

Note

The structurally characterised silyl complexes, $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)\text{-}(\text{SiMeCl}_2)(\text{CO})(\text{PPh}_3)_2$ and $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiCl}_3)(\text{CO})(\text{PPh}_3)_2$, which have remarkably unreactive Si–Cl bonds

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Abstract

Treatment of $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)\text{H}(\text{CO})(\text{PPh}_3)_2$ with HSiMeCl_2 or HSiCl_3 gives in high yield $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiMeCl}_2)(\text{CO})(\text{PPh}_3)_2$ (**1**) or $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiCl}_3)(\text{CO})(\text{PPh}_3)_2$ (**2**), respectively. The crystal structures of both compounds have been determined and the Os–Si distances are 2.3672(10) Å for **1** and 2.3449(12) Å for **2**. In solution, and under forcing conditions, both compounds are extraordinarily unreactive towards hydroxide ions.

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1. Introduction

Metal complexes with chloro-substituted silyl ligands, $\text{L}_n\text{M-SiR}_{3-n}\text{Cl}_n$ ($n = 1-3$), are often useful substrates, through nucleophilic substitution reactions, for the syntheses of silyl complexes with interesting functionalisation at silicon. Examples include the syntheses of compounds of the type, $\text{L}_n\text{M-SiR}_{3-n}\text{X}_n$, where X can be H [1], R [2], OH [3,4], OR [5], SR [6], NR_2 [7], and F [2,8]. However, the reactivity of the Si–Cl bonds in chlorosilyl ligands is variable and in some exceptional cases the Si–Cl bonds are quite unreactive towards hydrolysis. An example is provided by the ready hydrolysis of $\text{CpFe}(\text{CO})_2\text{SiR}_2\text{Cl}$ whereas the corresponding ruthenium derivative, $\text{CpRu}(\text{CO})_2\text{SiR}_2\text{Cl}$, is inert to hydrolysis [9]. A further example is that two electron-rich $\text{CpFe}(\text{CO})_2$ fragments attached to the one silicon atom in $[\text{CpFe}(\text{CO})_2]_2\text{SiCl}_2$ renders the Si–Cl bonds unreactive to Cl/OH exchange [10]. Furthermore, the number of chloride substituents on the silyl

ligand also affects the reactivity, and the general trend is that progressive chlorine replacement of organo-groups on silicon reduces the reactivity of the Si–Cl bonds. An example of this phenomenon is that when one of the chlorides in the inert compound $[\text{CpFe}(\text{CO})_2]_2\text{SiCl}_2$ is replaced by hydride to give $[\text{CpFe}(\text{CO})_2]_2\text{SiHCl}$ the remaining Si–Cl bond is readily hydrolysed. Interestingly, structural data suggests that both the Ru–Si and Si–Cl distances in $\text{Cp}(\text{PR}_3)_2\text{RuSiX}_3$ increase when chloride is replaced by either methyl or phenyl [11]. The increased Si–Cl distances have been attributed to $d(\text{Ru})-\sigma^*(\text{Si-Cl})$ π -back-bonding interactions and this may partly explain the increased Si–Cl bond reactivity.

We have previously reported that the unsaturated, five-coordinate, dimethylchlorosilyl complex, $\text{Os}(\text{SiMe}_2\text{Cl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$, is easily hydrolysed to $\text{Os}(\text{SiMe}_2\text{OH})\text{Cl}(\text{CO})(\text{PPh}_3)_2$, [12] just as $\text{Os}(\text{SiCl}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ is easily hydrolysed to $\text{Os}[\text{Si}(\text{OH})_3]\text{Cl}(\text{CO})(\text{PPh}_3)_2$ [3]. On the other hand, the saturated, six-coordinate, dimethylchlorosilyl complex, $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiMe}_2\text{Cl})(\text{CO})(\text{PPh}_3)_2$ [12], is quite difficult to hydrolyse under base conditions but is readily converted to $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiMe}_2\text{OH})(\text{CO})(\text{PPh}_3)_2$ upon chromatography on silica gel. In this paper,

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we report that the preparative procedure used to make $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiMe}_2\text{Cl})(\text{CO})(\text{PPh}_3)_2$ is equally effective for the preparation of the closely related chloro-silyl complexes, $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiMeCl}_2)(\text{CO})(\text{PPh}_3)_2$ (**1**) and $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiCl}_3)(\text{CO})(\text{PPh}_3)_2$ (**2**) and crystal structures for these two compounds are reported. However, the main purpose of this note is to draw attention to the remarkable lack of reactivity towards hydrolysis of the Si–Cl bonds in the two saturated complexes **1** and **2**.

