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Oxidative addition of silanes R₃SiH to the unsaturated cluster $[Os_3(\mu-H){\mu_3-Ph_2PCH_2PPh(C_6H_4)}(CO)_8]$: Evidence for reversible silane formation in the dynamic behaviour of $[Os_3(\mu-H) (SiR_3)(CO)_9(\mu-dppm)]$

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Oxidative addition of the silanes R_3SiH ($R_3 = Ph_3$, Et_3 , $EtMe_2$) to the unsaturated cluster [Os₃(μ -H){ μ_3 - $Ph_2PCH_2PPh(C_6H_4)$ (CO)₈ leads to the saturated clusters $[Os_3(\mu-H)(SiR_3)(CO)_9(\mu-dppm)]$ (SiR₃ = SiPh₃ 1, SiEt₃ 2 and SiEtMe₂ 3) and the unsaturated clusters $[Os_3(\mu-H)_2(SiR_3){\mu_3-Ph_2PCH_2PPh(C_6H_4)}(CO)_7]$ (SiR₃ = SiPh₃ 4, SiEt₃ 4 5 and SiEtMe₂ 6). Structures are based on spectroscopic evidence and a XRD structure of $[Os_3(\mu-H)(SiPh_3)(CO)_9(\mu-H)(SiPh_$ dppm)] 1 in which all non-CO ligands are coordinated equatorially and the hydride and the silyl groups are mutually cis. From variable-temperature ¹H NMR spectra of the SiEt₃ compound **2**, exchange of the P nuclei is clearly apparent. Simultaneous migrations of the SiEt₃ group and of the hydride from one Os–Os edge to another generate a time-averaged mirror plane in the molecule. VT ¹H NMR spectra of the somewhat less bulky compound $[Os_1(\mu-H)(SiMe_2Et)(CO)_9(\mu-dppm)]$ **3** have been analysed. Two isomers **3a** and **3b** are observed with the hydride ligand located on different Os-Os edges. Synchronous migration of the hydride and SiMe₂Et groups is faster than the observed interconversion of isomers which occurs by hydride migration alone. The synchronous motion of H and SiR₃ only occurs when these ligands are mutually cis as in the major isomer 3a and we propose that this process requires the formation of a transient silane complex of the type $[Os_3(\eta^2-HSiR_3)(CO)_9(\mu-dppm)]$. Turnstile rotation within an $Os(CO)_3(\eta^2-HSiR_3)$ group leads to the observed exchange within the major isomer **3a** without exchange with the minor isomer. This process is not observed for the minor isomer **3b** because the hydride and the silvl group are mutually *trans*. Protonation to give $[Os_3(\mu-H)_2(SiR_3)(CO)_9(\mu-dppm)]^+$ totally suppresses the dynamic behaviour because there are no edge vacancies.

Introduction

Complexes and clusters of transition metals containing M-Si bonds have been intensively studied in recent years because of theoretical challenges and applications (see, for example, ref. 1). The main entry into this chemistry is by the facile oxidative addition of silanes to unsaturated transition metal clusters which commonly generates clusters with bridging hydride and terminal silyl groups.² Agostic M-H-Si interactions are important in several clusters² and have been implicated in catalytic processes such as hydrosilation.3-5 Since agostic bonds are readily formed, they have been studied as analogues of the agostic M-H-C bonds and C-H bond activation. In some cases agostic M-H-Si bonds have been found in ground-state structures and have been characterised by XRD.2 In other cases they appear as intermediates in reactions.6

Examples of the oxidative addition of silanes to triosmium clusters are the addition of (EtO)₃SiH to [Os₃(CO)₁₀(MeCN)₂]^{7,8} and of Et₃SiH (and related Ge and Sn compounds) or Ph₂SiH₂ to [Os₃(µ-H)₂(CO)₁₀].^{6,9} Other examples of silyl osmium clusters^{10,11} and silyl ruthenium clusters have been reported.^{12,13}

In this paper we will describe examples of the oxidative addition of silanes R₃SiH to an unsaturated triosmium cluster $[Os_3(\mu\text{-}H)\{\mu_3\text{-}Ph_2PCH_2PPh(C_6H_4)\}(CO)_8]^{14}$ and present an analysis of dynamic behaviour of one of the products which is of the type [Os₃(µ-H)(SiR₃)(CO)₉(µ-dppm)]. Evidence is presented for the transient existence of an agostically bonded complex [Os₃(HSiR₃)(CO)₉(µ-dppm)] in the dynamic behaviour of one isomer of the cluster [Os₃(µ-H)(SiMe₂Et)(CO)₉(µdppm)].

