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The synthesis, structure, and reactivity of the osmium(IV) trihydrido silyl complex, $OsH_3(SiMe_3)(CO)(PPh_3)_2$

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Dedicated to Professor Fausto Calderazzo on the occasion of his 70th birthday.

Abstract

Reaction between the five coordinate complex, $Os(Ph)Cl(CO)(PPh_3)_2$, and $HSiMe_3$ produces the osmium(IV) trihydrido silyl complex, $OsH_3(SiMe_3)(CO)(PPh_3)_2$ (**1**). The structure of **1** has been determined by single crystal X-ray crystallography and by multi-nuclear NMR spectroscopy. The structure has an approximately tetrahedral disposition of silyl, carbonyl and the two PPh_3 ligands about osmium with the three classical hydride ligands located, one *trans* to CO, and the other two each approximately *trans* to a PPh_3. Treatment of complex **1** with $HSiR_3$ (R = Et, Ph), $HSn(p\text{-tolyl})_3$, or HC_2Ph gives $OsH_3(SiR_3)(CO)(PPh_3)_2$ (R = Et (**2**), Ph (**3**)), $OsH_2[Sn(p\text{-tolyl})_3]_2(CO)(PPh_3)_2$ (**4**) or $OsH(C_2Ph)(CO)(PPh_3)_3$ (**5**), respectively. A likely intermediate in these reactions is the coordinatively unsaturated complex, $OsH_2(CO)(PPh_3)_2$. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Hydride complexes; Silyl complexes; Osmium

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1. Introduction

Polyhydrido, silyl-containing transition metal complexes are postulated as intermediate species in reactions involving the oxidative addition of silanes to transition metal hydride compounds [1]. These complexes are often not isolated, but instead lose dihydrogen to afford transition metal silyl products [1,2]. As a consequence, relatively few polyhydrido transition metal silyl complexes have been characterised. Investigating the reactivity of complexes of this type may provide a better understanding of the role such complexes play in important industrial processes such as transition metal catalysed hydrosilation reactions [3].

The syntheses and characterisations of the first osmium trihydrido silyl complexes, $OsH_3(SiR_3)(CO)(P^iPr_3)_2$ ($SiR_3 = SiPh_2H$, $SiPh_3$, $SiPh(OMe)_2$), were reported recently by Esteruelas and co-workers [4]. These compounds were prepared by treatment of either $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2$ or $OsH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$ with the appropriate silane. Subsequently, we have described the synthesis and characterisation of the seven co-ordinate osmium trihydrido silyl complexes, $OsH_3(SiR_3)(PPh_3)_3$ (R = Pyr, Et, Ph; Pyr = 1-NC_4H_4), which were isolated after heating $OsH_4(PPh_3)_3$ and the appropriate silane in benzene [5]. The analogous ruthenium complex, $RuH_3(SiPyr_3)(PPh_3)_3$ was prepared in a similar manner. Several other ruthenium trihydrido silyl complexes of the type $RuH_3(SiR_3)L_n$ have also been characterised, having either alkyl [6,7], aryl [7,8], alkoxy [7,8], or halogen [8] substituents on the silicon. Examples of iron trihydrido silyl complexes include the series of complexes $FeH_3(SiR_3)(PR_3)_3$ and $FeH_3(SiR_3)(CO)(dppe)$ (dppe = $Ph_2CH_2CH_2PPh_2$) [9,10].

In this paper we describe the synthesis, structural and spectroscopic characterisation, and some reactions of the osmium(IV) trihydrido, silyl complex, $OsH_3(SiMe_3)(CO)(PPh_3)_2$ (**1**).

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2. Results and discussion

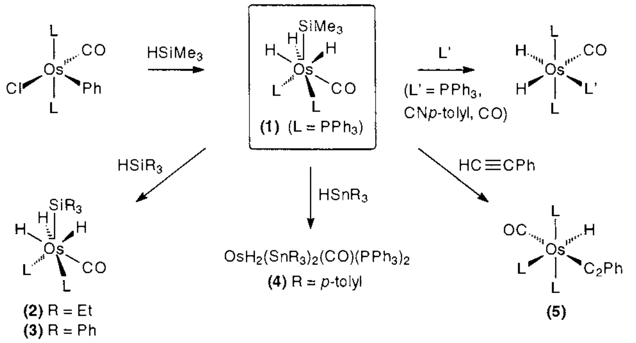
2.1. Synthesis and spectroscopic characterisation of $OsH_3(SiMe_3)(CO)(PPh_3)_2$ (1)

Treatment of a solution of $Os(Ph)Cl(CO)(PPh_3)_2$ with $HSiMe_3$ for 18 h at room temperature gives $OsH_3(SiMe_3)(CO)(PPh_3)_2$ (**1**) in 70% isolated yield (see Scheme 1). This unexpected product contrasts with the compounds derived from the reactions between $Os(Ph)Cl(CO)(PPh_3)_2$ and chlorosilanes. These are the co-ordinatively unsaturated osmium silyl complexes, $Os(SiR_3)Cl(CO)(PPh_3)_2$ (SiR_3=$SiCl_3$, $SiCl_2Me$, $SiClMe_2$), which have been reported previously [11]. Furthermore, the ruthenium analogue of $Os(Ph)Cl(CO)(PPh_3)_2$ gives the Ru(II) trimethylsilyl complex $Ru(SiMe_3)Cl(CO)(PPh_3)_2$, on treatment with $HSiMe_3$ [12,13].

