

# Metallacyclic complexes with *ortho*-silylated triphenylphosphine ligands, $L_n\text{Os}(\kappa^2(\text{Si},P)\text{-SiMe}_2\text{C}_6\text{H}_4\text{PPh}_2)$ , derived from thermal reactions of the coordinatively unsaturated trimethylsilyl, methyl complex, $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})(\text{PPh}_3)_2$

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Received 24 February 2005; accepted 25 March 2005

Available online 3 June 2005

## Abstract

Reaction between  $\text{Os}(\text{SiCl}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$  and five equivalents of MeLi produces a colourless intermediate, tentatively formulated as the lithium salt of the six-coordinate, dimethyl, trimethylsilyl-containing complex anion,  $\text{Li}[\text{Os}(\text{SiMe}_3)(\text{Me})_2(\text{CO})(\text{PPh}_3)_2]$ . Reaction of this material with ethanol releases methane and gives the red, coordinatively unsaturated methyl, trimethylsilyl-containing complex,  $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})(\text{PPh}_3)_2$  (**1**). An alternative synthesis of **1** is to add one equivalent of MeLi to  $\text{Os}(\text{SiMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ , which in turn is obtained by adding three equivalents of MeLi to  $\text{Os}(\text{SiCl}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ . Treatment of **1** with *p*-tolyl lithium, again gives a colourless intermediate which may be  $\text{Li}[\text{Os}(\text{SiMe}_3)(\text{Me})(p\text{-tolyl})(\text{CO})(\text{PPh}_3)_2]$ , and reaction with ethanol gives the red complex,  $\text{Os}(\text{SiMe}_3)(p\text{-tolyl})(\text{CO})(\text{PPh}_3)_2$  (**3**). Complexes **1** and **3** are readily carbonylated to  $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})_2(\text{PPh}_3)_2$  (**2**) and  $\text{Os}(\text{SiMe}_3)(p\text{-tolyl})(\text{CO})_2(\text{PPh}_3)_2$  (**4**), respectively. Heating  $\text{Os}(\text{SiMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$  in molten triphenylphosphine results only in loss of the trimethylsilyl ligand and formation of the previously known complex containing an *ortho*-metallated triphenylphosphine ligand,  $\text{Os}(\kappa^2(C,P)\text{-C}_6\text{H}_4\text{PPh}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ . In contrast, heating the five-coordinate osmium-methyl complex,  $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})(\text{PPh}_3)_2$  (**1**), in the presence of triphenylphosphine results mainly, not in tetramethylsilane elimination, but in *ortho*-silylation as well as *ortho*-metallation of different triphenylphosphine ligands giving,  $\text{Os}(\kappa^2(\text{Si},P)\text{-SiMe}_2\text{C}_6\text{H}_4\text{PPh}_2)(\kappa^2(C,P)\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$  (**5**). A byproduct of this reaction is the non-silicon containing di-*ortho*-metallated complex,  $\text{Os}(\kappa^2(C,P)\text{-C}_6\text{H}_4\text{PPh}_2)_2(\text{CO})(\text{PPh}_3)$  (**6**). A similar reaction occurs when  $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})(\text{PPh}_3)_2$  (**1**) is heated in the presence of tri(*N*-pyrrolyl)phosphine producing  $\text{Os}(\kappa^2(\text{Si},P)\text{-SiMe}_2\text{C}_6\text{H}_4\text{PPh}_2)(\kappa^2(C,P)\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})[\text{P}(\text{NC}_4\text{H}_4)_3]$  (**7**) but a better synthesis of **7** is to treat **5** directly with tri(*N*-pyrrolyl)phosphine. Heating the six-coordinate complex,  $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})_2(\text{PPh}_3)_2$  (**2**), gives two complexes both containing *ortho*-metallated triphenylphosphine, one with loss of the trimethylsilyl ligand, giving the known complex,  $\text{Os}(\kappa^2(C,P)\text{-C}_6\text{H}_4\text{PPh}_2)\text{H}(\text{CO})_2(\text{PPh}_3)$ , and the other with retention of the trimethylsilyl ligand, giving  $\text{Os}(\text{SiMe}_3)(\kappa^2(C,P)\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})_2(\text{PPh}_3)$  (**8**). Crystal structure determinations for **5**, **6**, **7** and **8** have been obtained.

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**Keywords:** Metallacyclic complex; *ortho*-Silylation; *ortho*-Metallation; Osmium; Silyl complexes; Methyl complexes; X-ray crystal structure

## 1. Introduction

C–Si bond formation, from reductive elimination of adjacent alkyl and silyl ligands in an alkyl, silyl-metal species, is widely postulated as one of two likely prod-

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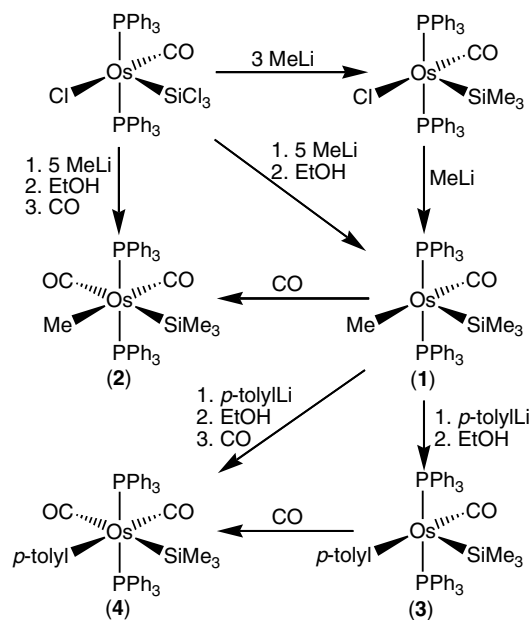
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uct-forming steps in metal-catalyzed hydrosilation [1]. There have been studies of this process, both theoretical [2] and experimental, using isolable alkyl, silyl–platinum [3] and alkyl, silyl–palladium [4] complexes. Fewer studies have been made with octahedral metal complexes, but important results include the observation that elimination of tetramethylsilane from *cis*-Fe(SiMe<sub>3</sub>)(Me)(CO)<sub>4</sub> was facile [5] and the demonstration that C–H and C–Si reductive elimination could be competitive for an iridium(III) complex containing hydride, alkyl, and silyl ligands [6]. We have previously shown that the coordinatively unsaturated silyl, aryl osmium(II) complexes, Os[Si(OEt)<sub>3</sub>](Aryl)(CO)(PPh<sub>3</sub>)<sub>2</sub> (Aryl = Ph, *o*-tolyl) are resistant to C–Si reductive elimination even at elevated temperatures [7]. This is no doubt in part because of the strong Os–Si bond in these complexes which is attributable to the electron-withdrawing ethoxy substituents on the silyl ligand [8]. To determine whether or not, related five-coordinate compounds bearing the more weakly-bound trimethylsilyl ligand would undergo C–Si reductive elimination more readily we set out to prepare and examine the thermal reactions of complexes of the type Os(SiMe<sub>3</sub>)(R)(CO)(PPh<sub>3</sub>)<sub>2</sub>. In this paper, we describe: (i) the reaction between Os(SiCl<sub>3</sub>)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub> and MeLi to give Os(SiMe<sub>3</sub>)(Me)(CO)(PPh<sub>3</sub>)<sub>2</sub> (**1**); (ii) the conversion of **1**, through reaction with *p*-tolylLi, to Os(SiMe<sub>3</sub>)(*p*-tolyl)(CO)(PPh<sub>3</sub>)<sub>2</sub> (**3**); (iii) the carbonylation of **1** and **3** to Os(SiMe<sub>3</sub>)(Me)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (**2**) and Os(SiMe<sub>3</sub>)(*p*-tolyl)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (**4**), respectively; (iv) the thermal reaction of Os(SiMe<sub>3</sub>)(Me)(CO)(PPh<sub>3</sub>)<sub>2</sub> (**1**) in the presence of PPh<sub>3</sub> to give Os(κ<sup>2</sup>(Si,P)-SiMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)(κ<sup>2</sup>(C,P)-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)(CO)(PPh<sub>3</sub>) (**5**) and Os(κ<sup>2</sup>(C,P)-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>) (**6**); (v) the thermal reaction of Os(SiMe<sub>3</sub>)(Me)(CO)(PPh<sub>3</sub>)<sub>2</sub> (**1**) in the presence of P(NC<sub>4</sub>H<sub>9</sub>)<sub>3</sub> to give Os(κ<sup>2</sup>(Si,P)-SiMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)(κ<sup>2</sup>(C,P)-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)(CO)[P(NC<sub>4</sub>H<sub>9</sub>)<sub>3</sub>] (**7**); (vi) the thermal reaction of Os(SiMe<sub>3</sub>)(Me)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (**2**) to give Os(κ<sup>2</sup>(C,P)-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)H(CO)<sub>2</sub>(PPh<sub>3</sub>), and Os(SiMe<sub>3</sub>)(κ<sup>2</sup>(C,P)-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)(CO)<sub>2</sub>(PPh<sub>3</sub>) (**8**); and (vii) the crystal structures of **5**, **6**, **7**, and **8**.