Results and discussion

Synthesis and characterisation of oxidative addition products

Treatment of the unsaturated cluster $[Os_3(\mu-H){\mu_3} Ph_2PCH_2PPh(C_6H_4)$ }(CO)₈] with a trisubstituted silane R₃SiH $(R_3 = Ph_3, Et_3, EtMe_2)$ in refluxing toluene for 8 to 10 hours leads to a mixture which can be separated chromatographically into the saturated product [Os₃(µ-H)(SiR₃)(CO)₉(µ-dppm)] (R = SiPh₃ 1, SiEt₃ 2 and SiEtMe₂ 3) and the unsaturated $[Os_3(\mu H_{2}(SiR_{3}){\mu_{3}-Ph_{2}PCH_{2}PPh(C_{6}H_{4})}(CO)_{7}]$ (R = SiPh_{3} 4, SiEt_{3} 5 and SiEtMe₂ 6) (Scheme 1) in similar yields. The Ph groups are omitted from dppm in this and following schemes.



These products have been characterised by the usual spectroscopic methods (see Experimental) and the structures confirmed by X-ray diffraction on the compounds 1 and 4. We report the structure of 1 in this paper because it is relevant to the dynamic behaviour of compounds 1 to 3 which is the subject of this paper. The structure of 4 will be reported in a following paper

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Table 1 Selected bond lengths (Å) and angles (°) for the cluster $[Os_3(\mu-H)(SiPh_3)(CO)_9(\mu-dppm)]$ 1

| Os(1)–Os(2) | 2.9008(3) | Os(1)–C(11) | 1.932(4) |
|----------------------|-----------|-----------------------|------------|
| Os(2)-Os(3) | 3.0220(2) | Os(1)–C(12) | 1.891(4) |
| Os(3) - Os(1) | 2.8711(3) | Os(1) - C(13) | 1.925(4) |
| Os(1) - P(1) | 2.3129(9) | Os(2) - C(21) | 1.949(4) |
| Os(2)-P(2) | 2.3517(9) | Os(2) - C(22) | 1.898(4) |
| Os(3)-Si(1) | 2.4503(9) | Os(2)–C(23) | 1.935(4) |
| Si(1) - C(65) | 1.892(4) | Os(3)–C(31) | 1.928(4) |
| Si(1)-C(71) | 1.902(4) | Os(3) - C(32) | 1.875(4) |
| Si(1)–C(77) | 1.910(4) | Os(3)–C(33) | 1.946(4) |
| Os(1)–Os(2)–P(1) | 89.19(2) | Os(1)-Os(3)-Si(1) | 174.22(2) |
| Os(2) - Os(1) - P(2) | 93.27(2) | Os(2) - Os(3) - C(32) | 146.34(12) |
| Os(3) - Os(2) - P(2) | 146.50(2) | Si(1) - Os(3) - C(32) | 97.20(12) |
| Os(3) - Os(1) - P(1) | 152.49(2) | Os(1) - Os(3) - C(32) | 87.49(12) |
| Os(2)–Os(3)–Si(1) | 116.46(2) | | |
| | | | |

which will describe the structures and full range of reactivities of compounds 1 to 6 and related compounds. Interestingly the compound $[Os_3(\mu-H){Si(OMe)_3}(CO)_{10}(dppm-P)]$ has been reported to be formed from the treatment of $[Os_3(\mu-H){Si-(OMe)_3}(CO)_{10}(MeCN)]$ with dppm.⁸ The monodentate nature of dppm was established spectroscopically but loss of CO to give $[Os_3(\mu-H){Si(OMe)_3}(CO)_9(\mu-dppm)]$ analogous to compounds 1 to 3 was not reported. We believe that compounds of the type 1 to 3 are reported here for the first time.

Crystal structure of the cluster [Os₃(µ-H)(SiPh₃)(CO)₉(µ-dppm)] 1

The molecular structure of compound 1 is shown in Fig. 1 and selected bond lengths and angles are in Table 1. Each Os atom has two equatorial and two axial ligands as in $[Os_3(CO)_{12}]$ and its simple substitution derivatives. Also the smaller (CO) ligands are positioned axially with longer Os–CO distances than those that are coordinated equatorially because of unfavourable competition of mutually *trans* CO for π -electron density.



