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Four isomers from the oxidative addition of Me_3SnH to $Os(CO)_2(PPh_3)_3$ and the crystal structure of $Os(SnMeI_2)I(CO)_2(PPh_3)_2$, in which the pairs of CO and PPh_3 ligands are mutually *trans*

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Abstract

Reaction between $Os(CO)_2(PPh_3)_3$ and Me_3SnH produces $Os(SnMe_3)H(CO)_2(PPh_3)_2$ (**1**). Multinuclear NMR studies of solutions of **1** reveal the presence of four geometrical isomers, the major one being that with mutually *cis* triphenylphosphine ligands and mutually *trans* CO ligands. $Os(SnMe_3)H(CO)_2(PPh_3)_2$ undergoes a redistribution reaction, at the trimethylstannyl ligand, when treated with Me_2SnCl_2 giving $Os(SnMe_2Cl)H(CO)_2(PPh_3)_2$ (**2**). Solutions of **2** again show the presence of four isomers but now the major isomer is that with mutually *trans* triphenylphosphine ligands and mutually *cis* CO ligands. The redistribution reaction of **1** with SnI_4 produces $Os(SnMeI_2)H(CO)_2(PPh_3)_2$ (**3**) which exists in solution as only one isomer, that with mutually *trans* triphenylphosphine ligands and mutually *trans* CO ligands. Treatment of **3** with I_2 cleaves the Os–H bond with retention of geometry giving $Os(SnMeI_2)I(CO)_2(PPh_3)_2$ (**4**). The crystal structure of **4** has been determined. No isomerization of the *trans* dicarbonyl complex **4** occurs when **4** is heated, instead there is a formal loss of "MeSnI" and formation of $OsI_2(CO)_2(PPh_3)_2$ (**5**).
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Keywords: Stannyl complex; Tin; Osmium; X-ray crystal structure

1. Introduction

We have demonstrated that $Os(CO)_2(PPh_3)_3$ is an excellent substrate for the syntheses of compounds with Os–E (E = main group element) bonds, through E–H oxidative addition reactions. Silanes [1,2], germanes [1], and boranes [3] all readily add. One stannane, $(tolyl)_3SnH$, has also been added to $Os(CO)_2(PPh_3)_3$ [1] and to $OsCl(NO)(PPh_3)_3$ [4]. Interestingly functionalised stannyl ligands are accessible through redistribution reactions beginning with the trimethylstannyl ligand, e.g., $Os(SnMe_3)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ with SnI_4 gives $Os(SnMeI_2)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ [5] and the iodide substituents on the stannyl ligand in the latter complex are susceptible to nucleophilic substitution reactions [6]. A simple and direct route to trimethylstannyl complexes of osmium is offered by the oxidative addition of Me_3SnH to $Os(CO)_2(PPh_3)_3$. Accordingly, in this paper we report: (i) the synthesis of $Os(SnMe_3)H(CO)_2(PPh_3)_2$ (**1**) as a mixture of four isomers, (ii) the synthesis of $Os(SnMe_2Cl)H(CO)_2(PPh_3)_2$ (**2**) as a mixture of four isomers, through a redistribution reaction of **1** with Me_2SnCl_2, (iii) the synthesis of $Os(SnMeI_2)H(CO)_2(PPh_3)_2$ (**3**) as a single isomer, through a redistribution reaction of **1** with SnI_4, and (iv) the synthesis and structure determination of $Os(SnMeI_2)I(CO)_2(PPh_3)_2$ (**4**), which again is a single isomer with mutually *trans* CO ligands and mutually *trans* PPh_3 ligands.

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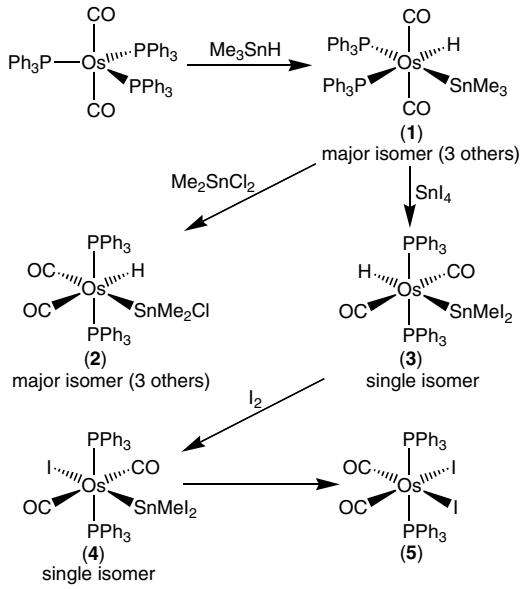
2. Results and discussion

2.1. Reaction of $Os(CO)_2(PPh_3)_3$ with Me_3SnH to give $Os(SnMe_3)H(CO)_2(PPh_3)_2$ (1) as a mixture of four isomers (1a–d)