## 2. Results and discussion

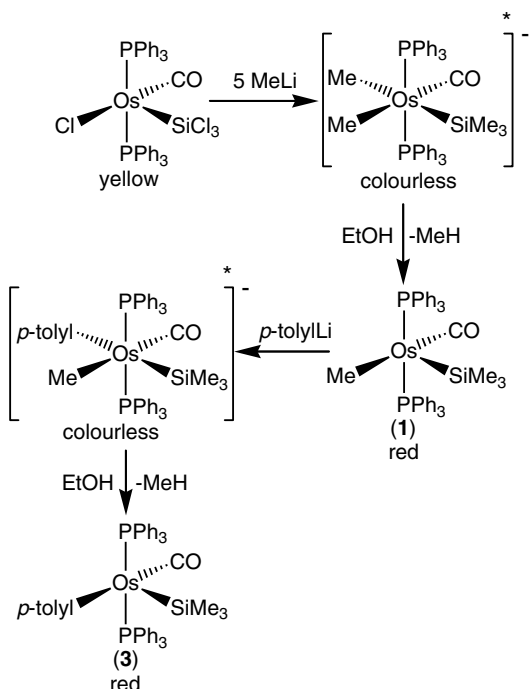
### 2.1. Preparation of Os(SiMe<sub>3</sub>)(Me)(CO)(PPh<sub>3</sub>)<sub>2</sub> (**1**) and Os(SiMe<sub>3</sub>)(*p*-tolyl)(CO)(PPh<sub>3</sub>)<sub>2</sub> (**3**)

We have previously reported that addition of three equivalents of MeLi to Os(SiCl<sub>3</sub>)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub> results in the formation of Os(SiMe<sub>3</sub>)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub> [8] (see Scheme 1). Since the Os–Cl bond in five coordinate complexes of this type is labile, it seemed likely that reaction with excess MeLi would afford Os(SiMe<sub>3</sub>)(Me)(CO)(PPh<sub>3</sub>)<sub>2</sub>. In fact, addition of five equivalents of MeLi to Os(SiCl<sub>3</sub>)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub> turned the originally yellow solution first red and then colourless with the



Scheme 1. Syntheses of Os(SiMe<sub>3</sub>)(Me)(CO)(PPh<sub>3</sub>)<sub>2</sub> (**1**), Os(SiMe<sub>3</sub>)(Me)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (**2**), Os(SiMe<sub>3</sub>)(*p*-tolyl)(CO)(PPh<sub>3</sub>)<sub>2</sub> (**3**), and Os(SiMe<sub>3</sub>)(*p*-tolyl)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (**4**).

formation of a white precipitate. This precipitate could not be fully characterized because of its extreme sensitivity to moisture and other protic solvents, but it was possible to record an IR spectrum as a Nujol mull. This revealed a ν(CO) band at 1754 cm<sup>−1</sup>. This extremely low ν(CO) is indicative of an anionic species and accordingly we formulate the white material as the lithium salt, Li[Os(SiMe<sub>3</sub>)(Me)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] where the osmium centre is coordinatively saturated and therefore colourless. This formulation is further supported by reactions depicted in Schemes 1 and 2. Thus, addition of ethanol to the white precipitate brings about dissolution with release of methane and the formation of a red solution from which can be isolated the red crystalline solid Os(SiMe<sub>3</sub>)(Me)(CO)(PPh<sub>3</sub>)<sub>2</sub> (**1**) in good yield (see Schemes 1 and 2). Complex **1** is stable in the solid state but slowly decomposes over several hours when in solution. Among the decomposition products is the hydride, OsHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>. Spectral data for **1** and all other new compounds are collected in Section 4. Compound **1** has ν(CO) at 1879 cm<sup>−1</sup> (in CH<sub>2</sub>Cl<sub>2</sub>), significantly lower than ν(CO) for the precursor Os(SiMe<sub>3</sub>)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>, at 1895 cm<sup>−1</sup> (in CH<sub>2</sub>Cl<sub>2</sub>), as expected. In the <sup>1</sup>H NMR spectrum the Os–Me signal is observed at 0.12 ppm as a triplet (<sup>3</sup>J<sub>PH</sub> = 8.7 Hz). The corresponding <sup>13</sup>C resonance is observed at 21.1 ppm as a triplet (<sup>2</sup>J<sub>PC</sub> = 9.6 Hz) and the resonance for the trimethylsilyl group is at 9.6 ppm. In the <sup>31</sup>P NMR spectrum there is a singlet resonance at 29.19 ppm. All these data are compatible with the pyramidal geometry shown for **1** in Scheme 1, i.e., mutually *trans* triphenylphosphine ligands and with a vacant site *trans* to the trimethylsilyl



Scheme 2. Formation of **1** and **3** via postulated anionic intermediates (compounds marked with an asterisk not fully characterised).

ligand. This same geometry has been verified crystallographically for numerous other five coordinate silyl derivatives of osmium(II) [7,8].

The red colour of a solution of complex **1** is immediately discharged by the addition of one or more equivalents of *p*-tolylLi suggesting that the saturated anion,  $[\text{Os}(\text{SiMe}_3)(\text{Me})(p\text{-tolyl})(\text{CO})(\text{PPh}_3)_2]^-$ , is formed (see Scheme 2). When ethanol is added to this colourless solution methane is liberated, the solution becomes red in colour and the *p*-tolyl analogue of **1**,  $\text{Os}(\text{SiMe}_3)(p\text{-tolyl})(\text{CO})(\text{PPh}_3)_2$  (**3**) can be isolated as a red crystalline solid. This is stable as a solid but like **1**, shows solution instability. It is interesting, that in the formation of **3** through protonolysis of the postulated anion, it is methane which is eliminated rather than toluene. The IR spectrum of **3** shows  $\nu(\text{CO})$  at  $1900\text{ cm}^{-1}$ . In the  $^{13}\text{C}$  NMR spectrum the resonance for the trimethylsilyl group is seen as a triplet at  $9.2\text{ ppm}$  ( $^3J_{\text{PC}} = 1.9\text{ Hz}$ ). In the  $^{31}\text{P}$  NMR spectrum there is a singlet resonance at  $22.31\text{ ppm}$ . The geometry depicted for complex **3** in Schemes 1 and 2 is based upon the known geometry of other related tolyl, silyl-complexes of osmium(II) [7].

## 2.2. Carbonylation of $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})(\text{PPh}_3)_2$ (**1**) and $\text{Os}(\text{SiMe}_3)(p\text{-tolyl})(\text{CO})(\text{PPh}_3)_2$ (**3**) to $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})_2(\text{PPh}_3)_2$ (**2**) and $\text{Os}(\text{SiMe}_3)(p\text{-tolyl})(\text{CO})_2(\text{PPh}_3)_2$ (**4**), respectively

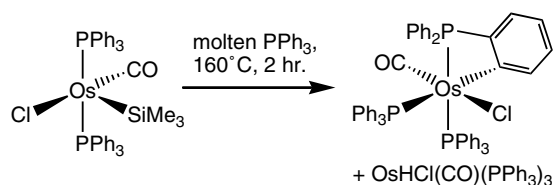
Like other five coordinate silyl-osmium(II) complexes, direct admission of CO to red solutions of

$\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})(\text{PPh}_3)_2$  (**1**) and  $\text{Os}(\text{SiMe}_3)(p\text{-tolyl})(\text{CO})(\text{PPh}_3)_2$  (**3**) brings about rapid discharge of the red colour and formation of the colourless, coordinatively saturated, complexes  $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})_2(\text{PPh}_3)_2$  (**2**) and  $\text{Os}(\text{SiMe}_3)(p\text{-tolyl})(\text{CO})_2(\text{PPh}_3)_2$  (**4**), respectively, in high yield. Experimentally, it is more convenient to add CO to red solutions of **1** and **3**, prepared in situ, avoiding isolation of the five coordinate compounds. Compound **2** has limited solution stability and attempts to grow a single crystal from  $\text{CH}_2\text{Cl}_2$  over several days resulted in the formation of  $\text{OsCl}_2(\text{CO})_2(\text{PPh}_3)_2$ . The IR spectra of both **2** and **4** show two  $\nu(\text{CO})$  bands consistent with a *cis* arrangement of the CO ligands. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra require no special comment, all the data being consistent with the structures depicted in Scheme 1. The  $^{31}\text{P}$  NMR spectra show singlet signals with chemical shifts at  $4.34\text{ ppm}$  for **2**,  $-4.16\text{ ppm}$  for **4**, both significantly upfield from the values observed for the five coordinate precursors ( $29.59\text{ ppm}$  for **1**,  $22.31\text{ ppm}$  for **3**).

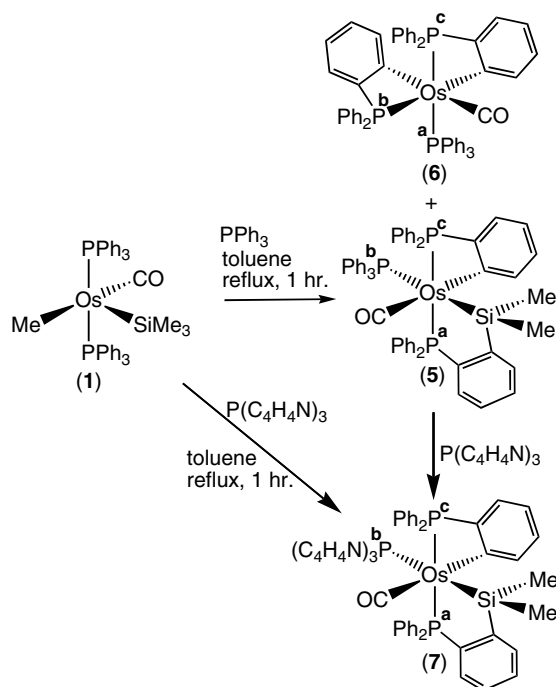
## 2.3. Thermal reactions of $\text{Os}(\text{SiMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ and $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})(\text{PPh}_3)_2$ (**1**) and the crystal structures of $\text{Os}(\kappa^2(\text{Si},\text{P})\text{-SiMe}_2\text{C}_6\text{H}_4\text{PPh}_2)(\kappa^2(\text{C},\text{P})\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$ (**5**) $\text{Os}(\kappa^2(\text{C},\text{P})\text{-C}_6\text{H}_4\text{PPh}_2)_2(\text{CO})(\text{PPh}_3)$ (**6**) and $\text{Os}(\kappa^2(\text{Si},\text{P})\text{-SiMe}_2\text{C}_6\text{H}_4\text{PPh}_2)(\kappa^2(\text{C},\text{P})\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})[\text{P}(\text{NC}_4\text{H}_4)_3]$ (**7**)

Before describing the thermal reactions of the silyl, methyl-complex,  $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})(\text{PPh}_3)_2$  (**1**), it is relevant to consider the thermal reaction of the silyl, chloride-complex,  $\text{Os}(\text{SiMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ . This is a very stable compound and it is only after heating in molten triphenylphosphine at  $160^\circ\text{C}$  for 2 h that decomposition occurs, the major products being the *ortho*-metallated complex,  $\text{Os}(\kappa^2(\text{C},\text{P})\text{-C}_6\text{H}_4\text{PPh}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2$  and  $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$ , both products involving loss of the silyl ligand (see Scheme 3).  $\text{Os}(\kappa^2(\text{C},\text{P})\text{-C}_6\text{H}_4\text{PPh}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2$  has been described previously as a product from transmetallation utilising  $\text{Hg}(\text{C}_6\text{H}_4\text{PPh}_2)_2$  [9].