The crystal structure of **1** (see details below) confirms the geometry shown in Scheme 1 and the following discussion of the NMR spectra of **1** is made on the basis of this geometry. At 300 K the ^1H-NMR spectrum of **1** shows the expected resonances for the trimethylsilyl and triphenylphosphine groups, as well as a broad resonance centred at -9.0 ppm due to the three hydride ligands. The $^{31}P\{^1H\}$-NMR spectrum (at 213 K) displays a single slightly broadened signal, at 13.43 ppm, for the two PPh_3 ligands.

In the ^1H-NMR spectrum at 213 K, the hydride resonance resolves to a pattern expected for the AA′BXX′ spin system (see Fig. 1). The signal at -8.82 ppm is immediately recognisable as a triplet of triplets ($^2J_{HP} = 19.4$ Hz; $^2J_{HH'} = 3.4$ Hz) and is assigned to the unique hydride *trans* to the CO ligand. The signal at -9.20 ppm, which has twice the integral of the signal at -8.82 ppm, appears as a complex multiplet. Using an NMR simulation/iteration program, together with the coupling constants derived above, the remaining coupling constants were obtained. These are given in Fig. 2 along with the nuclei numbering scheme that was used. The ^{31}P-NMR spectrum, which was proton-decoupled selectively in the aromatic region only, gave a complex multiplet that could be simulated by using the HP and PP′ coupling constants derived above. Differences between the spectra discussed here for **1** and those reported for the complexes $OsH_3(SiPh_2H)(CO)(P^iPr_3)_2$ [4], and $RuH_3(SiPh_2H)(CO)(P^tBu_2Me)_2$ [14] can be attributed to different geometries in these latter two compounds because of the very bulky phosphine ligands.

The ^1H-NMR signal at 213 K of the single hydride *trans* to CO, has a ^2J(HP) value of 19.4 Hz, which is similar to the ^2J(HP*cis*) values found in the complexes $OsH(SiR_3)(CO)_2(PPh_3)_2$ ($R_3 = Et_3$, Ph_3, Ph_2H) [15]. A smaller ^2J(HP) value would be expected if this hydrogen was involved in a $M(\eta^2\text{-}HSiR_3)$ bonding interaction [16], and therefore it is unlikely that there is any significant Si–H interaction in $OsH_3(SiMe_3)(CO)(PPh_3)_2$.



Scheme 1. Synthesis and reactions of $OsH_3(SiMe_3)(CO)(PPh_3)_2$ (**1**).

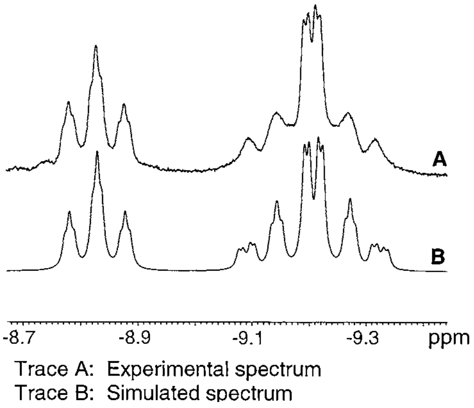
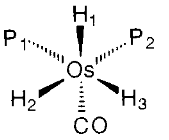


Fig. 1. Experimental (213 K) and simulated ^1H-NMR hydride resonances of $OsH_3(SiMe_3)(CO)(PPh_3)_2$ (**1**).



View down the Si-Os bond of **(1)** showing the donor atom numbering scheme (the $SiMe_3$ group has been omitted for clarity).

Coupling Constants

Measured from experimental spectrum:	$^2J(H_1H_{2,3}) = 3.4$ Hz $^2J(H_1P_{1,2}) = 19.4$ Hz
Calculated from simulated spectrum:	$^2J(H_2P_1/H_3P_2) = -29.9$ Hz $^2J(H_2P_2/H_3P_1) = 39.49$ Hz $^2J(H_2H_3) = 6.2$ Hz $^2J(P_1P_2) = -21.0$ Hz

Fig. 2. Coupling constants and nuclei numbering scheme for $OsH_3(SiMe_3)(CO)(PPh_3)_2$ (**1**).

