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Silatranyl, hydride complexes of osmium(II) and osmium(IV): crystal structure of $Os(Si\{OCH_2CH_2\}_3N)H_3(PPh_3)_3$

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Abstract

Reaction between $Os(CO)_2(PPh_3)_3$ and the silatrane, $HSi\{OCH_2CH_2\}_3N$, gives the osmium(II) silatranyl, hydride complex $Os(Si\{OCH_2CH_2\}_3N)H(CO)_2(PPh_3)_2$ (**1**), as a mixture of three isomers, the structures of which were determined by NMR spectroscopy. Reaction between $OsH_4(PPh_3)_3$ and the silatrane, $HSi\{OCH_2CH_2\}_3N$, gives the osmium(IV) silatranyl, trihydride complex $Os(Si\{OCH_2CH_2\}_3N)H_3(PPh_3)_3$ (**2**). The crystal structure of **2** has been determined and all three hydride ligands located. The three hydrides all make close approaches to the silicon atom but the distances between silicon and each of the hydrides suggests that any Si···H interactions must be weak. The interatomic distance between Si and N in the silatranyl ligand is large and the nitrogen atom has near planar geometry. Compound **2** can be methylated or protonated at nitrogen giving the complexes $[Os(Si\{OCH_2CH_2\}_3NMe)H_3(PPh_3)_3]I$ (**3**), and $[Os(Si\{OCH_2CH_2\}_3NH)H_3(PPh_3)_3]CF_3SO_3$ (**4**), respectively. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Hydride complexes; Silatranyl complexes; Osmium

1. Introduction

Silatranes are cyclic silicon ethers of tris(2-oxyalkyl)amine with general formula $X{-}Si\{OCH_2CH_2\}_3N$. They are interesting examples of hypervalent silicon compounds and have been intensively studied since their discovery in 1961 [1]. Points of interest related to the silatranes include the nature of any N–Si bond, the variation in the transannular N–Si distance and the dependence of this on the axial silicon substituent X, biological activity, reactivity, and even their architectural beauty [2]. Theoretical studies of the nature of the N–Si bond in silatranes suggest that it is best described in terms of a dative $N \rightarrow Si$ bond with some small contribution from a three-centre, four-electron interaction [3]. The calculated potential curve for deformation of the N–Si distance has been found to be very shallow [3c].

A feature of the chemical reactivity of silatranes is the reluctance of the bridgehead nitrogen to be quaternised. Indeed the first reported protonation and methylation of this nitrogen arose from our studies of the coordinatively unsaturated silatranyl complex, $Os(Si\{OCH_2CH_2\}_3N)Cl(CO)(PPh_3)_2$, where the axial silicon substituent is a transition metal ligand fragment [4]. Here, the ready quaternisation can be understood because structure determination of $Os(Si\{OCH_2CH_2\}_3N)Cl(CO)(PPh_3)_2$ revealed a greatly expanded silatrane cage with the nitrogen in a near planar environment. In an extension of this work we now describe the synthesis of coordinatively saturated silatranyl, hydride complexes of osmium(II) and osmium(IV), the crystal structure of $Os(Si\{OCH_2CH_2\}_3N)H_3(PPh_3)_3$, and quaternisation reactions of this complex.

2. Results and discussion

2.1. Oxidative addition of silatrane to $Os(CO)_2(PPh_3)_3$

In previous studies we have shown that oxidative addition of the silanes, $HSiR_3$ (R = $SiMe_3$, $SiEt_3$, $SiPh_3$, and $SiPh_2H$), to $Os(CO)_2(PPh_3)_3$ gives the correspond-

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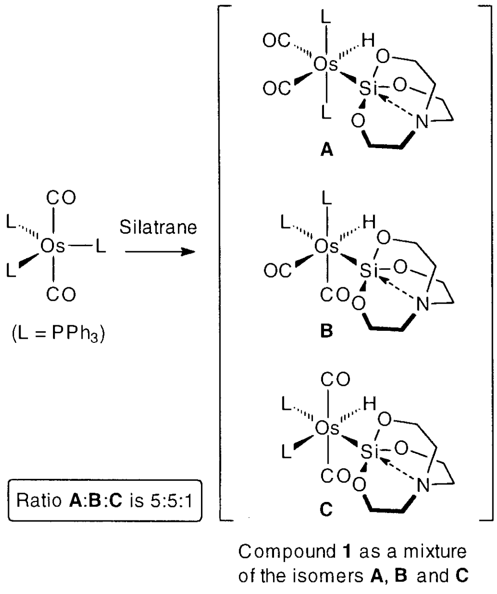
ing osmium(II) silyl, hydride complexes $Os(SiR_3)H(CO)_2(PPh_3)_2$ [5]. As an extension of this work we now report the oxidative addition of $HSi\{OCH_2CH_2\}_3N$ to $Os(CO)_2(PPh_3)_3$ which leads to the expected addition product as a mixture of three geometrical isomers.