In marked contrast to the stability of the silyl, chloride-complex,  $\text{Os}(\text{SiMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$  described above, the corresponding silyl, methyl-complex,  $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})(\text{PPh}_3)_2$  (**1**), shows solution instability and as depicted in Scheme 4 readily undergoes a thermal reaction (toluene reflux, 1 h) in the presence of



Scheme 3. Thermal reaction of  $\text{Os}(\text{SiMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ .



Scheme 4. Thermal reactions of  $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})(\text{PPh}_3)_2$  (**1**) (with phosphorus atoms labeled for NMR discussion).

triphenylphosphine, to give as major product, the *ortho*-silylated as well as *ortho*-metallated complex,  $\text{Os}(\kappa^2\text{-}(\text{Si},\text{P})\text{-SiMe}_2\text{C}_6\text{H}_4\text{PPh}_2)(\kappa^2\text{-}(\text{C},\text{P})\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$  (**5**). This unusual product, which retains the Os–Si bond, has been observed previously from the reaction of  $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$  and  $\text{Hg}(\text{SiMe}_3)_2$  [10]. The same *ortho*-silylated ligand,  $\kappa^2(\text{Si},\text{P})\text{-SiMe}_2\text{C}_6\text{H}_4\text{PPh}_2$ , is formed in the thermal reaction of a base-stabilised silylene, triphenylphosphine complex of ruthenium(II) [11]. This suggests the possibility of a dimethylsilylene intermediate in the formation of complex **5**. Such an intermediate could arise from a migration of a methyl group from the trimethylsilyl ligand to osmium. There is precedent for this sort of process on osmium in that a methyl group has been observed to migrate to osmium from a bound trimethylstannyl ligand [12]. However, the details of the mechanism are unknown and the reaction must be of some complexity since an *ortho*-metallated triphenylphosphine ligand is also formed. The focus of this study was to identify the metal complexes formed rather than the mechanism of their formation and in view of the complexity of this reaction, and the vigorous reaction conditions involved, no effort was made to detect and identify any gaseous by-products. In the IR spectrum of **5**, there is a  $\nu(\text{CO})$  at  $1906\text{ cm}^{-1}$ . In the  $^1\text{H}$  NMR spectrum, the two methyl groups of the  $\kappa^2(\text{Si},\text{P})\text{-SiMe}_2\text{C}_6\text{H}_4\text{PPh}_2$  ligand show separate resonances at  $-1.12$  and  $0.12\text{ ppm}$ . Likewise, in the  $^{13}\text{C}$  NMR spectrum, the two carbon atoms of these methyl groups also show separate resonances at  $-2.3$  and  $5.2\text{ ppm}$ . The

carbon atom of the carbonyl ligand appears as a multiplet at  $192.6\text{ ppm}$ , consistent with coupling to three inequivalent phosphorus atoms. In the  $^{31}\text{P}$  NMR spectrum, each of the phosphorus atoms appears as a doublet of doublets due to P–P coupling. The assignments and the accompanying coupling constants are presented in Section 4.6. The assignment of phosphorus atom (b) (see Scheme for phosphorus atom labeling) follows from coupling constants indicative of two *cis* phosphorus atoms. Distinction between phosphorus atoms (a) and (c), which both have one *cis* and one *trans* phosphorus atom, was made on the basis of the distinctly high-field chemical shift that is typically observed for *ortho*-metallated triphenylphosphine ligands (see Ref. [9] and the compounds **6**, **7**, and **8** described below).

Although some structural data for complex **5** have been reported in reference [10] complete X-ray structure determination for **5** is reported here to provide accurate bond length data for comparison with the other structure determinations in this paper. Crystallographic data for **5** and the other structures reported in this paper are given in Table 1. The molecular structure of **5** is depicted in Fig. 1 and selected bond lengths and angles for **5** are presented in Table 2. The overall geometry about osmium is octahedral with the phosphorus atoms of the two chelating ligands located mutually *trans*. The triphenylphosphine ligand is *trans* to the silyl ligand. The longest of the three Os–P distances is Os–P(1),  $2.4363(11)\text{ \AA}$  which is expected since P(1) is *trans* to Si. Os–P(3),  $2.3499(12)\text{ \AA}$ , which is part of the unstrained five membered chelate ring is significantly shorter than Os–P(2),  $2.3812(12)\text{ \AA}$ , which is part of the strained four membered chelate ring. All these Os–P distances are closely similar to values reported for other related osmium *ortho*-metallated complexes [9]. The Os–Si distance is  $2.4716(13)\text{ \AA}$ . The average for 10 entries for octahedral osmium silyl complexes in the Cambridge Crystallographic Data Base is  $2.4499$  (SD,  $0.0508$ )  $\text{\AA}$ . The Os–C(52) distance within the four-membered ring is  $2.190(5)\text{ \AA}$ .

A minor product from the thermal reaction of the silyl, methyl-complex,  $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})(\text{PPh}_3)_2$  (**1**) in the presence of triphenylphosphine does involve loss of the trimethylsilyl ligand and the methyl ligand giving eventually  $\text{Os}(\kappa^2\text{-}(\text{C},\text{P})\text{-C}_6\text{H}_4\text{PPh}_2)_2(\text{CO})(\text{PPh}_3)$  (**6**) which contains two *ortho*-metallated triphenylphosphine ligands (see Scheme 4). The IR spectrum of **6** shows  $\nu(\text{CO})$  at  $1888\text{ cm}^{-1}$ . There are no features requiring special comment in either the  $^1\text{H}$  NMR or the  $^{13}\text{C}$  NMR spectra of **6** but the  $^{31}\text{P}$  NMR spectrum is interesting. As for complex **5**, there are three inequivalent phosphorus atoms in a meridional arrangement and the signal for each phosphorus appears as a doublet of doublets due to P–P coupling. The assignments and the accompanying coupling constants are presented in Section 4.7. The assignment of phosphorus atom (a) follows from



Table 1  
Data collection and processing parameters for **5**, **6**, **7** and **8**

	<b>5</b> · 2H <sub>2</sub> O	<b>6</b> · 0.5C <sub>6</sub> H <sub>14</sub>	<b>7</b>	<b>8</b>
Formula	C <sub>57</sub> H <sub>49</sub> O <sub>3</sub> OsP <sub>3</sub> Si	C <sub>58</sub> H <sub>50</sub> O <sub>3</sub> OsP <sub>3</sub>	C <sub>51</sub> H <sub>46</sub> N <sub>3</sub> O <sub>3</sub> OsP <sub>3</sub> Si	C <sub>41</sub> H <sub>38</sub> O <sub>2</sub> OsP <sub>2</sub> Si
Molecular weight	1093.16	1046.09	1028.11	842.94
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>Unit cell dimensions</i>				
<i>a</i> (Å)	11.5539(1)	10.7694(2)	9.6783(1)	10.2287(1)
<i>b</i> (Å)	19.5272(2)	12.1558(2)	20.6293(1)	15.3207(1)
<i>c</i> (Å)	22.7764(1)	18.8593(3)	22.2438(3)	23.3242(2)
$\alpha$ (°)	90.0	75.886(1)	90.0	90.0
$\beta$ (°)	90.975(1)	87.315(1)	95.610(1)	96.263(1)
$\gamma$ (°)	90.0	69.919(1)	90.0	90.0
<i>V</i> (Å <sup>3</sup> )	5137.96(7)	2246.95(7)	4419.85(8)	3633.34(5)
<i>T</i> (K)	84	84	150	150
<i>Z</i>	4	2	4	4
<i>D</i> <sub>calc</sub> (g cm <sup>−3</sup> )	1.413	1.546	1.545	1.541
<i>F</i> (000)	2200	1054	2064	1680
$\mu$ (mm <sup>−1</sup> )	2.64	2.99	3.06	3.66
Crystal size (mm)	0.46 × 0.15 × 0.04	0.32 × 0.30 × 0.22	0.36 × 0.22 × 0.20	0.24 × 0.22 × 0.16
2 $\theta$ (Min–max) (°)	2.0–27.2	1.8–26.5	1.4–25.7	1.6–25.7
Reflections collected	50963	22087	39948	33266
Independent reflections ( <i>R</i> <sub>int</sub> )	11,300 (0.0253)	9198 (0.0235)	8389 (0.0253)	6916 (0.0292)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.376, 0.902	0.448, 0.559	0.405, 0.579	0.473, 0.592
Goodness of fit on <i>F</i> <sup>2</sup>	1.092	1.061	1.118	1.073
<i>R</i> (observed data)	<i>R</i> <sub>1</sub> = 0.0364 <i>wR</i> <sub>2</sub> = 0.1023	<i>R</i> <sub>1</sub> = 0.0365, <i>wR</i> <sub>2</sub> = 0.0932	<i>R</i> <sub>1</sub> = 0.0230 <i>wR</i> <sub>2</sub> = 0.0537	<i>R</i> <sub>1</sub> = 0.0192 <i>wR</i> <sub>2</sub> = 0.0409
<i>R</i> (all data)	<i>R</i> <sub>1</sub> = 0.0463 <i>wR</i> <sub>2</sub> = 0.1078	<i>R</i> <sub>1</sub> = 0.0437 <i>wR</i> <sub>2</sub> = 0.0976	<i>R</i> <sub>1</sub> = 0.0271 <i>wR</i> <sub>2</sub> = 0.0558	<i>R</i> <sub>1</sub> = 0.0247 <i>wR</i> <sub>2</sub> = 0.0429