Treatment of $Os(CO)_2(PPh_3)_3$ with Me_3SnH in benzene under irradiation with a quartz-halogen light source leads quickly to the colourless complex, $Os(SnMe_3)H(CO)_2(PPh_3)_2$ (**1**) in good yield (see Scheme 1). The IR spectrum of a solid sample of **1** shows a single band at 1913 cm^{-1} which is assigned to ν(CO) (or a combination of ν(CO) and ν(Os–H)). However, in dichloromethane solution three bands are observed at 2008, 1978, 1926 cm^{-1} and this spectrum did not change with time. It is possible that one isomer crystallises preferentially from an equilibrium mixture of isomers in solution. These IR data are insufficient to allow unambiguous assignment of one or more geometrical isomers. However, the solution NMR data do allow assignments to be made. Although more than four isomers are theoretically possible for complex **1** the NMR data identifies only four. These are shown in Chart 1. Compounds of composition, $OsX_2(CO)_2(PPh_3)_2$ usually have a *trans* arrangement of the bulky PPh_3 ligands. Unexpectedly, the major isomer, **1a** (54% from ^{1}H NMR data), has mutually *cis* PPh_3 ligands and mutually *trans* CO ligands. In the ^{1}H NMR spectrum, **1a** shows a high-field signal at δ, −10.54 ppm which is a doublet of doublets through coupling to both a *trans* and a *cis* PPh_3 ligand. In the ^{13}C NMR spectrum, **1a** shows a low-field signal at δ, 192.1 ppm for the mutually *trans* CO ligands, which is an apparent triplet through coupling to the two mutually *cis*, but inequivalent, PPh_3 ligands. In the ^{31}P NMR spectrum, **1a** shows two doublet signals, one at δ, 3.2 ppm and one at δ, 7.0 ppm. The ^{119}Sn NMR spectrum of **1a** shows a doublet of doublets at δ, −115.4 ppm through coupling to one *trans* and one *cis* PPh_3 ligand. Hetero-nuclear correlation experiments substantiate the above assignments. In a similar manner, the geometries of the other three isomers, **1b–d**, were assigned, with the aid of correlation experiments (H–C, H–Sn, and H–P), and details are in Section 4.



Scheme 1. Synthesis and reactions of $Os(SnMe_3)H(CO)_2(PPh_3)_2$ (**1**).

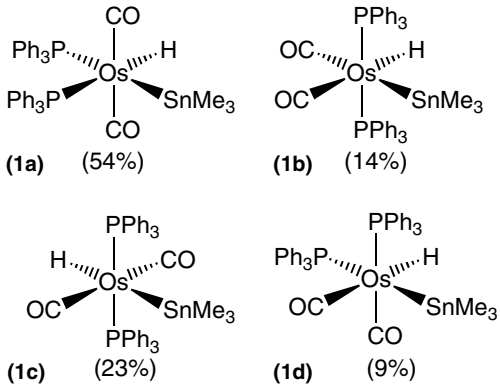


Chart 1. Geometrical isomers of $Os(SnMe_3)H(CO)_2(PPh_3)_2$ (**1**).

2.2. Redistribution of $Os(SnMe_3)H(CO)_2(PPh_3)_2$ (1) with Me_2SnCl_2 to give $Os(SnMe_2Cl)H(CO)_2(PPh_3)_2$ (2) as a mixture of four isomers (2a–d)

We have shown that a redistribution reaction of $Os(SnMe_3)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ with SnI_4 is an effective way of introducing iodo-substituents into the stannyl ligand, giving $Os(SnMeI_2)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ [5]. We now report that treatment of $Os(SnMe_3)H(CO)_2(PPh_3)_2$ with Me_2SnCl_2 is equally effective for the introduction of one chloro-substituent into the stannyl ligand forming $Os(SnMe_2Cl)H(CO)_2(PPh_3)_2$ (**2**) (see Scheme 1). The IR spectrum of a solid sample of **2** shows a single band at 1938 cm^{-1} which is assigned to ν(CO) (or a combination of ν(CO) and ν(Os–H)). However, in dichloromethane solution three bands are observed at 2026, 1989, 1948 cm^{-1}. When compared with the corresponding data for compound **1** all these bands are at higher wavenumber values as would be expected on replacing one methyl group by a more electron-withdrawing chloro-substituent. Again these IR data are insufficient to allow unambiguous assignment of geometrical isomers, but solution NMR data allows assignments to be made. The four identified isomers for complex **2** are shown in Chart 2. Two isomers are now dominant (**2b**, 46%; **2c**, 40%) and both are different from the major isomer present for complex **1** in that the pair of PPh_3 ligands are now mutually *trans*. The major isomer, **2b** (46% from ^{1}H NMR data), has mutually *trans* PPh_3 ligands and

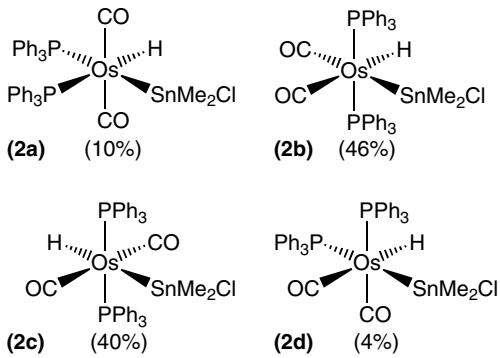


Chart 2. Geometrical isomers of $Os(SnMe_2Cl)H(CO)_2(PPh_3)_2$ (**2**).

mutually *cis* CO ligands. In the ^1H NMR spectrum, **2b** shows a high-field signal at δ, −7.70 ppm which is a triplet through coupling to the equivalent *trans* PPh_3 ligands. In the ^{13}C NMR spectrum, **2b** shows low-field triplet signals at δ, 180.9 and 186.0 ppm for the two *cis* CO ligands. In the ^{31}P NMR spectrum, **2b** shows a singlet resonance at δ, 6.1 ppm and in the ^{119}Sn NMR spectrum, **2b** shows a triplet resonance at δ, 114.0 ppm through coupling to two equivalent *trans* PPh_3 ligands. In a similar manner, the geometries of the other three isomers, **2a**, **c**, **d**, were assigned, with the aid of correlation experiments (H–C, H–Sn, and H–P), and details are in Section 4.

