

Syntheses, reactions, and structures of osmium(II) distannyl complexes, $L_n\text{Os-SnMe}_2\text{SnR}_3$ ($R = \text{Me, Ph}$), from reaction between $L_n\text{Os-SnClMe}_2$ and either LiSnMe_3 or KSnPh_3

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Abstract

Reaction between $\text{Os}(\text{SnClMe}_2)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ and either LiSnMe_3 or KSnPh_3 produces the distannyl complexes, $\text{Os}(\text{SnMe}_2\text{SnMe}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (**1**) or $\text{Os}(\text{SnMe}_2\text{SnPh}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (**3**), respectively. Similarly, reaction between $\text{Os}(\text{SnClMe}_2)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ (**6**) and KSnPh_3 produces the distannyl complex, $\text{Os}(\text{SnMe}_2\text{SnPh}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ (**7**). In the ^{119}Sn NMR spectra of these stable osmium(II) distannyl complexes both the α -Sn and β -Sn atoms show well-resolved ^{119}Sn – ^{119}Sn and ^{119}Sn – ^{117}Sn coupling. Each of these three distannyl complexes can be selectively functionalised at the α -Sn atom by reaction with SnCl_2Me_2 giving $\text{Os}(\text{SnClMeSnMe}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (**2**), $\text{Os}(\text{SnClMeSnPh}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (**4**), and $\text{Os}(\text{SnClMeSnPh}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ (**8**), respectively. Treatment of compounds **3** or **7** with iodine also cleaves one α -methyl group, selectively, to give $\text{Os}(\text{SnImeSnPh}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (**5**), or $\text{Os}(\text{SnImeSnPh}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ (**9**). Crystal structures for complexes **3** and **7** have been determined.

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1. Introduction

Disilanyl complexes of type $L_n\text{M-SiR}_2\text{-SiR}_3$, when coordinatively unsaturated, have proved to be interesting precursors for silylene complexes through reversible migration of the β -silyl group to the metal [1,2]. Furthermore, in regioselective reactions the α -silicon in $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{-SiMe}_3$ is bromodemethylated by reaction with BBR_3 to form $\text{Cp}^*(\text{CO})_2\text{FeSiBr}_2\text{SiMe}_3$ [3], and the α -Si-H bonds

in $\text{Cp}^*(\text{CO})_2\text{FeSiH}_2\text{SiH}_3$ react selectively with either CCl_4 or with dimethyldioxirane to give either $\text{Cp}^*(\text{CO})_2\text{FeSiCl}_2\text{SiH}_3$ [4] or $\text{Cp}^*(\text{CO})_2\text{FeSi}(\text{OH})_2\text{SiH}_3$ [5], respectively.

This interesting chemistry prompted us to examine corresponding distannyl complexes of type $L_n\text{M-SnR}_2\text{-SnR}_3$. Most disilanyl complexes of type $L_n\text{M-SiR}_2\text{-SiR}_3$ have been prepared beginning with a readily available and appropriately substituted disilane, and introducing the metal either as an anion or through an elimination reaction [1,2]. This approach for the corresponding distannyl complexes is less favourable because of the scarcity of suitably substituted distannanes. The very few reported distannyl complexes of type $L_n\text{M-SnR}_2\text{-SnR}_3$ include $(\text{PPh}_3)_2\text{PhPt-SnPh}_2\text{SnPh}_3$ (which was neither spectroscopically nor

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structurally characterised) from oxidative addition of a Sn–Ph bond in Sn_2Ph_6 to $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ [6] and $\text{CpCp}^*\text{ClHfSnPh}_2\text{SnHMes}_2$ (which was spectroscopically but not structurally characterised) from the complex reaction of $\text{CpCp}^*\text{ClHfSnHMes}_2$ with Ph_2SnH_2 [7]. Minor products also formed in this reaction include the tristannyl complex, $\text{CpCp}^*\text{ClHfSnPh}_2\text{SnPh}_2\text{SnHPh}_2$. Complexes involving the $\text{Sn}(\text{SnMe}_3)_3$ ligand, which result from reaction between $\text{LiSn}(\text{SnMe}_3)_3$ and the appropriate metal halide, include $\text{Cp}[\text{P}(\text{OPh})_3]_2\text{FeSn}(\text{SnMe}_3)_3$ [8] and $\text{Mo}_2[\text{Sn}(\text{SnMe}_3)_3]_2(\text{NMe}_2)_2$ [9]. Other distannanes substituted with transition metal fragments include the complex, $\text{H}_2\text{Sn}_2[\text{Mn}(\text{CO})_5]_4$, which results from the remarkable reaction between $\text{HMn}(\text{CO})_5$ and Cp_2Sn [10], $\text{Ph}_2\text{Sn}_2[\text{FeCp}(\text{CO})_2]_4$ produced by electrochemical reduction of $\text{PhClSn}[\text{FeCp}(\text{CO})_2]_2$ [11] and $\text{Ph}_4\text{Sn}_2[\text{Mn}(\text{CO})_5]_2$ [12]. This last complex results from the unexpected reaction between $\text{Ph}_2\text{ClSnMn}(\text{CO})_5$ and $\text{C}_6\text{F}_5\text{Li}$. The authors proposed that the reaction proceeds through an initial lithium-halogen exchange to produce the tin anion, $\text{Li}[\text{Ph}_2\text{SnMn}(\text{CO})_5]$, which then attacks $\text{Ph}_2\text{ClSnMn}(\text{CO})_5$ to give the observed product. This observation suggested that reaction between LiSnR_3 and a halostannyl complex, $\text{L}_n\text{M}-\text{SnR}_2-\text{X}$, could offer a general route to distannyl complexes, $\text{L}_n\text{M}-\text{SnR}_2-\text{SnR}_3$.