2. Results and discussion

2.1. Syntheses and crystal structures of $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiMeCl}_2)(\text{CO})(\text{PPh}_3)_2$ (**1**) and $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiCl}_3)(\text{CO})(\text{PPh}_3)_2$ (**2**)

As depicted in Scheme 1 the reaction between $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)\text{H}(\text{CO})(\text{PPh}_3)_2$ and the two chlorosilanes, HSiMeCl_2 and HSiCl_3 proceeds smoothly to give the corresponding colourless osmium silyl complexes, $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiMeCl}_2)(\text{CO})(\text{PPh}_3)_2$ (**1**) and $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiCl}_3)(\text{CO})(\text{PPh}_3)_2$ (**2**), respectively, in good yield. The IR spectrum of **1** shows $\nu(\text{CO})$ at 1893(s), 1877 cm^{-1} , the observation of two bands presumably arising from solid-state splitting. The IR spectrum of **2** shows $\nu(\text{CO})$ at 1901(s) cm^{-1} , this higher value being expected and attributable to the more electron-withdrawing SiCl_3 group [2]. That the geometry of **1** and **2** is as drawn in Scheme 1 is indicated by the presence of two signals for the methyl groups of the dimethyldithiocarbamate ligands (in both the ^1H and ^{13}C NMR spectra) and the observation of a singlet resonance in the ^{31}P NMR spectra of these compounds. Further spectroscopic data for these two compounds is collected in Section 4 and requires no special comment.

The crystal structures of **1** and **2** were determined, the crystal data and refinement details for both structures are in Table 1, the molecular geometries are shown in Figs. 1

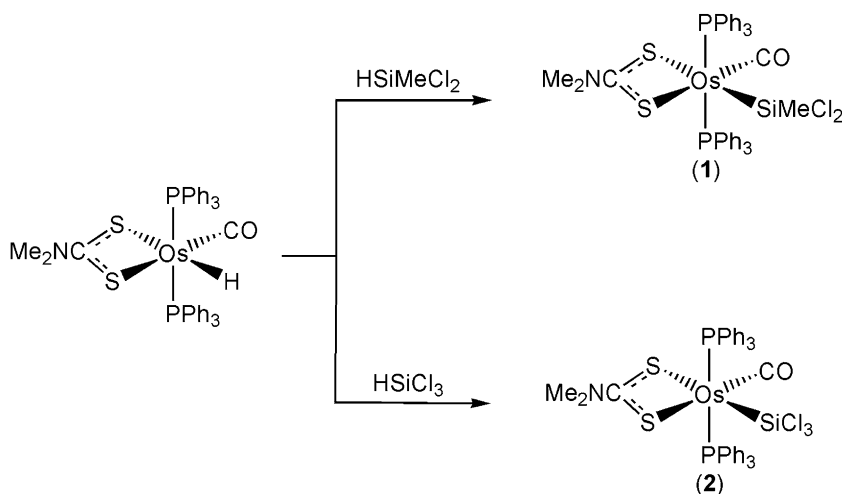
Table 1
Data collection and processing parameters for **1** and **2**