Fig. 1 Molecular structure of the cluster $[Os_3(\mu\text{-}H)(SiPh_3)(CO)_9(\mu\text{-}dppm)]$ (ORTEP plot with 30% thermal ellipsoids).

As expected the bulky SiPh₃ group is equatorially coordinated. The position of the hydride ligand was clearly established and refined in the X-ray analysis but various geometric features are totally consistent with its position as shown in Fig. 1. The hydride bridges the longest Os–Os edge [Os(2)–Os(3) 3.0220(2) Å] and significantly the SiPh₃ is *cis* to the hydride in the sterically least crowded equatorial site. The coordination geometries of the Os atoms are closely octahedral with the hydride occupying one of the octahedral sites at each of Os(2) and Os(3). As a consequence there is more crowding on the Os(1)–Os(3) edge than the Os(2)–Os(3) edge. For example, the Os(3)–Os(2)–C(22) angle is 115.29(11)° whereas the corresponding angle at the other edge, Os(3)–Os(1)–C(12) is 107.46(12)°. Related to this differ-

ence the Os(1)–Os(2)–P(2) angle of $89.19(2)^{\circ}$ is smaller than the Os(2)–Os(1)–P(1) angle of $93.27(2)^{\circ}$. Fig. 2 shows how the hydride location has a larger impact on the whole cluster, than its size alone would imply. This has consequences in considering the dynamic behaviour of the cluster (see below).



Fig. 2 Structure of the cluster $[Os_3(\mu-H)(SiPh_3)(CO)_9(\mu-dppm)]$ showing the effect of the bridging hydride on the positions of the other equatorial ligands.

Dynamic behaviour of the cluster $[Os_3(\mu\text{-}H)(SiEt_3)(CO)_9(\mu\text{-}dppm)]$ 2

The limiting low temperature and high temperature ¹H NMR spectra in the hydride region are a double doublet and a 1:2:1 triplet respectively. The limiting spectra are not fully achieved in Fig. 3 since higher and lower temperatures would be needed. The observed spectra can be well modelled by gNMR¹⁵ for a process which exchanges the P nuclei of the dppm ligand. It is reasonable to assume that it is the H, SiEt₃ and CO ligands that are in



Fig. 3 Observed and computed (using $gNMR^{15}$) ¹H NMR spectra for cluster $[Os_3(\mu-H)(SiEt_3)(CO)_9(\mu-dppm)]$ measured in CDCl₃ at 500 MHz.

motion rather than the dppm ligand. In the crystal structure of the SiPh₃ complex (Fig. 1) the dppm-bridge is non-planar and there are two axial and two equatorial Ph groups. Inversion of the dppm ligand is very rapid because the CH₂ group gives a 1:2:1 triplet at all temperatures. For the purposes of this discussion we can therefore consider the OsPCPOs set of atoms associated with the dppm bridge to be planar. Scheme 2 shows that hydride migration and motion of the Os(SiEt₃)(CO)₃ group are necessary to give P^A–P^B exchange which is a moderately complex process with the following activation parameters: ΔG^{\ddagger} (298 K) = (63.9 ± 2.3) kJ mol⁻¹, ΔH^{\ddagger} = (70.2 ± 2.3) kJ mol⁻¹, ΔS^{\ddagger} = (21.2 ± 7.7) J K⁻¹ mol⁻¹.



If the motion of the hydride occurs as a separate process from the motion of the $Os(SiEt_3)(CO)_3$ group we would expect another isomer with the hydride *trans* to $SiEt_3$ to be involved in the exchange.