We had previously developed preparative routes to several halostannyl complexes of osmium which undergo facile substitution reactions to yield novel products, e.g., a stannatranlyl complex from $\text{Os}(\text{SnI}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ and triethanolamine [13], a hydroxystannyl complex, $\text{Os}(\text{SnMe}_2(\text{OH}))(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ from $\text{Os}(\text{SnMe}_2\text{Cl})(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ with KOH [14], a trihydroxystannyl complex, $\text{Os}(\text{Sn}(\text{OH})_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ from $\text{Os}(\text{SnI}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ with KOH [15], and the simple SnH_3 complex, $\text{Os}(\text{SnH}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ from $\text{Os}(\text{SnI}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ with NaBH_4 [16]. Accordingly, we selected two chlorodimethylstannyl complexes, $\text{Os}(\text{SnMe}_2\text{Cl})(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ and $\text{Os}(\text{SnMe}_2\text{Cl})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$, and examined the reactivity of these two compounds towards the tin anions $[\text{SnMe}_3]^-$ and $[\text{SnPh}_3]^-$ in the salts LiSnMe_3 and KSnPh_3 .

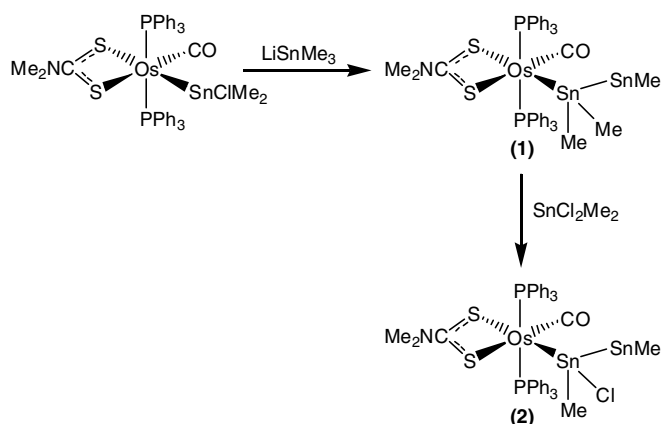
In this paper we report: (i) the syntheses of the distannyl complexes $\text{Os}(\text{SnMe}_2\text{SnMe}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (**1**), $\text{Os}(\text{SnMe}_2\text{SnPh}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (**3**), and $\text{Os}(\text{SnMe}_2\text{SnPh}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ (**7**) from reaction between $\text{Os}(\text{SnClMe}_2)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ and LiSnMe_3 , $\text{Os}(\text{SnClMe}_2)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ and KSnPh_3 , $\text{Os}(\text{SnClMe}_2)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ (**6**) and KSnPh_3 , respectively, (ii) ^{119}Sn NMR spectroscopic data for these stable osmium(II) distannyl complexes which reveal that both the α -Sn and β -Sn atoms show well-resolved $^{119}\text{Sn}-^{119}\text{Sn}$ and $^{119}\text{Sn}-^{117}\text{Sn}$ coupling, (iii) crystal structure determinations for distannyl complexes **3** and **7**, and (iv) selective functionalisation reactions at the α -tin atom in the distannyl complexes by reaction with either SnMe_2Cl_2 or I_2 .