2.3. Redistribution of $Os(SnMe_3)H(CO)_2(PPh_3)_2$ (1) with SnI_4 to give $Os(SnMeI_2)H(CO)_2(PPh_3)_2$ (3) as a single isomer

Treatment of $Os(SnMe_3)H(CO)_2(PPh_3)_2$ with excess SnI_4 is effective for the introduction of two iodo-substituents into the stannyl ligand forming $Os(SnMeI_2)H(CO)_2(PPh_3)_2$ (**3**) (see Scheme 1). The IR spectrum of a solid sample of **3** shows a single band at 1964 cm^{-1} which is assigned to ν(CO) (or a combination of ν(CO) and ν(Os–H)), higher than the corresponding band for compounds **1** and **2**. The trend is clear, the more methyl groups on tin that are replaced by halo-substituents, the higher ν(CO) becomes. Unlike compounds **1** and **2**, NMR data for **3** indicates that only one isomer is present in solution. This isomer has mutually *trans* PPh_3 ligands, mutually *trans* CO ligands, and the H and $SnMeI_2$ located *trans* to one another, as depicted in Scheme 1. In accordance with this assigned geometry the ^1H NMR spectrum shows a triplet signal at δ, −10.62 ppm with tin satellites ($^2J_{^{117}Sn-H} = 233$ Hz; $^2J_{^{119}Sn-H} = 244$ Hz). In the ^{13}C NMR spectrum one resonance, a triplet, is observed for the equivalent *trans* CO ligands at 185.8 ppm. In the ^{31}P NMR spectrum one resonance is observed at δ, 5.9 ppm with tin satellites ($^2J_{^{117}Sn-P} = 63.8$ Hz). In the ^{119}Sn NMR spectrum a triplet signal is observed at δ, 69.6 ppm ($^2J_{^{117}Sn-P} = 62.7$ Hz).

2.4. Reaction of $Os(SnMeI_2)H(CO)_2(PPh_3)_2$ (3) with I_2 to give $Os(SnMeI_2)I(CO)_2(PPh_3)_2$ (4) and the crystal structure of 4

$Os(SnMeI_2)H(CO)_2(PPh_3)_2$ (**3**) reacts with one equivalent of I_2 to selectively cleave the Os–H bond rather than the Sn–Me bond to form $Os(SnMeI_2)I(CO)_2(PPh_3)_2$ (**4**) (see Scheme 1). This reaction occurs with retention of geometry as indicated by IR and NMR data and confirmed by crystal structure determination (see below). One ν(CO) band is observed in the IR spectrum at 1957 cm^{-1}. In the ^{13}C NMR spectrum, one triplet signal is observed at δ, 183.2 ppm for the equivalent *trans* CO ligands and in the ^{31}P NMR spectrum a singlet resonance is observed at δ, 5.8 ppm with tin satellites ($^2J_{^{117}Sn-P} = 63.1$ Hz) for the equivalent *trans* PPh_3 ligands. In the ^{119}Sn NMR spectrum, a triplet signal is observed at δ, −66.0 ppm ($^2J_{^{117}Sn-P} = 65.7$ Hz).

The molecular geometry of **4** is shown in Fig. 1. Selected bond lengths and angles for **4** are collected in Table 2. The overall geometry about osmium is octahedral. Os–P and Os–CO distances are unremarkable and are not discussed further. The Os–I distance at 2.7718(4) Å is longer than the mean of reported Os–I distances (Os–I, mean = 2.705 Å, standard deviation = 0.061) [7] indicating the strong *trans* influence of the *trans* stannyl ligand. The Os–Sn distance of 2.6531(4) Å is intermediate between the values observed for the Os–trimethylstannyl distance (2.6616(13) Å) in the complex $Os(SnMe_3)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ [6] and the Os–triiodostannyl distance (2.6460(9) Å) in the complex $Os(SnI_3)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ [6]. The observed Sn–I distances of 2.7727(5) and 2.7739(5) Å are close to those observed in $Os(SnI_3)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ [6] (2.7598(12), 2.7688(11), 2.7602(11) Å).

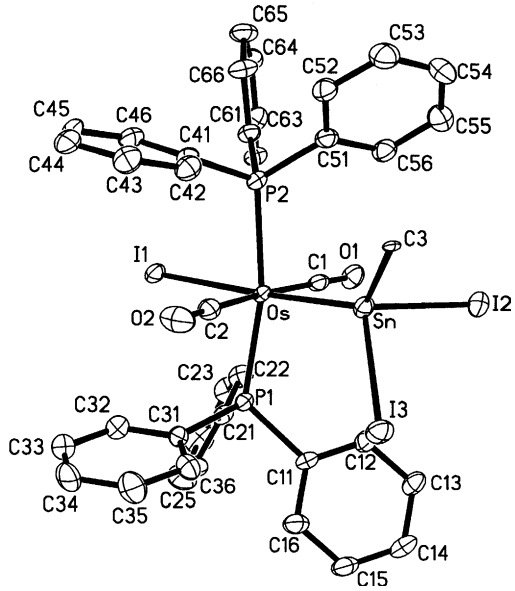


Fig. 1. Molecular geometry of $Os(SnMeI_2)I(CO)_2(PPh_3)_2$ (**4**).