	1 · 2CH ₂ Cl ₂	2 · 2CH ₂ Cl ₂
Formula	C ₄₃ H ₄₃ Cl ₆ NOOsP ₂ S ₂ Si	C ₄₂ H ₄₀ Cl ₇ NOOsP ₂ S ₂ Si
Molecular weight	1146.83	1167.25
Crystal system	Monoclinic	Monoclinic
Space group	C2/m	C2/m
<i>a</i> (Å)	28.0882(4)	28.0811(8)
<i>b</i> (Å)	15.1144(1)	15.0746(4)
<i>c</i> (Å)	11.4867(2)	11.4800(3)
α (°)		
β (°)	96.797(1)	96.810(1)
γ (°)		
<i>V</i> (Å ³)	4842.25(11)	4825.3(2)
<i>Z</i>	4	4
<i>D</i> _(calc) (g cm ⁻³)	1.573	1.607
<i>F</i> (000)	2280	2312
μ (mm ⁻¹)	3.17	3.24
Crystal size (mm)	0.34 × 0.18 × 0.10	0.42 × 0.22 × 0.04
2 θ (min–max) (°)	1.46–27.51	1.46–26.05
Reflections collected	14 775	14 285
Independent reflections [<i>R</i> _{int}]	5565 [0.0215]	4938 [0.0265]
<i>T</i> (min–max)	0.411, 0.742	0.343, 0.881
Goodness-of-fit on <i>F</i> ²	1.062	1.065
<i>R</i> (observed data)	<i>R</i> ₁ = 0.0276; <i>wR</i> ₂ = 0.0721	<i>R</i> ₁ = 0.0280; <i>wR</i> ₂ = 0.0738
<i>R</i> (all data)	<i>R</i> ₁ = 0.0296; <i>wR</i> ₂ = 0.0734	<i>R</i> ₁ = 0.0301; <i>wR</i> ₂ = 0.0751
Diff. map (min–max) (e Å ⁻³)	–1.72, 1.37	–1.58, 2.24

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)]}{\sum [w(F_o^2)]} \right\}^{1/2}$$

and **2**, respectively, and selected bond lengths and bond angles are listed in Tables 2 and 3, respectively. The geometries of both complexes are approximately octahedral with the two triphenylphosphine ligands arranged mutually *trans*. In both compounds the attachment of the bidentate dimethyldithiocarbamate ligand is unsymmetrical, with the Os–S distance greater when S is *trans* to the silyl ligand (2.5043(9) Å for **1**; 2.4968(11) Å for **2**) and less when S is



Scheme 1. Syntheses of $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiMeCl}_2)(\text{CO})(\text{PPh}_3)_2$ (**1**) and $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiCl}_3)(\text{CO})(\text{PPh}_3)_2$ (**2**).

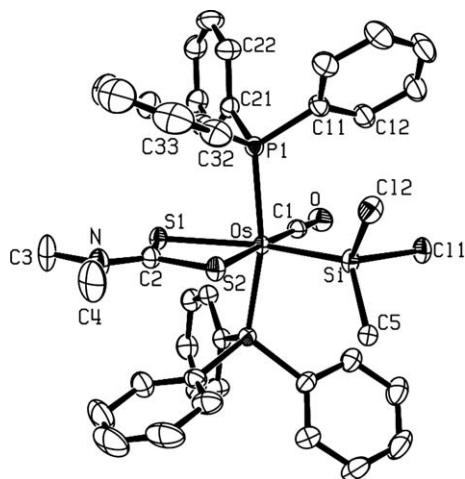


Fig. 1. Molecular geometry of $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiMeCl}_2)(\text{CO})(\text{PPh}_3)_2$ (**1**).

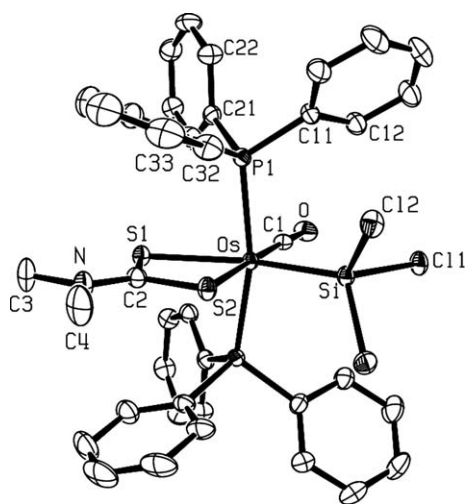


Fig. 2. Molecular geometry of $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiCl}_3)(\text{CO})(\text{PPh}_3)_2$ (**2**).

