

# Metallacyclic complexes with *ortho*-stannylated triphenylphosphine ligands, $L_n\text{Os}(\kappa^2(\text{Sn},P)\text{-SnMe}_2\text{C}_6\text{H}_4\text{PPh}_2)$ , derived from thermal reactions of the five-coordinate complex, $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$

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Received 10 March 2005; accepted 24 May 2005

## Abstract

Heating the five-coordinate trimethylstannyl complex,  $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ , in solution with triphenylphosphine induces an *ortho*-stannylation of one phenyl group of a triphenylphosphine ligand and an *ortho*-metallation of another triphenylphosphine ligand, to produce the metallacyclic complexes,  $\text{Os}(\kappa^2(\text{Sn},P)\text{-SnMe}_2\text{C}_6\text{H}_4\text{PPh}_2)(\kappa^2(C,P)\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$  (**1**) and  $\text{Os}(\kappa^2(\text{Sn},P)\text{-SnMe}_2\text{C}_6\text{H}_4\text{PPh}_2)(\kappa^2(C,P)\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$  (**2**), suggesting the possible intermediacy of a complex with a coordinated stannylene ligand. Spectroscopic data indicate that only one diastereomer of **1** is formed and crystal structure determination of **1** reveals that this is the diastereomer with chloride directed towards the CO ligand. Complex **2** is converted to **1** through a redistribution reaction with  $\text{SnMe}_2\text{Cl}_2$ . Heating the six-coordinate trimethylstannyl complex,  $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ , in solution produces the osmium(II) methyl complex,  $\text{Os}(\text{Me})(\text{SnMe}_2\text{Cl})(\text{CO})_2(\text{PPh}_3)_2$  (**3**), through an exchange of methyl and chloride groups on the tin and osmium. In this rearrangement, the relative locations of the two CO ligands and the two  $\text{PPh}_3$  ligands remains unchanged. However, when the six-coordinate trimethylstannyl complex,  $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$  is heated under CO, the same exchange reaction is observed but the mono-triphenylphosphine, tricarbonyl complex,  $\text{Os}(\text{Me})(\text{SnMe}_2\text{Cl})(\text{CO})_3(\text{PPh}_3)$  (**4**), is produced and here the  $\text{SnMe}_2\text{Cl}$  ligand is located *trans* to the  $\text{PPh}_3$  ligand. Crystal structure determinations for **1**, **2**, **3**, and **4** have been obtained.

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**Keywords:** Metallacyclic complex; *ortho*-Stannylation; Osmium; Stannyl complexes; X-ray crystal structure

## 1. Introduction

We have recently reported that the coordinatively unsaturated trimethylsilyl, methyl complex of osmium,  $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})(\text{PPh}_3)_2$ , when heated in the presence of triphenylphosphine, gives as the major product the *ortho*-silylated triphenylphosphine complex (which also contains an *ortho*-metallated triphenylphosphine ligand),

$\text{Os}(\kappa^2(\text{Si},P)\text{-SiMe}_2\text{C}_6\text{H}_4\text{PPh}_2)(\kappa^2(C,P)\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$  [**1**]. The nature of this product suggests that it was formed by electrophilic attack of a dimethylsilylene ligand (in an intermediate complex) at the *ortho* position of a phenyl ring of a resident triphenylphosphine ligand. Since we have previously observed that the related coordinatively unsaturated trimethylstannyl complex,  $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ , undergoes reactions in which a methyl moves to osmium accompanied by chloride moving to tin [**2**], we thought it worthwhile to explore thermal reactions of  $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$  in the expectation of perhaps seeing stannylene ligand attack at the phenyl

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ring of a triphenylphosphine, so generating the  $\kappa^2(\text{Sn},P)$ - $\text{SnMe}_2\text{C}_6\text{H}_4\text{PPh}_2$  ligand.

We describe herein: (i) the thermal reaction of the five-coordinate trimethylstannyl complex,  $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ , in the presence of triphenylphosphine to give a mixture of  $\text{Os}(\kappa^2(\text{Sn},P)\text{-SnMeClC}_6\text{H}_4\text{PPh}_2)(\kappa^2(\text{C},P)\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$  (**1**) and  $\text{Os}(\kappa^2(\text{Sn},P)\text{-SnMe}_2\text{C}_6\text{H}_4\text{PPh}_2)(\kappa^2(\text{C},P)\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$  (**2**) both containing an *ortho*-stannylated triphenylphosphine ligand and an *ortho*-metallated triphenylphosphine ligand; (ii) the conversion of **2** to **1** through reaction with  $\text{SnMe}_2\text{Cl}_2$ ; (iii) the thermal reaction of the six-coordinate trimethylstannyl complex,  $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ , to give the rearranged osmium methyl complex,  $\text{Os}(\text{Me})(\text{SnMe}_2\text{Cl})(\text{CO})_2(\text{PPh}_3)_2$  (**3**); (iv) the thermal reaction of the six-coordinate trimethylstannyl complex,  $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ , in the presence of CO to give  $\text{Os}(\text{Me})(\text{SnMe}_2\text{Cl})(\text{CO})_3(\text{PPh}_3)$  (**4**) and (v) the crystal structures of **1–4**.

## 2. Results and discussion

**2.1. The thermal reaction of  $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$  in the presence of triphenylphosphine to produce a mixture of  $\text{Os}(\kappa^2(\text{Sn},P)\text{-SnMeClC}_6\text{H}_4\text{PPh}_2)(\kappa^2(\text{C},P)\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$  (**1**) and  $\text{Os}(\kappa^2(\text{Sn},P)\text{-SnMe}_2\text{C}_6\text{H}_4\text{PPh}_2)(\kappa^2(\text{C},P)\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$  (**2**) and the structures of **1** and **2****

When the red complex  $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$  is heated with triphenylphosphine in toluene under reflux the red colour fades and after chromatography the major product obtained is the colourless complex,  $\text{Os}(\kappa^2(\text{Sn},P)\text{-SnMeClC}_6\text{H}_4\text{PPh}_2)(\kappa^2(\text{C},P)\text{-C}_6\text{H}_4\text{PPh}_2)$ -

$(\text{CO})(\text{PPh}_3)$  (**1**), and the minor product is the closely related colourless complex,  $\text{Os}(\kappa^2(\text{Sn},P)\text{-SnMe}_2\text{C}_6\text{H}_4\text{PPh}_2)(\kappa^2(\text{C},P)\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$  (**2**) (see Scheme 1). Complex **2** is smoothly converted into complex **1** through treatment with  $\text{SnMe}_2\text{Cl}_2$  [3]. Both these complexes contain an *ortho*-stannylated triphenylphosphine ligand in which the Os–Sn bond is retained. This ligand has been previously identified in the product isolated from reaction between the osmastannol,  $\text{Os}(\text{SnMe}_2\text{OH})(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$  and  $t\text{BuLi}$  [3]. In addition, complexes **1** and **2** incorporate an *ortho*-metallated triphenylphosphine ligand. As mentioned in Section 1, the silicon analogue of complex **2** is formed when the trimethylsilyl, methyl complex,  $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})(\text{PPh}_3)_2$  is heated in the presence of triphenylphosphine [1]. The formation of complexes **1** and **2** could be envisaged as arising from electrophilic attack by a stannylene ligand at the phenyl ring of a coordinated triphenylphosphine. There are examples of both carbene and silylene electrophilic attack at the phenyl ring of a coordinated triphenylphosphine to form closely related 5-membered ring systems as depicted in Chart 2, the examples given coming from Refs. [4,5]. A coordinated stannylene complex such as A in Chart 1 could be formed as a transient species by methyl migration

