0.5 mol per mol Os_3) in toluene (20 cm^3) was heated at 40 °C overnight. The solvent was evaporated and the residue chromatographed using t.l.c. Three yellow bands were eluted in order of decreasing R_f: $[Os_3H(CO)_{10}\{Si(OEt)_3\}(\text{dppe-}P)]$ **(3b)** (0.005 g, 7%), $[\{Os_3H(CO)_{10}[Si(OEt)_3]\}_2(\mu\text{-dppe})]$ **(4b)** (0.02 g, 42%), and orange-yellow **(5)** (0.006 g, 10%). A similar reaction between **(1b)** (0.050 g, 0.05 mmol) and dppe (0.019 g, 1.0 mol per mol Os_3) was carried out in toluene (20 cm^3) at 40 °C for 18 h. T.l.c. work-up gave as a first fraction a yellow solid which was crystallized from hexane solutions at 0 °C affording orange flat crystals of **(3b)** (0.023 g, 35%), **(4b)** (0.012 g, 21%) as a second fraction, and finally **(5)** as yellow-orange platelets from hexane solutions at 0 °C (0.021 g, 31%).

Synthesis of $[\{Os_3(CO)_{10}(MeCN)\}_2(\mu\text{-dppe})]$ **(6)**.—To a CH_2Cl_2 solution (25 cm^3) containing $[\{Os_3(CO)_{11}\}_2(\mu\text{-dppe})]$ (0.060 g, 0.03 mmol) were added MeCN (5 cm^3) and a CH_2Cl_2 solution of freshly sublimed Me_3NO (0.005 g, 0.06 mmol) and the reaction mixture was allowed to stir at room temperature for 1 h. The solution was filtered through a short silica column under N_2 to eliminate the unreacted Me_3NO and the solvent was evaporated under vacuum affording $[\{Os_3(CO)_{10}(MeCN)\}_2(\mu\text{-dppe})]$ (0.055 g, 90%).

Syntheses of $[\{Os_3H(CO)_{10}[Si(OR)_3]\}_2(\mu\text{-dppe})]$ [R = Me, **(4a)**; *or* Et, **(4b)**].—An excess of $SiH(OMe)_3$ was added to a solution of $[\{Os_3(CO)_{10}(MeCN)\}_2(\mu\text{-dppe})]$ (0.050 g, 0.02 mmol). The solution changed from dark yellow to light yellow upon addition of the silane and the solvent was removed under vacuum after 0.5 h. T.l.c. of the residue separated three yellow fractions of which the first and the third were in trace amount. The second yellow fraction yielded compound **(4a)** (0.024 g, 44%).

Similarly, an excess of $SiH(OEt)_3$ was added to a CH_2Cl_2 solution of compound **(6)** and the reaction was stopped after 0.5 h. Subsequent t.l.c. work-up of the residue afforded compound **(4b)** (0.041 g, 73%) as the major product.

Thermolysis of $[Os_3H(CO)_{10}\{Si(OEt)_3\}(\text{dppe-}P)]$.—Compound **(3b)** (0.040 g, 0.03 mmol) was dissolved in toluene and refluxed for 15 h at 75 °C until a spot t.l.c. revealed the disappearance of the starting material. Evaporation of the solvent followed by t.l.c. eluting with Et_2O–hexane (7:5, v/v) afforded the orange compound, $[\{Os_3H(CO)_{10}[Si(OEt)_3]\}\{Os_3(CO)_9(\text{dppe})\}(\mu\text{-dppe})]$ (0.028 g, 75%, m/z 2 645 (M^+, ^{192}Os). I.r. ν(CO) (n-hexane): 2 105w, 2 062m, 2 040m, 2 021vs, 2 000s, and 1 977s cm^{-1}. N.m.r.: ^{1}H (CD_2Cl_2), δ 7.34 (m, Ph), 3.78 [q, $Si(OCH_2CH_3)_3$] (minor isomer), 3.64 [q, $Si(OCH_2CH_3)_3$], 2.36 [m(br), $P(CH_2)_2P$], 1.13 [t, $Si(OCH_2CH_3)_3$] (minor isomer), 1.07 [t, $Si(OCH_2CH_3)_3$], −18.70 (d, J_{PH} 12.5) (minor isomer), −19.14 (d, J_{PH} 10.30 Hz); ^{31}P-{^{1}H} ($CDCl_3$), δ −139.4 (s), −142.5 (s), −150.3 (d, J_{PH} 30), −150.9 (d, J_{PH} 30), −152.4 (d, J_{PH} 30), and −154.1 p.p.m. (d, J_{PH} 30 Hz).