Dynamic behaviour of the cluster $[Os_3(\mu-H)(SiMe_2Et)(CO)_9(\mu-dppm)]$ 3

There are significant differences between the solution behaviour of the SiEt₃ and the SiMe₂Et clusters, most notable the presence of a second minor isomer 3b in dynamic equilibrium with the major isomer of $[Os_3(\mu-H)(SiMe_2Et)(CO)_9(\mu-dppm)]$ 3a. Fig. 4 shows the variation in hydride ¹H NMR spectra with temperature. Species 3a gives a low-temperature double doublet at δ -18.75 [J_{PH} = 24.0 and 5.0 Hz] which corresponds to that at δ -18.90 for the compound [Os₃(μ -H)(SiEt₃)(CO)₉(μ -dppm)]. In addition there is a smaller double doublet at $\delta - 17.75 [J_{PH} = 26.5]$ and 4.5 Hz] with essentially the same two coupling constants to ³¹P as **3a**. The hydride and the dppm ligand must be similarly disposed with respect to each other in both isomers. The isomer 3a corresponds to that in the crystal of [Os₃(µ-H)(SiPh₃)(CO)₉(µdppm)] 1 and in solution for [Os₃(µ-H)(SiEt₃)(CO)₉(µ-dppm)] 2. Since 3a is in exchange with 3b, the two isomers must be closely related. Isomer **3b** cannot have an axially coordinated SiPh₃ since the CH₂ (dppm) ¹H NMR signals appear as 1:2:1 triplets for both 3a and 3b indicating that both have a plane of symmetry through the Os₃ plane. We therefore propose that isomer **3b** is as shown in Scheme 3 with a mutually trans arrangement of the hydride and silvl group.

Isomer **3a** follows the same pattern of exchange as $[Os_3(\mu-H)(SiEt_3)(CO)_9(\mu-dppm)]$ with exchange of the two P nuclei but this occurs by a *process independent of isomer 3b*. Over the temperature range 258 to 298 K there is no evidence for a similar exchange for isomer **3b**. The first indication of dynamic behaviour for **3b** is an exchange between **3a** and **3b**.

Simulation of the NMR spectra of compound 3 by an intraisomer process A for 3a (rate coefficient k_a , see Scheme 3) and a slower 3a–3b isomerisation B (rate coefficient k_b) leads to the spectra in Fig. 5. Good matches of observed and experimental spectra are obtained with the rate coefficients given in the figure. The intraisomer process A is about 15 times faster than isomer interconversion B. *Therefore isomer* 3b cannot be an intermediate in process A for 3a. The intraisomer process C shown in Scheme 3 is too slow to be detected. An independent measure of the rate of 3a–3b isomerisation was obtained by analysis of the line-shapes of the coalescing dppm methylene triplets for the two isomers. The rate data are



Fig. 4 Observed ¹H NMR spectra in the hydride region for the cluster $[Os_3(\mu-H)(SiMe_2Et)(CO)_9(\mu-dppm)]$ measured in CDCl₃ at 500 MHz. The signal for major isomer **3a** is on the right and for the minor isomer **3b** on the left.



presented together as the Eyring plots shown in Fig. 6. From these the activation parameters were obtained: process **A**, ΔG^{\ddagger} (298 K) = (63.7 ± 2.3) kJ mol⁻¹, ΔH^{\ddagger} = (62.7 ± 2.3) kJ mol⁻¹, ΔS^{\ddagger} = (-3.3 ± 7.1) J K⁻¹ mol⁻¹ while those for process **B** are ΔG^{\ddagger} (298 K) = (70.5 ± 2.6) kJ mol⁻¹, ΔH^{\ddagger} = (62.0 ± 2.6) kJ mol⁻¹, ΔS^{\ddagger} = (-28.5 ± 10.0) J K⁻¹ mol⁻¹.



Fig. 5 gNMR¹⁵ simulated ¹H NMR spectra in the hydride region for the cluster $[Os_3(\mu-H)(SiMe_2Et)(CO)_9(\mu-dppm)]$ **3a** and **3b**, where k_a is for the faster process (P–P exchange) and k_b for the slower process (interconversion of isomer **3a** with **3b**). The signal for major isomer **3a** is on the right and for the minor isomer **3b** on left.



Fig. 6 Plots of $\ln(k_a/T)$ against 1/T (points \diamondsuit) and of $\ln(k_b/T)$ against 1/T (points Δ and \Box) for the two processes **A** and **B** occurring for isomers **3a** and **3b** of the cluster $[Os_3(\mu-H)(SiMe_2Et)(CO)_9(\mu-dppm)]$. Points Δ are from the coalescence of the CH₂ NMR triplets and \diamondsuit and \Box from changes in the hydride signals with temperature.