Photolysis (with a tungsten/halogen lamp), of a mixture of $Os(CO)_2(PPh_3)_3$ and silatrane in benzene, causes the initially yellow solution to become colourless over a period of 20 min. The colourless product isolated has an elemental analysis and a FAB^+ mass spectrum consistent with the formulation $Os(Si\{OCH_2CH_2\}_3N)H(CO)_2(PPh_3)_2$ (see Scheme 1). However, the spectral data clearly reveal that this compound is a mixture of isomers and these isomers could not be separated. In the IR spectrum, there are five absorptions in the region associated with $\nu(CO)$ and $\nu(OsH)$, at 1902, 1942, 1976, 2015 and 2092 cm^{-1}. All six possible isomers for compound **1** are illustrated in Fig. 1, however, the NMR spectral data indicate that the three isomers, **A**, **B**, and **C** are present in an approximate ratio of 5:5:1.



Scheme 1. Synthesis of $Os(Si\{OCH_2CH_2\}_3N)H(CO)_2(PPh_3)_2$ (**1**) as three isomers.

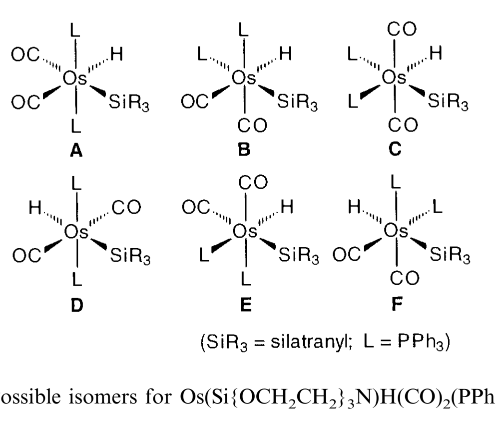
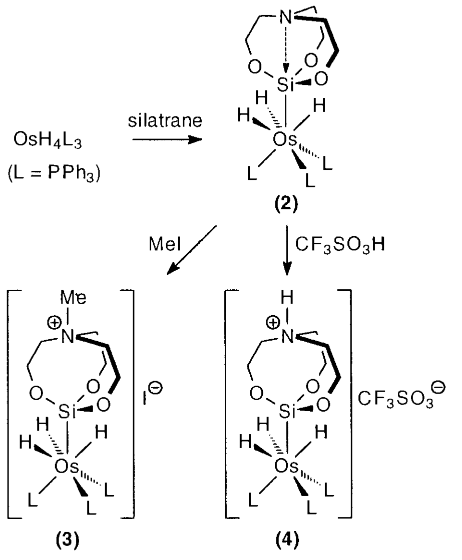


Fig. 1. Possible isomers for $Os(Si\{OCH_2CH_2\}_3N)H(CO)_2(PPh_3)_2$ (**1**).

The ^1H-NMR spectrum of the mixture of isomers reveals three hydride signals at high-field. The triplet hydride resonance appearing at -7.63 ppm ($^2J_{HP} = 17.6$ Hz) is assigned to isomer **A**. An unresolved overlapping doublet of doublets (an apparent triplet) at -7.12 (‘$^2J_{HP}$’ $= 20.4$ Hz) is assigned to isomer **B**. These two signals are in a ratio of ca. 1:1. A third signal, in this case a well-resolved doublet of doublets, at -9.64 ppm ($^2J_{HP\mathit{trans}} = 37.2$ Hz, $^3J_{HP\mathit{cis}} = 20.8$ Hz) is attributed to isomer **C**. This signal is smaller than the other two and the ratio of **A**:**B**:**C** is ca. 5:5:1.

All remaining NMR data are consistent with the three isomers in the mixture being **A**, **B**, and **C**. In the ^{31}P-NMR spectrum the singlet at 9.95 ppm is assigned to isomer **A** which has two-equivalent, mutually *trans* triphenylphosphine ligands. The two other isomers which could give rise to a singlet in the ^{31}P-NMR spectrum (and a triplet in the ^1H-NMR spectrum) are **D** and **F**, but these isomers are excluded by the ^{13}C-NMR data discussed below. Doublet signals at 3.81 ppm ($^2J_{PP} = 25.3$ Hz) and 8.98 ppm ($^2J_{PP} = 25.1$ Hz), are assigned to isomer **B** which has two inequivalent *cis* triphenylphosphine ligands. Isomer **E** would also be compatible with this assignment but is incompatible with the ^1H- and ^{13}C-NMR data discussed below. A third smaller set of two doublet resonances at 3.68 ppm ($^2J_{PP} = 14.7$ Hz) and 4.11 ppm ($^2J_{PP} = 14.7$ Hz) is assigned to isomer **C**. In the ^{13}C-NMR spectrum the signals for the silatrane cage methylene carbons of the three isomers appear at 52.49, 52.71, and 52.84 ppm and at 61.11, 61.09, and 60.13 ppm. The carbonyl region also reveals the existence of three isomers. The two triplet resonances, one at 189.35 ppm (t, *C*O, $^2J_{CP} = 8.6$ Hz) and a second at 186.57 (t, *C*O, $^2J_{CP} = 10.6$ Hz), are assigned to the two inequivalent carbonyls of isomer **A**. Likewise, the two doublet of doublet resonances at 182.95 (dd, *C*O, $^2J_{CP\mathit{trans}} = 74.5$ Hz, $^2J_{CP\mathit{cis}} = 6.0$ Hz), and 187.68 (dd, *C*O, $^2J_{CP\mathit{cis}} = 8.6$ Hz, $^2J_{CP\mathit{cis}} = 4.5$ Hz) are assigned to the two inequivalent carbonyls of isomer **B**, the first resonance being for the carbonyl *trans* to triphenylphosphine. A much weaker and poorly resolved signal at 188.68 (dd, *C*O, $^2J_{CP\mathit{cis}} = 10.0$ Hz, $^2J_{CP\mathit{cis}} = 6.0$ Hz) is assigned to isomer **C**. A ^{29}Si-NMR spectrum of the mixture of isomers was obtained although the signal-to-noise ratio was very low. A triplet signal at -39.10 ($^2J_{SiP} = 10.8$ Hz) is assigned to isomer **A** but the high level of background noise in this spectrum makes it impossible to assign further peaks.