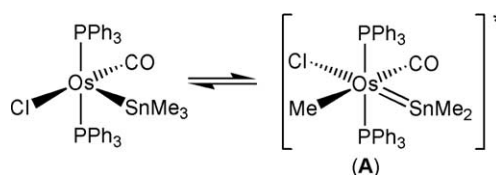
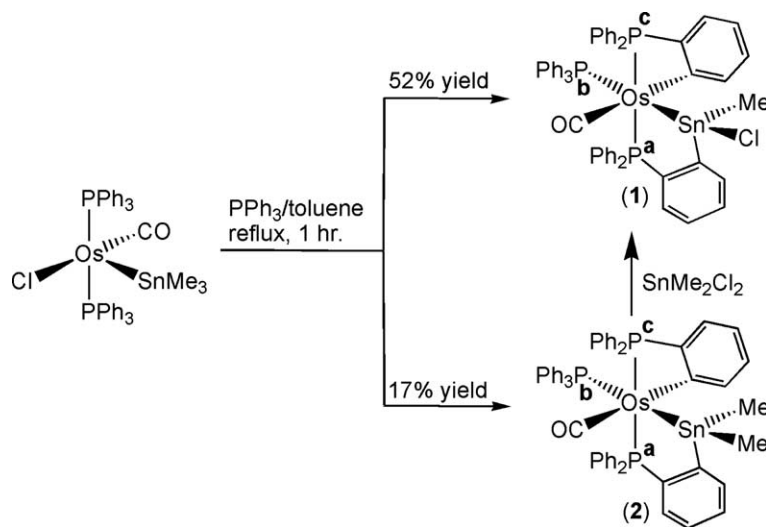


Chart 1. Possible equilibrium of a coordinatively unsaturated trimethylstannyl complex with a saturated methyl, “dimethylstannylene” complex via methyl migration.



Scheme 1. Syntheses of  $\text{Os}(\kappa^2(\text{Sn},P)\text{-SnMeClC}_6\text{H}_4\text{PPh}_2)(\kappa^2(\text{C},P)\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$  (**1**) and  $\text{Os}(\kappa^2(\text{Sn},P)\text{-SnMe}_2\text{C}_6\text{H}_4\text{PPh}_2)(\kappa^2(\text{C},P)\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$  (**2**) (Phosphorus atoms labeled for NMR discussion).

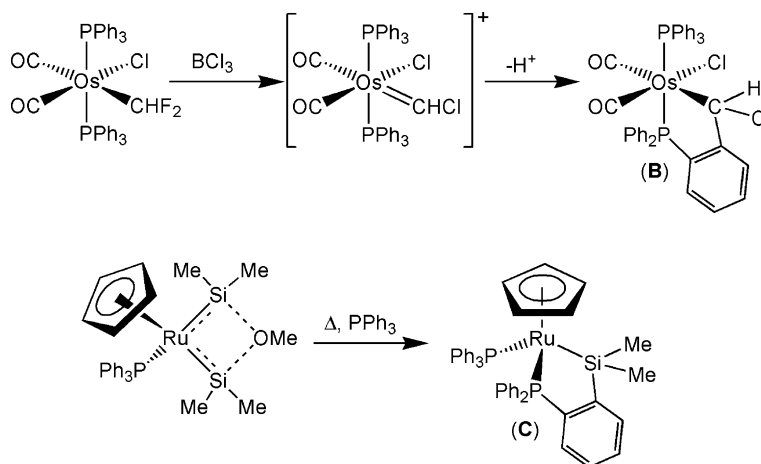


Chart 2. Examples of electrophilic carbene and silylene ligands attacking the *ortho*-position of a phenyl ring in a PPh<sub>3</sub> ligand.

to osmium in the coordinatively unsaturated Os(SnMe<sub>3</sub>)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>. The Sn–Cl bond observed in complex **1** (the major product) may arise through an initial exchange of methyl and chloride between tin and osmium [2] to form Os(SnMe<sub>2</sub>Cl)(Me)(CO)(PPh<sub>3</sub>)<sub>2</sub> which could be the source of a methylchlorostannylene ligand. The mechanism of this reaction is clearly complex and further speculation is unwarranted. Nevertheless, the overall conversion to complex **1** plus complex **2** is quite high in yield (69%) and no other products were formed in isolable amounts. There is also a literature precedent for an isolated stannylene complex of palladium, Pd(SnR<sub>2</sub>)L<sub>2</sub> in which the Sn centre behaves as an electrophile towards ethyne in the formation of a palladastannete complex. This complex is involved in the catalytic formation of a stannole [6,7]. Furthermore, the electrophilicity of the Sn centre in Pd(SnR<sub>2</sub>)L<sub>2</sub> is revealed by the reaction with water and methanol to give PdH(SnR<sub>2</sub>OH)L<sub>2</sub> and PdH(SnR<sub>2</sub>OMe)L<sub>2</sub>, respectively [8].

Full spectroscopic data for the new compounds described in this paper are collected in Section 2. Selected data, deserving of special comment, are discussed in what follows. The IR spectrum of complex **1** shows  $\nu(\text{CO})$  at 1926 cm<sup>-1</sup>. In the <sup>1</sup>H NMR spectrum, the single methyl group resonance is observed at -0.81 ppm as a singlet with Sn satellites (<sup>2</sup>J<sub>Sn(119/117)H</sub> = 43.8 Hz). It is significant that only one methyl signal is observed indicating that only one diastereomer is present. This conclusion is further supported by the <sup>13</sup>C NMR spectrum (a singlet at -5.0 ppm) and also by the X-ray crystal structure determination described below. In the related complex containing the  $\kappa^2(\text{Sn}, P)\text{-SnMeClC}_6\text{H}_4\text{PPh}_2$  ligand, Os( $\kappa^2(\text{Sn}, P)\text{-SnMeClC}_6\text{H}_4\text{PPh}_2$ )( $\kappa^2\text{-S}_2\text{CNMe}_2$ )(CO)(PPh<sub>3</sub>), both diastereomers were present in the crystal [3]. Complex **1** has a very characteristic <sup>31</sup>P NMR spectrum showing three doublet of doublets signals, each with Sn satellites. The triphenylphosphine

ligand (P<sup>b</sup> see Scheme 1) is located *trans* to Sn and shows very large Sn–P coupling of 1157.1 Hz. The other phosphorus atoms which are both *cis* to Sn, (P<sup>a</sup> and P<sup>c</sup>) show much smaller coupling constants of 123.1 and 138.5 Hz, respectively. Since P<sup>a</sup> and P<sup>c</sup> are mutually *trans* the P<sup>a</sup>–P<sup>c</sup> coupling constant is 222.8 Hz, whereas P<sup>a</sup>–P<sup>b</sup> and P<sup>b</sup>–P<sup>c</sup> have much smaller values of 13.7 and 21.5 Hz, respectively. The chemical shift of the *ortho*-metallated triphenylphosphine ligand (P<sup>c</sup>) occurs at the characteristically high-field value of -66.57 ppm [1].