X-*Ray Structural Determination*.— Crystal data and details of measurements for compounds **(3b)**, **(4a)**, and **(5)** are reported in Table 6. Diffraction intensities were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer equipped with Mo-K_α radiation, corrected for Lorentz-polarization effects and reduced to F_o. No correction for decay was necessary. The metal-atom positions were determined by direct methods and all remaining atoms located from subsequent Fourier difference syntheses. An absorption correction was applied by the Walker and Stuart[17] method once the structural models were completely defined and all atoms refined isotropically. For all computations the SHELX 76 package of crystallographic programs was used.[18] In compound **(5)** all atoms, except the H atoms, were allowed to vibrate anisotropically; in **(3b)** also the phenyl C atoms were treated isotropically. In **(4a)** the Os, P, and Si atoms only could be treated anisotropically. In both **(3b)** and **(4a)** geometrical constraints were used for the phenyl groups (C–C–C 120°, C–C 1.395 Å). Hydrogen atoms were added in calculated positions (C–H 1.08 Å) and refined 'riding' on their corresponding C atoms. In compound **(5)** simple isotropic thermal parameters for the H(Ph) and H(CH_2) groups were refined [0.080(6) and 0.059(10) Å^2, respectively], while in **(3b)** and **(4a)** H-atom thermal motion was assigned the value 0.090 Å^2 and not refined. Attempts to locate the H(hydride) atom

Table 6. Crystal data and details of measurements for compounds (**3b**), (**4a**), and (**5**)[a]

	(**5**)	(**4a**)	(**3b**)
Formula	$C_{36}H_{24}O_{10}Os_3P_2$	$C_{26}H_{22}O_{13}Os_3PSi$	$C_{42}H_{40}O_{13}Os_3P_2Si$
M_r	1 248.5	1 172.1	1 413.4
Crystal size (mm)	0.10 × 0.15 × 0.20	0.10 × 0.12 × 0.18	0.11 × 0.15 × 0.10
Space group	$P2_1/c$	$C2/c$	$P2_1/c$
a/Å	15.527(2)	18.07(2)	18.092(4)
b/Å	10.405(5)	14.134(3)	11.924(1)
c/Å	22.519(3)	26.60(1)	23.210(5)
β/°	94.01(1)	111.72(5)	108.29(2)
U/Å^3	3 628.9	6 309.8	4 754.0
Z	4	8	4
$F(000)$	2 311	4 312	2 671
D_c/g cm^{-3}	2.28	2.47	1.97
μ(Mo-K_α)/cm^{-1}	101.9	117.1	78.1
ω scan width/°	0.75	1.5	1.0
Prescan rate/min^{-1}	8	8	5
Prescan acceptance $\sigma(I)/I$	0.5	0.5	0.5
Maximum scan time/s	100	90	100
Measured reflections	5 767	4 511	5 516
Unique observed reflections	4 677	3 860	4 133
Absorption correction[b] (min., max.)	0.78, 1.00	0.25, 1.00	0.86, 1.00
R, R', S[c]	0.023, 0.024, 1.78	0.068, 0.078, 2.32	0.035, 0.035, 1.62
K, g	1.86, 0.0003	1.00, 0.0001	1.41, 0.0004

[a] Details in common: monoclinic; λ(Mo-K_α) 0.710 69 Å; scan mode ω—2θ; θ range 2.5—25°; $\sigma(I)/I$ requested 0.02; octants explored $\pm h$, $+k$, $+l$. [b] Applied by the Walker and Stuart[17] method. [c] $R' = \Sigma[(F_o - F_c)w^{\frac{1}{2}}]/\Sigma(F_o w^{\frac{1}{2}})$, where $w = k/[\sigma^2(F) + |g|F^2]$.