It is noteworthy that in each of the observed isomers **A**, **B**, and **C** the hyride and silatranyl ligands are *cis* to one another as would be expected on both kinetic and thermodynamic grounds. Steric effects are also apparent in that in each of the three isomers **A**, **B**, and **C**, the



Scheme 2. Synthesis and reactions of $Os(Si\{OCH_2CH_2\}_3N)H_3(PPh_3)_3$ (**2**).

three bulkiest ligands (the two triphenylphosphines and the silatranyl ligand) are found in a meridional arrangement. Previous products obtained from the oxidative addition of silanes to $Os(CO)_2(PPh_3)_3$ usually have the silyl and H groups *cis*, the carbonyl groups *cis*, and the phosphine groups *trans*, i.e. the geometry of isomer **A** [5]. An exception is that in the addition of SiH_2Ph_2 to $Os(CO)_2(PPh_3)_3$ to form $Os(SiPh_2H)H(CO)_2(PPh_3)_2$, two isomers were observed corresponding to isomers **A** and **B** in Fig. 1. The NMR data for compound **1** (isomer **B**) and the corresponding isomer of $Os(SiPh_2H)H(CO)_2(PPh_3)_2$ are closely similar.

2.2. Reaction of silatrane with $OsH_4(PPh_3)_3$

The osmium(IV) complex, $OsH_4(PPh_3)_3$ reacts with the silanes $HSiR_3$ (R = Et, Ph, Pyrrolyl) to form the corresponding metal complexes, $Os(SiR_3)H_3(PPh_3)_3$ [6]. The bonding situation in these complexes was explored through X-ray crystal structure determination of the complex, $Os(SiPyrrolyl_3)H_3(PPh_3)_3$ (although the hydride ligands were not located), and through theoretical calculations of the model compounds $Os(SiR_3)H_3(PH_3)_3$ (R = H, NH_2, Pyrrolyl). The conclusion was that there was a small but significant bonding interaction between the silicon and all three hydride ligands, the major source of this interaction involving overlap between the hydrogen s orbitals and the σ*(Os–Si). Related weak Si···H interactions for situations involving one silicon, one hydrogen, and one metal centre, have been widely documented and discussed by Schubert [7] and by others [8]. For early metal complexes, several examples where one hydride ligand and two silyl ligands are involved, have been recognised [8]. Study of the compound $Os(Si\{OCH_2CH_2\}_3N)H_3(PPh_3)_3$ prepared here, provides the opportunity to obtain further information about the structure and bonding interactions in compounds of the class $Os(SiR_3)H_3L_3$.

Attachment of the silatranyl ligand to osmium(II) in either a coordinatively unsaturated [4] or saturated [9] complex results in a cage geometry with an unusually long Si to N distance. It was also of interest, therefore, to determine whether the silatranyl cage in an osmium(IV) complex would have a similarly expanded cage geometry.

The reaction between $OsH_4(PPh_3)_3$ and $HSi\{OCH_2CH_2\}_3N$ gave the expected silatranyl, trihydride complex, $Os(Si\{OCH_2CH_2\}_3N)H_3(PPh_3)_3$ (**2**) (see Scheme 2). The infrared (IR) spectrum of **2** in the solid state, shows three bands in the Os–H stretching region, at 2105, 2059, and 2033 cm^{-1}. In dichloromethane solution only one broad band at 2053 cm^{-1} is observed. Elemental analysis and FAB^+ mass spectroscopy are both consistent with the formulation $Os(Si\{OCH_2CH_2\}_3N)H_3(PPh_3)_3$ (**2**).