2. Results and discussion

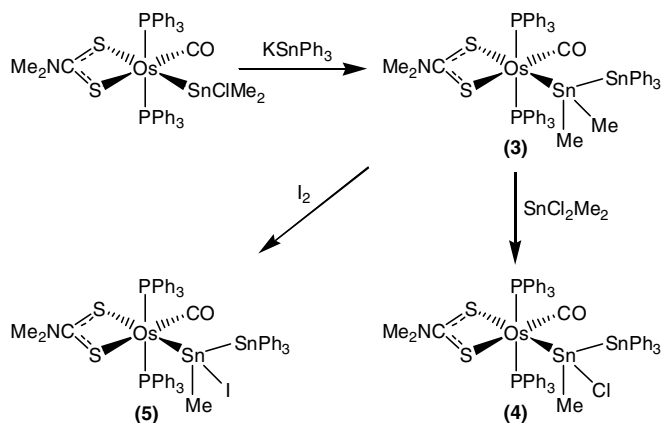
2.1. The syntheses of the distannyl complexes,

$\text{Os}(\text{SnMe}_2\text{SnMe}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (**1**), $\text{Os}(\text{SnMe}_2\text{SnPh}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (**3**), and $\text{Os}(\text{SnMe}_2\text{SnPh}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ (**7**) from reaction between $\text{Os}(\text{SnClMe}_2)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ and LiSnMe_3 , $\text{Os}(\text{SnClMe}_2)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ and KSnPh_3 , $\text{Os}(\text{SnClMe}_2)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ (**6**) and KSnPh_3 , respectively

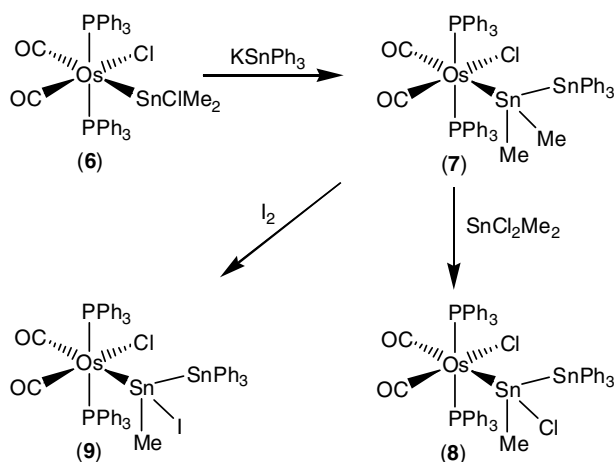
As illustrated in Schemes 1–3, LiSnMe_3 and KSnPh_3 readily displaces chloride from the SnClMe_2 ligands in $\text{Os}(\text{SnClMe}_2)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ and $\text{Os}(\text{SnClMe}_2)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ (**6**) to form the distannyl complexes **1**, **3**, and **7** in good yields. All three complexes are colourless crystalline solids and show good solution stability. The IR spectra of **1** and **3** show $\nu(\text{CO})$ bands at 1907 and 1895 cm^{-1} , respectively, and the dicarbonyl complex **7** shows two $\nu(\text{CO})$ bands at 2017, 1958 cm^{-1} as expected for a *cis* arrangement of CO ligands. Full spectroscopic data for all the compounds appears in Section 4. The ^1H



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



Scheme 2. Synthesis and reactions of $\text{Os}(\text{SnMe}_2\text{SnPh}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (**3**).



Scheme 3. Synthesis and reactions of $\text{Os}(\text{SnMe}_2\text{SnPh}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ (**6**).

NMR spectra of **1**, **3**, and **7** all show a singlet signal for the two equivalent methyl groups on the α -Sn. Each of these signals shows satellites arising from coupling ($J_{\text{Sn}(117/119)\text{H}}$) to both the α -Sn and the β -Sn atoms. In the case of **1** the three equivalent methyl groups on the β -Sn also appear as a singlet with satellites arising from coupling to both the α -Sn and the β -Sn atoms. Likewise, the ^{13}C NMR spectra of **1**, **3**, and **7** all show a singlet signal for the two equivalent methyl groups on the α -Sn. The signals for **1** and **3** again show satellites arising from coupling ($J_{\text{Sn}(117/119)\text{C}}$) to both the α -Sn and the β -Sn atoms. However, in **7**, no satellites were observed for the singlet signal for the two methyl groups on the α -Sn. The three equivalent methyl groups on the β -Sn in **1** also appear as a singlet with satellites arising from coupling to both the α -Sn and the β -Sn atoms and in this case the one-bond coupling to ^{117}Sn and ^{119}Sn is resolved.

The three compounds, **1**, **3**, and **7**, each show a singlet in the ^{31}P NMR spectrum which is consistent with a *trans* arrangement of the triphenylphosphine ligands, subsequently confirmed by crystal structure determination (see below). Each singlet in the ^{31}P NMR spectrum shows Sn satellites, resulting from coupling with the α -Sn for **1**, **3**, and **7** and with the β -Sn as well for **1**.