The IR spectrum of complex **2** shows  $\nu(\text{CO})$  at 1907 cm<sup>-1</sup> a value significantly lower than found for **1** as would be expected for replacement of the electronegative chloride group on tin by a methyl group. In the <sup>1</sup>H NMR spectrum, there are two methyl group resonances at -1.29 and -0.08 ppm both with Sn satellites (<sup>2</sup>J<sub>Sn(119/117)H</sub> = 43.8 and <sup>2</sup>J<sub>Sn(119/117)H</sub> = 39.8 Hz, respectively). Similarly, in the <sup>13</sup>C NMR spectrum there are two methyl group resonances at -12.7 and -7.7 ppm. The <sup>31</sup>P NMR spectrum of **2** shows the same overall pattern as observed for **1** with similar chemical shift values and will not be discussed in detail here (details are in Section 4.3).

The molecular geometries of **1** and **2** are depicted in Figs. 1 and 2. Crystal data pertaining to these structures and other structures reported in this paper are presented in Table 1. Selected bond lengths and angles for **1** and **2** are collected in Tables 2 and 3, respectively. The coordination sphere for both complexes is the same and the overall geometry about osmium for each compound can be described as octahedral with the three phosphorus donor atoms and the Sn all lying in one plane with the triphenylphosphine ligand *trans* to Sn. The greatest distortion from regular octahedral geometry is associated with the strain introduced by the the 4-membered ring of the *ortho*-metallated triphenylphosphine ligand (P(2)–Os–P(3)) is 161.20(2)°, whereas P(1)–Os–Sn is 176.10(2)°. The silicon analogue of compound **2** has

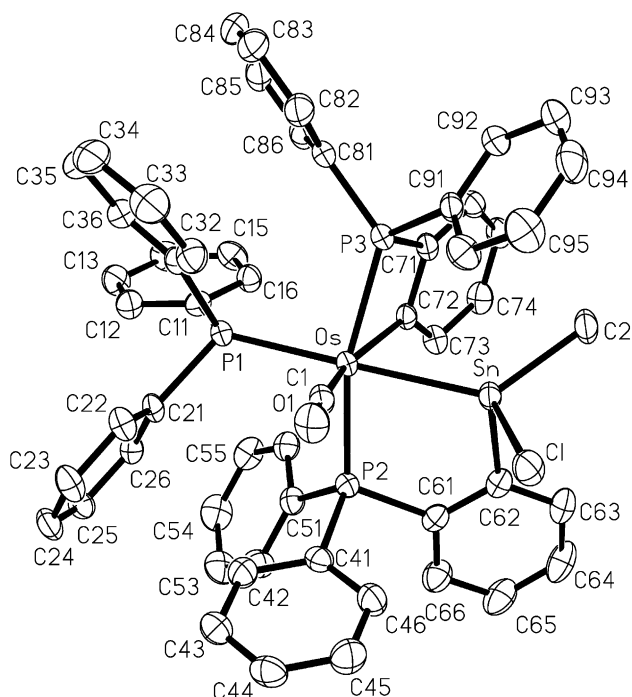


Fig. 1. Molecular geometry of  $\text{Os}(\kappa^2(\text{Sn},\text{P})\text{-SnMeClC}_6\text{H}_4\text{PPh}_2)(\kappa^2(\text{C},\text{P})\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$  (**1**).

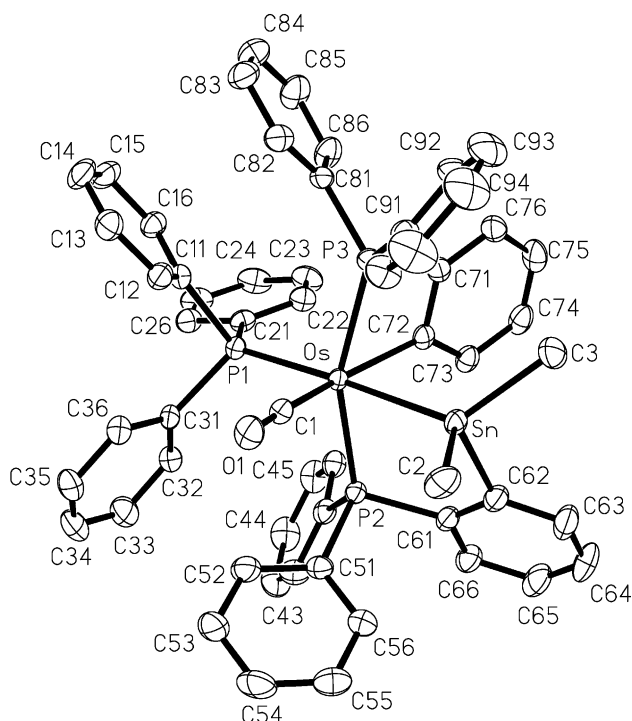


Fig. 2. Molecular geometry of  $\text{Os}(\kappa^2(\text{Sn},\text{P})\text{-SnMe}_2\text{C}_6\text{H}_4\text{PPh}_2)(\kappa^2(\text{C},\text{P})\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$  (**2**).

this same geometry [1,9]. As expected, the Os–Sn distance in **1** (2.6430(2) Å) is less than the Os–Sn distance in **2** (2.7074(3) Å), because of the electronegative chloride substituent on Sn in complex **1**. These Os–Sn

distances are similar to values found for related complexes e.g., in  $\text{Os}(\text{SnR}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$  the Os–Sn distances are 2.6616(13) (R<sub>3</sub> = Me<sub>3</sub>) [10]; 2.6260(9) (R<sub>3</sub> = I<sub>3</sub>) [10]; 2.6441(3) (R<sub>3</sub> = Me<sub>2</sub>Cl) [3]; 2.6065(3) Å (R<sub>3</sub> = MeBr<sub>2</sub>) [10]. The Sn–Cl distance is 2.4338(7) Å which is longer than the average of 2.396 Å (SD of 0.080 Å) for 791 recorded observations (Cambridge Crystallographic Data Base). In both complexes, the Os–P distances to the triphenylphosphine ligand *trans* to Sn (2.4088(7) for **1** and 2.4056(12) Å for **2**) are considerably longer than the mutually *trans* Os–P distances involving the *ortho*-stannylated (2.3790(7) for **1** and 2.3753(12) Å for **2**) and *ortho*-metallated triphenylphosphine ligands (2.3816(7) for **1** and 2.3787(12) Å for **2**). It can be noted that the shorter Os–Sn distance in **1** is associated with the longer Os–P distance to the *trans* triphenylphosphine ligand. The overall dimensions of the 4-membered ring associated with the *ortho*-metallated triphenylphosphine ligand are closely similar to those found in the silicon analogue of compound **2** [1].

**2.2. The thermal reactions of  $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$  to produce  $\text{Os}(\text{Me})(\text{SnMe}_2\text{Cl})(\text{CO})_2(\text{PPh}_3)_2$  (**3**) and, in the presence of CO,  $\text{Os}(\text{Me})(\text{SnMe}_2\text{Cl})(\text{CO})_3(\text{PPh}_3)$  (**4**) and the structures of **3** and **4****

To contrast the thermal reaction of the coordinatively unsaturated complex  $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ , with that of a coordinatively saturated analogue, we examined the thermal reactions of  $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ . This parallels the studies already completed with coordinatively unsaturated and coordinatively saturated trimethylsilyl complexes [1].