The $^{31}P\{^1H\}$-NMR spectrum of **2** shows a singlet at 7.62 ppm, suggesting that the three phosphorus nuclei are equivalent on the NMR time scale. In the $^{29}Si\{^1H\}$-NMR spectrum the silicon nucleus appears as a quartet at − 15.22 ppm ($^2J_{SiP} = 16.2$ Hz). The ^1H-NMR spectrum shows a complex multiplet at − 11.19 ppm for the three hydride ligands, together with triplet signals for the silatranyl methylene protons. The multiplet at − 11.19 ppm becomes a singlet in the $^1H\{^{31}P\}$-NMR spectrum which suggests that the three hydride ligands are also equivalent on the NMR time scale. Variable temperature ^1H-NMR studies show that the multiplet at − 11.19 ppm broadens as the temperature is lowered from 298 to 233 K. The spin lattice relaxation times, T_1, measured between 298 and 233 K were close to 342 ms. The T_1 value of an η^2-H_2 is expected to be less than 20 ms, whereas the T_1 value for a classical hydride would lie between 50 and 500 ms [10]. Clearly, the T_1 values observed for **2** are in the region expected for a classical hydride complex. Similar observations were made for $Os(Si\{Pyrrolyl\}_3)H_3(PPh_3)_3$ [6].

2.3. Crystallographic study of $Os(Si\{OCH_2CH_2\}_3N)H_3(PPh_3)_3$ (2)

The structure of **2** was obtained by an X-ray crystal structure determination (see Table 1), and the molecular geometry is depicted in Fig. 2. The silicon and the three phosphorus atoms are arranged in an approximately tetrahedral manner about osmium and selected bond lengths and bond angles are presented in Table 2. All three hydride ligands were located and refined (Os–H(1), 1.52(3); Os–H(2), 1.66(3); Os–H(3), 1.57(3) Å). Each hydrogen atom is approximately *trans* to a phosphorus atom. The calculated distances between Si and H are Si···H(1), 2.06(4); Si···H(2), 2.00(4); Si···H(3), 1.96(3) Å. This is indicative of, at best, a very weak interaction since Schubert has suggested that the shortest possible non-bonding contact between Si and H centres is 2.0 Å [7,11]. There is approximately threefold symmetry about the osmium–silicon axis. The three O atoms bound to Si and the three H atoms bound to Os, are in a staggered arrangement. The average P–Os–P angle is ca. 101° and the average Si–Os–P angle is larger at 117°. Each hydride ligand can be viewed as capping one of the three SiP_2 faces of the distorted tetrahedron. It should be noted that the three hydrides were found to be located in the positions predicted by theoretical calculations for the closely related complex, $Os(SiPyrrolyl_3)H_3(PPh_3)_3$ [6]. The Os–Si bond distance (2.3442(8) Å) is slightly longer than the value of 2.2293 Å observed for $Os(SiPyrrolyl_3)H_3(PPh_3)_3$ [6]. The interatomic distance between silicon and nitrogen of 3.242(3) Å is longer even than the values observed in the five-coordinate osmium(II) silatranyl complexes previously reported [4] and must represent a situation where there is effectively no bonding interaction between Si and N. The sum of the angles around the nitrogen atom is 357.8°, and the deviation of nitrogen from the plane through C(2), C(4), and C(6) is 0.124(4) Å, with the nitrogen pointing away from the silicon.

Table 1
Crystal data and structure refinement for **2**

Formula	$C_{60}H_{60}NO_3OsP_3Si$
Molecular weight	1154.29
Temperature (K)	203
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	13.8391(1)
b (Å)	16.8507(2)
c (Å)	21.9290(1)
V (Å^3)	5113.86(7)
Z	4
D_{calc} (g cm^{-3})	1.499
F(000)	2344
μ (mm^{-1})	2.658
Crystal size (mm)	$0.45 \times 0.24 \times 0.18$
A (min, max)	0.381, 0.646
2θ (min, max) (°)	3, 56
Reflections collected	31 768
Independent reflections	11 615, $R_{int} = 0.0207$
Observed reflections	10 871
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.042
R (observed data)	$R_1 = 0.0236$, $wR_2 = 0.0525$
R (all data)	$R_1 = 0.0274$, $wR_2 = 0.0548$
Difference map (min, max) e Å^{-3}	+0.86, −0.66

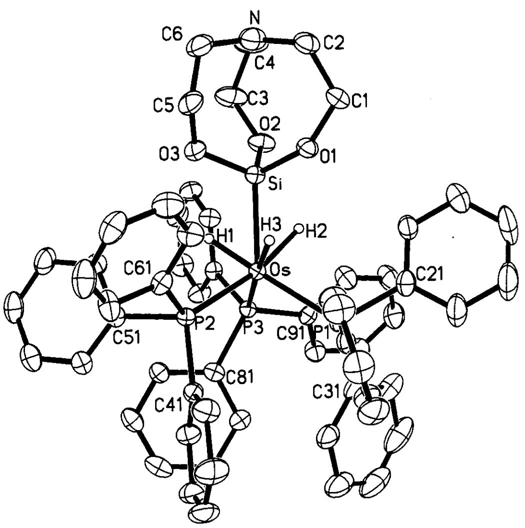


Fig. 2. Molecular geometry of $Os(Si\{OCH_2CH_2\}_3N)H_3(PPh_3)_3$ (**2**).