The ^{119}Sn NMR spectra of **1**, **3**, and **7** are quite complex but detailed analysis is especially revealing of the Os–Sn–Sn linkage. Each compound will be discussed separately. The ^{119}Sn NMR spectrum of **1** is depicted in Fig. 1 and it can be seen that the α -Sn resonance occurs at -283.3 ppm and the β -Sn resonance occurs at -170.8 ppm. This pattern of the metal-bound tin signal appearing at higher field relative to the β -Sn signal is common to the organo-substituted distannyl complexes **1**, **3**, and **7**, but is reversed for all the α -halo-substituted complexes, **2**, **4**, **5**, **8**, and **9**, reported in this paper (see below). In **1**, both the α -Sn and β -Sn resonances at -283.3 and -170.8 ppm, respectively, are observed as triplets through coupling to phosphorus (see Fig. 1). The two-bond coupling of the α -Sn is 88 Hz and the three-bond coupling of

the β -Sn is 9 Hz. The values and relative magnitudes of these two coupling constants are typical of all the distannyl compounds reported in this paper. Each of these triplets show two sets of satellites arising through one bond Sn–Sn coupling to the adjacent tin atom, when present as either the ^{117}Sn isotope or the ^{119}Sn isotope. Inspection of Fig. 1 indicates that the satellite signals are not symmetrically distributed about the central triplet signal, a feature most clearly seen in trace (B). This is because the chemical shift of the ^{119}Sn resonance changes according to whether the adjacent isotope is ^{117}Sn or ^{119}Sn . The assignments of the appropriate pairs of satellite triplets, for determination of the coupling constants, are based upon the requirement that the ratio $J_{\text{Sn}(119)\text{Sn}(119)}/J_{\text{Sn}(119)\text{Sn}(117)}$ is the same as ratio of the magnetogyric ratios for $^{119}\text{Sn}/^{117}\text{Sn}$, that is 1.0462 [17a]. The coupling constants so measured for the α -Sn in complex **1** are $^1J_{\text{Sn}(117)\text{Sn}(119)} = 2333$, $^1J_{\text{Sn}(119)\text{Sn}(119)} = 2442$ Hz and for the β -Sn are $^1J_{\text{Sn}(117)\text{Sn}(119)} = 2332$, $^1J_{\text{Sn}(119)\text{Sn}(119)} = 2441$ Hz. The corresponding one-bond coupling constants, determined in the same manner, for all the remaining distannyl complexes reported in this paper are to be found in Section 4. The Sn–Sn coupling constants measured for $\text{Os}(\text{SnMe}_2\text{SnMe}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (**1**) are far less than that reported for $\text{Me}_3\text{SnSnMe}_3$ ($^1J_{\text{Sn}(119)\text{Sn}(119)} = 4404$ Hz) [17a]. We are aware of only two other transition metal distannyl complexes where the one bond Sn–Sn coupling constants have been measured and these are $\text{CpCp}^*\text{ClHfSnPh}_2\text{SnHMe}_2$ for which $^1J_{\text{Sn}(117/119)\text{Sn}(119)}$ is 185 Hz [7] and $\text{Cp}[\text{P}(\text{O}^i\text{Pr})_3]_2\text{FeSn}(\text{SnMe}_3)_3$ [17b] for which a value near to zero was measured by a heteronuclear double-resonance experiment. It is clear that the presence of a transition metal and associated ligands as a substituent on a ditin fragment has the effect of reducing the one bond Sn–Sn coupling constant. The corresponding values observed for complexes **2**, **3**, **4**, **5**, **7**, **8**, and **9** are less than those for complex **1**. For example, replacement of the β -trimethylstannyl group in **1** with the β -triphenylstannyl group in **3** reduces the values to $^1J_{\text{Sn}(117)\text{Sn}(119)} = 1074$, $^1J_{\text{Sn}(119)\text{Sn}(119)} = 1119$ Hz (measured for the α -Sn) and to $^1J_{\text{Sn}(117)\text{Sn}(119)} = 1061$, $^1J_{\text{Sn}(119)\text{Sn}(119)} = 1120$ Hz (measured for the β -Sn). One bond Sn–Sn coupling has been correlated with the Taft σ^* values of the substituents on tin [17b] and with the s-overlap integral for the Sn–Sn bond [17c]. One piece of evidence suggesting that electronegative substituents increase the Sn–Sn coupling constant is that the value for $\text{Bu}_2(\text{OAc})\text{SnSnBu}_2(\text{OAc})$ (14,980 Hz) is much greater than the value for $\text{Bu}_3\text{SnSnBu}_3$ (2,748 Hz) [17b]. However, the coordination number of tin in $\text{Bu}_2(\text{OAc})\text{SnSnBu}_2(\text{OAc})$ is 5 and direct comparisons should be made with caution. The lowest values measured in this work were for complex (**5**) (see below) where the α -Sn has an iodo-substituent, $^1J_{\text{Sn}(117)\text{Sn}(119)} = 525$, $^1J_{\text{Sn}(119)\text{Sn}(119)} = 531$ Hz (measured for the α -Sn) and to $^1J_{\text{Sn}(117)\text{Sn}(119)} = 522$, $^1J_{\text{Sn}(119)\text{Sn}(119)} = 537$ Hz (measured for the β -Sn). We cannot explain this unexpected reduction in coupling constant associated with halogen substitution of the α -tin and further measurements