No *ortho*-stannylated triphenylphosphine-containing products were isolated from heating  $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$  under vigorous conditions (see Scheme 2). Rather, the compound containing methyl on osmium and chloride on tin,  $\text{Os}(\text{Me})(\text{SnMe}_2\text{Cl})(\text{CO})_2(\text{PPh}_3)_2$  (**3**) was formed in good yield. Exchange of a methyl group on tin for a chloride on osmium has been observed previously, under quite mild conditions, when pyridine coordinates to  $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$  to give  $\text{Os}(\text{SnMe}_2\text{Cl})(\text{Me})(\text{pyridine})(\text{CO})(\text{PPh}_3)_2$  [2]. Interestingly, when CO replaces pyridine in  $\text{Os}(\text{SnMe}_2\text{Cl})(\text{Me})(\text{pyridine})(\text{CO})(\text{PPh}_3)_2$  at room temperature, the methyl group returns to tin forming  $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$  [2]. The thermal reaction depicted in Scheme 2 implies that  $\text{Os}(\text{Me})(\text{SnMe}_2\text{Cl})(\text{CO})_2(\text{PPh}_3)_2$  is more stable thermodynamically than  $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ . If this is so, then when  $\text{Os}(\text{SnMe}_2\text{Cl})(\text{Me})(\text{pyridine})(\text{CO})(\text{PPh}_3)_2$  is carbonylated the methyl migration must precede the CO addition.

The IR spectrum of **3** shows  $\nu(\text{CO})$  at 2003, 1920 and 1906  $\text{cm}^{-1}$ . The appearance of three bands must be attributed to solid-state splitting. The crystal structure reported below and the two carbonyl signals observed

Table 1  
Data collection and processing parameters for **1**, **2**, **3**, and **4**

	<b>1</b>	<b>2</b> · CHCl <sub>3</sub>	<b>3</b>	<b>4</b>
Formula	C <sub>56</sub> H <sub>46</sub> ClO <sub>3</sub> OsP <sub>3</sub> Sn	C <sub>58</sub> H <sub>50</sub> Cl <sub>3</sub> O <sub>3</sub> OsP <sub>3</sub> Sn	C <sub>41</sub> H <sub>39</sub> ClO <sub>2</sub> OsP <sub>2</sub> Sn	C <sub>24</sub> H <sub>24</sub> ClO <sub>3</sub> OsP <sub>3</sub> Sn
Molecular weight	1172.18	1271.13	970.00	735.74
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/n</i>
<i>a</i> (Å)	12.0499(1)	12.6401(2)	10.8434(2)	10.1943(2)
<i>b</i> (Å)	20.1324(1)	25.5707(2)	28.0855(1)	22.7547(3)
<i>c</i> (Å)	19.8367(1)	18.1429(2)	12.6913(1)	11.2088(1)
$\alpha$ (°)				
$\beta$ (°)	101.347(1)	93.856(1)	101.309(1)	101.707(1)
$\gamma$ (°)				
<i>V</i> (Å <sup>3</sup> )	4718.19(5)	5850.80(12)	3789.99(8)	2546.00(6)
<i>Z</i>	4	4	4	4
<i>D</i> <sub>(calc)</sub> (g cm <sup>-3</sup> )	1.650	1.443	1.700	1.919
<i>F</i> (0 0 0)	2312	2512	1896	1400
$\mu$ (mm <sup>-1</sup> )	3.42	2.85	4.19	6.15
Crystal size (mm)	0.26 × 0.18 × 0.08	0.32 × 0.30 × 0.22	0.36 × 0.20 × 0.20	0.42 × 0.26 × 0.08
2 $\theta$ (min–max) (°)	1.8–26.1	1.4–26.0	1.5–25.7	1.8–25.8
Reflections collected	26,875	53,564	21,827	14,624
Independent reflections ( <i>R</i> <sub>int</sub> )	9248 (0.0210)	11363 (0.0201)	7204 (0.0190)	4870 (0.0303)
<i>T</i> (min–max)	0.470–0.772	0.462–0.573	0.313–0.487	0.182–0.639
Goodness of fit on <i>F</i> <sup>2</sup>	1.072	1.043	1.183	1.099
<i>R</i> (observed data)	<i>R</i> <sub>1</sub> = 0.0208 <i>wR</i> <sub>2</sub> = 0.0468	<i>R</i> <sub>1</sub> = 0.0377 <i>wR</i> <sub>2</sub> = 0.1052	<i>R</i> <sub>1</sub> = 0.0225 <i>wR</i> <sub>2</sub> = 0.0529	<i>R</i> <sub>1</sub> = 0.0291 <i>wR</i> <sub>2</sub> = 0.0721
<i>R</i> (all data)	<i>R</i> <sub>1</sub> = 0.0268 <i>wR</i> <sub>2</sub> = 0.0494	<i>R</i> <sub>1</sub> = 0.0400 <i>wR</i> <sub>2</sub> = 0.1069	<i>R</i> <sub>1</sub> = 0.0247 <i>wR</i> <sub>2</sub> = 0.0536	<i>R</i> <sub>1</sub> = 0.0304 <i>wR</i> <sub>2</sub> = 0.0728
Difference map (min, max) (e Å <sup>-3</sup> )	–0.53, +0.59	–2.30, +2.57	–0.67, +1.57	–2.39, +1.52

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

in the <sup>13</sup>C NMR spectrum confirm that the two CO ligands are coordinated mutually *cis*. In the <sup>1</sup>H NMR spectrum of **3**, the osmium methyl signal is a triplet with Sn satellites at –1.06 ppm (<sup>3</sup>*J*<sub>PH</sub> = 6.9 Hz, <sup>3</sup>*J*<sub>Sn(119/117)H</sub> = 51.6 Hz) and the two methyl groups on tin appear as a singlet signal with Sn satellites at –0.12 ppm (<sup>2</sup>*J*<sub>Sn(119/117)H</sub> = 31.8 Hz). In the <sup>13</sup>C NMR spectrum, the osmium methyl signal is a triplet with Sn satellites at –26.0 ppm (<sup>2</sup>*J*<sub>PC</sub> = 6.0 Hz, <sup>2</sup>*J*<sub>Sn(119/117)C</sub> = 74.4 Hz). The two carbonyl carbons appear as triplets at 182.4 (<sup>2</sup>*J*<sub>PC</sub> = 10.1 Hz) and 184.8 ppm (<sup>2</sup>*J*<sub>PC</sub> = 9.1 Hz), respectively. The phosphorus atoms of the mutually *trans* triphenylphosphine ligands appear as a singlet with Sn satellites at 3.83 ppm (<sup>2</sup>*J*<sub>Sn(119/117)P</sub> = 177.4 Hz).

When Os(SnMe<sub>3</sub>)Cl(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> is heated under an atmosphere of CO the same methyl/chloride exchange is observed but the tricarbonyl, mono-triphenylphosphine complex, Os(Me)(SnMe<sub>2</sub>Cl)(CO)<sub>3</sub>(PPh<sub>3</sub>) (**4**), is formed (see Scheme 2). Simple replacement of a triphenylphosphine by CO would lead to a tricarbonyl complex with the three CO ligands arranged facially but in fact the compound isolated, presumably the most stable isomer, has a meridional arrangement of CO ligands and with triphenylphosphine *trans* to tin. The IR spectrum of **4** shows  $\nu$ (CO) at 2078m, 2009vs, and 1988vs cm<sup>-1</sup> as expected for a meridional arrangement of the three CO's. In the <sup>1</sup>H NMR spectrum, the osmium methyl signal is a doublet with Sn satellites at