The T_1 values for the ^1H-NMR resonances of the hydrides in complex (**1**) were determined. The T_1(min) for the resonance of the hydride *trans* to CO occurs close to 223 K and is 309 ms. A T_1(min) was not located for the other hydrides, however, at all tempera-

Table 1
Crystal data and structure refinement for **1**

Empirical formula	$C_{40}H_{42}OOsP_2Si$
Formula weight	818.97
Temperature (K)	203(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	9.929
b (Å)	23.2622(3)
c (Å)	16.0141(2)
β (°)	103.0840(10)
Volume (Å^3)	3602.83(6)
Z	4
$D_{calc.}$ (g cm^{-3})	1.510
Absorption coefficient (mm^{-1})	3.691
$F(000)$	1640
Crystal size (mm)	$0.32 \times 0.12 \times 0.10$
θ range for data collection (°)	1.75–27.49
Reflections collected	22333
Unique reflections	7944 [$R_{int} = 0.0246$]
Observed reflections [$I > 2\sigma(I)$]	6885
Max. and min. transmission	0.7091–0.3846
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.014
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0223$, $wR_2 = 0.0496$
R indices (all data)	$R_1 = 0.0303$, $wR_2 = 0.0526$
Largest difference peak and hole (e Å^{-3})	0.870 and -0.655

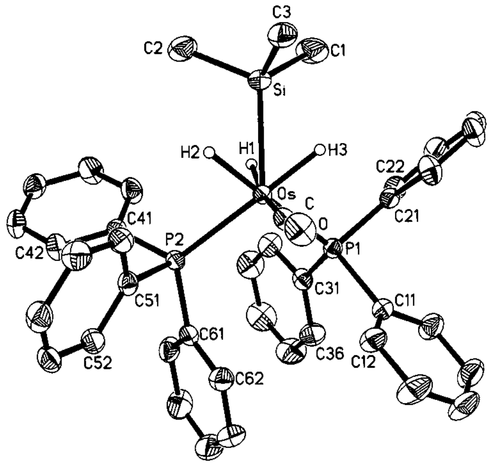


Fig. 3. Molecular geometry of $OsH_3(SiMe_3)(CO)(PPh_3)_2$ (**1**).

tures, the determined T_1 values for both signals ranged from 300 to 537 ms. This strongly implies that both resonances originate from classical terminal hydride ligands [17].

2.2. Crystallographic study of $OsH_3(SiMe_3)(CO)(PPh_3)_2$ (1)

The structure of **1** was obtained by an X-ray crystal structure determination (see Table 1), and the molecular geometry is depicted in Fig. 3. The non-hydrogen donor atoms are arranged in an approximately tetrahedral manner about osmium and representative bond lengths and bond angles are presented in Table 2. The Si–Os–CO angle is 108.16(9)°, and the Si–Os–P angles are 124.97(2) and 119.41(2)°. Surprisingly, the angle between the two quite bulky triphenylphosphine ligands is only 99.85(2)°. Two phenyl rings, one from each triphenylphosphine, make a close face-to-face approach. In contrast, the P1–Os–P2 angle between the very bulky P^iPr_3 ligands in $OsH_3(SiHPh_2)(CO)(P^iPr_3)_2$ is 146.06° [4]. The skeletal geometry suggests that the hydride ligands should be located between the trimethylsilyl group and the CO and two PPh_3 ligands. Indeed this is where the crystal structure revealed the hydrides to be. A convenient description of their positions is as *trans* to CO, and approximately *trans* to each of the two PPh_3 ligands. The position of the hydride *trans* to CO was determined more precisely than the positions of the other two. The Os–Si bond length is 2.4533(8) Å, similar to that found in $OsH_3(SiHPh_2)(CO)(P^iPr_3)_2$ of 2.448 (2) Å [4], and falling at the longer end of the range of observed osmium–silicon bond distances [15]. The Si–$C_{(methyl)}$ bonds are the same within estimated S.D.s and the C–Si–C angles are all uniform at approx. 105°. The Os–Si–C angles are also very similar (between 112.0(1) and 114.2(1)°) implying that the $SiMe_3$ group is symmetrically bonded to the metal centre in $OsH_3(SiMe_3)(CO)(PPh_3)_2$.