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

Bond lengths			
Os–P1	2.3921(9)	Os–H1	1.52(3)
Os–P2	2.3735(8)	Os–H2	1.66(3)
Os–P3	2.3854(8)	Os–H3	1.57(3)
Os–Si	2.3442(8)		
Bond angles			
Si–Os–P1	118.82(3)	P2–Os–H2	167.4(12)
Si–Os–P2	110.77(3)	P3–Os–H3	174.1(13)
Si–Os–P3	121.00(3)	Os–Si–O1	113.42(9)
P1–Os–P2	100.59(3)	Os–Si–O2	114.08(9)
P1–Os–P3	98.44(3)	Os–Si–O3	113.61(10)
P2–Os–P3	104.44(3)	O1–Si–O2	103.98(13)
P1–Os–H1	176.8(13)	O1–Si–O2	105.46(13)
		O2–Si–O3	105.33(14)

2.4. Methylation and protonation of the silatranyl nitrogen in $Os(Si\{OCH_2CH_2\}_3N)H_3(PPh_3)_3$ (2)

In silatranes, excluding those examples where the silatrane is bound as a silatranyl ligand, the nitrogen is pyramidal and points inwardly towards the silicon with an accompanying weak Si–N interaction. The structure of compound **2** reveals an elongated cage geometry with the nitrogen only slightly pyramidal but pointing *away* from silicon. In the osmium(II) silatranyl complexes previously described [4] and in the platinum(II) silatranyl complex, $Pt(Si\{OCH_2CH_2\}_3N)Cl(PMe_2Ph)_2$ [12], the silatrane cages are also expanded with the nitrogens in near-planar arrangements. Since the osmium(II) complexes were readily quaternised at nitrogen it was expected that compound **2** would behave similarly. Indeed this was found to be the case and treatment of **2** with methyl iodide gives the complex, $[Os(Si\{OCH_2CH_2\}_3NMe)H_3(PPh_3)_3]I$ (**3**) (see Scheme 2). In the ^{1}H-NMR spectrum for **3** the quaternary methyl group protons appear as a singlet resonance at 3.42 ppm, while the osmium–hydride signals appear at a position (−10.62 ppm) similar to those observed in the starting material. The carbon resonance for the methyl group on nitrogen is at 62.60 ppm in the ^{13}C-NMR spectrum. The ^{29}Si-NMR spectrum shows a poorly resolved multiplet at −3.50 ppm, ca. 12 ppm downfield from the Si chemical shift in the parent complex.

Protonation of **2** with one equivalent of triflic acid also proceeds as expected (see Scheme 2). The resulting complex, $[Os(Si\{OCH_2CH_2\}_3NH)H_3(PPh_3)_3]CF_3SO_3$ (**4**), shows a broad singlet at 10.55 ppm in the ^{1}H-NMR spectrum (which disappears when D_2O is added) and this is assigned to the NH. The ^{29}Si-NMR spectrum of **4** shows a multiplet at −3.40 ppm, similar to the value recorded for complex **3**. The Os–H signals are almost unchanged, appearing in the ^{1}H-NMR spectrum as a multiplet centred at −10.52 ppm.

3. Conclusion

We have shown that the silatrane, $HSi\{OCH_2CH_2\}_3N$, in common with other silanes, undergoes an oxidative addition reaction with $Os(CO)_2(PPh_3)_3$. The silatranyl, hydide product, $Os(Si\{OCH_2CH_2\}_3N)H(CO)_2(PPh_3)_2$ (**1**), consists of an inseparable mixture of three isomers, the geometries of which have been determined by multinuclear NMR spectroscopy. $HSi\{OCH_2CH_2\}_3N$ also reacts with $OsH_4(PPh_3)_3$ to give the silaranyl, trihydride, $Os(Si\{OCH_2CH_2\}_3N)H_3(PPh_3)_3$ (**2**), the structure of which has been determined by X-ray crystallography, complete with the location of the hydride ligands. The structure also reveals an expanded cage geometry for the silatranyl ligand with the nitrogen atom pointing away from silicon. This nitrogen atom is readily quaternised. Thus, both osmium(II) and osmium(IV) have a similar effect upon silatranyl ligand geometry and silatranyl nitrogen reactivity.

4. Experimental

4.1. General procedures and instruments

Standard laboratory procedures were followed as have been described previously [13]. The compounds $Os(CO)_2(PPh_3)_3$ [14] and $OsH_4(PPh_3)_3$ [15] were prepared according to literature methods.