trans to the CO ligand (2.4553(10) Å for **1**; 2.4539(11) Å for **2**). This observation relates to the *trans* influence of the silyl ligand and the distances suggest that the *trans* influence is slightly greater for SiMeCl_2 than for SiCl_3 . The Os–Si distance in $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiMeCl}_2)(\text{CO})(\text{PPh}_3)_2$ (**1**) is 2.3672(10) Å, which is much less than the average (2.4499 with SD 0.0508 Å) of 10 measured Os–Si distances recorded in the Cambridge Crystallographic Data Base for octahedral osmium silyl complexes where silicon is four-coordinate. It is also less than the corresponding value for the related $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiMe}_2\text{Cl})(\text{CO})(\text{PPh}_3)_2$ at 2.4021(11) Å [12]. The Os–Si distance in **2** (2.3449(12) Å) is shorter than in either $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiMe}_2\text{Cl})(\text{CO})(\text{PPh}_3)_2$ or **1**, as would be expected for a trichlorosilyl ligand [2]. The overall trend is that the Os–Si distance decreases with increasing chloride substitution on silicon. The Si–Cl distances are 2.1252(14) Å for the non-disordered chloride in **1** and 2.1084(16) and 2.0983(12) Å in **2**. All of these are long when compared with the average of recorded Si–Cl distances of 2.0579 Å, SD 0.0435 Å

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

Bond lengths	
Os–C(1)	1.855(4)
Os–Si	2.3672(10)
Os–P(1)	2.3948(7)
Os–S(2)	2.4553(10)
Os–S(1)	2.5043(9)
Cl(1)–Si	2.1252(14)
Cl(2)–Si	2.066(8)
C(5)–Si	1.93(3)
S(1)–C(2)	1.718(4)
S(2)–C(2)	1.709(4)
O–C(1)	1.159(5)
N–C(2)	1.330(5)
Bond angles	
C(1)–Os–Si	90.45(13)
C(1)–Os–P(1)	89.84(2)
Si–Os–P(1)	97.249(17)
P(1)–Os–P(1)#1	165.50(3)
C(1)–Os–S(2)	177.00(12)
Si–Os–S(2)	86.56(3)
P(1)–Os–S(2)	90.533(17)
C(1)–Os–S(1)	112.20(12)
Si–Os–S(1)	157.35(4)
P(1)–Os–S(1)	83.351(17)
S(2)–Os–S(1)	70.80(3)
O–C(1)–Os	176.7(4)

Symmetry transformations used to generate equivalent atoms: (#1) $x, -y, z$.

Table 3
Selected bond lengths (Å) and bond angles (°) for **2**

Bond lengths	
Os–C(1)	1.860(5)
Os–Si	2.3449(12)
Os–P(1)	2.4005(8)
Os–S(2)	2.4539(11)
Os–S(1)	2.4968(11)
Cl(1)–Si	2.1084(16)
Cl(2)–Si	2.0983(12)
S(1)–C(2)	1.723(5)
S(2)–C(2)	1.711(5)
O–C(1)	1.163(6)
N–C(2)	1.324(6)
N–C(3)	1.460(7)
N–C(4)	1.471(7)
Bond angles	
C(1)–Os–Si	90.77(14)
C(1)–Os–P(1)	89.82(2)
Si–Os–P(1)	97.063(19)
P(1)#1–Os–P(1)	165.87(4)
C(1)–Os–S(2)	178.12(14)
Si–Os–S(2)	87.35(4)
P(1)–Os–S(2)	90.414(19)
C(1)–Os–S(1)	110.96(14)
Si–Os–S(1)	158.27(4)
P(1)–Os–S(1)	83.474(19)
S(2)–Os–S(1)	70.92(4)
Cl(2)#1–Si–Cl(2)	97.31(7)
Cl(2)–Si–Cl(1)	101.15(5)
Cl(2)–Si–Os	116.96(4)
Cl(1)–Si–Os	119.65(6)

Symmetry transformations used to generate equivalent atoms: (#1) $x, -y, z$.

(Cambridge Crystallographic Data Base) but no convincing trends with respect to chloride substitution are apparent.