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

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

P–P coupling constants indicative of one *cis* and one *trans* phosphorus atom together with a chemical shift position appropriate for a PPh<sub>3</sub> ligand. The phosphorus

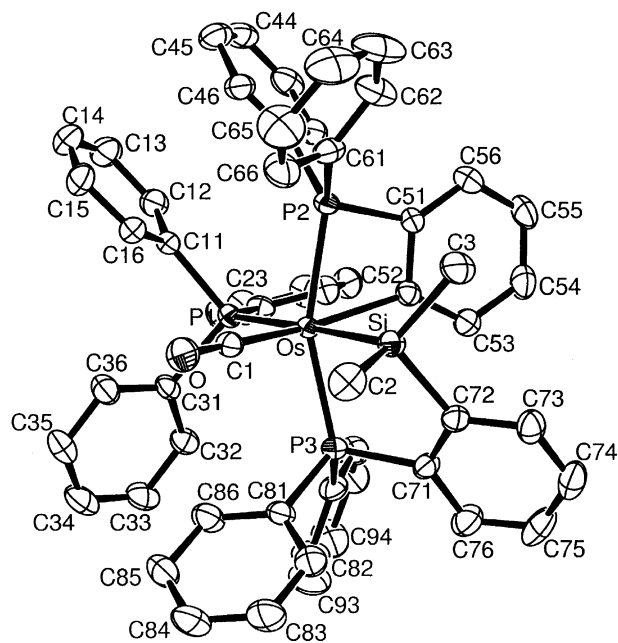


Fig. 1. Molecular geometry of Os( $\kappa^2$ (Si,*P*)-SiMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)( $\kappa^2$ (C,*P*)-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)(CO)(PPh<sub>3</sub>) (**5**).

atoms of the two *ortho*-metallated triphenylphosphine ligands appear at unusually high-field positions (see discussion for complex **5**) and are distinguished by (b) having P–P coupling constants appropriate for two *cis* phosphorus atoms and by (c) having P–P coupling constants appropriate for one *cis* and one *trans* P atoms.

The molecular structure of **6** is depicted in Fig. 2 and selected bond lengths and angles for **6** are presented in Table 3. The overall geometry about osmium is octahedral with the phosphorus atoms of the two *ortho*-metallated ligands located mutually *cis*. The triphenylphosphine ligand is *trans* to a phosphorus atom of one of the *ortho*-metallated ligands. The Os–P distances in the *ortho*-metallated ligands (Os–P(1), 2.3786(10) and Os–P(2), 2.3871(11) Å) are almost identical despite one being *trans* to carbon and the other *trans* to phosphorus. The Os–PPh<sub>3</sub> distance is slightly shorter at 2.3454(11) Å. The Os–C distances within the four-membered rings are Os–C(32), 2.133(4) and Os–C(2), 2.149(4) Å, are both shorter than the corresponding distance in **5** (2.190(5) Å).

When Os(SiMe<sub>3</sub>)(Me)(CO)(PPh<sub>3</sub>)<sub>2</sub> (**1**), undergoes a thermal reaction (toluene reflux, 1 h) in the presence of tris(*N*-pyrrolyl)phosphine instead of triphenylphosphine, the tris(*N*-pyrrolyl)phosphine analogue of **5**, Os( $\kappa^2$ (Si,*P*)-SiMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)( $\kappa^2$ (C,*P*)-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)(CO)-

Table 2  
Selected bond lengths (Å) and angles (°) for **5**

<i>Bond lengths</i>	
Os–Si	2.4716(13)
Os–P(1)	2.4363(11)
Os–P(2)	2.3812(12)
Os–P(3)	2.3499(12)
Os–C(1)	1.883(5)
Os–C(52)	2.190(5)
Si–C(2)	1.886(6)
Si–C(3)	1.891(6)
Si–C(72)	1.913(5)
P(2)–C(51)	1.801(5)
C(51)–C(52)	1.420(7)
<i>Bond angles</i>	
Si–Os–P(1)	178.02(4)
Si–Os–P(2)	88.92(4)
Si–Os–P(3)	78.94(4)
Si–Os–C(1)	87.83(15)
Si–Os–C(52)	77.59(12)
P1–Os–P(2)	92.56(4)
P1–Os–P(3)	100.03(4)
P(2)–Os–P(3)	159.13(4)
P(2)–Os–C(52)	66.01(12)
Os–P(2)–C(51)	87.14(16)
Os–Si–C(72)	103.01(16)
Os–C(52)–C(51)	105.6(3)
Os–P(3)–C(71)	109.79(17)
P(3)–C(71)–C(72)	115.3(4)
Si–C(72)–C(71)	117.5(4)

Table 3  
Selected bond lengths (Å) and angles (°) for **6**

<i>Bond lengths</i>	
Os–P(1)	2.3786(10)
Os–P(2)	2.3871(11)
Os–P(3)	2.3454(11)
Os–C	1.897(4)
Os–C(2)	2.149(4)
Os–C(32)	2.133(4)
P(1)–C(1)	1.816(4)
C(1)–C(2)	1.406(6)
P(2)–C(31)	1.799(4)
C(31)–C(32)	1.401(6)
<i>Bond angles</i>	
P(1)–Os–P(2)	100.58(4)
P(1)–Os–P(3)	98.09(4)
P(1)–Os–C	101.73(12)
P(1)–Os–C(2)	66.47(12)
P(1)–Os–C(32)	156.65(12)
P(2)–Os–P(3)	158.65(4)
P(2)–Os–C	91.86(13)
P(2)–Os–C(2)	88.06(12)
P(2)–Os–C(32)	66.13(12)
P(3)–Os–C	94.41(13)
P(3)–Os–C(2)	89.97(12)
P(3)–Os–C(32)	92.76(12)
P(1)–C(1)–C(2)	100.4(3)
Os–C(2)–C(1)	107.0(3)
P(2)–C(31)–C(32)	100.6(3)
Os–C(32)–C(31)	107.2(3)
Os–P(2)–C(31)	85.64(15)
Os–P(1)–C(1)	86.04(14)

[P(NC<sub>4</sub>H<sub>4</sub>)<sub>3</sub>] (**7**), can be detected amongst numerous uncharacterised products (see Scheme 4). A clean high-yield preparation of **7** involves direct replacement of triphenylphosphine in **5** by reaction with tris(*N*-pyrrolyl)phosphine. The IR spectrum of **7** shows  $\nu(\text{CO})$  at 1941 cm<sup>−1</sup>, a value markedly higher than observed for **5**, consistent with the introduction of a very good  $\pi$ -

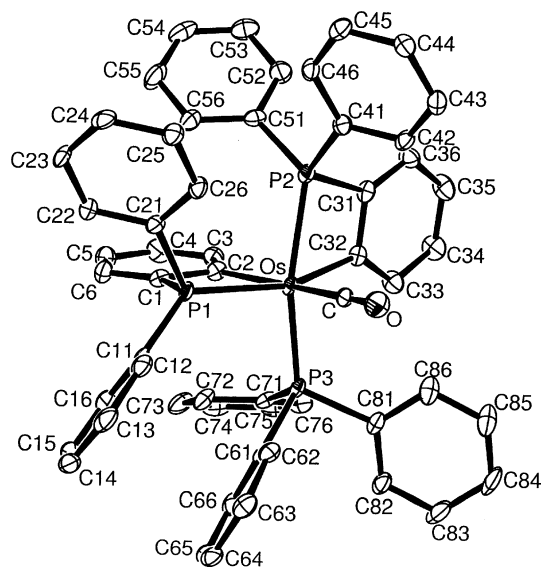


Fig. 2. Molecular geometry of Os( $\kappa^2$ (C,P)-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>) (**6**).

acceptor ligand (tris(*N*-pyrrolyl)phosphine) [13]. In the <sup>1</sup>H NMR spectrum the two methyl groups of the  $\kappa^2$ (Si,P)-SiMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub> ligand again show separate resonances at −1.15 and 0.13 ppm. Likewise, in the <sup>13</sup>C NMR spectrum, the two carbon atoms of these methyl groups also show separate resonances at −2.3 and 5.3 ppm. The carbon atom of the carbonyl ligand appears as a multiplet at 190.1 ppm, consistent with coupling to three inequivalent phosphorus atoms. All these chemical shifts are close to those observed for complex **5**. In the <sup>31</sup>P NMR spectrum each of the phosphorus atoms appears as a doublet of doublets due to P–P coupling. The assignments and the accompanying coupling constants are presented in Section 4.8. The assignment of phosphorus atom (b) (P(NC<sub>4</sub>H<sub>4</sub>)<sub>3</sub>) follows from the very low-field chemical shift (70.15 ppm) [13b] and coupling constants indicative of two *cis* phosphorus atoms. Distinction between phosphorus atoms (a) and (c), which both have a *cis* and a *trans* phosphorus atom, was made on the basis of the distinctly high-field chemical shift that is typically observed for *ortho*-metallated triphenylphosphine ligands.

The molecular structure of **7** is depicted in Fig. 3 and selected bond lengths and angles for **7** are presented in Table 4. The overall geometry of **7** is the same as that for **5** with tris(*N*-pyrrolyl)phosphine replacing triphenyl-

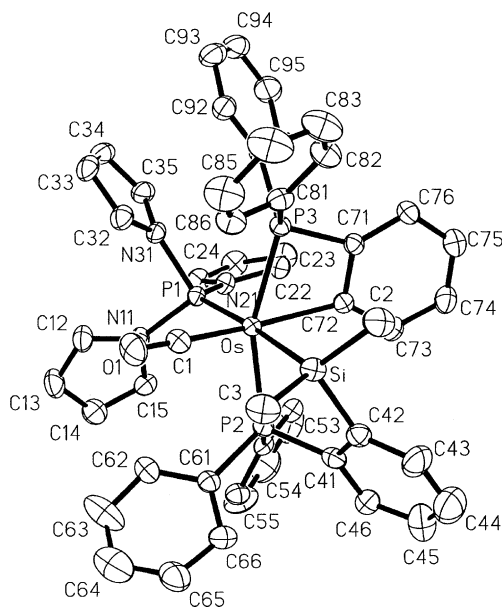


Fig. 3. Molecular geometry of  $\text{Os}(\kappa^2(\text{Si},\text{P})\text{-SiMe}_2\text{C}_6\text{H}_4\text{PPh}_2)(\kappa^2(\text{C},\text{P})\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})[\text{P}(\text{NC}_4\text{H}_9)_3]$  (**7**).