–0.38 ppm (<sup>3</sup>*J*<sub>PH</sub> = 7.7 Hz, <sup>3</sup>*J*<sub>Sn(119/117)H</sub> = 25.6 Hz) and the two methyl groups on tin appear as a singlet signal with well resolved satellites for <sup>119</sup>Sn and <sup>117</sup>Sn at 0.80 ppm (<sup>2</sup>*J*<sub>Sn(119)H</sub> = 42.5 Hz, <sup>2</sup>*J*<sub>Sn(117)H</sub> = 40.8 Hz). In the <sup>13</sup>C NMR spectrum, the osmium methyl signal is a doublet with Sn satellites at –36.6 ppm (<sup>2</sup>*J*<sub>PC</sub> = 5.8 Hz, <sup>2</sup>*J*<sub>Sn(119/117)C</sub> = 30.0 Hz). The carbonyl carbons appear as doublets with Sn satellites at 176.5 (<sup>2</sup>*J*<sub>PC</sub> = 5.1 Hz, <sup>2</sup>*J*<sub>Sn(119/117)C</sub> = 37.3 Hz, CO *trans* to methyl) and 183.3 ppm (<sup>2</sup>*J*<sub>PC</sub> = 7.6 Hz, <sup>2</sup>*J*<sub>Sn(119/117)C</sub> = 67.0 Hz, CO's mutually *trans*). The phosphorus atom of the triphenylphosphine ligand appears as a singlet with well resolved satellites for <sup>119</sup>Sn and <sup>117</sup>Sn at –0.30 ppm (<sup>2</sup>*J*<sub>Sn(119)P</sub> = 700.9 Hz, <sup>2</sup>*J*<sub>Sn(117)P</sub> = 668.3 Hz).

The molecular geometries of **3** and **4** are depicted in Figs. 3 and 4. Selected bond lengths and angles for **3** and **4** are collected in Tables 4 and 5, respectively. The coordination sphere for both complexes is octahedral. In **3**, the two triphenylphosphine ligands are mutually *trans* and the two carbonyl ligands are mutually *cis*. The Os–Sn distance is 2.6913(2) Å which can be compared with the value of 2.6441(3) Å found in another osmium octahedral complex with a dimethylchlorostannyl ligand, Os(SnMe<sub>2</sub>Cl)(κ<sup>2</sup>-S<sub>2</sub>CNMe<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> [**3**]. The Os–methyl distance is 2.209(4) Å which can be compared with the distance found in Os(Me)(SnClMe<sub>2</sub>)(py)(CO)(PPh<sub>3</sub>)<sub>2</sub> of 2.249(5) Å [**3**]. In **4**, the three carbonyl ligands are arranged meridionally and the



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

Bond lengths (Å)	
Os–C(1)	1.886(3)
Os–C(72)	2.197(3)
Os–P(2)	2.3790(7)
Os–P(3)	2.3816(7)
Os–P(1)	2.4088(7)
Os–Sn	2.6430(2)
Sn–C(2)	2.144(3)
Sn–C(62)	2.154(3)
Sn–Cl	2.4338(7)
O(1)–C(1)	1.156(3)
C(61)–C(62)	1.388(4)
C(61)–C(66)	1.398(4)
C(62)–C(63)	1.400(4)
C(63)–C(64)	1.394(5)
C(64)–C(65)	1.370(5)
C(65)–C(66)	1.385(5)
C(71)–C(76)	1.395(4)
C(71)–C(72)	1.415(4)
C(72)–C(73)	1.401(4)
C(73)–C(74)	1.400(4)
C(74)–C(75)	1.381(4)
C(75)–C(76)	1.385(4)
Bond angles (°)	
C(1)–Os–C(72)	160.87(11)
C(1)–Os–P(2)	90.38(9)
C(72)–Os–P(2)	96.89(7)
C(1)–Os–P(3)	103.26(9)
C(72)–Os–P(3)	66.25(7)
P(2)–Os–P(3)	161.20(2)
C(1)–Os–P(1)	92.46(8)
C(72)–Os–P(1)	103.86(7)
P(2)–Os–P(1)	98.56(2)
P(3)–Os–P(1)	93.78(2)
C(1)–Os–Sn	91.40(8)
C(72)–Os–Sn	72.45(7)
P(2)–Os–Sn	80.830(17)
P(3)–Os–Sn	85.888(17)
P(1)–Os–Sn	176.100(17)
C(2)–Sn–C(62)	106.66(12)
C(2)–Sn–Cl	100.48(9)
C(62)–Sn–Cl	98.88(8)
C(2)–Sn–Os	130.19(8)
C(62)–Sn–Os	101.15(7)
Cl–Sn–Os	115.14(2)

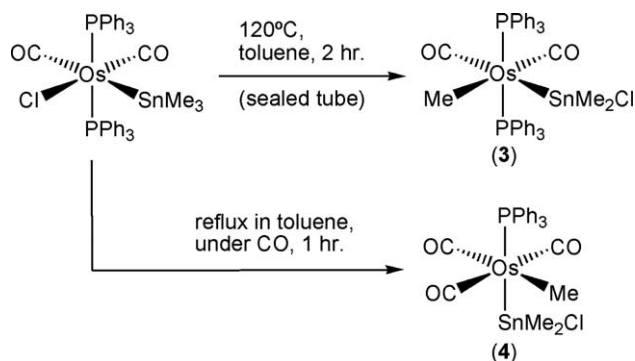
triphenylphosphine is *trans* to the stannyl ligand. The Os–Sn (2.6642(3) Å) distance and the Os–methyl (2.227(4) Å) distance are close to the corresponding values found in **3**. The Os–P distance in **4** of 2.3839(10) Å does not differ significantly from the distances in complex **3** (Os–P(1), 2.3986(8); Os–P(2), 2.3880(8) Å).

### 3. Conclusions

It has been demonstrated that the coordinatively unsaturated trimethylstannyl complex, Os(SnMe<sub>3</sub>)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub> undergoes a thermal reaction to form a mixture of Os(κ<sup>2</sup>(*Sn,P*)-SnMeClC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)(κ<sup>2</sup>(*C,P*)-

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

Bond lengths (Å)	
Os–C(1)	1.889(5)
Os–C(72)	2.202(5)
Os–P(2)	2.3753(12)
Os–P(3)	2.3787(12)
Os–P(1)	2.4056(12)
Os–Sn	2.7074(3)
Sn–C(3)	2.173(6)
Sn–C(62)	2.182(5)
Sn–C(2)	2.183(5)
O(1)–C(1)	1.176(6)
Bond angles (°)	
C(1)–Os–C(72)	161.18(18)
C(1)–Os–P(2)	94.45(15)
C(72)–Os–P(2)	92.37(13)
C(1)–Os–P(3)	103.27(15)
C(72)–Os–P(3)	66.26(13)
P(2)–Os–P(3)	156.67(4)
C(1)–Os–P(1)	90.72(14)
C(72)–Os–P(1)	105.37(12)
P(2)–Os–P(1)	99.81(4)
P(3)–Os–P(1)	95.08(4)
C(1)–Os–Sn	86.02(14)
C(72)–Os–Sn	78.03(11)
P(2)–Os–Sn	79.37(3)
P(3)–Os–Sn	86.75(3)
P(1)–Os–Sn	176.56(3)
C(3)–Sn–C(62)	101.0(2)
C(3)–Sn–C(2)	104.2(2)
C(62)–Sn–C(2)	107.7(2)
C(3)–Sn–Os	123.69(15)
C(62)–Sn–Os	99.01(14)
C(2)–Sn–Os	118.63(16)
O(1)–C(1)–Os	174.3(4)



Scheme 2. Thermal reactions of Os(SnMe<sub>3</sub>)Cl(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.