IR spectra (4000–400 cm^{-1}) were recorded as Nujol mulls between KBr plates on a Perkin–Elmer Paragon 1000 spectrometer. NMR spectra were obtained on a Bruker DRX 400 at 25 °C. ^{1}H-, ^{13}C-, ^{31}P-, and ^{29}Si-NMR spectra were obtained operating at 400.1 (^{1}H), 100.6 (^{13}C), 162.0 (^{31}P), and 79.5 (^{29}Si) MHz, respectively. Resonances are quoted in ppm and ^{1}H-NMR spectra referenced to either tetramethylsilane (0.00 ppm) or the proteo-impurity in the solvent (7.25 ppm for $CHCl_3$). ^{13}C-NMR spectra were referenced to $CDCl_3$ (77.00 ppm), ^{31}P-NMR spectra to 85% orthophosphoric acid (0.00 ppm) as an external standard, and ^{29}Si-NMR spectra to tetramethylsilane (0.00 ppm). Mass spectra were recorded using the fast atom bombardment technique with a Varian VG 70-SE mass spectrometer. Melting points (uncorrected) were determined on a Reichert hot stage microscope. Elemental analyses were obtained from the Microanalytical Laboratory, University of Otago.

4.2. $Os(Si\{OCH_2CH_2\}_3N)H(CO)_2(PPh_3)_2$ (**1**)

$Os(CO)_2(PPh_3)_3$ (200 mg, 0.194 mmol) was added to deoxgenated benzene containing $HSi\{OCH_2CH_2\}_3N$ (37 mg, 0.21 mmol). The bright-yellow solution was subjected to photolysis using a 1000 W tungsten/halogen lamp. After 20 min, the resulting colourless solution was reduced in volume in vacuo and ethanol (15 ml) was added. The colourless solid was removed by filtration and recrystallised from dichloromethane/ethanol (25 ml:10 ml) to give **1** as a mixture of three isomers, **A**, **B**, and **C** (152 mg, 83%). M.p. 220–223 °C. *m*/*z* 948.2044: $C_{42}H_{42}ClN_2O_4OsP_2Si$ requires 948.2079. Anal. Calc. for $C_{42}H_{42}ClN_2O_4OsP_2Si$: C, 56.07; H, 4.47; N, 1.42. Found: C, 56.00; H, 4.11; N, 1.63%. IR (cm^{-1}): 1902, 1942, 1976, 2015 (CO); 2092, 1402, 1384, 1329, 1115, 1099, 1022, 939, 916, 860, 798. ^{1}H-NMR ($CDCl_3$; δ): −9.64 ppm (dd, 0.1H, Os*H* (isomer **C**), $^2J_{HP\mathit{trans}} = 37.2$ Hz, $^2J_{HP\mathit{cis}} = 20.8$ Hz), −7.63 (t, 0.45H, Os*H* (isomer **A**), $^2J_{HP} = 17.6$ Hz) −7.12 ('t' [overlapping dd], 0.45H, Os*H* (isomer **B**), $^2J_{HP} = 20.4$ Hz); 2.5–2.9 (m, C*H* silatranyl, all isomers) 3.1–3.5 (m, C*H* silatranyl, all isomers), 7.10–7.71 (m, 30H, PPh_3). ^{13}C-NMR ($CDCl_3$; δ): 52.49 (s, *C*H_2N); 52.71 (s, *C*H_2N), 52.84 (s, *C*H_2N), 60.13 (s, O*C*H_2), 61.09 (s, O*C*H_2); 127.0–128.0 (m, PPh_3), 128.6–129.3 (m, PPh_3), 133.1–134.2 (m, PPh_3); 189.35 (t, *C*O isomer **A**, $^2J_{CP} = 8.6$ Hz), 186.57 (t, *C*O isomer **A**, $^2J_{CP} = 10.6$ Hz); 187.68 (dd, *C*O isomer **B**, $^2J_{CP\mathit{cis}} = 8.6$ Hz, $^2J_{CP\mathit{cis}} = 4.5$ Hz); 182.95 (dd, *C*O isomer **B**, $^2J_{CP\mathit{trans}} = 74.5$ Hz, $^2J_{CP\mathit{cis}} = 6.0$ Hz); 188.68 (dd, *C*O isomer **C**, $^2J_{CP\mathit{cis}} = 10.0$ Hz, $^2J_{CP\mathit{cis}} = 6.0$ Hz). ^{29}Si-NMR ($CDCl_3$; δ): −39.10 (t, Os*Si* isomer **A**, $^2J_{SiP} = 10.8$ Hz). ^{31}P-NMR ($CDCl_3$; δ): 9.95 (s, isomer **A**); 8.98 (d, isomer **B**, $^2J_{PP} = 25.1$ Hz); 3.81 (d, isomer **B**, $^2J_{PP} = 25.3$ Hz); 4.11 (d, isomer **C**, $^2J_{PP} = 14.7$ Hz); 3.68 (d, isomer **C**, $^2J_{PP} = 14.7$ Hz).