Table 4  
Selected bond lengths [Å] and angles [°] for **7**

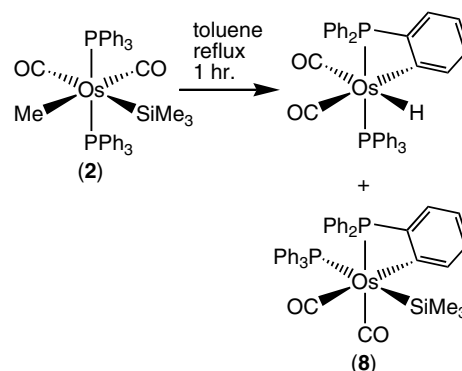
Bond lengths	
Os–C(1)	1.897(3)
Os–C(72)	2.179(3)
Os–P(1)	2.3169(7)
Os–P(2)	2.3338(7)
Os–P(3)	2.3807(7)
Os–Si	2.5110(8)
Si–C(2)	1.888(3)
Si–C(3)	1.893(3)
Si–C(42)	1.901(3)
O(1)–C(1)	1.151(4)
Bond angles	
C(1)–Os–C(72)	161.59(12)
C(1)–Os–P(1)	90.20(10)
C(72)–Os–P(1)	104.83(7)
C(1)–Os–P(2)	93.86(10)
C(72)–Os–P(2)	94.22(8)
P(1)–Os–P(2)	98.90(3)
C(1)–Os–P(3)	102.84(9)
C(72)–Os–P(3)	66.00(8)
P(1)–Os–P(3)	94.52(3)
P(2)–Os–P(3)	158.51(3)
C(1)–Os–Si	87.46(10)
C(72)–Os–Si	78.00(7)
P(1)–Os–Si	176.38(3)
P(2)–Os–Si	78.53(3)
P(3)–Os–Si	88.68(3)
C(2)–Si–C(3)	104.58(17)
C(2)–Si–C(42)	102.95(16)
C(3)–Si–C(42)	106.32(15)
C(2)–Si–Os	123.17(11)
C(3)–Si–Os	115.02(12)
C(42)–Si–Os	103.02(10)
O(1)–C(1)–Os	176.7(3)
Os–P(3)–C(71)	86.88(10)

phosphine. The Os–P(NC<sub>4</sub>H<sub>9</sub>)<sub>3</sub> distance is 2.3169(7) Å and this can be compared with the Os–PPh<sub>3</sub> distance in **5** of 2.4363(11) Å. This pronounced shortening of the Os–P bond for the tris(*N*-pyrrolyl)phosphine ligand has been observed previously and attributed to the strong  $\pi$ -accepting capability of this ligand [13]. Accompanying this shortening of the Os–P bond is a marked lengthening of the Os–Si bond in the *trans* position. In **7** the Os–Si distance is 2.5110(8) Å which can be compared with the value for **5** which is 2.4716(13) Å. 2.5110(8) Å is longer than any recorded Os–Si distance for an octahedral osmium silyl complex (the average for 10 entries in the Cambridge Crystallographic Data Base is 2.4499 (SD, 0.0508) Å). The Os–C(72) distance within the four-membered ring is 2.179(3) Å, close to the corresponding value in **5**.

#### 2.4. Thermal reaction of $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})_2(\text{PPh}_3)_2$ (**2**) and the crystal structure of $\text{Os}(\text{SiMe}_3)(\kappa^2(\text{C},\text{P})\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})_2(\text{PPh}_3)$ (**8**)

For comparison with the thermal reactions of the coordinatively unsaturated  $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})_2(\text{PPh}_3)_2$  (**1**) described above the coordinatively saturated dicarbonyl complex,  $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})_2(\text{PPh}_3)_2$  (**2**) was heated under reflux in toluene. Two products were isolated from this reaction after chromatography, the major one being  $\text{Os}(\text{SiMe}_3)(\kappa^2(\text{C},\text{P})\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})_2(\text{PPh}_3)$  (**8**) (see Scheme 5). Complex **8** retains the trimethylsilyl ligand and incorporates an *ortho*-metalated triphenylphosphine. The minor product is  $\text{Os}(\kappa^2(\text{C},\text{P})\text{-C}_6\text{H}_4\text{PPh}_2)\text{H}(\text{CO})_2(\text{PPh}_3)$ , with loss of both the trimethylsilyl and methyl ligands.  $\text{Os}(\kappa^2(\text{C},\text{P})\text{-C}_6\text{H}_4\text{PPh}_2)\text{H}(\text{CO})_2(\text{PPh}_3)$  has also been reported from the thermal reactions of  $\text{Os}(\eta^2\text{-CH}_2\text{O})(\text{CO})_2(\text{PPh}_3)_2$  [14] and  $\text{Os}(\text{Bcat})(o\text{-tolyl})(\text{CO})_2(\text{PPh}_3)_2$  [15].

The IR spectrum of complex **8** shows two  $\nu(\text{CO})$  bands at 2001 and 1933  $\text{cm}^{-1}$  indicating a *cis* disposition of these ligands. In the <sup>1</sup>H NMR spectrum the methyl signal for the trimethylsilyl ligand appears as a doublet



Scheme 5. Thermal reactions of  $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})_2(\text{PPh}_3)_2$  (**2**).

at  $-0.20$  ppm, with weak coupling observed only to the *trans* phosphorus atom. In the  $^{13}\text{C}$  NMR spectrum the methyl signal for the trimethylsilyl ligand appears as a multiplet at  $4.8$  ppm. The carbon signals for the two carbonyl ligands each appear as doublets of doublets, the CO *trans* to phosphorus with  $J_{\text{PC}}$  values of  $77.0$  and  $5.6$  Hz, the CO *cis* to both phosphorus atoms with  $J_{\text{PC}}$  values of  $8.2$  and  $5.7$  Hz. In the  $^{31}\text{P}$  NMR spectrum there are two doublet signals. One has a chemical shift of  $-77.10$  ppm and this is assigned to the *ortho*-metallated triphenylphosphine ligand. All these NMR spectroscopic data are compatible with the geometry shown in Scheme 5 and this was confirmed by an X-ray crystallographic study.

The molecular structure of **8** is depicted in Fig. 4 and selected bond lengths and angles for **8** are presented in Table 5. The overall geometry about osmium is octahedral with the phosphorus atoms of the *ortho*-metallated ligand and the triphenylphosphine ligand located mutually *cis*. The trimethylsilyl ligand is located *trans* to the triphenylphosphine ligand and the Os–Si distance is  $2.5166(7)$  Å. This is even longer than the Os–Si distance found in **7** ( $2.5110(8)$ ). The Os–P distance in the *ortho*-metallated ligand, Os–P(1) is  $2.4074(6)$  and the Os–PPh<sub>3</sub> distance is slightly longer at  $2.4230(6)$  Å, probably because of the *trans* trimethylsilyl ligand. The Os–C distance within the four-membered ring, Os–C(12) is  $2.148(3)$  close in value to the other corresponding Os–C distances reported in this paper.

Table 5

Selected bond lengths [Å] and angles [°] for **8**

Bond lengths	
Os–C(1)	1.894(3)
Os–C(2)	1.902(3)
Os–C(12)	2.148(3)
Os–P(1)	2.4074(6)
Os–P(2)	2.4230(6)
Os–Si	2.5166(7)
Si–C(4)	1.888(3)
Si–C(5)	1.893(3)
Si–C(3)	1.897(3)
O(1)–C(1)	1.155(3)
O(2)–C(2)	1.155(3)
Bond angles	
C(1)–Os–C(2)	96.42(12)
C(1)–Os–C(12)	93.97(11)
C(2)–Os–C(12)	165.04(11)
C(1)–Os–P(1)	159.77(9)
C(2)–Os–P(1)	103.12(9)
C(12)–Os–P(1)	65.86(7)
C(1)–Os–P(2)	89.03(8)
C(2)–Os–P(2)	91.07(8)
C(12)–Os–P(2)	99.85(7)
P(1)–Os–P(2)	95.70(2)
C(1)–Os–Si	83.83(8)
C(2)–Os–Si	89.16(8)
C(12)–Os–Si	81.27(7)
P(1)–Os–Si	91.22(2)
P(2)–Os–Si	172.84(2)
C(4)–Si–C(5)	102.30(14)
C(4)–Si–C(3)	102.34(13)
C(5)–Si–C(3)	106.58(14)
C(4)–Si–Os	110.97(10)
C(5)–Si–Os	114.28(10)
C(3)–Si–Os	118.55(9)
O(1)–C(1)–Os	177.1(3)
O(2)–C(2)–Os	177.6(3)
Os–P(1)–C(11)	85.86(9)

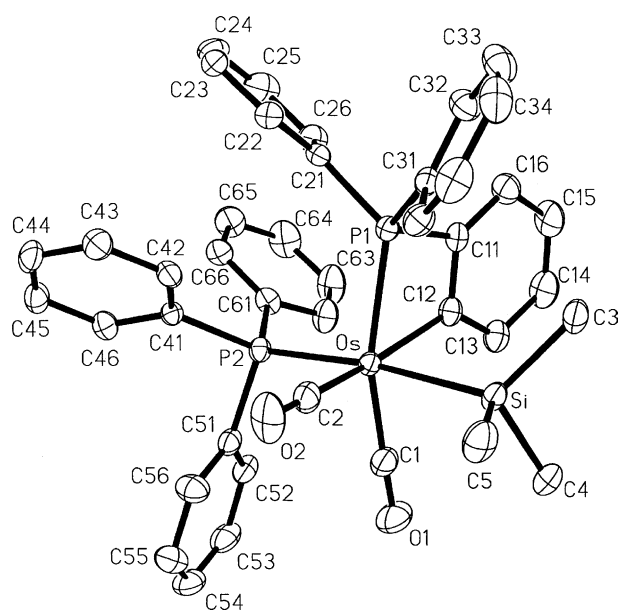


Fig. 4. Molecular geometry of  $\text{Os}(\text{SiMe}_3)(\kappa^2(\text{C},\text{P})\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})_2(\text{PPh}_3)$  (**8**).