C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)(CO)(PPh<sub>3</sub>) (**1**) and Os(κ<sup>2</sup>(*Sn,P*)-SnMe<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>) (**2**), each complex containing both *ortho*-stannylated and *ortho*-metallated triphenylphosphine ligands. It is proposed that the *ortho*-stannylation reaction could proceed through the intermediacy of a stannylene complex. In contrast, similar thermal reactions of the coordinatively saturated trimethylstannyl complex, Os(SnMe<sub>3</sub>)Cl(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, do not

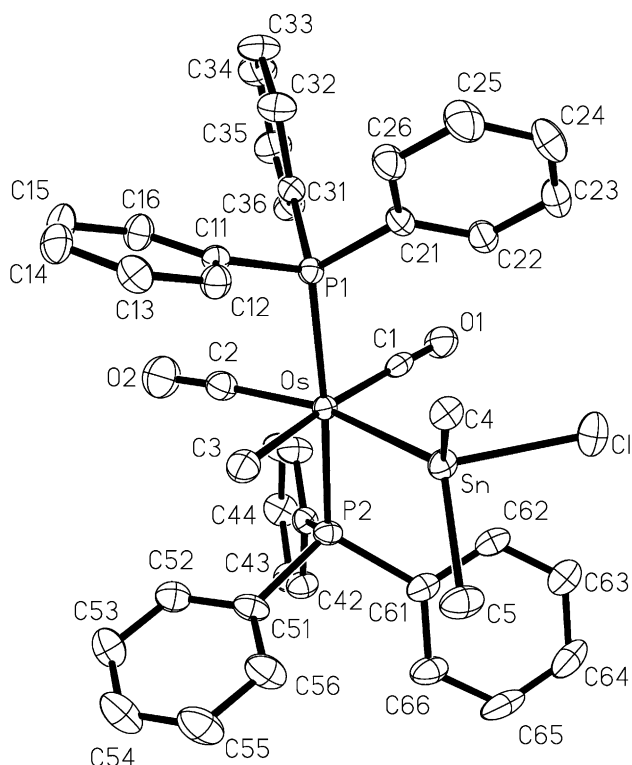


Fig. 3. Molecular geometry of  $\text{Os}(\text{Me})(\text{SnMe}_2\text{Cl})(\text{CO})_2(\text{PPh}_3)_2$  (**3**).

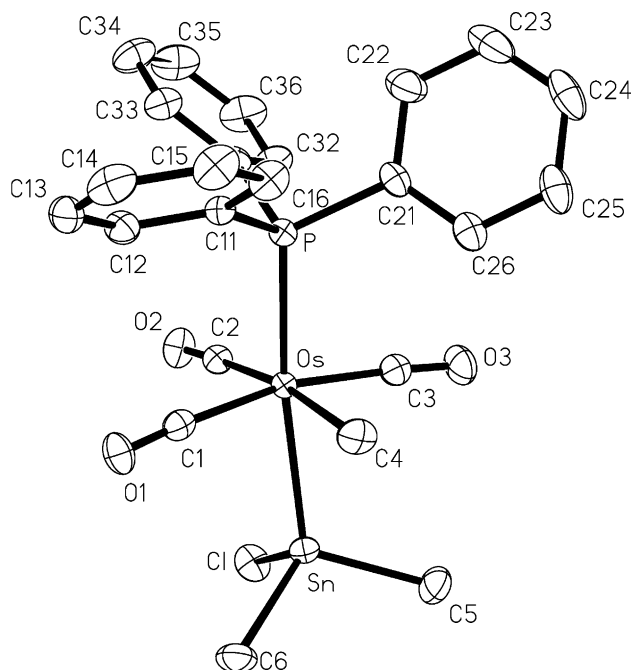


Fig. 4. Molecular geometry of  $\text{Os}(\text{Me})(\text{SnMe}_2\text{Cl})(\text{CO})_3(\text{PPh}_3)$  (**4**).

result in formation of either *ortho*-stannylated or *ortho*-metallated triphenylphosphine ligands but rather result only in exchange of methyl and chloride between tin and osmium. Complexes **1** and **2** are of a structural type previously recognised in thermal reactions of the coordin-

Table 4  
Selected bond lengths (Å) and angles (°) for **3**

Bond lengths (Å)	
Os–C(1)	1.920(4)
Os–C(2)	1.931(4)
Os–C(3)	2.209(4)
Os–P(2)	2.3880(8)
Os–P(1)	2.3986(8)
Os–Sn	2.6913(2)
Sn–C(5)	2.159(4)
Sn–C(4)	2.179(3)
Sn–Cl	2.4400(9)
O(1)–C(1)	1.130(4)
O(2)–C(2)	1.108(5)
Bond angles (°)	
C(1)–Os–C(2)	102.65(14)
C(1)–Os–C(3)	174.38(13)
C(2)–Os–C(3)	82.89(14)
C(1)–Os–P(2)	89.33(9)
C(2)–Os–P(2)	88.54(11)
C(3)–Os–P(2)	89.90(9)
C(1)–Os–P(1)	90.35(9)
C(2)–Os–P(1)	86.16(10)
C(3)–Os–P(1)	90.94(9)
P(2)–Os–P(1)	174.48(3)
C(1)–Os–Sn	96.89(10)
C(2)–Os–Sn	160.45(11)
C(3)–Os–Sn	77.57(10)
P(2)–Os–Sn	91.32(2)
P(1)–Os–Sn	94.19(2)
C(5)–Sn–C(4)	99.58(13)
C(5)–Sn–Cl	95.51(12)
C(4)–Sn–Cl	95.72(9)
C(5)–Sn–Os	122.32(11)
C(4)–Sn–Os	118.89(8)
Cl–Sn–Os	119.20(2)
O(1)–C(1)–Os	178.7(3)
O(2)–C(2)–Os	174.8(3)

atively unsaturated trimethylsilyl, methyl complex,  $\text{Os}(\text{SiMe}_3)(\text{Me})(\text{CO})(\text{PPh}_3)_2$  [**1**]. Crystal structure determinations of **1**, **2**, **3**, and **4** verify the formulations of the new compounds.

## 4. Experimental

### 4.1. General procedures and instruments

Standard laboratory procedures were followed as have been described previously [11]. The compounds  $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$  [12],  $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$  [12] and  $\text{SnMe}_3(\text{CH}=\text{CH}_2)$  [13] were prepared according to the literature methods.

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  $25\text{ }^\circ\text{C}$ . 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

Table 5  
Selected bond lengths (Å) and angles (°) for **4**

<i>Bond lengths (Å)</i>	
Os–C(2)	1.922(4)
Os–C(1)	1.938(4)
Os–C(3)	1.939(4)
Os–C(4)	2.227(4)
Os–P	2.3839(10)
Os–Sn	2.6642(3)
Sn–C(6)	2.141(5)
Sn–C(5)	2.144(5)
Sn–Cl	2.4214(11)
O(1)–C(1)	1.138(5)
O(2)–C(2)	1.139(5)
O(3)–C(3)	1.133(5)
<i>Bond angles (°)</i>	
C(2)–Os–C(1)	93.74(17)
C(2)–Os–C(3)	95.60(18)
C(1)–Os–C(3)	167.22(18)
C(2)–Os–C(4)	171.79(17)
C(1)–Os–C(4)	80.37(18)
C(3)–Os–C(4)	89.41(18)
C(2)–Os–P	94.14(12)
C(1)–Os–P	95.65(12)
C(3)–Os–P	92.36(13)
C(4)–Os–P	92.14(12)
C(2)–Os–Sn	91.87(12)
C(1)–Os–Sn	87.59(12)
C(3)–Os–Sn	83.41(13)
C(4)–Os–Sn	82.23(12)
P–Os–Sn	172.97(3)
C(6)–Sn–C(5)	110.2(2)
C(6)–Sn–Cl	101.89(15)
C(5)–Sn–Cl	97.62(16)
C(6)–Sn–Os	118.39(14)
C(5)–Sn–Os	114.39(14)
Cl–Sn–Os	111.61(3)

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. Elemental analyses were obtained from the Microanalytical Laboratory, University of Otago.