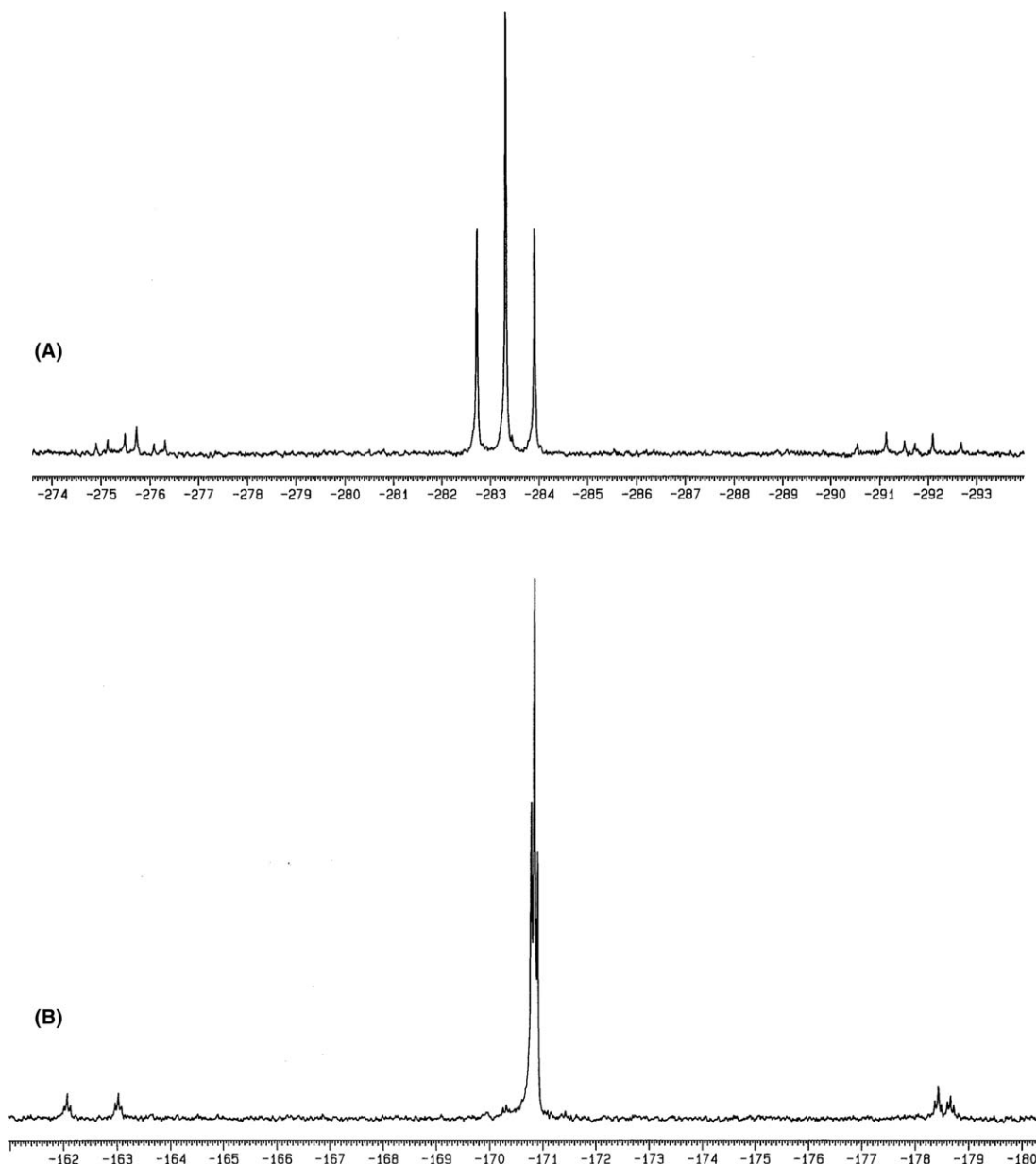


Fig. 1. The ^{119}Sn NMR spectrum of $\text{Os}(\text{SnMe}_2\text{SnMe}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (**1**): the α -Sn resonance with satellites is shown in trace (A) and the β -Sn resonance with satellites is shown in trace (B).

on a greater range of compounds in conjunction with theoretical studies will be required to rationalise these observations.