Table 2
Selected bond lengths (Å) and angles (°) for **1**

Bond lengths	
Os–C	1.893(3)
Os–P(2)	2.3820(7)
Os–P(1)	2.3900(7)
Os–Si	2.4533(8)
Os–H(1)	1.58(9)
Os–H(2)	1.55(9)
Os–H(3)	1.45(10)
Si–C(2)	1.879(3)
Si–C(1)	1.881(3)
Si–C(3)	1.884(3)
O–C	1.155(3)
Bond angles	
C–Os–P(2)	97.36(8)
C–Os–P(1)	103.21(8)
P(2)–Os–P(1)	99.85(2)
C–Os–Si	108.16(9)
P(2)–Os–Si	124.97(2)
P(1)–Os–Si	119.41(2)
C–Os–H(1)	169(1)
P(2)–Os–H(3)	173(1)
P(1)–Os–H(2)	171(1)

2.3. Reactions of $OsH_3(SiMe_3)(CO)(PPh_3)_2$ (1) with Lewis Bases L (L = CO, CNp-tolyl, PPh_3), $HSiR_3$ (R = Et, Ph), $HSn(p\text{-tolyl})_3$, and phenylacetylene

In solution, $OsH_3(SiMe_3)(CO)(PPh_3)_2$ appears to react via loss of $HSiMe_3$ to form the highly reactive, coordinatively unsaturated species, $OsH_2(CO)(PPh_3)_2$ which then undergoes reaction with another ligand or addition reactions with suitable H–Si, H–Sn, and H–C bonds.

Addition of the Lewis bases, L, to solutions of complex **1** in toluene resulted in the formation of the known compounds $OsH_2(CO)L(PPh_3)_2$ (L = CO, CN*p*-tolyl, PPh_3). The addition of CO at 400 kPa for 2 h at room temperature generated $OsH_2(CO)_2(PPh_3)_2$. Addition of CN(*p*-tolyl) formed $OsH_2(CO)(CNp\text{-tolyl})(PPh_3)_2$ and $OsH_2(CO)(PPh_3)_3$ was isolated after heating a solution containing **1** and PPh_3 in toluene at ca. 50°C for 0.5 h. A similar reactivity pattern has been observed for the ruthenium (IV) trihydrido, silyl complexes, $RuH_3(SiR_3)(PPh_3)_3$ [8].

Heating solutions of $OsH_3(SiMe_3)(CO)(PPh_3)_2$ (**1**) in the presence of excess triethylsilane resulted in the formation of $OsH_3(SiEt_3)(CO)(PPh_3)_2$ (**2**), which was isolated as a colourless crystalline solid. The methyl and methylene resonances of the ethyl groups appear in the ^1H-NMR spectrum of **2** as overlapping triplet and quartet signals. At 298 K, resonances for the hydride ligands occur as two broad signals at -8.92 and -9.82 ppm. At 263 K, the signals resolve into patterns closely resembling the low temperature hydride resonances of complex **1**, suggesting a similar structure. A triplet of triplets at -9.04 ppm ($^2J(HP) = 19.3$ Hz; $^2J(HH') = 3.6$ Hz) was assigned to the unique hydride ligand *trans* to CO. The other two hydride ligands give a complex signal at -9.85 ppm, having the same appearance as signal assigned to the other two hydrides in $OsH_3(SiMe_3)(CO)(PPh_3)_2$. Again, the hydrides were designated as classical hydride ligands, based on T_1 measurements (see Section 3). Heating complex **2** in the presence of excess $HSiMe_3$ returned $OsH_3(SiMe_3)(CO)(PPh_3)_2$ (**1**).

Similarly, $OsH_3(SiPh_3)(CO)(PPh_3)_2$ (**3**) was synthesised by reacting complex **1** with $HSiPh_3$. A broad resonance for the hydride ligands at -9.01 ppm in the ^1H-NMR spectrum of complex **3** at 298 K, separates into two signals at 233 K, one at -8.09 (triplet, $^2J(HP) = 20.0$ Hz) and the other at -9.32 ppm (multiplet). The splitting pattern was very similar to that observed for complex **1** at 213 K indicating again a similar structure.

The reaction between $OsH_3(SiMe_3)(CO)(PPh_3)_2$ and $HSn(p\text{-tolyl})_3$ yielded $OsH_2[Sn(p\text{-tolyl})_3]_2(CO)(PPh_3)_2$ (**4**). This reaction most likely proceeded through successive oxidative additions of H–Sn bonds. Two equivalents of $HSn(p\text{-tolyl})_3$ were required for complete reaction. $OsH_2[Sn(p\text{-tolyl})_3]_2(CO)(PPh_3)_2$ (**4**) was isolated as a stable, colourless solid. The equivalence of the stannyl ligands is revealed by the observation of a single methyl resonance in the ^1H-NMR spectrum at 2.28 ppm, and also by only one set of *p*-tolyl signals in the ^{13}C-NMR spectrum. In contrast, two sets of signals for the carbon atoms of the phenyl groups are observed, indicating that the PPh_3 ligands are inequivalent. Consistent with this, the carbonyl signal in the ^{13}C-NMR spectrum appears as a doublet of doublets ($^2J(CP) = 75.4$ Hz; $^2J(CP') = 10.8$ Hz). The coupling constant values suggest that the carbonyl ligand is positioned approximately *trans* to one PPh_3 ligand and *cis* to the other. Inequivalent PPh_3 ligands are identified by two doublets at 1.36 and -6.84 ppm ($^2J(PP') = 26.5$ Hz) in the ^{31}P-NMR spectrum. A broad signal at -7.67 ppm in the ^1H-NMR spectrum of complex (**4**) indicates that the hydride ligands are involved in a dynamic process at 298 K. At 223 K, this signal resolves into two signals, each of which appears as a doublet of doublets of doublets, centred at -6.98 and -8.26 ppm. T_1 values (223 K, 200 MHz) for each of these signals of 231 and 219 ms, verify that terminal hydride ligands are present. On the basis of the above data, complex **4** appears to be very similar to the trimethylstannyl analogue, $OsH_2(SnMe_3)_2(CO)(PPh_3)_2$, which has been previously reported [15]. It is not possible to propose a definitive structure for **4** based on the above NMR data alone.