#### 4.2. Preparation of $\text{Os}(\kappa^2(\text{Sn},\text{P})\text{-SnMeClC}_6\text{H}_4\text{PPh}_2)\text{-}(\kappa^2(\text{C},\text{P})\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$ (**1**)

The required starting material,  $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})\text{-}(\text{PPh}_3)_2$ , was prepared in situ by the following procedure. A two-necked 100 mL flask equipped with a condenser was charged with  $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$  (1.042 g, 1.0 mmol),  $\text{SnMe}_3(\text{CH}=\text{CH}_2)$  (0.8 mL, 5.0 mmol), benzene (10 mL) and toluene (20 mL). This mixture was photolysed for 10 min with 1000 W tungsten/halogen lamp the heat from the lamp being sufficient to keep

the mixture under reflux. The resulting red solution was concentrated under reduced pressure to give a dark red oily solid, which was identified by NMR ( $^1\text{H}$  and  $^{31}\text{P}$ ) to be a mixture of  $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$  and  $\text{PPh}_3$  in an approximately 50:50 ratio. Triphenylphosphine (0.262 g, 1.0 mmol) and toluene (20 mL) were added and the new mixture was heated under reflux for 1 h to give a pale solution. The solvent was removed under reduced pressure and the residue was recrystallized from  $\text{CH}_2\text{Cl}_2$  and EtOH to remove excess  $\text{PPh}_3$ . The crude product was subjected to column chromatography on silica gel. Upon elution with a mixture of  $\text{CH}_2\text{Cl}_2$ /hexane (1:3) the first fraction was collected and set aside for the isolation of  $\text{Os}(\kappa^2(\text{Sn},\text{P})\text{-SnMe}_2\text{C}_6\text{H}_4\text{PPh}_2)(\kappa^2(\text{C},\text{P})\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$  (**2**), see Section 4.3. Further elution with acetone/hexane (1:3) gave another fraction which after solvent removal gave a white solid which was recrystallised from  $\text{CH}_2\text{Cl}_2$ /EtOH to give pure **1** as a colourless microcrystalline solid (0.605 g, 52%). Complex **1** can also be obtained, quantitatively, by treating **2** (see Section 4.3) with  $\text{SnMe}_2\text{Cl}_2$  in  $\text{CH}_2\text{Cl}_2$  for 16 h. Anal. Calc. for  $\text{C}_{56}\text{H}_{46}\text{ClOOSn}_2\text{P}_3$ : C, 57.38; H, 3.96. Found: C, 57.68; H, 4.25%. IR ( $\text{cm}^{-1}$ ): 1926s  $\nu(\text{CO})$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ):  $-0.81$  (s with Sn satellites, 3H,  $^2J_{\text{Sn}(119/117)\text{H}} = 43.8$  Hz, *SnMe*), 5.70 (m, 2H,  $\text{C}_6\text{H}_4$ ), 6.45–7.72 (m, 41H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ):  $-5.0$  (m, *SnMe*), 122.4–158.7 (numerous unassigned resonances from aromatic carbons of  $\text{PPh}_3$  and  $\text{C}_6\text{H}_4$  groups), 188.6 (m, CO).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) (see Scheme 1 for phosphorus atom labeling): 33.81 (dd with Sn satellites,  $^2J_{\text{P(a)P(b)}} = 13.7$ ,  $^2J_{\text{P(a)P(c)}} = 222.8$ ,  $^2J_{\text{Sn}(119/117)\text{P}} = 123.1$  Hz,  $\text{Ph}_2\text{PC}_6\text{H}_4\text{SnMeCl}$  [ $\text{P}^{\text{a}}$ ]),  $-2.67$  (dd with Sn satellites,  $^2J_{\text{P(a)P(b)}} = 13.7$ ,  $^2J_{\text{P(b)P(c)}} = 21.5$ ,  $^2J_{\text{Sn}(119/117)\text{P}} = 1157.1$  Hz,  $\text{PPh}_3$  [ $\text{P}^{\text{b}}$ ]),  $-66.57$  (dd with Sn satellites,  $^2J_{\text{P(a)P(c)}} = 222.8$ ,  $^2J_{\text{P(b)P(c)}} = 21.5$ ,  $^2J_{\text{Sn}(119/117)\text{P}} = 138.5$  Hz,  $\text{Ph}_2\text{PC}_6\text{H}_4$  [ $\text{P}^{\text{c}}$ ]).

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

The first fraction from the chromatographic procedure described in Section 4.2 was collected and after solvent removal the resulting white solid was recrystallised from  $\text{CH}_2\text{Cl}_2$ /EtOH to give pure **2** as a colourless microcrystalline solid (0.195 g, 17%). Anal. Calc. for  $\text{C}_{57}\text{H}_{49}\text{OOSn}_2\text{P}_3$ : C, 59.44; H, 4.29. Found: C, 59.65; H, 4.49%. The crystal selected for X-ray crystallographic study was grown from  $\text{CHCl}_3$  and proved to be a 1:1  $\text{CHCl}_3$  solvate (see Table 1). IR ( $\text{cm}^{-1}$ ): 1907s  $\nu(\text{CO})$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ):  $-1.29$  (s with Sn satellites, 3H,  $^2J_{\text{Sn}(119/117)\text{H}} = 43.8$  Hz, *SnMe*),  $-0.08$  (s with Sn satellites, 3H,  $^2J_{\text{Sn}(119/117)\text{H}} = 39.8$  Hz, *SnMe*), 5.64 (m, 2H,  $\text{C}_6\text{H}_4$ ), 6.64–7.52 (m, 41H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ):  $-12.7$  (m, *SnMe*),  $-7.7$  (apparent d,  $^3J_{\text{PC}} = 6.0$  Hz, *SnMe*), 120.9–157.5 (numerous unassigned resonances



from aromatic carbons of  $\text{PPh}_3$  and  $\text{C}_6\text{H}_4$  groups), 191.7 (apparent q,  $^2J_{\text{PC}} = 6.0$  Hz, CO).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 31.35 (dd with Sn satellites,  $^2J_{\text{P(a)P(b)}} = 13.3$ ,  $^2J_{\text{P(a)P(c)}} = 225.9$ ,  $^2J_{\text{Sn(119/117)P}} = 98.6$  Hz,  $\text{Ph}_2\text{PC}_6\text{H}_4\text{-SnMe}_2$  [ $\text{P}^{\text{a}}$ ]),  $-3.61$  (dd with Sn satellites,  $^2J_{\text{P(a)P(b)}} = 13.3$ ,  $^2J_{\text{P(b)P(c)}} = 20.5$ ,  $^2J_{\text{Sn(119/117)P}} = 833.6$  Hz,  $\text{PPh}_3$  [ $\text{P}^{\text{b}}$ ]),  $-66.30$  (dd with Sn satellites,  $^2J_{\text{P(a)P(c)}} = 225.9$ ,  $^2J_{\text{P(b)P(c)}} = 20.5$ ,  $^2J_{\text{Sn(119/117)P}} = 114.2$  Hz,  $\text{Ph}_2\text{PC}_6\text{H}_4$  [ $\text{P}^{\text{c}}$ ]).