The geometrical isomer observed for complex **4**, with mutually *trans* CO ligands might be expected to be unstable with respect to the isomer with mutually *cis* CO ligands. However, heating **4** in toluene under reflux for 16 h did not lead to a rearranged product but instead led to a formal loss of "MeSnI" and gave $OsI_2(CO)_2(PPh_3)_2$ (**5**). Complex **5** had mutually *trans* PPh_3 ligands and mutually *cis* CO ligands.

3. Conclusions

Oxidative addition of Me_3SnH to $Os(CO)_2(PPh_3)_2$ is a simple way to introduce the trimethylstannyl ligand to an osmium(II) complex. $Os(SnMe_3)H(CO)_2(PPh_3)_2$ undergoes redistribution reactions with either Me_2SnCl_2 or SnI_4 to give $Os(SnMe_2Cl)H(CO)_2(PPh_3)_2$ or $Os(SnMeI_2)H(CO)_2(PPh_3)_2$, respectively. Spectroscopic studies indicate that in solution $Os(SnMe_3)H(CO)_2(PPh_3)_2$ and $Os(SnMe_2Cl)H(CO)_2(PPh_3)_2$ exist as a mixture of four isomers whereas $Os(SnMeI_2)H(CO)_2(PPh_3)_2$ exists as a single isomer. The preferred isomer depends on the substituents on the stannyl ligand in these compounds: $SnMe_3$ favours the isomer with mutually *cis* PPh_3 ligands and mutually *trans* CO ligands, $SnMe_2Cl$ favours the isomer with mutually *trans* PPh_3 ligands and mutually *cis* CO ligands, and $SnMeI_2$ favours exclusively the isomer with mutually *trans* PPh_3 ligands and mutually *trans* CO ligands. The particular isomer distribution for any given compound is clearly a sensitive balance between steric and electronic effects, particularly of the stannyl ligand. It is interesting that the preferred isomer for each of the three compounds, $Os(SnMe_3)H(CO)_2(PPh_3)_2$, $Os(SnMe_2Cl)H(CO)_2(PPh_3)_2$, $Os(SnMeI_2)H(CO)_2(PPh_3)_2$, always has the three largest ligands (two triphenyphosphines and the stannyl ligand) arranged meridionally, although each compound has a different overall geometry. Further rationalisation of the preferred geometries, especially the frequent observation of isomers with mutually *trans* carbonyl ligands, will require detailed theoretical studies.

4. Experimental

4.1. General procedures and instruments

Standard laboratory procedures were followed as have been described previously [8]. The compound $Os(CO)_2(PPh_3)_3$ [9] was prepared according to the literature method.

Infrared spectra (4000–400 cm^{-1}) were recorded as Nujol mulls between KBr plates on a Perkin–Elmer Paragon 1000 spectrometer. NMR spectra were obtained on a Bruker DRX 400 at 25 °C. ^1H, ^{13}C, ^{119}Sn, and ^{31}P NMR spectra were obtained operating at 400.1 (^1H), 100.6 (^{13}C), 149.2 (^{119}Sn), and 162.0 (^{31}P) MHz, respectively. Resonances are quoted in ppm and ^1H NMR spectra referenced to either tetramethylsilane (0.00 ppm) or the proteo-impurity in the solvent (7.25 ppm for $CHCl_3$). ^{13}C NMR spectra were referenced to $CDCl_3$ (77.00 ppm), ^{119}Sn NMR spectra to $SnMe_4$ (0.00 ppm), and ^{31}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 $Os(SnMe_3)H(CO)_2(PPh_3)_2$ (**1**)

Under a nitrogen atmosphere, Me_3SnH (0.098 g, 0.592 mmol) was added to a yellow suspension of $Os(CO)_2(PPh_3)_3$ (0.510 g, 0.494 mmol) in C_6H_6 (30 mL). The reaction mixture was then irradiated with a 1000 W quartz-halogen lamp at room temperature for ca. 30 min, after which time it had become clear and colourless. The volume of the solution was reduced, in vacuo, to ca. 5 mL and ethanol (20 mL) added. Further concentration afforded a colourless precipitate from which all solvent was subsequently removed in vacuo. Recrystallisation from dichloromethane–ethanol afforeded pure **1** as colourless crystals (0.443 g, 96%). *Anal.* Calc. for $C_{41}H_{40}O_2OsP_2Sn$: C, 52.63; H, 4.31. Found: C, 52.62; H, 4.30%. IR (cm^{-1}): 1913 ν(CO) and/or ν(OsH); 2008, 1978, 1926 (CH_2Cl_2 solution) ν(CO) and/or ν(OsH).