### 3. Conclusions

It has been demonstrated that introducing a methyl group into the coordinatively unsaturated, but rather inert complex,  $\text{Os}(\text{SiMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ , to produce  $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})(\text{PPh}_3)_2$  (**1**), opens a pathway to a facile thermal reaction which leads to a product retaining the Os–Si bond in the *ortho*-silylated as well as *ortho*-metallated complex,  $\text{Os}(\kappa^2(\text{Si},\text{P})\text{-SiMe}_2\text{C}_6\text{H}_4\text{PPh}_2)(\kappa^2(\text{C},\text{P})\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$  (**5**). This reaction product may indicate the intermediacy of a silylene complex. Replacement of triphenylphosphine in **5** by the superior  $\pi$ -bonding ligand tris(*N*-pyrrolyl)phosphine leads to  $\text{Os}(\kappa^2(\text{Si},\text{P})\text{-SiMe}_2\text{C}_6\text{H}_4\text{PPh}_2)(\kappa^2(\text{C},\text{P})\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})\text{-}[\text{P}(\text{NC}_4\text{H}_4)_3]$  (**7**). A structural comparison between **5** and **7** reveals that the Os–Si bond is considerably lengthened by this substitution. Thermal reaction of the coordinatively saturated methyl complex,  $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})_2(\text{PPh}_3)_2$  (**2**), leads to *ortho*-metallated products again, but none of these contain an *ortho*-silylated ligand.



## 4. Experimental

### 4.1. General procedures and instruments

Standard laboratory procedures were followed as have been described previously [16]. The compounds  $\text{Os}(\text{SiCl}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$  and  $\text{Os}(\text{SiMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$  were prepared according to the literature methods [8].

Infrared spectra ( $4000\text{--}400\text{ cm}^{-1}$ ) 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  $25^\circ\text{C}$ . For the Bruker DRX 400,  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectra were obtained operating at 400.1 ( $^1\text{H}$ ), 100.6 ( $^{13}\text{C}$ ), and 162.0 ( $^{31}\text{P}$ ) MHz, respectively. For the Bruker Avance 300,  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectra were obtained operating at 300.13 ( $^1\text{H}$ ), 75.48 ( $^{13}\text{C}$ ), and 121.50 ( $^{31}\text{P}$ ) MHz, respectively. Resonances are quoted in ppm and  $^1\text{H}$  NMR spectra referenced to either tetramethylsilane (0.00 ppm) or the proteo-impurity in the solvent (7.25 ppm for  $\text{CHCl}_3$ ).  $^{13}\text{C}$  NMR spectra were referenced to  $\text{CDCl}_3$  (77.00 ppm), and  $^{31}\text{P}$  NMR spectra to 85% orthophosphoric acid (0.00 ppm) as an external standard. In recording  $^{13}\text{C}$  NMR data the symbol  $t'$  is used to indicate a virtual triplet where only three of the expected five lines in the X part of an  $\text{AA}'\text{X}$  system are observed. This is frequently the case in the spectra of complexes containing mutually *trans* bis(triphenylphosphine) ligands [16]. Elemental analyses were obtained from the Microanalytical Laboratory, University of Otago.

### 4.2. Preparation of $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})(\text{PPh}_3)_2$ (**1**)

$\text{MeLi}$  (3.5 mL of a  $1.28\text{ mol L}^{-1}$  in  $\text{Et}_2\text{O}$ , 4.5 mmol) was added dropwise, at  $0^\circ\text{C}$ , to a yellow-orange solution of  $\text{Os}(\text{SiCl}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (0.821 g, 0.9 mmol) in toluene (45 mL). During the addition the colour of the reaction mixture changed from orange to red, and then to colourless, with the formation of a white precipitate. (This white solid is tentatively formulated as  $\text{Li}[\text{Os}(\text{SiMe}_3)(\text{Me})_2(\text{CO})(\text{PPh}_3)_2]$  and an IR spectrum recorded as a Nujol mull shows  $\nu(\text{CO})$  at  $1754\text{ cm}^{-1}$ ).  $\text{EtOH}$  (1 mL) was added to the colourless suspension and the mixture was stirred at room temperature for 0.5 h to give eventually a clear red solution. The resulting solution was concentrated to half volume, and passed down a short (5 cm) silica gel column under nitrogen using toluene as eluent. The eluent was concentrated to 2 mL and  $\text{EtOH}$  (10 mL) was added and after standing for half an hour a red crystalline solid formed. This was collected and washed with  $\text{EtOH}$  and hexane to give pure **1** (0.530 g, 71%). Anal. Calc. for  $\text{C}_{41}\text{H}_{42}\text{OOSiP}_2$ : C, 59.26; H, 5.09. Found: C, 59.46; H, 5.25%. IR ( $\text{cm}^{-1}$ ): 1893s, 1867s (1879s in  $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{CO})$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 0.01 (s, 9H,  $\text{SiMe}_3$ ), 0.12 (t, 3H,  $^3J_{\text{PH}} = 8.7\text{ Hz}$ ,  $\text{OsMe}$ ), 7.32–7.52 (m, 30H,  $\text{PPh}_3$ ).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 0.51 (s, 9H,  $\text{SiMe}_3$ ), 0.69 (t, 3H,

$^3J_{\text{PH}} = 8.6\text{ Hz}$ ,  $\text{OsMe}$ ) 7.02–7.75 (m, 30H,  $\text{PPh}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 9.6 (s,  $\text{SiMe}_3$ ), 21.1 (t,  $^2J_{\text{PC}} = 9.6\text{ Hz}$ ,  $\text{OsMe}$ ), 128.0 (t',  $^{2,4}J_{\text{PC}} = 8.6\text{ Hz}$ , *o-Ph*), 129.8 (s, *p-Ph*), 133.7 (t',  $^{1,3}J_{\text{PC}} = 46.6\text{ Hz}$ , *i-Ph*), 134.4 (t',  $^{3,5}J_{\text{PC}} = 10.4\text{ Hz}$ , *m-Ph*), 194.1 (t,  $^2J_{\text{PC}} = 8.2\text{ Hz}$ , C O).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 10.4 (s,  $\text{SiMe}_3$ ), 22.1 (t,  $^2J_{\text{PC}} = 9.5\text{ Hz}$ ,  $\text{OsMe}$ ), *o-Ph* obscured by solvent peaks, 130.0 (s, *p-Ph*), 134.4 (t',  $^{1,3}J_{\text{PC}} = 46.8\text{ Hz}$ , *i-Ph*), 134.8 (t',  $^{3,5}J_{\text{PC}} = 11.4\text{ Hz}$ , *m-Ph*), 194.4 (t,  $^2J_{\text{PC}} = 7.0\text{ Hz}$ , C O).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 29.19 (s).  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 29.59 (s).

### 4.3. Preparation of $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})_2(\text{PPh}_3)_2$ (**2**)

$\text{CO}$  gas was bubbled through a red solution of  $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})(\text{PPh}_3)_2$  (**1**) (0.166 g, 0.2 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) whereupon the solution immediately became colourless.  $\text{EtOH}$  (10 mL) was added and the mixture concentrated to effect the precipitation of pure **2** as a colourless crystalline solid (0.164 g, 95%). An alternative procedure involved preparing compound **1** in situ by adding five equivalents of  $\text{MeLi}$  to  $\text{Os}(\text{SiCl}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$  followed by addition of ethanol and carbonylation. Details of this procedure are as follows:  $\text{MeLi}$  (3.75 mL of a  $1.28\text{ mol L}^{-1}$  solution, 4.8 mmol) was added dropwise at  $0^\circ\text{C}$  to a yellow-orange solution of  $\text{OsCl}(\text{SiCl}_3)(\text{CO})(\text{PPh}_3)_2$  (0.730 g, 0.8 mmol) in toluene (20 mL). The colour of the reaction mixture changed from orange to red and then to colourless with formation of a colourless solid.  $\text{EtOH}$  (1 mL) was added to this mixture and stirring continued for 30 min at room temperature to give a red clear solution.  $\text{CO}$  gas (1 atm.) was then introduced to give immediately a colourless solution. All volatiles were removed under reduced pressure and the residue dissolved in  $\text{CH}_2\text{Cl}_2$  and filtered through a thin layer of Celite. The filtrate was concentrated and  $\text{EtOH}$  was added. Further concentration yielded pure **2** as a colourless crystalline solid, which was collected, washed with  $\text{EtOH}$  and hexane and dried in vacuo (0.667 g, 97%). Anal. Calc. for  $\text{C}_{42}\text{H}_{42}\text{O}_2\text{OsP}_2\text{Si}$ : C, 58.72; H, 4.93. Found: C, 58.64; H, 4.88%. IR ( $\text{cm}^{-1}$ ): 1992s, 1927m, 1896s (1985s, 1910s in  $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{CO})$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ):  $-0.96$  (t, 3H,  $^3J_{\text{PH}} = 7.2\text{ Hz}$ ,  $\text{OsMe}$ ),  $-0.12$  (s, 9H,  $\text{SiMe}_3$ ), 7.35–7.65 (m, 30H,  $\text{PPh}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ):  $-19.8$  (t,  $^2J_{\text{PC}} = 6.6\text{ Hz}$ ,  $\text{OsMe}$ ), 5.5 (t,  $^3J_{\text{PC}} = 1.8\text{ Hz}$ ,  $\text{SiMe}_3$ ), 127.8 (t',  $^{2,4}J_{\text{PC}} = 9.8\text{ Hz}$ , *o-Ph*), 129.8 (s, *p-Ph*), 134.0 (t',  $^{3,5}J_{\text{PC}} = 10.8\text{ Hz}$ , *m-Ph*), 134.6 (t',  $^{1,3}J_{\text{PC}} = 50.6\text{ Hz}$ , *i-Ph*), 183.0 (t,  $^2J_{\text{PC}} = 11.0\text{ Hz}$ , C O), 188.9 (t,  $^2J_{\text{PC}} = 9.0\text{ Hz}$ , C O).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 4.34 (s).