4.3. $Os(Si\{OCH_2CH_2\}_3N)H_3(PPh_3)_3$ (**2**)

$OsH_4(PPh_3)_3$ (200 mg, 0.204 mmol) and $HSi\{OCH_2CH_2\}_3N$ (72 mg, 0.41 mmol) were heated under reflux in toluene for 3 h. The toluene was removed from the black solution in vacuo and the product was dissolved in dichloromethane and filtered through a Celite pad. Ethanol (20 ml) was added, and the dichloromethane was removed on a rotary evaporator. The light-grey solid was collected and recrystallised a further time from dichloromethane:ethanol (25 ml:10 ml) to yield colourless crystals of pure **2** (148 mg, 63%). M.p. 175–179°C. *m*/*z* 1156.3270, $C_{60}H_{60}NO_3OsP_3Si$ requires 1156.3249. Anal. Calc. for $C_{60}H_{60}NO_3OsP_3Si\cdot 1/2CH_2Cl_2C$: 60.72; H, 5.14; N, 1.17. Found: C, 60.88; H, 5.10; N, 1.15%. IR (cm^{-1}): 2105, 2059, 2033 ν(OsH); 1586, 1384, 1328, 1125, 1085, 1079, 906, 863, 660. ^{1}H-NMR (CDCl$_3$; δ): -11.19 (m, 3H, Os*H*); 2.84 (t, 6H, C*H*$_2$N, $^3J_{HH} = 4.0$ Hz); 3.48 (t, 6H, OC*H*$_2$, $^3J_{HH} = 4.0$ Hz); 6.95–7.36 (m, 30H, PPh$_3$). ^{13}C-NMR (CDCl$_3$; δ): 53.34 (s, *C*H$_2$N); 61.55 (s, O*C*H$_2$); 126.96 (m, PPh$_3$); 128.15 (m, PPh$_3$); 133.99 (m, PPh$_3$); 133.99 (m, PPh$_3$). ^{29}Si-NMR (CDCl$_3$; δ): -15.22 (q, Os*Si*, $^2J_{SiP} = 16.2$). ^{31}P-NMR (CDCl$_3$; δ) 7.62 (s, *P*Ph$_3$). 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 (K) and T_1 (ms) are: 298, 342.2; 278, 341.4; 233, 342.6.

4.4. *[Os(Si{OCH$_2$CH$_2$}$_3$NMe)H$_3$(PPh$_3$)$_3$]I (**3**)*

Os(Si{OCH$_2$CH$_2$}$_3$N)H$_3$(PPh$_3$)$_3$ (200 mg, 0.173 mmol) was heated under reflux in MeI for 45 min. Ethanol (10 ml) was added to the dark-grey solution and the MeI removed. The resulting dark-grey product was recrystallised from dichloromethane:ethanol (25 ml:10 ml) to give colourless crystals of pure **3** (175 mg, 78%). M.p. 176–178°C. *m*/*z* 1168.3353; $C_{61}H_{63}NO_3OsP_3Si$ requires 1168.3375. Anal. Calc. for $C_{61}H_{63}INO_3OsP_3Si.CH_2Cl_2$: C, 53.92; H, 4.74; N, 1.01. Found: C, 54.35; H, 4.92; N, 1.00%. IR (cm^{-1}) 2037br (OsH); 1586, 1573, 1401, 1257, 1224, 1127, 1065, 1088, 910, 832, 743, 697, 636, 520. ^{1}H-NMR (CDCl$_3$; δ): -10.62 (m, 3H, Os*H*); 3.42 (s, 3H, C*H*$_3$); 3.57 (s broad, 6H, C*H*$_2$N); 3.79 (s broad, 6H, OC*H*$_2$); 6.97–7.33 (m, 30H, PPh$_3$). ^{13}C-NMR (CDCl$_3$; δ): 57.29 (s, *C*H$_2$N); 62.60 (s, *C*H$_3$); 65.48 (s, O*C*H$_2$); 127.12 (m, PPh$_3$); 128.22 (s, PPh$_3$); 133.52 (m, PPh$_3$); 134.05 (m, PPh$_3$). ^{29}Si-NMR (CDCl$_3$; δ): -3.50 (m, Os*Si*).

4.5. *[Os(Si{OCH$_2$CH$_2$}$_3$NH)H$_3$(PPh$_3$)$_3$]CF$_3$SO$_3$ (**4**)*

Triflic acid (18 µl, 0.17 mmol) and ethanol (1 ml) were added to a dichloromethane (25 ml) solution containing Os(Si{OCH$_2$CH$_2$}$_3$N)H$_3$(PPh$_3$)$_3$ (200 mg, 0.173 mmol). The resulting grey solution was stirred for 30 min, further ethanol (10 ml) was added, and the dichloromethane was removed. The resulting product was recrystallised from dichloromethane:ethanol (25 ml:10 ml) to give pure **4** as colourless crystals (194 mg, 86%). Anal. Calc. for $C_{61}H_{61}F_3NO_6OsP_3SSi$: C, 56.17; H, 4.71; N, 1.07. Found: C, 56.56; H, 4.99; N, 1.25%. IR (cm^{-1}) 3433br (NH); 2025br (OsH); 1585, 1571, 1401, 1257, 1220, 1127, 1070, 1090, 912, 829, 740, 690, 634. ^{1}H-NMR (CDCl$_3$; δ): -10.52 (m, 1H, Os*H*); 3.62 (s broad, 6H, C*H*$_2$N); 3.85 (s broad, 6H, OC*H*$_2$); 10.55 (s broad, 1H, N*H*); 6.97–7.33 (m, 30H, PPh$_3$). ^{13}C-NMR (CDCl$_3$; δ): 53.55 (s, *C*H$_2$N); 61.42 (s, O*C*H$_2$); 127.96 (m, PPh$_3$); 128.22 (s, PPh$_3$); 133.97 (m, PPh$_3$); 134.01 (m, PPh$_3$). ^{29}Si-NMR (CDCl$_3$; δ): -3.40 (m, Os*Si*).