When $OsH_3(SiMe_3)(CO)(PPh_3)_2$ was treated with phenylacetylene the product was characterised as $OsH(C_2Ph)(CO)(PPh_3)_3$ (**5**). Initial reactions gave only small amounts of this product, but almost quantitative yields of **5** could be achieved by the addition of further PPh_3 to the reaction mixture after an initial period of heating. In the IR spectrum, a strong $\nu(CO)$ band is observed at 1931 cm^{-1} and a medium intensity band at 2091 cm^{-1} is assigned as $\nu(C\equiv C)$. A weaker, broader band at 2078 cm^{-1}, appearing as a shoulder of $\nu(C\equiv C)$, is most likely $\nu(Os–H)$. The presence of the hydride ligand is clearly seen in the ^1H-NMR spectrum of complex **5** as a doublet of triplets centred at -8.49 ppm which integrates for one proton. The splitting pattern is consistent with a geometry where the hydride ligand is *trans* to one triphenylphosphine ligand and *cis* to the remaining two equivalent PPh_3 ligands. The remaining acetylide and carbonyl ligands must therefore be positioned mutually *trans*.

The formation of complex **5** most likely involves oxidative addition of HC_2Ph to $OsH_2(CO)(PPh_3)_2$ followed by reductive elimination of dihydrogen to generate the coordinatively unsaturated complex $OsH(C_2Ph)(CO)(PPh_3)_2$. This complex could not be isolated, however, addition of PPh_3 forms the stable coordinatively saturated product $OsH(C_2Ph)(CO)(PPh_3)_3$ (**5**) in good yield.

In conclusion, we have demonstrated that the simple and easily accessible osmium(IV) trihydrido, silyl complex, $OsH_3(SiMe_3)(CO)(PPh_3)_2$, has a structure closely similar to that of the $OsH_3(SiR_3)(PPh_3)_3$ family of compounds [5], with CO replacing one triphenylphosphine ligand but with the positions of the remaining ligands substantially unchanged. Furthermore, in contrast to $OsH_3(SiR_3)(PPh_3)_3$, $OsH_3(SiMe_3)(CO)(PPh_3)_2$ has a marked tendency to lose silane in solution and is therefore a useful precursor to the reactive, coordinatively unsaturated, intermediate, $OsH_2(CO)(PPh_3)_2$.

3. Experimental

3.1. General procedures and instruments

Solvents were freshly distilled from appropriate drying agents prior to use [18]. Schlenk tubes with Teflon screw caps were used as reaction vessels. Reactions were carried out under an inert atmosphere of oxygen-free nitrogen or sealed under vacuum (once the contents had been frozen) when heating was involved. Schlenk tubes were partly immersed in hot oil baths for those reactions requiring heating. Reactions carried out at room temperature were in the range 18–22°C. Crystallizations were achieved in the reaction vessel by removing most of the solvent by reduced pressure then slowly adding another solvent in which the compound is insoluble. Once the solid had formed, the tube was opened and the compound collected in a glass sinter. Recrystallization was accomplished in most cases by dissolving the sample in a low boiling point solvent, then adding an equivalent amount of a higher boiling point solvent, in which the compound is insoluble. Slow evaporation at reduced pressure was performed using a rotary evaporator resulted in gradual crystallisation. The compounds $Os(Ph)Cl(CO)(PPh_3)_2$ and $HSiMe_3$ were prepared according to literature methods [19,20].