The following NMR data are grouped according to the isomers depicted in Chart 1. The isomer ratios given in Chart 1 are derived from integral measurements made in the ^1H NMR spectra of the isomer mixture. The ^{13}C triphenylphosphine resonances could not be assigned to individual isomers and these data are presented under a separate heading, only once, along with the data which could be unambiguously assigned to isomer **1a**.

*Isomer **1a**.* ^1H NMR ($CDCl_3$, δ): −10.54 (dd, 1H, Os*H*, $^2J_{PH} = 40.0$ Hz, $^2J_{PH} = 24.0$ Hz, $^2J_{117/119SnH} = 58.0$ Hz), 0.06 (s, 9H, $^2J_{117/119SnH} = 42.8$ Hz, Sn*Me*$_3$), 6.90–8.00 (m, P*Ph*$_3$ all isomers). ^{13}C NMR ($CDCl_3$, δ): −6.1 (s, $^1J_{117/119SnC} = 116.1$ Hz, Sn*Me*$_3$), 192.1 (apparent t, $^2J_{PC} = 8.0$ Hz, $^2J_{117/119SnC} = 52.3$ Hz, *C*O). The following PPh_3 *resonances are due to all four isomers.* 127.9 (apparent d, $J_{PC} = 2.0$ Hz), 128.0 (apparent d, $J_{PC} = 3.0$ Hz), 129.4 (apparent d, $J_{PC} = 9.1$ Hz), 129.9 (s), 130.0 (s), 133.2 (t' [8], $J_{PC} = 12.1$ Hz), 133.3 (t', $J_{PC} = 12.1$ Hz), 133.4 (br), 134.0 (t', $J_{PC} = 6.0$ Hz), 136.2 (t', $^{1,3}J_{PC} = 52.3$ Hz, *i*-PPh_3), 137.1 (t', $^{1,3}J_{PC} = 52.3$ Hz, *i*-PPh_3), 137.7 (apparent d, $J_{PC} = 43.3$ Hz), 137.9 (apparent d, $J_{PC} = 46.3$ Hz). ^{31}P NMR ($CDCl_3/CH_2Cl_2$, δ): 3.2 (d, $^2J_{PC} = 8.8$ Hz, $^2J_{117/119SnP} = 53.5$ Hz), 7.0 (d, $^2J_{PC} = 8.6$ Hz, $^2J_{117/119SnP} = 395.2$ Hz). ^{119}Sn NMR ($CDCl_3$, δ): −115.4 (dd, $^2J_{119SnP} = 417.8$ Hz, $^2J_{119SnP} = 59.7$ Hz).

*Isomer **1b**.* ^1H NMR ($CDCl_3$, δ): −7.77 (t, 1H, $^2J_{PH} = 20.0$ Hz, $^2J_{117/119SnH} = 44.0$ Hz, Os*H*), −0.58 (s, $^2J_{117/119SnH} = 36.8$ Hz, Sn*Me*$_3$), 6.90–8.00 (m, P*Ph*$_3$ all

isomers). ^{13}C NMR ($CDCl_3$, δ): −5.0 (s, $^1J_{117/119SnC}$ = 165.5 Hz, Sn*Me*$_3$), 181.3 (t, $^2J_{PC}$ = 9.1 Hz, *C*O), 189.1 (t, $^2J_{PC}$ = 7.0 Hz, *C*O). See under isomer **1a** for other unassigned ^{13}C resonances. ^{31}P NMR ($CDCl_3/CH_2Cl_2$, δ): 8.8 (s, $^2J_{117/119SnP}$ = 166.2 Hz). ^{119}Sn NMR ($CDCl_3$, δ): −166.8 (t, $^2J_{119SnP}$ = 164.1 Hz).

Isomer ***1c***. ^{1}H NMR ($CDCl_3$, δ): −8.31(br t, 1H, $^2J_{PH}$ = 20.0 Hz, Os*H*), −0.24 (br s 9H, $^2J_{117/119SnH}$ = 38.0 Hz, Sn*Me*$_3$), 6.90–8.00 (m, P*Ph*$_3$ all isomers). ^{13}C NMR ($CDCl_3$, δ): −8.1 (s, $^1J_{117/119SnC}$ = 193.8 Hz, Sn*Me*$_3$). See under isomer **1a** for other unassigned ^{13}C resonances. ^{31}P NMR ($CDCl_3/CH_2Cl_2$, δ): 10.2 (s, $^2J_{117/119SnP}$ = 41.6 Hz). ^{119}Sn NMR ($CDCl_3$, δ): −127.2 (t, $^2J_{119SnP}$ = 37.3 Hz).

Isomer ***1d***. ^{1}H NMR ($CDCl_3$, δ): −7.88 (br apparent t, 1H, $^2J_{PH}$ = 24.0 Hz, Os*H*), 0.09 (s, Sn*Me*$_3$), 6.90–8.00 (m, P*Ph*$_3$ all isomers). ^{13}C NMR ($CDCl_3$, δ): −5.7 (s, Sn*Me*$_3$). See under isomer **1a** for other unassigned ^{13}C resonances. ^{31}P NMR ($CDCl_3/CH_2Cl_2$, δ): 5.6 (br d, $^2J_{PC}$ = 21.7 Hz), 9.5 (br d, $^2J_{PC}$ = 22.4 Hz). ^{119}Sn NMR ($CDCl_3$, δ): −127.2 (dd, $^2J_{119SnP}$ = 581.9, $^2J_{119SnP}$ = 164.1 Hz).