2.2. Reactivity towards hydrolysis of compounds

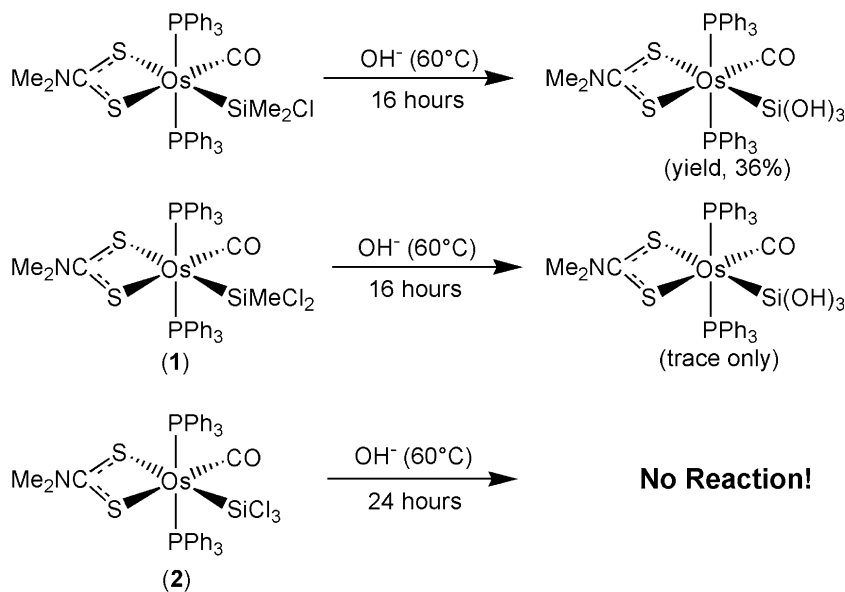
$\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiMe}_2\text{Cl})(\text{CO})(\text{PPh}_3)_2$,
 $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiMeCl}_2)(\text{CO})(\text{PPh}_3)_2$ (**1**), and
 $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiCl}_3)(\text{CO})(\text{PPh}_3)_2$ (**2**)

We have previously reported all three of the five-coordinate, coordinatively unsaturated derivatives, $\text{Os}(\text{SiMe}_2\text{Cl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$, $\text{Os}(\text{SiMeCl}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2$, and $\text{Os}(\text{SiCl}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$, are readily hydrolysed (KOH/H₂O/THF at room temperature within minutes) to the corresponding osmasilanols, $\text{Os}[\text{SiMe}_2(\text{OH})]\text{Cl}(\text{CO})(\text{PPh}_3)_2$ [12], $\text{Os}[\text{SiMe}(\text{OH})_2]\text{Cl}(\text{CO})(\text{PPh}_3)_2$ [13], and $\text{Os}[\text{Si}(\text{OH})_3]\text{Cl}(\text{CO})(\text{PPh}_3)_2$ [2,3]. Replacement of the osmium-bound chloride ligand in $\text{Os}(\text{SiMe}_2\text{Cl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ by the bidentate dimethyldithiocarbamate ligand to give $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiMe}_2\text{Cl})(\text{CO})(\text{PPh}_3)_2$ brings about a marked change in the reactivity of the Si–Cl bond. Similar base hydrolysis conditions to those given above are ineffective for this six-coordinate, coordinatively saturated compound and forcing conditions (KOH/H₂O/THF at 60 °C, 16 h) produce $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)[\text{SiMe}_2(\text{OH})]\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (10%) and $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)[\text{Si}(\text{OH})_3]\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (36%) [12] and $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)\text{H}(\text{CO})(\text{PPh}_3)_2$ (20%) (see Scheme 2). Likewise, as shown in Scheme 2, vigorous base conditions with $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiMeCl}_2)(\text{CO})(\text{PPh}_3)_2$ (**1**) return unreacted **1** with small amounts of $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)[\text{Si}(\text{OH})_3]\text{Cl}(\text{CO})(\text{PPh}_3)_2$. Significantly, no $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)[\text{SiMe}(\text{OH})_2]\text{Cl}(\text{CO})(\text{PPh}_3)_2$ was isolated. $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiCl}_3)(\text{CO})(\text{PPh}_3)_2$ (**2**), when subjected to these same forcing conditions for 24 h returned unreacted **2** only. These