Table 7. Fractional atomic co-ordinates for compound (**3b**)

Atom	*x*	*y*	*z*
Os(1)	0.524 42(3)	0.151 04(5)	0.146 52(2)
Os(2)	0.410 60(3)	0.147 04(4)	0.212 31(2)
Os(3)	0.361 80(3)	0.145 50(5)	0.074 91(2)
P(1)	0.305 7(2)	0.142 3(3)	0.252 4(1)
P(2)	0.125 0(2)	−0.089 5(3)	0.132 8(2)
Si	0.224 3(2)	0.136 0(4)	0.023 6(2)
C(1)	0.619 1(9)	0.167 4(14)	0.212 9(8)
O(1)	0.675 8(6)	0.179 8(10)	0.251 3(6)
C(2)	0.566 9(9)	0.147 8(13)	0.082 3(8)
O(2)	0.596 1(8)	0.149 2(11)	0.043 9(6)
C(3)	0.508 9(9)	0.310 8(12)	0.138 6(8)
O(3)	0.504 0(6)	0.404 5(9)	0.133 1(5)
C(4)	0.524 4(7)	−0.012 4(13)	0.146 7(6)
O(4)	0.529 6(6)	−0.107 2(8)	0.149 0(5)
C(5)	0.385 0(8)	0.145 2(12)	0.001 1(6)
O(5)	0.401 3(7)	0.143 2(10)	−0.042 9(4)
C(6)	0.360 4(7)	−0.016 6(11)	0.073 2(6)
O(6)	0.357 1(6)	−0.112 9(8)	0.071 8(5)
C(7)	0.345 4(8)	0.306 7(13)	0.071 4(6)
O(7)	0.331 0(7)	0.398 2(8)	0.066 4(5)
C(8)	0.408 0(7)	0.311 5(11)	0.210 1(6)
O(8)	0.404 0(6)	0.406 2(8)	0.211 6(4)
C(9)	0.413 7(7)	−0.014 5(10)	0.213 7(5)
O(9)	0.412 8(5)	−0.110 1(7)	0.217 0(4)
C(10)	0.495 0(8)	0.151 0(10)	0.287 1(6)
O(10)	0.546 8(5)	0.153 4(9)	0.330 2(4)
O(11)	0.195 8(7)	0.004 1(9)	0.013 3(5)
C(11)	0.131 1(12)	−0.044 0(17)	−0.036 0(9)
C(12)	0.158 1(14)	−0.138 5(19)	−0.058 2(11)
O(12)	0.175 9(6)	0.198 7(8)	0.063 0(5)
C(13)	0.092 0(10)	0.203 7(15)	0.041 7(9)
C(14)	0.059 7(11)	0.262 5(16)	0.079 5(9)
O(13)	0.194 9(6)	0.183 8(9)	−0.046 0(5)
C(15)	0.192 6(11)	0.298 3(13)	−0.061 8(8)
C(16)	0.129 3(12)	0.319 9(16)	−0.118 7(9)
C(17)	0.215 5(7)	0.075 7(10)	0.202 5(5)
C(18)	0.223 8(6)	−0.036 7(9)	0.175 9(5)
C(20)	0.113 3(6)	−0.215 1(8)	0.233 0(6)
C(21)	0.083 6(6)	−0.233 5(8)	0.280 9(6)
C(22)	0.028 5(6)	−0.160 2(8)	0.290 4(6)
C(23)	0.003 1(6)	−0.068 3(8)	0.252 0(6)
C(24)	0.032 8(6)	−0.049 9(8)	0.204 2(6)
C(19)	0.087 9(6)	−0.123 2(8)	0.194 7(6)
C(26)	0.385 8(5)	0.112 4(6)	0.375 0(4)
C(27)	0.402 1(5)	0.061 0(6)	0.431 6(4)
C(28)	0.357 9(5)	−0.030 4(6)	0.439 0(4)
C(29)	0.297 4(5)	−0.070 5(6)	0.389 8(4)
C(30)	0.281 1(5)	−0.019 1(6)	0.333 2(4)
C(25)	0.325 3(5)	0.072 3(6)	0.325 8(4)
C(32)	0.273 3(5)	0.320 7(6)	0.321 4(3)
C(33)	0.244 5(5)	0.426 8(6)	0.328 0(3)
C(34)	0.211 1(5)	0.493 3(6)	0.277 0(3)
C(35)	0.206 6(5)	0.453 8(6)	0.219 4(3)
C(36)	0.235 4(5)	0.347 6(6)	0.212 9(3)
C(31)	0.268 8(5)	0.281 1(6)	0.263 9(3)
C(38)	0.084 0(4)	−0.298 8(8)	0.083 4(5)
C(39)	0.095 2(4)	−0.402 8(8)	0.059 9(5)
C(40)	0.169 7(4)	−0.435 8(8)	0.061 2(5)
C(41)	0.232 9(4)	−0.364 7(8)	0.085 9(5)
C(42)	0.221 7(4)	−0.260 6(8)	0.109 3(5)
C(37)	0.147 2(4)	−0.227 6(8)	0.108 1(5)