4.3. Preparation of $Os(SnMe_2Cl)H(CO)_2(PPh_3)_2$ (2)

A small Schlenk tube was charged with $OsH(SnMe_3)(CO)_2(PPh_3)_2$ (0.199 g, 0.213 mmol) and $SnMe_2Cl_2$ (0.046 g, 0.213 mmol). CH_2Cl_2 (5 mL) was added and the resulting clear, colourless solution stirred at room temperature for ca. 16 h. All volatiles were removed in vacuo and the residual colourless solid was recrystallised from CH_2Cl_2/EtOH. This afforded pure **2** as colourless crystals which were collected by vacuum filtration, washed with EtOH (3 × 10 mL) and heptane (10 mL), and dried in vacuo (yield 0.194 g, 91%). *Anal.* Calc. for $C_{40}H_{37}ClO_2OsP_2Sn$: C 50.25; H 3.90. Found: C 49.97; H 4.00%. IR (cm^{-1}): 1938 ν(CO) and/or ν(OsH); 2026, 1989, 1948 (CH_2Cl_2 solution) ν(CO) and/or ν(OsH).

Isomer ***2a***. ^{1}H NMR ($CDCl_3$, δ): −10.14 (dd, 1H, $^2J_{PH}$ = 40.0 Hz, $^2J_{PH}$ = 20.0 Hz, Os*H*), 0.48 (s, 6H, $^2J_{117/119SnH}$ = 38.8 Hz, Sn*Me*$_2$), 7.25–7.63 (m, P*Ph*$_3$ all isomers). ^{13}C NMR ($CDCl_3$, δ): 2.8 (s, Sn*Me*$_2$), 188.6 (t, $^2J_{PC}$ = 9.1 Hz, *C*O). The following PPh_3 *resonances are due to all four isomers.* 128.3 (t', $^{2,4}J_{PC}$ = 10.1 Hz, $^4J_{117/119SnC}$ = 65.4 Hz, *o*-PPh$_3$), 129.9 (s), 130.0 (s), 130.4 (s), 130.4 (s), 132.9 (apparent d, J_{PC} = 11.1 Hz), 133.3 (apparent d, J_{PC} = 11.1 Hz), 133.5 (t', $^{3,5}J_{PC}$ = 12.1 Hz, *m*-PPh$_3$), 133.7 (t', $^{3,5}J_{PC}$ = 10.1 Hz, *m*-PPh$_3$), 135.1 (t', $^{1,3}J_{PC}$ = 54.3 Hz, *i*-PPh$_3$), 135.9 (t', $^{1,3}J_{PC}$ = 53.3 Hz, *i*-PPh$_3$). ^{31}P NMR ($CDCl_3/CH_2Cl_2$, δ): 0.4 (br m). ^{119}Sn NMR ($CDCl_3$, δ): 106.5 (dd, $^2J_{119SnP}$ = 614.7 Hz, $^2J_{119SnP}$ = 45.1 Hz).

Isomer ***2b***. ^{1}H NMR ($CDCl_3$, δ): −7.70 (t, 1H, $^2J_{PH}$ = 16.0 Hz, $^2J_{117SnH}$ = 148.0 Hz, $^2J_{119SnH}$ = 152.0 Hz, Os*H*), 0.25 (s, 6H, $^2J_{117/119SnH}$ = 31.2 Hz, Sn*Me*$_2$), 7.25–7.63 (m, P*Ph*$_3$ all isomers). ^{13}C NMR ($CDCl_3$, δ): 2.9 (s, $^1J_{117/119SnC}$ = 147.6 Hz, Sn*Me*$_2$), 180.9 (t, $^2J_{PC}$ = 9.1 Hz, *C*O), 186.0 (t, $^2J_{PC}$ = 8.0 Hz, *C*O). See under isomer **2a** for other unassigned ^{13}C resonances. ^{31}P NMR ($CDCl_3/CH_2Cl_2$, δ): 6.1 (s, $^2J_{117SnP}$ = 179.3 Hz, $^2J_{119SnP}$ = 186.9 Hz). ^{119}Sn NMR ($CDCl_3$, δ): 114.0 (t, $^2J_{119SnP}$ = 188.0 Hz).

Isomer ***2c***. ^{1}H NMR ($CDCl_3$, δ): −9.25 (t, 1H, $^2J_{PH}$ = 20.0 Hz, $^2J_{117/119SnH}$ = 76.0 Hz, Os*H*), −0.36 (s, 6H, $^2J_{117/119SnH}$ = 33.2 Hz, Sn*Me*$_2$), 7.25–7.63 (m, P*Ph*$_3$ all isomers). ^{13}C NMR ($CDCl_3$, δ): 4.9 (s, $^1J_{117/119SnC}$ = 170.4 Hz, Sn*Me*$_2$), 188.0 (t, $^2J_{PC}$ = 10.1 Hz, *C*O). See under isomer **2a** for other unassigned ^{13}C resonances. ^{31}P NMR ($CDCl_3/CH_2Cl_2$, δ): 7.4 (s, $^2J_{117/119SnP}$ = 58.3 Hz). ^{119}Sn NMR ($CDCl_3$, δ): 125.7 (t, $^2J_{119SnP}$ = 58.3 Hz).