qualitative observations of the relative reactivity of the Si–Cl bonds in these complexes lead to the following conclusions. The remarkable inertness of the trichlorosilyl derivative **2**, contrasts strongly with the ease of hydrolysis of the coordinatively unsaturated trichlorosilyl complex, $\text{Os}(\text{SiCl}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ and this difference must be attributed to the availability of a vacant coordination site at osmium in $\text{Os}(\text{SiCl}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ which offers the opportunity for anion coordination at osmium, i.e., the anion $[\text{Os}(\text{SiCl}_3)(\text{OH})\text{Cl}(\text{CO})(\text{PPh}_3)_2]^-$ may be formed as a prelude to hydrolysis. Hydrolysis could then become an intramolecular ligand reaction. Support for this idea comes from the fact that chloride ion coordinates to $\text{Os}(\text{SiCl}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ with formation of the colourless, coordinatively saturated anion, $[\text{Os}(\text{SiCl}_3)\text{Cl}_2(\text{CO})(\text{PPh}_3)_2]^-$. We have isolated this anion as the dimethylammonium salt, $[\text{NMe}_2\text{H}_2][\text{Os}(\text{SiCl}_3)\text{Cl}_2(\text{CO})(\text{PPh}_3)_2]$, and characterized it by crystal structure determination [14]. Other related osmium anions containing silyl ligands are also known, e.g., $[\text{Os}(\text{SiMe}_3)(\text{Me})_2(\text{CO})(\text{PPh}_3)_2]^-$ [15]. There is also the report of a ruthenium anion containing two trichlorosilyl ligands, $[\text{PCy}_3\text{H}][\text{Ru}(\text{SiCl}_3)_2\text{Cl}(\text{CO})(\text{PCy}_3)]$ [16]. Within the set of coordinatively saturated complexes, $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiMe}_2\text{Cl})(\text{CO})(\text{PPh}_3)_2$, $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiMeCl}_2)(\text{CO})(\text{PPh}_3)_2$, and $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiCl}_3)(\text{CO})(\text{PPh}_3)_2$ it appears that the SiCl_3 ligand is least reactive and the SiMe_2Cl ligand the most reactive.

3. Conclusions

It has been demonstrated that the two coordinatively saturated chlorosilyl-complexes, $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiMeCl}_2)(\text{CO})(\text{PPh}_3)_2$ (**1**) and $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiCl}_3)(\text{CO})$



Scheme 2. Reactivity towards hydrolysis of $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiMe}_2\text{Cl})(\text{CO})(\text{PPh}_3)_2$, $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiMeCl}_2)(\text{CO})(\text{PPh}_3)_2$ (**1**), and $\text{Os}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{SiCl}_3)(\text{CO})(\text{PPh}_3)_2$ (**2**).

(PPh₃)₂ (**2**) are readily prepared from reaction between Os(κ^2 -S₂CNMe₂)H(CO)(PPh₃)₂ and the appropriate silane. The most remarkable chemical feature of these molecules is the inertness of the Si–Cl bonds, which resist hydrolysis even under very forcing conditions. It is suggested that this inertness is associated with the coordinative saturation of the osmium centre since the closely related, coordinatively unsaturated analogues, Os(SiMeCl₂)Cl(CO)(PPh₃)₂ and Os(SiCl₃)Cl(CO)(PPh₃)₂ are easily hydrolysed, perhaps because osmium offers an alternative site for hydroxide attack and the ensuing hydrolysis then becomes intramolecular.

4. Experimental

4.1. General procedures and instruments

Standard laboratory procedures were followed as have been described previously [17]. The compound Os(κ^2 -S₂CNMe₂)H(CO)(PPh₃)₂ [18] was prepared by the literature method.

Infrared 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 either a Bruker DRX 400 or a Bruker Avance 300 at 25 °C. For the Bruker DRX 400, ¹H, ¹³C, and ³¹P NMR spectra were obtained operating at 400.1 (¹H), 100.6 (¹³C), and 162.0 (³¹P) MHz, respectively. For the Bruker Avance 300, ¹H, ¹³C, and ³¹P NMR spectra were obtained operating at 300.13 (¹H), 75.48 (¹³C), and 121.50 (³¹P) MHz, respectively. Resonances are quoted in ppm and ¹H NMR spectra referenced to either tetramethylsilane (0.00 ppm) or the proteo-impurity in the solvent (7.25 ppm for CHCl₃). ¹³C NMR spectra were referenced to CDCl₃ (77.00 ppm), and ³¹P NMR spectra to 85% orthophosphoric acid (0.00 ppm) as an external standard. Elemental analyses were obtained from the Microanalytical Laboratory, University of Otago.