position from Fourier difference maps for (**3b**) and (**4a**) gave untrustworthy results and were abandoned. Residual peaks were not higher than 0.8 e Å^{-3} for (**3b**) and located mainly in the proximity of the Os atoms. Larger residual peaks (*ca.* 2.5 e Å^{-3}) were observed for (**4a**), probably caused by unsatisfactory correction for absorption. Final atomic co-ordinates are reported in Tables 7—9, respectively.

Additional material available from the Cambridge Crystallo-

Table 8. Fractional atomic co-ordinates for compound (**4a**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.362 78(4)	0.049 41(6)	0.360 13(3)	C(9)	0.150 6(13)	0.086 2(15)	0.285 1(9)
Os(2)	0.383 08(5)	0.263 69(6)	0.368 97(3)	O(9)	0.095 5(12)	0.033 6(14)	0.262 3(8)
Os(3)	0.229 22(5)	0.177 19(6)	0.312 43(3)	C(10)	0.175 8(18)	0.289 4(22)	0.288 2(12)
P(1)	0.476 7(3)	−0.037 3(4)	0.412 4(2)	O(10)	0.142 0(12)	0.362 3(14)	0.275 7(8)
Si	0.517 0(3)	0.317 5(5)	0.417 1(2)	C(11)	0.581 9(17)	0.474 2(20)	0.475 3(11)
C(14)	0.489 2(3)	−0.046 1(4)	0.485 7(2)	O(11)	0.513 9(12)	0.427 9(14)	0.439 8(7)
C(1)	0.316 6(13)	0.039 4(14)	0.415 2(9)	C(12)	0.581 0(18)	0.395 5(21)	0.347 9(12)
O(1)	0.293 4(12)	0.026 1(14)	0.446 7(8)	O(12)	0.574 4(9)	0.321 9(11)	0.381 7(6)
C(2)	0.302 5(13)	−0.055 9(15)	0.330 0(9)	C(13)	0.652 0(21)	0.239 2(26)	0.489 5(14)
O(2)	0.261 6(12)	−0.118 4(15)	0.307 0(8)	O(13)	0.567 1(9)	0.248 4(10)	0.468 1(6)
C(3)	0.396 6(14)	0.053 4(15)	0.297 0(10)	C(16)	0.447 5(9)	−0.231 5(10)	0.416 9(5)
O(3)	0.419 3(14)	0.053 8(16)	0.265 1(9)	C(17)	0.444 4(9)	−0.324 1(10)	0.398 2(5)
C(4)	0.375 5(13)	0.270 0(15)	0.437 7(9)	C(18)	0.464 8(9)	−0.343 5(10)	0.353 5(5)
O(4)	0.370 9(11)	0.272 5(12)	0.479 8(7)	C(19)	0.488 5(9)	−0.270 3(10)	0.327 7(5)
C(5)	0.406 5(14)	0.259 4(16)	0.303 4(9)	C(20)	0.491 6(9)	−0.177 6(10)	0.346 4(5)
O(5)	0.428 0(14)	0.268 0(15)	0.268 9(9)	C(15)	0.471 2(9)	−0.158 2(10)	0.391 0(5)
C(6)	0.348 7(14)	0.391 9(17)	0.354 2(10)	C(22)	0.581 1(7)	0.083 0(8)	0.385 6(5)
O(6)	0.330 2(13)	0.462 9(15)	0.338 1(8)	C(23)	0.654 3(7)	0.106 0(8)	0.382 3(5)
C(7)	0.216 0(14)	0.190 1(16)	0.380 0(10)	C(24)	0.719 1(7)	0.045 0(8)	0.404 0(5)
O(7)	0.197 9(15)	0.199 4(18)	0.417 3(9)	C(25)	0.710 7(7)	−0.039 0(8)	0.428 9(5)
C(8)	0.251 9(14)	0.170 9(16)	0.246 8(10)	C(26)	0.637 5(7)	−0.062 0(8)	0.432 2(5)
O(8)	0.267 8(12)	0.166 4(13)	0.210 0(8)	C(21)	0.572 7(7)	−0.001 0(8)	0.410 5(5)