Mechanisms of the dynamic behaviour for isomers 3a

Neither hydride migration or turnstile rotation at the Os(CO)₃(SiMe₂Et) group in 3a are sufficient to account for process A. A combination of the two are necessary to account for the exchange shown in Scheme 2 and furthermore these must occur without the intermediacy of isomer 3b. Also we believe it is fundamental to process A that the hydride and SiMe₂Et group are mutually *cis*. We propose that the *cis* arrangement allows the reductive elimination of the silane which remains agostically bonded. A turnstile process at the resultant $Os(CO)_3(\eta^2-$ HSiMe₂Et) group as in Scheme 4 followed by an oxidative addition regenerate isomer 3a with exchange of the P-nuclei of the dppm ligand. This explains why there is no analogous process when the H and SiMe2Et ligands are trans as in isomer 3b because reductive elimination is not possible in that case. There are examples of agostic bonding in compounds such as $[Ru_2(\mu-\eta^2-SiTol_2H)(SiTol_2H)(CO)_5(\mu-dppm)]$ which contain the fragment shown in Fig. 7. Such a unit might possibly be on the reaction path of the process shown in Scheme 4.



Fig. 7 Agostically bonded silyl unit found in metal-metal bonded systems.

Treatment of cluster **3** with CO at atmospheric pressure displaces Me_2EtSiH and forms the cluster $[Os_3(CO)_{10}(dppm)]$. This provides circumstantial evidence that the reductive elimination is facile.

Protonation of cluster 1

Treatment of a CD_2Cl_2 solution of the cluster $[Os_3(\mu-H)-(SiPh_3)(CO)_9(\mu-dppm)]$ 1 with HBF₄·Et₂O leads to the formation of a non-fluxional cationic dihydride $[Os_3(\mu-H)_2(SiPh_3)(CO)_9(\mu-dppm)]$ [BF₄] 7.

The ¹H NMR spectrum of **7** shows two closely positioned hydride signals at $\delta - 17.49$ ($J_{PH} = 16.8$, 1.8 Hz and $J_{HH} =$ 1.8 Hz) and $\delta - 17.57$ ($J_{PH} = 12.0$, 1.0 Hz and $J_{HH} = 1.8$ Hz). Each signal appears as a doublet of triplets, but these are more correctly analysed (gNMR¹⁵) as double double doublets. Since the hydrides are different and not exchanging, as expected, there are also two corresponding ³¹P{¹H} NMR signals appearing as two AB doublets at $\delta - 35.80$ and -35.21($J_{PP} = 18.0$ Hz). A structure consistent with these data is shown in Scheme 5. Significantly the cluster is not dynamic at the same

HBF4.Et2O/CD2CI2 S ç Os(CO)₃ Os(CO)₃ (CO),08 (CO).09 7 1 Scheme 5

temperatures as the neutral precursor and this is likely to be because there are no edge vacancies to allow the migration of hydride ligands.

Experimental

The cluster $[Os_3(\mu-H){\mu_3-Ph_2PCH_2PPh(C_6H_4)}(CO)_8]$ was synthesised by a reported method¹⁴ and the silanes Ph₃SiH, Et₃SiH and Me₂EtSiH were obtained from Aldrich plc and used as supplied.

Reaction of the cluster $[Os_3(\mu-H){\mu_3-Ph_2PCH_2PPh(C_6H_4)}-$ (CO)₈ with triphenylsilane