### 4.4. Preparation of $\text{Os}(\text{SiMe}_3)(p\text{-tolyl})(\text{CO})(\text{PPh}_3)_2$ (**3**)

$p\text{-TolLi}$  (0.50 mL of  $0.77\text{ mol L}^{-1}$  in  $\text{Et}_2\text{O}$ , 0.4 mmol) was added dropwise at room temperature to a deep red

solution of  $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})(\text{PPh}_3)_2$  (**1**) (0.166 g, 0.20 mmol) in toluene (10 mL) to produce an almost colourless solution. After the mixture had been stirred for 30 min EtOH (1 mL) was added slowly to give a deep red solution. All volatiles were removed under reduced pressure and the red residue dissolved in  $\text{CH}_2\text{Cl}_2$  and filtered through a thin layer of silica gel (5 cm) under nitrogen. The volume of the red filtrate was reduced in vacuo to ca. 5 mL before EtOH (5 mL) was added. Further concentration yielded pure **3** as a red crystalline solid, which was collected and washed with EtOH and hexane (0.143 g, 79%). Anal. Calc. for  $\text{C}_{47}\text{H}_{46}\text{OOSiP}_2$ : C, 62.23; H, 5.11. Found: C, 62.12; H, 5.09%. IR ( $\text{cm}^{-1}$ ): 1900s  $\nu(\text{CO})$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 0.20 (s, 9H,  $\text{SiMe}_3$ ), 2.22 (s, 3H,  $p$ -Me  $\text{C}_6\text{H}_4$ ), 6.59–7.35 (m, 34H,  $p$ -Me  $\text{C}_6\text{H}_4$  and  $\text{PPh}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 9.2 (t,  $^3J_{\text{CP}} = 1.9$  Hz,  $\text{SiMe}_3$ ), 21.0 (s,  $p$ -Me  $\text{C}_6\text{H}_4$ ), 125.3 (s,  $p$ -Me  $\text{C}_6\text{H}_4$ ), 127.8 (br,  $o$ - $\text{PPh}_3$ ), 128.2 (s,  $p$ -Me  $\text{C}_6\text{H}_4$ ), 129.0 (s,  $p$ -Me  $\text{C}_6\text{H}_4$ ), 129.6 (br,  $p$ - $\text{PPh}_3$ ), 131.0 (s,  $p$ -Me  $\text{C}_6\text{H}_4$ ), 133.5 (br,  $i$ - $\text{PPh}_3$ ), 134.6 (br,  $m$ - $\text{PPh}_3$ ), 137.9 (s,  $p$ -Me  $\text{C}_6\text{H}_4$ ), 174.0 (t,  $^2J_{\text{PC}} = 12.9$  Hz, Os– $\text{C}_6\text{H}_4\text{Me}$ -4), 194.6 (t,  $^2J_{\text{PC}} = 8.6$  Hz, CO).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 22.31 (s).

#### 4.5. Preparation of $\text{Os}(\text{SiMe}_3)(p\text{-tolyl})(\text{CO})_2(\text{PPh}_3)_2$ (**4**)

$p$ -TolLi (0.50 mL of a 0.77 mol  $\text{L}^{-1}$  solution in  $\text{Et}_2\text{O}$ , 0.4 mmol), at room temperature, was added dropwise to a deep red solution of  $\text{Os}(\text{SiMe}_3)\text{Me}(\text{CO})(\text{PPh}_3)_2$  (0.166 g, 0.20 mmol) in toluene (10 mL) to produce an almost colourless solution. After the mixture was stirred for half an hour, EtOH (1 mL) was added slowly to give a deep red solution. Introduction of CO gas at atmospheric pressure into the reaction solution resulted immediately in a colourless solution. All the volatiles were removed under reduced pressure and the residue dissolved in a minimum volume of  $\text{CH}_2\text{Cl}_2$ . This solution was then subjected to flash column chromatography on a silica gel support using as eluent  $\text{CH}_2\text{Cl}_2/n$ -hexane ( $v/v = 1:3$ ). The main colourless band from the column was collected and the solvent removed under reduced pressure. Recrystallisation of the resulting solid using  $\text{CH}_2\text{Cl}_2/n$ -heptane yielded pure **4** as a colourless crystalline solid (0.156 g, 83%). Anal. Calc. for  $\text{C}_{48}\text{H}_{46}\text{O}_2\text{OsP}_2\text{Si}$ : C, 61.65; H, 4.96. Found: C, 61.87; H, 5.00%. IR ( $\text{cm}^{-1}$ ): 2002, 1925  $\nu(\text{CO})$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): –0.04 (s, 9H,  $\text{SiMe}_3$ ), 2.13 (s, 3H,  $p$ -Me  $\text{C}_6\text{H}_4$ ), 6.23 (m, 2H,  $p$ -Me  $\text{C}_6\text{H}_4$ ), 6.98 (m, 2H,  $p$ -Me  $\text{C}_6\text{H}_4$ ), 7.14–7.29 (m, 30H,  $2\text{PPh}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 7.6 (s,  $\text{SiMe}_3$ ), 20.7 (s,  $p$ -Me  $\text{C}_6\text{H}_4$ ), 127.3 (t',  $^{2,4}J_{\text{PC}} = 9.7$  Hz,  $o$ -Ph), 127.8 (s,  $p$ -Me  $\text{C}_6\text{H}_4$ ), 129.4 (s,  $p$ -Ph), 134.4 (t',  $^{3,5}J_{\text{PC}} = 10.3$  Hz,  $m$ -Ph), 134.5 (t',  $^{1,3}J_{\text{PC}} = 50.8$  Hz,  $i$ -Ph), 136.2 (t,  $^2J_{\text{PC}} = 11.9$  Hz, Os– $\text{C}_6\text{H}_4\text{Me}$ -4), 147.0 (s,  $p$ -Me  $\text{C}_6\text{H}_4$ ), 181.0 (t,  $^2J_{\text{PC}} = 9.1$  Hz, CO), 188.4 (t,  $^2J_{\text{PC}} = 7.7$  Hz, CO).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): –4.16 (s).

#### 4.6. Thermal reaction of $\text{Os}(\text{SiMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$

A mixture of  $\text{Os}(\text{SiMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (0.082 g, 0.1 mmol),  $\text{PPh}_3$  (0.079 g, 0.3 mmol) was heated under nitrogen at 160–200 °C for 2–4 h, during which time the red oil became almost colourless. After cooling, the resulting mixture was re-dissolved in a minimum of  $\text{CH}_2\text{Cl}_2$  and subjected to preparative thin-layer chromatography on silica gel using  $\text{CH}_2\text{Cl}_2$ /hexane ( $v/v = 1:1$ ) as eluent. From the first and second major colourless bands were obtained  $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$  (ca. 50%) and  $\text{Os}(\kappa^2(\text{C},\text{P})\text{-C}_6\text{H}_4\text{PPh}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (ca. 40%), respectively. Both compounds were identified by comparison with reported IR and NMR spectral data ( $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$  [17];  $\text{Os}(\kappa^2(\text{C},\text{P})\text{-C}_6\text{H}_4\text{PPh}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2$  [9]).

#### 4.7. Preparation of $\text{Os}(\kappa^2(\text{Si},\text{P})\text{-SiMe}_2\text{C}_6\text{H}_4\text{PPh}_2)(\kappa^2(\text{C},\text{P})\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)_2$ (**5**)

A mixture of  $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})(\text{PPh}_3)_2$  (**1**) (0.050 g, 0.06 mmol),  $\text{PPh}_3$  (0.032 g, 0.12 mmol) and toluene (10 mL) was heated under reflux for 1 h during which time the red solution became almost colourless. The solvent was removed under reduced pressure and the resulting residue re-dissolved in a minimum of  $\text{CH}_2\text{Cl}_2$  and subjected to preparative thin-layer chromatography on silica gel using  $\text{CH}_2\text{Cl}_2$  and hexane ( $v/v = 1:2$ ) as eluent. The fastest moving band is  $\text{PPh}_3$ . From the second, colourless band, after recrystallisation from  $\text{CH}_2\text{Cl}_2$  and hexane, pure **5** was obtained as a colourless crystalline solid (0.032 g, 50%). (From a third band was obtained another colourless product, compound **6**, see below). Anal. Calc. for  $\text{C}_{57}\text{H}_{49}\text{OOSiP}_3$ · $0.5(\text{C}_6\text{H}_{14})$ : C, 65.26; H, 5.11. Found: C, 65.17; H, 5.12 (the hexane of solvation was seen in both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra). The single crystal for X-ray structural analysis was grown from a different solvent combination ( $\text{CH}_2\text{Cl}_2$  and ethanol) over several days and proved to solvated with two molecules of water (see Section 4.10). IR ( $\text{cm}^{-1}$ ): 1906 (s)  $\nu(\text{CO})$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): –1.12 (s, 3H,  $\text{SiMe}$ ), 0.12 (s, 3H,  $\text{SiMe}$ ), 5.65–8.34 (m, 43H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): –2.3 (s,  $\text{SiMe}$ ), 5.2 (br,  $\text{SiMe}$ ), 121.0–157.9 (m, aromatic carbons), 192.6 (m, CO).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): [Note: the phosphorus atom labels are given in Scheme 4] 29.26 (dd,  $^2J_{\text{P(a)}-\text{P(c)}} = 222.5$  Hz,  $^2J_{\text{P(a)}-\text{P(b)}} = 16.1$  Hz,  $\text{P(a)}$ ), –6.11 (dd,  $^2J_{\text{P(a)}-\text{P(b)}} = 16.1$  Hz,  $^2J_{\text{P(b)}-\text{P(c)}} = 20.5$  Hz,  $\text{P(b)}$ ), –62.46 (dd,  $^2J_{\text{P(a)}-\text{P(c)}} = 222.5$  Hz,  $^2J_{\text{P(b)}-\text{P(c)}} = 20.5$  Hz,  $\text{P(c)}$ ).