Isomer ***2d***. ^{1}H NMR ($CDCl_3$, δ): −7.53 (dd, 1H, $^2J_{PH}$ = 20.0 Hz, $^2J_{PH}$ = 20.0 Hz, Os*H*), 0.18 (s, 6H, $^2J_{117/119SnH}$ = 37.6 Hz, Sn*Me*$_2$), 7.25–7.63 (m, P*Ph*$_3$ all isomers). ^{13}C NMR ($CDCl_3$, δ): 2.8 (s, Sn*Me*$_2$). See under isomer **2a** for other unassigned ^{13}C resonances. ^{31}P NMR ($CDCl_3/CH_2Cl_2$, δ): 5.0 (br s), 5.7 (br s). ^{119}Sn NMR ($CDCl_3$, δ): 95.3 (dd, $^2J_{119SnP}$ = 808.7 Hz, $^2J_{119SnP}$ = 189.5 Hz).

4.4. Preparation of $Os(SnMeI_2)H(CO)_2(PPh_3)_2$ (3)

$Os(SnMe_3)H(CO)_2(PPh_3)_2$ (0.352 g, 0.376 mmol) and SnI_4 (1.178 g, 1.881 mmol) were dissolved in dichloromethane (20 mL) and the resulting orange suspension stirred at room temperature for ca. 16 h. All volatiles were removed in vacuo and the residual orange solid recrystallised from dichloromethane–ethanol to afford pure **3** as a pale yellow microcrystalline solid (0.392 g, 90%). *Anal.* Calc. for $C_{39}H_{34}I_2O_2OsP_2Sn$: C, 40.41; H, 2.96. Found: C, 40.13; H, 2.90%. IR (cm^{-1}): 1964 ν(CO). ^{1}H NMR ($CDCl_3$, δ): −10.62 (t, 1H, $^2J_{PH}$ = 19.1 Hz, $^2J_{117SnH}$ = 233.4 Hz, $^2J_{119SnH}$ = 244.1 Hz, Os*H*), 1.09 (s, 3H, $^2J_{117/119SnH}$ = 19.1 Hz, Sn*Me*), 7.37 (m, 22H, PPh$_3$), 7.50 (m, 8H, PPh$_3$). ^{13}C NMR ($CDCl_3$, δ): 12.5 (s, Sn*Me*), 128.6 (t', $^{2,4}J_{PC}$ = 10.1 Hz, *o*-PPh$_3$), 130.8 (s, *p*-PPh$_3$), 133.6 (t', $^{3,5}J_{PC}$ = 11.1 Hz, *m*-PPh$_3$), 134.4 (t', $^{1,3}J_{PC}$ = 54.3 Hz, *i*-PPh$_3$), 185.8 (t, $^2J_{PC}$ = 11.1 Hz, *C*O). ^{31}P NMR ($CDCl_3/CH_2Cl_2$, δ): 5.9 (s, $^2J_{117/119SnP}$ = 63.8 Hz). ^{119}Sn NMR ($CDCl_3$, δ): 69.6 (t, $^2J_{117SnP}$ = 62.7 Hz).

4.5. Preparation of $Os(SnMeI_2)I(CO)_2(PPh_3)_2$ (4)

A pale yellow solution of $Os(SnMeI_2)H(CO)_2(PPh_3)_2$ (0.300 g, 0.259 mmol) in dichloromethane (10 mL) was cooled in an ice-bath and a solution of I_2 (0.069 g, 0.272 mmol) in dichloromethane (10 mL) added dropwise while stirring rapidly. All volatiles were then removed from the resulting dark orange solution, in vacuo, and the residual glassy orange solid recrystallised from dichloromethane–ethanol to afford pure **4** as a bright yellow microcrystalline solid (0.292 g, 88%). *Anal.* Calc.

for $C_{39}H_{33}I_3O_2OsP_2Sn$: C, 36.45; H, 2.59. Found: C, 36.64; H, 2.37%. IR (cm^{-1}): 1957 ν(CO). ^{1}H NMR ($CDCl_3$, δ): 1.11 (s, 3H, $^2J_{117/119SnH} = 37.1$ Hz, Sn*Me*), 7.41 (m, 22H, PPh_3), 7.75 (m, 8H, PPh_3). ^{13}C NMR ($CDCl_3$, δ): 13.5 (s, Sn*Me*), 128.4 (t', $^{2,4}J_{PC} = 10.1$ Hz, *o*-PPh_3), 130.8 (s, *p*-PPh_3), 133.9 (t', $^{1,3}J_{PC} = 56.3$Hz, *i*-PPh_3), 134.6 (t', $^{3,5}J_{PC} = 10.1$ Hz, *m*-PPh_3), 183.2 (t, $^2J_{PC} = 10.1$ Hz, *C*O). ^{31}P NMR ($CDCl_3/CH_2Cl_2$, δ): 5.8 (s, $^2J_{117/119SnP} = 63.1$ Hz). ^{119}Sn NMR ($CDCl_3$, δ): −66.0 (t, $^2J_{119SnP} = 65.7$ Hz).