2.2. The crystal structures of $\text{Os}(\text{SnMe}_2\text{SnPh}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (**3**), and $\text{Os}(\text{SnMe}_2\text{SnPh}_3)\text{-Cl}(\text{CO})_2(\text{PPh}_3)_2$ (**7**)

Further confirmation of the presence of distanny ligands in these complexes was provided by crystal structure determinations of **3** and **7**. The molecular geometries of **3** and **7** are shown in Figs. 2 and 3, respectively, and crystal data pertaining to these structures are presented in Table 1. Selected bond lengths and angles for **3** and **7** are

collected in Tables 2 and 3, respectively. In the structure of **3** the overall geometry about osmium can be described as octahedral with the two triphenylphosphine ligands arranged mutually *trans*. The dimethyldithiocarbamate ligand is reasonably symmetrically attached (Os–S(1), 2.4662(15) and Os–S(2), 2.4772(15) Å). Related osmium stannyl, dimethyldithiocarbamate complexes also show symmetrical attachment of this bidentate ligand [15]. The Os–Sn(1) distance in **3** is 2.6928(5) Å (the average for 33 observations listed in the CCDC is 2.7037 Å with an SD of 0.0586 Å) which is longer than the value found for the corresponding SnMe_3 complex, $\text{Os}(\text{SnMe}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (2.6616(13) Å) [15] but reasonable in view of the increased steric demands of the distanny ligand.

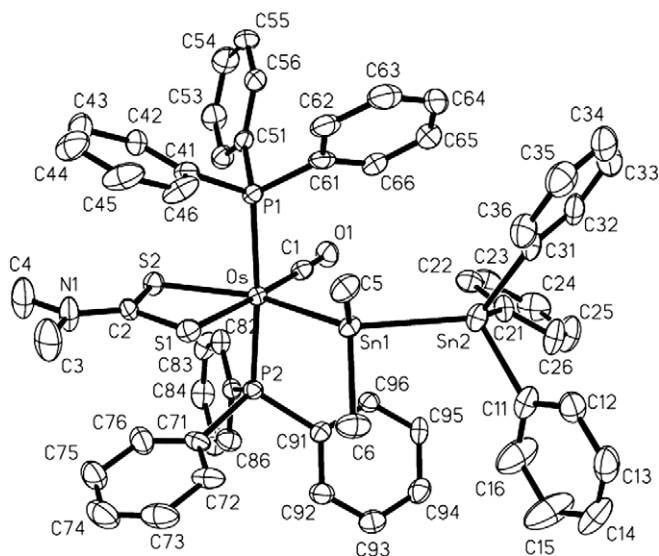


Fig. 2. Molecular geometry of $\text{Os}(\text{SnMe}_2\text{SnPh}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (**3**).

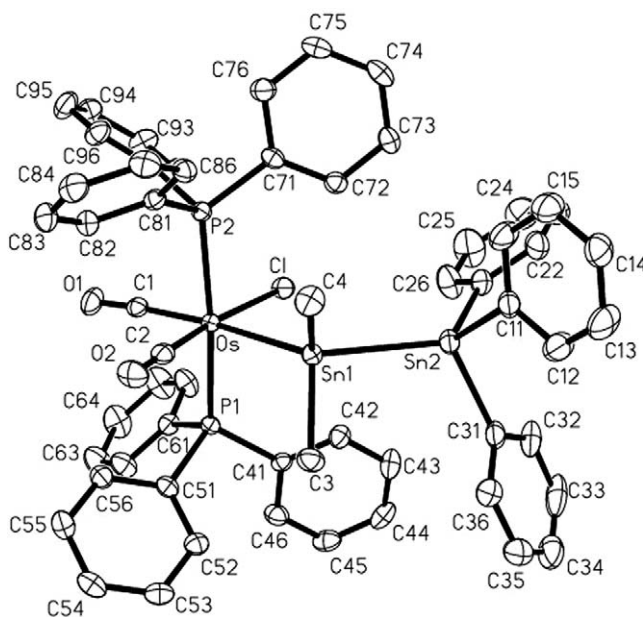


Fig. 3. Molecular geometry of $\text{Os}(\text{SnMe}_2\text{SnPh}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ (**7**).

Further support for the idea that replacement of a methyl group on the trimethylstannyl ligand by a triphenylstannyl group introduces considerable steric pressures is provided by the large $\text{Os-Sn}(1)\text{-Sn}(2)$ angle of $129.816(18)^\circ$. The $\text{Sn}(1)\text{-Sn}(2)$ distance in **3** is unremarkable at $2.8236(6)$ Å. It is probably not very meaningful to compare this value with the average of 281 observations of all Sn–Sn distances listed in the CCDC (2.8708 Å with an SD of 0.0950 Å) since this compilation includes many examples which are complex tin cluster compounds including tin Zintl ions. A more meaningful comparison is with the Sn–Sn distances in simple organo-polystannanes, e.g., Ph_6Sn_2 ($2.770(4)$ Å [18]) and the cyclic hexamer of diphenyltin (2.78 Å [19]).