#### 4.8. Preparation of $\text{Os}(\kappa^2(\text{C},\text{P})\text{-C}_6\text{H}_4\text{PPh}_2)_2(\text{CO})(\text{PPh}_3)$ (**6**)

From the thermal reaction between  $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})(\text{PPh}_3)_2$  and  $\text{PPh}_3$  in toluene described in detail

above (Section 4.6), the third colourless band obtained from the preparative thin-layer chromatography procedure was collected. This solid was recrystallised from  $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_5\text{OH}$  to give pure **6** in low and variable yield from repeated experiments (ca. 25%). Anal. Calc. for  $\text{C}_{55}\text{H}_{43}\text{OOSiP}_3$ : C, 65.86; H, 4.32. Found: C, 65.20; H, 4.67%. The single crystal for X-ray structure determination was grown from  $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$  and proved to be a 0.5 hexane solvate (see Section 4.10). IR ( $\text{cm}^{-1}$ ): 1888  $\nu(\text{CO})$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 5.87–7.40 (m, 43H, aromatic hydrogens).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 121.2–160.1 (m, aromatic carbons), 195.5 (m, CO).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): [Note: the phosphorus atom labels are given in Scheme 4] 15.16 (dd,  $^2J_{\text{P(a)}-\text{P(c)}} = 256.1$  Hz,  $^2J_{\text{P(a)}-\text{P(b)}} = 8.1$  Hz,  $P(a)$ ),  $-72.81$  (dd,  $^2J_{\text{P(a)}-\text{P(b)}} = 8.5$  Hz,  $^2J_{\text{P(b)}-\text{P(c)}} = 16.8$  Hz,  $P(b)$ ),  $-68.78$  (dd,  $^2J_{\text{P(a)}-\text{P(c)}} = 256.4$  Hz,  $^2J_{\text{P(b)}-\text{P(c)}} = 17.1$  Hz,  $P(c)$ ).

#### 4.9. Preparation of $\text{Os}(\kappa^2(\text{Si,P})\text{-SiMe}_2\text{C}_6\text{H}_4\text{PPh}_2)(\kappa^2(\text{C,P})\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})[\text{P}(\text{NC}_4\text{H}_4)_3]$ (**7**)

A mixture of  $\text{Os}(\kappa^2(\text{Si,P})\text{-SiMe}_2\text{C}_6\text{H}_4\text{PPh}_2)(\kappa^2(\text{C,P})\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$  (**5**) (0.053 g, 0.05 mmol),  $\text{P}(\text{NC}_4\text{H}_4)_3$  (0.013 g, 0.055 mmol) and benzene (10 mL) was heated under reflux for 1 h. The solvent was removed under reduced pressure and the resulting residue was recrystallised from  $\text{CH}_2\text{Cl}_2$  and hexane to give pure **7** as a colourless crystalline solid (0.045 g, 88%). Compound **7** was also detected by  $^{31}\text{P}$  NMR spectroscopy in mixtures obtained from the thermal reaction of  $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})(\text{PPh}_3)_2$  (**1**) and  $\text{P}(\text{NC}_4\text{H}_4)_3$  but a pure sample could not be extracted by this procedure. Anal. Calc. for  $\text{C}_{51}\text{H}_{46}\text{N}_3\text{OOSiP}_3\text{Si} \cdot 0.25\text{C}_6\text{H}_{14}$ : C, 60.07; H, 4.75; N, 4.00. Found: C, 60.21; H, 4.73; N, 4.10%.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the analytical sample confirmed the presence of hexane. The single crystal for X-ray structure determination was grown from  $\text{CH}_2\text{Cl}_2$  and hexane over a period of one week and the crystal did not contain solvent (see Table 1). IR ( $\text{cm}^{-1}$ ): 1941  $\nu(\text{CO})$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ):  $-1.15$  (s, 3H,  $\text{SiMe}$ ),  $0.13$  (d,  $^4J_{\text{PH}} = 2.3$  Hz, 3H,  $\text{SiMe}$ ),  $5.85$ – $8.23$  (m, 40H,  $\text{Ph}$  and  $\text{NC}_4\text{H}_4$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ):  $-2.3$  (m,  $\text{SiMe}$ ),  $5.3$  (d,  $^3J_{\text{PC}} = 6.7$  Hz,  $\text{SiMe}$ ),  $111.0$ – $156.8$  (m, aromatic carbons),  $190.1$  (m, CO).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): [Note: the phosphorus atom labels are given in Scheme 4]  $28.53$  (dd,  $^2J_{\text{P(a)}-\text{P(c)}} = 208.8$  Hz,  $^2J_{\text{P(a)}-\text{P(b)}} = 20.2$  Hz,  $P(a)$ ),  $70.15$  (dd,  $^2J_{\text{P(a)}-\text{P(b)}} = 20.2$  Hz,  $^2J_{\text{P(b)}-\text{P(c)}} = 25.4$  Hz,  $P(b)$ ),  $-64.68$  (dd,  $^2J_{\text{P(a)}-\text{P(c)}} = 208.8$  Hz,  $^2J_{\text{P(b)}-\text{P(c)}} = 25.4$  Hz,  $P(c)$ ).

#### 4.10. Preparation of $\text{Os}(\text{SiMe}_3)(\kappa^2(\text{C,P})\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})_2(\text{PPh}_3)$ (**8**)

$\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})_2(\text{PPh}_3)_2$  (**2**) (0.687 g, 0.80 mmol) in toluene (30 mL) was heated under reflux for 1 h, during which time the colour of the solution changed from

colourless to red and then to almost colourless. The solvent was removed under reduced pressure and the resulting residue was dissolved in a minimum of  $\text{CH}_2\text{Cl}_2$  and purified by preparative thin-layer chromatography on silica gel using  $\text{CH}_2\text{Cl}_2$  and hexane ( $v/v = 1:2$ ) as eluent. The second colourless band was collected and from this was obtained after recrystallisation from  $\text{CH}_2\text{Cl}_2/\text{EtOH}$  pure **8** as a colourless crystalline solid (0.190 g, 28%). A single crystal for X-ray crystal structure determination was grown from  $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ . Anal. Calc. for  $\text{C}_{41}\text{H}_{38}\text{O}_2\text{OsP}_2\text{Si}$ : C, 58.42; H, 4.54. Found: C, 58.34; H, 4.49%. IR ( $\text{cm}^{-1}$ ): 2001s, 1933s  $\nu(\text{CO})$ , 843m ( $\text{SiMe}_3$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ):  $-0.20$  (apparent d,  $^4J_{\text{P(trans)H}} = 1.2$  Hz, 9H,  $\text{SiMe}_3$ ),  $6.50$ – $7.85$  (m, 29H, aromatic protons).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ):  $4.8$  (m,  $\text{SiMe}_3$ ),  $121.6$ – $150.7$  (m, aromatic carbons),  $186.6$  (dd,  $^2J_{\text{P(trans)C}} = 77.0$  Hz,  $^2J_{\text{P(cis)C}} = 5.6$  Hz, CO(*trans* to phosphorus of *ortho*-metallated phosphine)),  $189.4$  (dd,  $^2J_{\text{P(cis)C}} = 8.2$  Hz, and  $^2J_{\text{P(cis)C}} = 5.7$  Hz, CO(*cis* to both phosphorus atoms)).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ):  $-77.10$  (d,  $^2J_{\text{PP}} = 27.5$  Hz, phosphorus of *ortho*-metallated phosphine),  $-3.38$  (d,  $^2J_{\text{PP}} = 27.5$  Hz,  $\text{PPh}_3$ ).

From the chromatography procedure detailed above the third colourless band was collected and yielded, after recrystallisation from  $\text{CH}_2\text{Cl}_2/\text{EtOH}$ , pure  $\text{Os}(\kappa^2(\text{C,P})\text{-C}_6\text{H}_4\text{PPh}_2)\text{H}(\text{CO})_2(\text{PPh}_3)$  as a colourless crystalline solid (0.061 g, 10%) which was identified by comparison of spectroscopic data reported for an authentic sample [14,15].

#### 4.11. X-ray crystal structure determinations for complexes **5**, **6**, **7**, and **8**.

X-ray data collections were by a Siemens SMART diffractometer with a CCD area detector using graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) at 84 K for **5** and **6**, 150 K for **7** and **8**. Data were integrated and corrected for Lorentz and polarisation effects using SAINT [18]. Semi-empirical absorption corrections were applied based on equivalent reflections using SADABS [19]. The structures were solved by Patterson or direct methods and refined by full-matrix least-squares on  $F^2$  using programs SHELXS [20] and SHELXL [21]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located geometrically and refined using a riding model. Compound **5** contains two molecules of water of crystallization with an  $\text{O}(2) \cdots \text{O}(3)$  separation of 2.724 Å. There are no other H-bonding contacts in the crystal structure. Compound **6** contains 0.5 molecules of hexane of crystallization, for which five carbon atoms were refined isotropically with no hydrogen atoms included, but the sixth carbon could not be reliably located. Crystal data and refinement details for all four structures 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. 2632126–263129 for **5**, **6**, **7** and **8**, 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>).

## Acknowledgements

We thank the Marsden Fund, administered by the Royal Society of New Zealand, for granting a Post Doctoral Fellowship to G.-L.L. We also thank The University of Auckland Research Committee for partial support of this work through grants-in-aid. Dr. D.M. Salter is thanked for providing some data for complex **5**.

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