4.6. Preparation of $OsI_2(CO)_2(PPh_3)_2$ (5)

A stirred, bright yellow suspension of $Os(SnMeI_2)I(CO)_2(PPh_3)_2$ (0.081 g, 0.063 mmol) in toluene (10 mL) was heated under reflux for ca. 16 h, during which time a slightly cloudy, colourless solution resulted. All volatiles were then removed in vacuo and the residual colourless solid recrystallised from dichloromethane–ethanol to afford pure **5** as a colourless microcrystalline solid (0.054 g, 84%). *Anal.* Calc. for $C_{38}H_{30}I_2O_2OsP_2Sn$: C, 44.55; H, 2.95. Found: C,44.31; H,2.67%. IR (cm^{-1}): 2035, 1973 ν(CO). ^{1}H NMR ($CDCl_3$, δ): 7.38 (m, 22H, PPh_3), 7.90 (m, 8H, PPh_3). ^{13}C NMR ($CDCl_3$, δ): 127.8 (t',$^{2,4}J_{PC} = 10.3$ Hz, *o*-PPh_3), 130.7 (s, *p*-PPh_3), 132.0 (t', $^{1,3}J_{PC} = 54.7$ Hz, *i*-PPh_3), 134.9 (t', $^{3,5}J_{PC} = 9.7$ Hz, *m*-PPh_3), 169.9 (t, $^2J_{PC} = 6.9$ Hz, *C*O). ^{31}P NMR ($CDCl_3/CH_2Cl_2$, δ): −28.4 (s).

Table 1
Data collection and processing parameters for $\mathbf{4}\cdot 0.5CH_2Cl_2$

Formula	$C_{39}H_{33}I_3O_2OsP_2Sn\cdot 0.5CH_2Cl_2$
Molecular weight	1327.65
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	12.1419(1)
b (Å)	23.4363(3)
c (Å)	16.3552(2)
β (°)	94.783(1)
V (Å^3)	4637.85(9)
Z	4
d(calc) (g cm^{-3})	1.90
$F(000)$	2476
μ (mm^{-1})	5.43
Crystal size (mm)	$0.28 \times 0.26 \times 0.26$
2θ (minimum and maximum) (°)	1.5 and 27.1
Reflections collected	27,781
Independent reflections	9982 [$R_{int} = 0.0281$]
A (minimum and maximum)	0.312 and 0.333
Function minimised	$\sum w(F_o^2 - F_c^2)^2$
Goodness-of-fit on F^2	1.089
R, wR_2 (observed data)	0.0323, 0.0858
R, wR_2 (all data)	0.0360, 0.0885
Difference map (minimum and maximum) (e Å^{-3})	+2.88 and −1.26
$R = \sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \sum \lvert F_o\rvert$	$wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$

$w = 1.0/[\sigma^2(F_o^2) + aP^2 + bP],\ P = (F_o^2 + 2F_c^2)/3.$

4.7. X-ray crystal structure determination for complex 4

X-ray data collection was by Siemens SMART diffractometer with a CCD area detector using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were integrated and corrected for Lorentz and polarisation effects using SAINT [10]. Semi-empirical absorption corrections were applied based on equivalent reflections using SADABS [11]. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares using programs SHELXS [11] and SHELXL [12]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located geometrically and refined using a riding model. The final electron density map contained numerous electron density peaks, three of which could be resolved into a half-weighted molecule of dichloromethane. The remaining peaks could not be resolved, sensibly, into molecules and presumably represent further disordered dichloromethane molecules. This density was removed using the 'squeeze' function of PLATON [13] before the final refinement.

Crystal data and refinement details for both structures are given in Table 1.

Table 2
Selected bond lengths (Å) and angles (°) for **4**

Os–C(1)	1.933(6)
Os–C(2)	1.952(5)
Os–P(2)	2.4151(13)
Os–P(1)	2.4332(13)
Os–Sn	2.6531(4)
Os–I(1)	2.7718(4)
Sn–C(3)	2.294(5)
Sn–I(2)	2.7727(5)
Sn–I(3)	2.7739(5)
O(1)–C(1)	1.142(7)
O(2)–C(2)	1.138(7)
C(1)–Os–C(2)	172.9(2)
C(1)–Os–P(2)	91.47(15)
C(2)–Os–P(2)	90.17(15)
C(1)–Os–P(1)	92.92(15)
C(2)–Os–P(1)	86.87(16)
P(2)–Os–P(1)	167.74(4)
C(1)–Os–Sn	87.54(15)
C(2)–Os–Sn	85.51(16)
P(2)–Os–Sn	92.03(3)
P(1)–Os–Sn	99.58(3)
C(1)–Os–I(1)	99.03(15)
C(2)–Os–I(1)	88.00(16)
P(2)–Os–I(1)	83.36(3)
P(1)–Os–I(1)	84.65(3)
Sn–Os–I(1)	172.035(13)
C(3)–Sn–Os	126.62(11)
C(3)–Sn–I(2)	100.18(11)
Os–Sn–I(2)	116.270(16)
C(3)–Sn–I(3)	93.13(11)
Os–Sn–I(3)	116.646(16)
I(2)–Sn–I(3)	98.465(15)
O(1)–C(1)–Os	176.2(5)
O(2)–C(2)–Os	178.2(5)

5. Supplementary material

Crystallographic data (excluding structure factors) for **4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 219511. 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 http://www.ccdc.cam.ac.uk).

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