4.6. *X-ray crystal structure determination of Os(Si{OCH$_2$CH$_2$}$_3$N)H$_3$(PPh$_3$)$_3$ (**2**)*

A suitable crystal was grown from dichloromethane/ethanol. Data were collected on a Siemens SMART diffractometer with a CCD area detector and covered a nominal hemisphere. Lorentz and polarisation corrections were applied and absorption corrections using the program SADABS [16] yielding 31 768 measured reflections.

The structure was solved by Patterson and Fourier techniques using SHELXS-97 [17] and refined by full-matrix least-squares on F^2 using SHELXL-97 [18]. All non-hydrogen atoms were allowed to refine anisotropically. 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 difference maps and their coordinates allowed to refine with thermal parameters fixed at 20% greater than the osmium atom. Refinement converged to conventional $R = 0.0236$ for the 10 871 reflections with $I > 2\sigma(I)$. Crystal data and refinement parameters are given in Table 1 and selected bond lengths and angles in Table 2.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 138312. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Rd., Cambridge CB2 1EX, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.com.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] C.L. Frye, G.E. Vogel, J.A. Hall, J. Am. Chem. Soc. 83 (1961) 996.

[2] (a) J.G. Verkade, Acc. Chem. Res. 26 (1993) 483. (b) M.G. Voronkov, V.M. Dyakov, S.V. Kirpichenko, J. Organomet. Chem. 233 (1982) 1. (c) S.N. Tandura, M.G. Voronkov, N.V. Alekseev, Top. Cur. Chem. 131 (1986) 99. (d) E. Lukevits, O. Pudova, R. Sturkovich, Molecular Structure of Organosilicon Compounds, Ellis Horwood, Chichester, 1989. (e) C. Chuit, R.J.P. Corriu, C. Reye, J.C. Young, Chem. Rev. 93 (1993) 1371.

[3] (a) A. Haaland, Angew. Chem. Int. Ed. Engl. 28 (1989) 992. (b) M.S. Gordon, M.T. Carrol, J.H. Jensen, L.P. Davis, L.W. Burggraf, R.M. Guidry, Organometallics 10 (1991) 2657. (c) M.W. Schmidt, T.L. Windus, M.S. Gordon, J. Am. Chem. Soc. 117 (1995) 7480.

[4] M.T. Attar-Bashi, C.E.F. Rickard, W.R. Roper, L.J. Wright, S.D. Woodgate, Organometallics 17 (1998) 504.

[5] G.R. Clark, K.R. Flower, C.E.F. Rickard, D.M. Salter, L.J. Wright, J. Organomet. Chem. 462 (1993) 331.

[6] K. Hübler, U. Hübler, W.R. Roper, P. Schwerdtfeger, L.J. Wright, Chem. Eur. J. 3 (1997) 1608.

[7] U. Schubert, Adv. Organomet. Chem. 30 (1990) 151.

[8] G.I. Nikonov, L.G. Kuzmina, S.F. Vyboishchikov, D.A. Lemenovskii, and J.A.K. Howard, Chem. Eur. J. 5 (1999) 2947.

[9] C.E.F. Rickard, W.R. Roper, T.J. Woodman, L.J. Wright, Chem. Commun. (1999) 837.

[10] M. Buil, P. Espinet, M.A. Esteruelas, F.J. Lahoz, A. Lledós, J.M. Martínez-Ilarduya, F. Maseras, J. Modrego, E. Oñate, L.A. Oro, E. Sola, C. Valero, Inorg. Chem. 35 (1996) 1250.

[11] R.S. Simons, C.A. Tessier, Organometallics 15 (1996) 2604.

[12] C. Eaborn, K.J. Odell, A. Pidcock, G.R. Scollary, J. Chem. Soc. Chem. Comm. (1971) 317.

[13] S.M. Maddock, C.E.F. Rickard, W.R. Roper, L.J. Wright, Organometallics 15 (1996) 1793.

[14] T.J. Collins, K.R. Grundy, W.R. Roper, J. Organomet. Chem. 231 (1982) 161.

[15] J.J. Levison, S.D. Robinson, J. Chem. Soc. (A) (1970) 2947.

[16] G.M. Sheldrick, SADABS, Program for Absorption Corrections, University of Göttingen, Germany, 1997.

[17] G.M. Sheldrick, Acta Crystallogr. A46 (1990) 467.

[18] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.