4.2. Preparation of Os(κ^2 -S₂CNMe₂)-(SiMeCl₂)(CO)(PPh₃)₂ (**1**)

Os(κ^2 -S₂CNMe₂)H(CO)(PPh₃)₂ (0.150 g, 0.17 mmol) was placed in a 250 mL Schlenk tube and toluene (10 mL) and HSiMeCl₂ (0.300 g, 2.55 mmol) added. The tube was sealed, cooled in liquid nitrogen and then evacuated. After warming to ambient temperature, the sealed tube was shielded with a safety shield (*Caution*. Pressure increases as reaction proceeds) and heated in an oil bath at 90 °C for 1 h. During this time the yellow solution turned to a paler yellow colour. After cooling, the solvent volume was reduced under vacuum and hexane added slowly to induce crystallisation of a colourless solid. This was collected and recrystallised from dry dichloromethane–hexane to give pure **1** (0.116 g, 70%). Anal. Calc. for C₄₁H₃₉NOCl₂SiP₂OsS₂: C, 50.40; H, 4.02; N, 1.43. Found: C, 50.29; H, 3.82; N, 1.40%. IR (cm⁻¹): 1893(s), 1877

v(CO). ¹H NMR (CDCl₃, δ): 0.64 (s, 3H, Si(CH₃)), 1.98 (s, 3H, N(CH₃)₂), 2.23 (s, 3H, N(CH₃)₂), 7.31–7.32 (m, 18H, PPh₃), 7.71–7.74 (m, 12H, PPh₃). ¹³C NMR (CDCl₃, δ): 14.9 (Si(CH₃)), 36.7, 36.8 (N(CH₃)₂), 127.1 (br, *o*-C₆H₅), 129.5 (s, *p*-C₆H₅), 135.1 (br, *m*-C₆H₅), 186.6 (t, ²J_{CP} = 11.6 Hz, CO), 208.4 (S₂CNMe₂). ³¹P NMR (CDCl₃, δ): 7.27 (s).

4.3. Preparation of Os(κ^2 -S₂CNMe₂)(SiCl₃)(CO)(PPh₃)₂ (**2**)

Os(κ^2 -S₂CNMe₂)H(CO)(PPh₃)₂ (0.086 g, 0.10 mmol) was placed in a 250 mL Schlenk tube and toluene (5 mL) and HSiCl₃ (0.200 mL, 2.0 mmol) added. The tube was sealed, cooled in liquid nitrogen and then evacuated. After warming to ambient temperature, the sealed tube was shielded with a safety shield (*Caution*. Pressure increases as reaction proceeds) and heated in an oil bath at 100 °C for 12 h. During this time the yellow solution turned to a paler yellow colour. After cooling, the solvent volume was reduced under vacuum and hexane added slowly to induce crystallisation of a colourless solid. This was collected and recrystallised from dry dichloromethane–ethanol to give pure **2** (0.094 g, 94%). Anal. Calc. for C₄₀H₃₆Cl₃NOOsP₂S₂Si: C, 48.17; H, 3.64; N, 1.38. Found: C, 48.06; H, 3.86; N, 1.60%. IR (cm⁻¹): 1901(s) v(CO). ¹H NMR (CDCl₃, δ): 1.99 (s, 3H, N(CH₃)₂), 2.24 (s, 3H, N(CH₃)₂), 7.32–7.34 (m, 18H, PPh₃), 7.70–7.74 (m, 12H, PPh₃). ¹³C NMR (CDCl₃, δ): 36.6, 36.7 (N(CH₃)₂), 127.3 (br, *o*-C₆H₅), 129.7 (s, *p*-C₆H₅), 135.1 (br, *m*-C₆H₅), 184.9 (br, CO), 208.0 (S₂CNMe₂). ³¹P NMR (CDCl₃, δ): 6.72 (s).

4.4. X-ray crystal structure determinations for complexes **1** and **2**

X-ray data collection was by Siemens SMART diffractometer with a CCD area detector using graphite monochromated Mo K α radiation (λ = 0.71073 Å) at 150 K. Data were integrated and corrected for Lorentz and polarisation effects using SAINT [19]. Semi-empirical absorption corrections were applied based on equivalent reflections using SADABS [20]. The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares on *F*² using programs SHELXS [21] and SHELXL [22]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located geometrically and refined using a riding model. The two structures are isostructural and both contain residual electron density which could not be assigned to ordered solvent molecules. In both cases the residual density has been treated as disordered solvent and removed with the Squeeze function of PLATON [23] before the final refinement. For **1** there is disorder between one chlorine atom and the methyl group of the dichloromethylsilyl ligand. This disorder has been modeled with half-weighted atoms. Crystal data and refinement details for **1** and **2** are given in Table 1.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. 288557 and 288558 for **1** and **2**, respectively. Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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