The observed distance in **3** is only slightly longer than these distances and in fact lies between these values and the measured distance in $\text{Br}_2\text{Sn}_2[\text{Mn}(\text{CO})_5]_4$ ($2.885(1)$ Å [10b]). The two $\alpha\text{-Sn-CH}_3$ distances at $2.188(7)$ and $2.198(7)$ Å are similar to those reported for $\text{Os}(\text{SnMe}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ [15] and are right at the long end of the range of Sn–CH₃ distances recorded in the CCDC (1569 observations, average 2.1367 Å with an SD of 0.0267 Å). This may be related to the unusual reactivity associated with these methyl groups to be discussed below.

In the structure of **7** the overall geometry about osmium is close to regular octahedral with the two triphenylphosphine ligands arranged mutually *trans* and the two CO ligands mutually *cis*. The $\text{Os-Sn}(1)$ distance in **7** is $2.7925(2)$ Å is significantly longer than the corresponding distance in **3** and this no doubt reflects the *trans* influence of the CO ligand. The CO ligand *trans* to the distannyl ligand is associated with a longer Os–CO bond ($1.928(3)$ Å) than the CO ligand *trans* to chloride ($1.882(3)$ Å) in turn reflecting the *trans* influence of the distannyl ligand. The $\text{Os-Sn}(1)\text{-Sn}(2)$ angle in **7** is $128.496(8)^\circ$, very close to the value found in **3**. The $\text{Sn}(1)\text{-Sn}(2)$ distance in **7** is unremarkable at $2.8367(2)$ Å and again is very close to the value found in **3**. Clearly, changing the accompanying ligands in the two distannyl complexes, **3** and **7**, makes very little difference to the geometrical parameters of the Os–distannyl moiety. Once again the two $\alpha\text{-Sn-CH}_3$ distances at $2.169(3)$ and $2.171(3)$ Å are at the long end of the range of Sn–CH₃ distances recorded in the CCDC (1569 observations, average 2.1367 Å with an SD of 0.0267 Å) but the lengthening of these bonds is not as pronounced as for **3**.

2.3. Selective $\alpha\text{-Sn}$ functionalisation of distannyl complexes **1**, **3**, and **7** with SnCl_2Me_2 giving $\text{Os}(\text{SnClMeSnMe}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (**2**), $\text{Os}(\text{SnClMeSnPh}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (**4**), and $\text{Os}(\text{SnClMeSnPh}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ (**8**), respectively

It is well established that simple stannyl complexes, $\text{L}_n\text{M-SnR}_3$, readily undergo exchange reactions with halo-substituted stannanes to form $\text{L}_n\text{M-SnR}_2\text{X}$, $\text{L}_n\text{M-SnRX}_2$, or $\text{L}_n\text{M-SnX}_3$, depending upon the particular halo-stannane and the particular reaction conditions [20,15]. Accordingly reaction between the distannyl complexes **1**, **3**, and **7**, and SnCl_2Me_2 were investigated. As depicted in Schemes 1–3 these reactions proceeded cleanly and in high yield to give exclusively the reaction products from exchange at the $\alpha\text{-Sn}$ atom, $\text{Os}(\text{SnClMeSnMe}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (**2**), $\text{Os}(\text{SnClMeSnPh}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (**4**), and $\text{Os}(\text{SnClMeSnPh}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ (**8**). That the integrity of the Sn–Sn bond retained in all of these complexes is clear from the ^1H and ^{119}Sn NMR spectra of **2**, **4**, and **8**. In the ^1H NMR spectra the methyl signal on the $\alpha\text{-Sn}$ shows both two- and three-bond coupling to the $\alpha\text{-Sn}$ and $\beta\text{-Sn}$ atoms, respectively. In the ^{119}Sn NMR spectra of these complexes separate triplet signals are seen for both the $\alpha\text{-Sn}$