A benzene solution (60 cm³) of the cluster $[Os_3(\mu-H){\mu_3 Ph_2PCH_2PPh(C_6H_4)$ (CO)₈ (0.165 g, 0.140 mmol) and Ph_3SiH (0.182 g, 0.699 mmol) was heated to reflux for 8 h during which time the colour changed from green to orange. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica. Elution with hexane-dichloromethane (2:2 by volume) gave two bands. The faster moving band gave $[Os_3(\mu-H)_2(SiPh_3){\mu_3-Ph_2PCH_2PPh(C_6H_4)}(CO)_7]$ 4 (0.099 g, 50%) as yellow crystals from a hexane-CH₂Cl₂ mixture at 4 °C. Anal. for 4: calc. for C₅₀H₃₈O₇Os₃P₂Si, C, 42.54; H, 2.72. Found: C, 42.64; H, 2.78%; IR [v(CO), CH₂Cl₂]: 2070vs, 2020s, 2004s, 1993s, 1950m cm⁻¹; ¹H NMR (CD₂Cl₂): δ 7.82-6.68 (m, 30H), 6.96 (m, 1H), 6.63 (m, 1H), 6.21 (m, 1H), 6.46 (t, 1H), 4.81 (m, 1H), 3.76 (m, 1H), -12.43 (dd, 1H, J = 36.0, 8.8 Hz), -15.05 (d, 1H, J = 10.8 Hz); ${}^{31}P{}^{1}H$ NMR (CD₂Cl₂): δ -14.7 (d, J = 62.6 Hz), -22.2 (d, J = 62.6 Hz). The slower band gave the cluster [Os₂H(SiPh₂)(CO)₀(dppm)] 1 (0.092 g, 45%) as orange crystals from a hexane-CH₂Cl₂ mixture at 4 °C. Anal. for 1: calc. for C₅₂H₃₈O₉Os₃P₂Si, C, 42.56; H, 2.62. Found: C, 42.69; H, 2.72%; IR [v(CO), CH₂Cl₂]: 2087m, 2049s, 2004vs, 1977m cm⁻¹; ¹H NMR (CD₂Cl₂): δ 7.60–7.18 (m, 35H), 5.25 (t, 2H, J = 10.8 Hz), -18.32 (apparent d similar to the spectrum at 298 K in Fig. 3, 1H, J = 30.4 Hz); ³¹P{¹H} NMR (CD₂Cl₂): δ -30.2 (d, J = 46.5 Hz), -41.8 (d, J = 46.5 Hz).

Reaction of the cluster $[Os_3(\mu-H){\mu_3-Ph_2PCH_2PPh(C_6H_4)}-$ (CO)₈] with triethylsilane

A similar reaction to that above using $[Os_3(\mu-H){\mu_3-Ph_2PCH_2-}$ $PPh(C_6H_4)$ {(CO)₈] (0.097 g, 0.082 mmol) with Et₃SiH (262 µL, 1.643 mmol) for 10 h followed by a similar chromatographic separation gave two bands. The first band gave $[Os_3(\mu H_{2}(SiEt_{3}){\mu_{3}-Ph_{2}PCH_{2}PPh(C_{6}H_{4})}(CO)_{7}]$ 5 (0.055 g, 53%) as yellow crystals from a hexane-CH₂Cl₂ mixture at 0 °C. Anal. for 5: calc. for C₃₈H₃₈O₇Os₃P₂Si, C, 36.01; H, 3.03. Found: C, 36.12; H, 3.15%; IR [v(CO), CH₂Cl₂]: 2064s, 2015s, 2000vs, 1989s, 1940s cm⁻¹. The other band gave the cluster $[Os_3H(SiEt_3)(CO)_9(dppm)]$ 2 (0.092 g, 45%) as orange crystals from a hexane-CH₂Cl₂ mixture at 4 °C. Anal. for 2: calc. for C40H38O9Os3P2Si, C, 36.30; H, 2.90. Found: C, 36.42; H, 2.98%; IR [v(CO), CH₂Cl₂]: 2082w, 2042s, 2000vs, 1967m, 1957m cm⁻¹.

Reaction of the cluster [Os₃(µ-H){µ₃-Ph₂PCH₂PPh(C₆H₄)}-(CO)₈] with dimethylethylsilane

Similarly $[Os_3(\mu-H){\mu_3-Ph_2PCH_2PPh(C_6H_4)}(CO)_8]$ using (0.102 g, 0.087 mmol) with Me₂EtSiH (210 µL, 1.74 mmol)

gave $[Os_3(\mu-H)_2(SiMe_2Et)\{\mu_3-Ph_2PCH_2PPh(C_6H_4)\}(CO)_7]$ 6 (0.058 g, 54%) as yellow crystals from a hexane-CH₂Cl₂ mixture at 0 °C. Anal. for 6: calc. for C₃₆H₃₄O₇Os₃P₂Si, C, 34.89; H, 2.77. Found: C, 34.98; H, 2.86%; IR [v(CO), CH₂Cl₂]: 2065s, 2012s, 1998vs, 1989s, 1940s cm⁻¹ and the cluster [Os₃(µ-H)(SiMe₂Et)(CO)₉(dppm)] 3 (0.036 g, 32%) as orange crystals from a hexane-CH₂Cl₂ mixture at 0 °C. Anal. for 3: calc. for C₃₈H₃₄O₉Os₃P₂Si, C, 35.23; H, 2.65. Found: C, 35.38; H, 2.78%; IR [v(CO), CH₂Cl₂]: 2082w, 2042s, 2000vs, 1968m, 1958m cm⁻¹.