Table 9. Fractional atomic co-ordinates for compound (**5**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.253 08(1)	0.296 21(2)	0.158 92(1)	C(12)	0.098 1(4)	0.360 6(6)	0.249 3(3)
Os(2)	0.418 13(1)	0.248 36(3)	0.108 92(1)	C(111)	0.081 9(3)	0.532 2(6)	0.151 4(3)
Os(3)	0.289 03(2)	0.402 56(2)	0.043 53(1)	C(112)	0.129 3(4)	0.634 7(7)	0.176 7(4)
P(1)	0.248 34(10)	0.216 03(15)	0.254 15(7)	C(113)	0.107 7(5)	0.760 7(7)	0.163 8(4)
P(2)	0.114 65(9)	0.367 47(15)	0.169 53(7)	C(114)	0.038 4(5)	0.786 1(7)	0.124 9(4)
C(1)	0.209 5(4)	0.137 4(6)	0.126 3(3)	C(115)	−0.010 1(5)	0.687 9(8)	0.099 2(4)
O(1)	0.179 7(3)	0.039 1(5)	0.110 9(2)	C(116)	0.011 2(4)	0.561 2(7)	0.112 2(3)
C(2)	0.303 3(4)	0.448 4(6)	0.196 1(3)	C(121)	0.026 4(4)	0.270 2(6)	0.134 4(3)
O(2)	0.330 4(3)	0.533 3(4)	0.222 7(2)	C(122)	0.028 4(4)	0.240 8(7)	0.074 9(3)
C(3)	0.470 6(4)	0.152 9(7)	0.173 9(3)	C(123)	−0.036 7(5)	0.164 3(8)	0.046 6(4)
O(3)	0.503 9(4)	0.097 8(6)	0.212 3(2)	C(124)	−0.103 1(5)	0.119 7(8)	0.078 4(4)
C(4)	0.508 5(5)	0.249 1(7)	0.054 8(3)	C(125)	−0.104 8(5)	0.149 0(8)	0.137 5(4)
O(4)	0.563 8(4)	0.244 1(6)	0.025 3(3)	C(126)	−0.041 2(4)	0.224 4(7)	0.165 3(4)
C(5)	0.368 7(4)	0.091 6(7)	0.073 2(3)	C(211)	0.313 6(4)	0.297 7(6)	0.313 6(3)
O(5)	0.345 7(4)	−0.002 2(5)	0.053 2(3)	C(212)	0.279 9(5)	0.384 2(7)	0.352 5(3)
C(6)	0.462 4(4)	0.408 4(7)	0.144 0(3)	C(213)	0.333 3(5)	0.443 7(8)	0.395 5(3)
O(6)	0.493 4(3)	0.496 2(6)	0.164 8(2)	C(214)	0.420 0(5)	0.414 6(7)	0.402 6(3)
C(7)	0.326 7(4)	0.558 2(7)	0.084 9(3)	C(215)	0.453 3(5)	0.327 9(8)	0.364 6(4)
O(7)	0.344 8(4)	0.655 8(5)	0.105 0(3)	C(216)	0.401 5(4)	0.269 8(7)	0.320 7(3)
C(8)	0.190 3(5)	0.494 5(7)	0.012 9(3)	C(221)	0.271 4(4)	0.048 7(6)	0.272 8(3)
O(8)	0.132 5(4)	0.550 4(7)	−0.007 2(3)	C(222)	0.254 2(5)	0.004 3(7)	0.329 2(3)
C(9)	0.368 2(5)	0.424 4(7)	−0.017 3(3)	C(223)	0.274 2(6)	−0.123 1(7)	0.344 4(4)
O(9)	0.415 7(4)	0.439 7(7)	−0.052 5(3)	C(224)	0.309 5(5)	−0.204 2(7)	0.305 7(4)
C(10)	0.238 5(4)	0.245 4(7)	0.011 6(3)	C(225)	0.328 5(5)	−0.160 2(6)	0.250 2(4)
O(10)	0.202 5(3)	0.159 6(5)	−0.009 5(2)	C(226)	0.308 2(4)	−0.034 0(6)	0.234 2(3)
C(11)	0.136 4(4)	0.235 0(7)	0.275 5(3)				

graphic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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