#### 4.4. Preparation of $\text{Os}(\text{Me})(\text{SnMe}_2\text{Cl})(\text{CO})_2(\text{PPh}_3)_2$ (**3**)

A solution of  $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$  (0.485 g, 0.50 mmol) in of toluene (25 mL) in a Schlenk tube was deoxygenated, frozen, evacuated and sealed and then heated in an oil-bath at 120 °C (CAUTION: Safety Shield) for 2 hour. The toluene was then removed under reduced pressure. The resulting residue was recrystallised from  $\text{CH}_2\text{Cl}_2$ /ethanol to give a crude product which contained ~10% of an impurity formulated as  $\text{Os}(\text{SnMe}_2\text{Cl})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$  on the basis of  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectral data. This crude product was dissolved in a little  $\text{CH}_2\text{Cl}_2$  and subjected to column chromatography on silica gel. Elution with a mixture of  $\text{CH}_2\text{Cl}_2$ /hexane (1:1) removed some minor impurities. The eluent was then changed to acetone/hexane (1:3) and the band containing the major product was collected (the elution of fractions from the column was monitored by TLC). Removal of solvents gave a white solid, which was recrystallised from  $\text{CH}_2\text{Cl}_2$ /ethanol to give pure **3** as a colourless crystalline solid (0.250 g, 52% yield). Anal. Calc.  $\text{C}_{41}\text{H}_{39}\text{ClO}_2\text{OsP}_2\text{Sn}$ : C, 50.77; H, 4.05. Found: C, 50.70; H, 3.99%. IR ( $\text{cm}^{-1}$ ): 2003vs, 1920vs, 1906s  $\nu$  (CO).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ):  $-1.06$  (t with Sn satellites, 3H,  $^3J_{\text{PH}} = 6.9$  Hz,  $^3J_{\text{Sn(119/117)H}} = 51.6$  Hz,  $\text{OsMe}$ ),  $-0.12$  (s with Sn satellites, 6H,  $^2J_{\text{Sn(119/117)H}} = 31.8$  Hz,  $\text{SnMe}_2$ ), 7.26–7.68 (m, 30H,  $\text{PPh}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ):  $-26.0$  (t with Sn satellites,  $^2J_{\text{PC}} = 6.0$  Hz,  $^2J_{\text{Sn(119/117)C}} = 74.4$  Hz,  $\text{OsMe}$ ), 0.7 (s with Sn satellites,  $^1J_{\text{Sn(119/117)C}} = 159.0$  Hz,  $\text{SnMe}_2$ ), 128.3 (t' [11],  $^{2,4}J_{\text{PC}} = 9.0$  Hz,  $o\text{-PPh}_3$ ), 130.4 (s,  $p\text{-PPh}_3$ ), 133.4 (t',  $^{1,3}J_{\text{PC}} = 53.4$  Hz,  $i\text{-PPh}_3$ ), 134.0 (t',  $^{3,5}J_{\text{PC}} = 11.0$  Hz,  $o\text{-PPh}_3$ ), 182.4 (t,  $^2J_{\text{PC}} = 10.1$  Hz, CO), 184.8 (t,  $^2J_{\text{PC}} = 9.1$  Hz, CO).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 3.83 (s with Sn satellites,  $^2J_{\text{Sn(119/117)P}} = 177.4$  Hz).

#### 4.5. Preparation of $\text{Os}(\text{Me})(\text{SnMe}_2\text{Cl})(\text{CO})_3(\text{PPh}_3)$ (**4**)

A solution of  $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$  (0.400 g, 0.41 mmol) in toluene (20 mL) was heated under reflux for 1 h with CO bubbling slowly through the solution. The toluene was then removed under reduced pressure. The resulting residue was dissolved in a little  $\text{CH}_2\text{Cl}_2$  and subjected to column chromatography on silica gel.

Elution with a mixture of  $\text{CH}_2\text{Cl}_2$ /hexane (1:2) removed minor impurities. This was followed by elution with acetone to give a band containing the crude product which was further purified by preparative TLC using acetone/hexane (1:3) as eluent. From the first major band on the plate was obtained a white solid which after recrystallisation from  $\text{CH}_2\text{Cl}_2$ /heptane gave pure **4** as a colourless microcrystalline solid (0.100 g, 33%). Anal. Calc. for  $\text{C}_{24}\text{H}_{24}\text{ClO}_3\text{OsPSn}$ : C, 39.18; H, 3.29. Found: 39.18; H, 3.30%. IR ( $\text{cm}^{-1}$ ): 2078m, 2009vs, 1988vs  $\nu$  (CO).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ):  $-0.38$  (d with Sn satellites, 3H,  $^3J_{\text{PH}} = 7.7$  Hz,  $^3J_{\text{Sn(119/117)H}} = 25.6$  Hz,  $\text{OsMe}$ ), 0.80 (s with Sn satellites, 6H,  $^2J_{\text{Sn(119)H}} = 42.5$ ,  $^2J_{\text{Sn(117)H}} = 40.8$  Hz,  $\text{SnMe}_2$ ), 7.39–7.48 (m, 15H,  $\text{PPh}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ):  $-36.6$  (d with Sn satellites,  $^2J_{\text{PC}} = 5.8$  Hz,  $^2J_{\text{Sn(119/117)C}} = 30.0$  Hz,  $\text{OsMe}$ ), 0.3 (d with Sn satellites,  $^3J_{\text{PC}} = 5.7$  Hz,  $^1J_{\text{Sn(119/117)C}} = 229.9$  Hz,  $\text{SnMe}_2$ ), 128.8 (d,  $^2J_{\text{PC}} = 10.6$  Hz,  $o\text{-PPh}_3$ ), 131.0 (d,  $^4J_{\text{PC}} = 2.3$  Hz,  $p\text{-PPh}_3$ ), 132.3 (d,  $^1J_{\text{PC}} = 50.1$  Hz,  $i\text{-PPh}_3$ ), 133.0 (d,  $^3J_{\text{PC}} = 10.9$  Hz,  $m\text{-PPh}_3$ ), 176.5 (d with Sn satellites,  $^2J_{\text{PC}} = 5.1$  Hz,  $^2J_{\text{Sn(119/117)C}} = 37.3$  Hz, CO *trans* to Me), 183.3 (d with Sn satellites,  $^2J_{\text{PC}} = 7.6$  Hz,  $^2J_{\text{Sn(119/117)C}} = 67.0$  Hz, CO's mutually *trans*).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ):  $-0.30$  (s with Sn satellites,  $^2J_{\text{Sn(119)P}} = 700.9$  Hz,  $^2J_{\text{Sn(117)P}} = 668.3$  Hz).

#### 4.6. X-ray crystal structure determinations for complexes **1**, **2**, **3**, and **4**

X-ray data collection was by Siemens SMART diffractometer with a CCD area detector using graphite monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073$  Å) at 150 K. Data were integrated and corrected for Lorentz and polarisation effects using SAINT [14]. Semi-empirical absorption corrections were applied based on equivalent reflections using SADABS [15]. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares on  $F^2$  using programs SHELXS [16] and SHELXL [17]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located geometrically and refined using a riding model. Crystal data and refinement details 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. 263203–263206 for **1**, **2**, **3**, and **4**, 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.

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