Crystal structure determination for compound 1

All geometric and intensity data were obtained for a red single crystal of compound 1 on a Bruker SMART APEX CCD diffractometer using Mo-K α radiation ($\lambda = 0.71073$ Å) at 150 ± 2 K. Data reduction and integration was carried out with SAINT+ and absorption corrections were applied using the programme SADABS.¹⁶ Structures were solved by direct methods and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms, except that bonded to Os, were placed in calculated positions and their thermal parameters linked to those of the atoms to which they were attached (riding model). The hydrogen atom bridging Os atoms was located and its position refined using fixed isotropic thermal parameters. There is an indication of disorder of one phenyl ring, C(47)–C(52), but this was not included in the model. The SHELXTL PLUS V6.10 program package was used for structure solution and refinement.17

Crystal data. $C_{52}H_{38}O_9Os_3P_2Si$, M = 1467.45, monoclinic, $a = 19.3866(16), \quad b = 10.2591(8), \quad c = 24.713(2)$ Å, $\beta =$ $102.8060(10)^\circ$, $U = 4793.0(7) \text{ Å}^3$, T = 150 K, space group $P2_1/c$, Z = 4, μ (Mo-K α) = 8.082 mm⁻¹, 41583 reflections measured, 11406 unique ($R_{int} = 0.0280$) which were used in all calculations. The final R1 = 0.0269 and wR2 = 0.0555 (all data).

CCDC reference number 246431.

See http://www.rsc.org/suppdata/dt/b4/b411833b/ for crystallographic data in CIF or other electronic format.

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References

- 1 P. Braunstein and M. Knorr, J. Organomet. Chem., 1995, 500, 21; P. Braunstein, M. Knorr and C. Stern, Coord. Chem. Rev., 1998, 178-180, 903.
- 2 H. Hashimoto, Y. Hayashi, I. Aratani, C. Kabuto and M. Kira, Organometallics, 2002, 21, 1534 and references therein.
- 3 R. D. Adams, J. E. Cortopassi and M. P. Pompeo, Organometallics, 1992. 11. 1.
- 4 H. Nagashima, A. Suzuki, T. Iura, K. Ryu and K. Matsubara, Organometallics, 2000, 19, 3579.
- 5 K. Matsubara, K. Ryu, T. Maki, T. Iura and H. Nagashima, Organometallics, 2002, 21, 3023.
- 6 R. J. Hall, P. Serguievski and J. B. Keister, Organometallics, 2000, 19, 4499
- 7 R. D. Adams, J. E. Cortopassi and M. P. Pompeo, Inorg. Chem., 1991, 30, 2960 and R. D. Adams, J. E. Cortopassi and M. P. Pompeo, Inorg. Chem., 1992, 31, 2563.
- 8 B. F. G. Johnson, J. Lewis, M. Monari, D. Braga, F. Grepioni and C. Gradella, J. Chem. Soc., Dalton Trans., 1990, 2863.
- 9 F. W. B. Einstein, R. K. Pomeroy and A. C. Willis, J. Organomet. Chem., 1986, 311, 257.



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- H. G. Ang, B. Chang, W. L. Kwik and E. S. H. Sim, *J. Organomet. Chem.*, 1994, **474**, 153.
 R. D. Adams, J. E. Cortopassi, J. Aust and M. Myrick, *J. Am. Chem.*
- Soc., 1993, 115, 8877.
- R. D. Adams, B. Captain and W. Fu, *Organometallics*, 2000, **19**, 3670.
 P. Braunstein, J. R. Galworthy and W. Massa, *J. Chem. Soc., Dalton* Trans., 1997, 4677.
- 14 J. A. Clucas, D. F. Foster, M. M. Harding and A. K. Smith, *J. Chem. Soc., Chem. Commun.*, 1984, 949.
 15 gNMR, Ver. 4.1, Cherwell Scientific Ltd., Oxford, UK, 1995.
 16 SMART and SAINT+ software for CCD diffractometers, version 6.1,
- Bruker AXS, Madison, WI, 2000.
- 17 G. M. Sheldrick, SHELXTL PLUS, version 6.1, Bruker AXS Inc., Madison, WI, 2000.