Infrared spectra (4000–400 cm^{-1}) were recorded on a Digilab FTS-7 infrared spectrometer as Nujol mulls between KBr plates. ^1H-NMR spectra were recorded on a Bruker AM-400 or DRX-400 instrument operating at 400 MHz. Resonances are quoted in ppm and referenced to either tetramethylsilane (0.00 ppm) or the proteo-impurity in the solvent (7.25 ppm for $CHCl_3$). ^{13}C- and ^{31}P-NMR spectra were obtained with a Bruker AM-400 or DRX-400 instrument operating at 100.6 (^{13}C) and 162.0 (^{31}P) MHz, respectively. ^{13}C-NMR spectra were referenced to $CDCl_3$ (77.00 ppm) and ^{31}P-NMR to 85% orthophosphoric acid (0.00 ppm) as an external standard. Melting points (uncorrected) were determined on a Reichert hot stage microscope. Elemental analyses were obtained from the Microanalytical Laboratory, University of Otago.

3.2. $OsH_3(SiMe_3)(CO)(PPh_3)_2$ (**1**)

$HSiMe_3$ was vigorously bubbled for ca. 20 s through a solution of $Os(Ph)Cl(CO)(PPh_3)_2$ (0.200g; 0.23 mmol) dissolved in toluene (10 ml) and contained in a Schlenk tube. The Schlenk tube with the atmosphere of $HSiMe_3$ still above the toluene solution was then sealed and the solution stirred at room temperature for 18 h. The resulting clear, orange solution was reduced in volume to ca. 3 ml in vacuo and dry hexane (ca. 20 ml) added to precipitate (**1**) as a cream solid. This solid was collected by filtration and washed with several small portions of hexane. Recrystallization from dichloromethane–ethanol yielded large, off-white crystals of (**1**) (0.134 g, 70%). m.p. 133–135°C. Anal. Calc. for $C_{40}H_{42}OOsP_2Si$: C, 58.66; H, 5.17. Found: C, 58.83; H, 5.00. IR (cm^{-1}): 1983s (CO); 2054w, 2033w, 1888s (OsH). ^1H-NMR ($CDCl_3$; δ): 7.40–7.12 (m, 30H, PPh_3); 0.51 (s, 9H, $Si(CH_3)_3$); -9.03 (broad, 3H, OsH_3). ^{13}C-NMR ($CDCl_3$; δ): 186.9 (t, CO, $^2J_{CP} = 9.4$ Hz); 138.0 (t′, PPh_3 *ipso*, $^{1,3}J_{CP} = 52$ Hz) (the meaning of t′ and $^{m,n}J$ are described in Ref. [13]); 133.8 (t′, PPh_3 *meta*, $^{3,5}J_{CP} = 11.8$ Hz); 129.2 (s, PPh_3 *para*); 127.6 (t′, PPh_3 *ortho*, $^{2,4}J_{CP} = 9.2$ Hz); 1.35 (s, $Si(CH_3)_3$). ^{31}P-NMR ($CH_2Cl_2/CDCl_3$; δ): 13.43 (s, broad). Determination of the T_1 values for the hydride resonances of **1** were carried out by an inversion recovery NMR experiment at 400 MHz. Values for temperature (°C), chemical shift (ppm), T_1 (ms) are: -40.0, -8.82, 334; -40.0, -9.26, 385; -50, -8.84, 309; -50, -9.26, 412; -60, -8.87, 330; -60, -9.26, 460; -75, -8.91, 415; -75, -9.27, 537.

3.3. $OsH_3(SiEt_3)(CO)(PPh_3)_2$ (**2**)

$OsH_3(SiMe_3)(CO)(PPh_3)_2$ (0.200 g; 0.24 mmol) and $HSiEt_3$ (0.160 g; 1.38 mmol) were heated in toluene (15 ml) in a sealed Schlenk tube at 55°C for 2 h. The volume of the solution was reduced in vacuo to a small volume (ca. 3 ml) and then dry hexane added to precipitate (**2**). Recrystallization using dichloromethane–ethanol afforded colourless crystals of (**2**) (0.096 g, 46%). m.p. 138–140°C. Anal. Calc. for $C_{43}H_{48}OOsP_2Si$: C, 59.98; H, 5.62. Found: C, 60.02; H, 5.56. IR (cm^{-1}): 1983s (CO); 2050w, 1892s (OsH). ^1H-NMR ($CDCl_3$; δ): 7.65–7.10 (m, 30H, PPh_3); 0.70 (overlapping t and q, 15H, $Si(CH_2CH_3)_3$); -8.92 (broad, ca. 1H, OsH); -9.81 (broad, 2H, OsH_2). ^{13}C-NMR ($CDCl_3$; δ): 187.3 (t, CO, $^2J_{CP} = 5$ Hz); 137.7 (t′, PPh_3 *ipso*, $^{1,3}J_{CP} = 47.0$ Hz); 133.8 (t′, PPh_3 *meta*, $^{3,5}J_{CP} = 11.2$ Hz); 129.1 (s, PPh_3 *para*); 127.5 (t′, PPh_3 *ortho*, $^{2,4}J_{CP} = 9.0$ Hz); 16.02 (s, $Si(CH_2CH_3)_3$); 8.71 (s, $Si(CH_2CH_3)_3$). ^{31}P-NMR ($CH_2Cl_2/CDCl_3$; δ): 12.76 (s, broad). Determination of the T_1 values for the hydride resonances of **2** were carried out by an inversion recovery NMR experiment at 400 MHz. Values for temperature (°C), chemical shift (ppm), T_1 (ms) are: −30, −8.08, 258; −30, −9.29, 381; −40, −8.09, 273; −40, −9.32, 372; −50, −8.11, 316; −50, −9.33, 439; −60, −8.12, 357; −60, −9.36, 497.

3.4. *$OsH_3(SiPh_3)(CO)(PPh_3)_2$* (**3**)

$OsH_3(SiMe_3)(CO)(PPh_3)_2$ (0.200 g; 0.24 mmol) and $HSiPh_3$ (0.317 g; 1.22 mmol) were heated in toluene (15 ml) under a nitrogen atmosphere at 55°C for 3 h. The volume of the solution was reduced in vacuo to a small volume (ca. 3 ml) and then dry hexane added to precipitate (**3**). Recrystallization using dichloromethane–ethanol afforded colourless crystals of (**3**) (0.145 g, 59%). m.p. 169–172°C. Anal. Calc. for $C_{55}H_{48}OOsP_2Si$: C, 65.72; H, 4.81. Found: C, 65.44; H, 5.05. IR (cm^{-1}): 1987s (CO); 2071w, 2016w, 1900s (OsH). ^1H-NMR ($CDCl_3$; δ): 7.24–6.97 (m, 45H, PPh_3 and $SiPh_3$); −9.01 (broad, ca. 3H, OsH_3). ^{13}C-NMR ($CDCl_3$; δ): 187.6 (t, CO, $^2J_{CP} = 5.1$ Hz); 145.8 (s, $SiPh_3$); 136.7 (t′, PPh_3 *ipso*, $^{1,3}J_{CP} = 47.8$ Hz); 133.6 (t′, PPh_3 *meta*, $^{3,5}J_{CP} = 11.2$ Hz); 129.3 (s, PPh_3 *para*); 127.6 (t′, PPh_3 *ortho*, $^{2,4}J_{CP} = 9.4$ Hz); 127.1 (s, $SiPh_3$); 126.7 (s, $SiPh_3$). ^{31}P-NMR ($CH_2Cl_2/CDCl_3$; δ): 10.30 (s, broad). Determination of the T_1 values for the hydride resonances of **3** were carried out by an inversion recovery NMR experiment at 400 MHz. Values for temperature (°C), chemical shift (ppm), T_1 (ms) are: −20, −9.10, 215; −20, −9.89, 291; −30, −9.12, 228; −30, −9.91, 315; −40, −9.14, 252; −40, −9.93, 372.

3.5. *$OsH_2[Sn(p-tolyl)_3]_2(CO)(PPh_3)_2$* (**4**)

$OsH_3(SiMe_3)(CO)(PPh_3)_2$ (0.200 g; 0.24 mmol) and $HSn(p\text{-tolyl})_3$ (0.200 g; 0.50 mmol) were heated in toluene (15 ml) at 55°C for 3 h. The volume of the solution was reduced in vacuo to a small volume (ca. 3 ml) and then dry hexane added to precipitate (**4**). This solid was collected by filtration and washed with several portions (4 ml) of ethanol and then hexane. Recrystallization twice from dichloromethane–hot ethanol gave (**4**) as a colourless, micro-crystalline solid (0.119 g, 32%). m.p. 173–174°C. Anal. Calc. for $C_{79}H_{74}OOsP_2Sn_2$: C, 62.06; H, 4.88. Found: C, 61.49; H, 5.34. IR (cm^{-1}): 1966s (CO); 1911w, 1901w, (OsH). ^1H-NMR ($CDCl_3$; δ): 7.30–6.57 (m, 38H, PPh_3 and *p*-tolyl); 2.27 (s, 6H, $C_6H_4CH_3$); −7.67 (broad, ca. 2H, OsH_2). ^{13}C-NMR ($CDCl_3$; δ): 180.9 (d/d, CO, $^2J_{CP} = 75.4$ Hz, $^2J_{CP'} = 10.8$ Hz); 137.5 (s, $Sn(C_6H_4CH_3)_3$ *meta*, broad); 136.3 (d, PPh_3 *ipso*, $^1J_{CP} = 44.9$ Hz); 136.2 (s, $Sn(C_6H_4CH_3)_3$ *ipso*, broad); 135.0 (d, PPh_3 *ipso*, $^1J_{CP} = 45.4$ Hz); 134.4 (d, PPh_3 *meta*, $^3J_{CP} = 10.4$ Hz); 129.9 (s, PPh_3 *para*); 129.4 (s, PPh_3 *para*); 128.2 (s, $Sn(C_6H_4CH_3)_3$ *para*, broad); 128.0 (s, $Sn(C_6H_4CH_3)_3$ *ortho*); 127.7 (t′, PPh_3 *ortho*, $^{2,4}J_{CP} = 19.6$ Hz); 127.3 (t′, PPh_3 *ortho*, $^{2,4}J_{CP} = 19.6$ Hz); 21.4 (s, $Sn(C_6H_4CH_3)_3$). ^{31}P-NMR ($CH_2Cl_2/CDCl_3$; δ): 1.36 (d, $^2J_{PP} = 26.5$ Hz); −6.84 (d, $^2J_{PP} = 26.5$ Hz). Determination of the T_1 values for the hydride resonances of **4** were carried out by an inversion recovery NMR experiment at 400 MHz. Values for temperature (°C), chemical shift (ppm), T_1 (ms) are: −30, −6.91, 184; −30, −8.20, 196; −40, −6.92, 207; −40, −8.22, 195; −50, −6.98, 231; −50, −8.26, 219.

3.6. *$OsH(C_2Ph)(CO)(PPh_3)_3$* (**5**)

$OsH_3(SiMe_3)(CO)(PPh_3)_2$ (0.200 g; 0.24 mmol) and phenylacetylene (0.135 g; 1.32 mmol) were heated in toluene (15 ml) under vacuum in a sealed Schlenk tube at 55°C for 10 min, resulting in a yellow–orange solution. The solution was frozen in liquid nitrogen and PPh_3 (0.065 g, 0.24 mmol) added. The Schlenk tube was then evacuated again and sealed. The solution was heated at 55°C for a further 0.5 h. The volume of the solution was reduced in vacuo to a small volume (ca. 3 ml) and then dry hexane added to precipitate (**5**). This solid was collected by filtration and washed with several small portions (ca. 5 ml) of hexane. The solid was then dissolved in dichloromethane (5 ml) and passed down a short column (8 × 4 cm) of silica gel using dichloromethane as eluent. Addition of ethanol and reduction of the solvent volume under reduced pressure yielded (**5**) as a colourless powder (0.158 g, 60%). m.p. 170–172°C. Anal. Calc. for $C_{63}H_{51}OOsP_3$: C, 68.34; H, 4.64. Found: C, 68.59; H, 5.41. IR (cm^{-1}): 1931s (CO); 2091m (C≡C); 2078w (OsH). ^1H-NMR ($CDCl_3$; δ): 8.00–6.48 (m, 50H, PPh_3 and C_2Ph); −8.49 (d/t, ca. 1H, OsH, $^2J_{HP(trans)} = 68.1$ Hz, $^2J_{HP(cis)} = 25.2$ Hz) ^{13}C-NMR ($CDCl_3$; δ): 189.5 (d/t, CO, $^2J_{CP} = 7.2$ Hz, $^2J_{CP'} = 6.7$ Hz); 137.5–123.7 (multiple signals, PPh_3 and Ph); the quaternary acetylide carbons were not observed. ^{31}P-NMR ($CH_2Cl_2/CDCl_3$; δ): 4.02 (d, $^2J_{PP} = 11.5$ Hz); −9.90 (t, $^2J_{PP} = 11.5$ Hz).

3.7. *X-ray crystal structure determination of $OsH_3(SiMe_3)(CO)(PPh_3)_2$* (**1**)

A suitable crystal was grown from toluene. Data were collected on a Siemens SMART diffractometer with a CCD area detector. Data collection covered a nominal hemisphere of data by a combination of three sets of exposures each exposure covering 0.3° in ω. Lorentz and polarisation corrections were applied and absorption corrections by the method of Blessing [21] yielding 22 333 measurements and equivalent reflections averaged yielding 7944 unique reflections ($R_{int} = 0.0246$).

The structure was solved by Patterson and Fourier techniques using SHELXS-97 [22] and SHELXL-97 [23]. Refinement was by full-matrix least-squares with all non-hydrogen atoms being allowed to assume anisotropic thermal motion. Hydrogen atoms, other than those bonded to osmium, were placed geometrically and refined with a riding model with U_{iso} 20% greater than the carrier atom. The hydrogen atoms bonded to osmium were located from a difference map, that *trans* to the carbonyl group being clearly resolved and the remaining two less so. The coordinates of these hydrides were allowed to refine with thermal parameter fixed at 20% greater than that of osmium. Refinement converged to conventional $R = 0.0223$ for the 6885 data with $[I > 2\sigma(I)]$. Crystal data and refinement parameters are given in Table 1 and selected bond lengths and angles in Table 2.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 127541. Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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