Table 1
Data collection and processing parameters for **3** and **7**

	3 · 2CH ₂ Cl ₂	7
Formula	C ₆₂ H ₆₁ Cl ₄ NOOsP ₂ S ₂ Sn ₂	C ₅₈ H ₅₁ ClO ₂ OsP ₂ Sn ₂
Molecular weight	1531.56	1304.96
Crystal system	Monoclinic	Triclinic
Space group	C2/c	P $\bar{1}$
<i>a</i> (Å)	36.2935(4)	12.1286(3)
<i>b</i> (Å)	15.0172(1)	13.5793(4)
<i>c</i> (Å)	24.2814(1)	17.1334(4)
α (°)		93.637(1)
β (°)	109.611(1)	103.200(1)
γ (°)		107.759(1)
<i>V</i> (Å ³)	12466.34(17)	2589.23(12)
<i>Z</i>	8	2
<i>D</i> _(calc) (g cm ⁻³)	1.632	1.674
<i>F</i> (000)	6032	1276
μ (mm ⁻¹)	3.16	3.56
Crystal size (mm)	0.30 × 0.28 × 0.16	0.38 × 0.16 × 0.14
θ (min–max) (°)	1.6–26.4	1.6–26.1
Reflections collected	34 551	24 109
Independent reflections (<i>R</i> _{int})	12666 (0.0266)	10117 (0.0213)
<i>T</i> (min–max)	0.451–0.632	0.345–0.636
Goodness of fit on <i>F</i> ²	1.207	1.066
<i>R</i> (observed data)	<i>R</i> ₁ = 0.0425, <i>wR</i> ₂ = 0.1075	<i>R</i> ₁ = 0.0192, <i>wR</i> ₂ = 0.0454
<i>R</i> (all data)	<i>R</i> ₁ = 0.0509, <i>wR</i> ₂ = 0.1113	<i>R</i> ₁ = 0.0228, <i>wR</i> ₂ = 0.0470
Diff. map (min–max) (e Å ⁻³)	–1.15 and +2.67	–0.74 and +0.73

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

and β -Sn atoms and one-bond Sn–Sn coupling is observed for each signal. Replacement of a methyl group on the α -Sn by a chloride in each case results in a reduction of the Sn–Sn coupling constants (see discussion in Section 2.3). A feature of the ³¹P NMR spectrum of complex **8** is that two resonances are observed (–10.7 and –10.5 ppm) indicating that the two phosphorus atoms are slightly inequivalent. This same feature is observed in the ³¹P NMR spectra of complexes **5** and **9** to be described below. In principle, in complexes **2**, **4**, **5**, **8**, and **9** where a chiral tin centre is directly bound to the osmium atom, the two phosphorus atoms will be inequivalent. However, the difference in the chemical shift values may be very small and is not observed in complexes **2** and **4**.

2.4. Selective α -Sn functionalisation of distanny complexes **3**, and **7** with iodine to give Os(SnIMeSnPh₃)-(κ^2 -S₂CNMe₂)(CO)(PPh₃)₂ (**5**), or Os(SnIMeSnPh₃)Cl(CO)₂(PPh₃)₂ (**9**)

In view of the facility with which Sn–phenyl bonds are usually cleaved by reaction with iodine [17a], the two complexes bearing phenyl substituents on the β -Sn atom, complexes **3** and **7** were treated with iodine in the hope of functionalising the β -Sn atom. Of course, a possible competing reaction would be cleavage of the Sn–Sn bond and this has been demonstrated to occur when Cp[P(OPh)₃]₂-FeSn(SnMe₃)₃ is treated with iodine [21]. In fact, complexes **3** and **7** react cleanly with one equivalent of iodine at low temperature to form again the products from cleavage of a methyl group from the α -Sn atom (see Schemes 2

and 3), Os(SnIMeSnPh₃)(κ^2 -S₂CNMe₂)(CO)(PPh₃)₂ (**5**), and Os(SnIMeSnPh₃)Cl(CO)₂(PPh₃)₂ (**9**). These reactions testify to both the unusually high reactivity of the Sn–methyl bonds on the α -Sn atom and to the robustness of the Sn–Sn bond. Once again the ¹H and ¹¹⁹Sn NMR spectra of **5** and **9** indicate the Sn–Sn bond is retained in both complexes. Replacement of a methyl group on the α -Sn by an iodide in each case results in a further reduction of the Sn–Sn coupling constants relative to the corresponding chloride derivatives. The ³¹P NMR spectrum of complexes **5** and **9** again shows two resonances (2.3 and 3.2 ppm for **5**, –10.2 and –10.4 ppm for **9**) indicating that the two phosphorus atoms (P_a and P_b) are slightly inequivalent as discussed above.

3. Conclusions

It has been demonstrated that a possibly general route to distanny complexes involves reaction between an appropriate complex with a chloro-substituted stanny ligand, L_nM–SnR₂Cl, and a tri-organo tin anion, SnR₃[–]. Three distanny complexes prepared in this way, Os(SnMe₂SnMe₃)(κ^2 -S₂CNMe₂)(CO)(PPh₃)₂ (**1**), Os(SnMe₂-SnPh₃)(κ^2 -S₂CNMe₂)(CO)(PPh₃)₂ (**3**), and Os(SnMe₂SnPh₃)-Cl(CO)₂(PPh₃)₂ (**7**), have been thoroughly characterised by multinuclear NMR studies and for **3** and **7** by X-ray crystallography. In the ¹¹⁹Sn NMR spectra of these stable osmium(II) distanny complexes both the α -Sn and β -Sn atoms show well-resolved one-bond ¹¹⁹Sn–¹¹⁹Sn and ¹¹⁹Sn–¹¹⁷Sn coupling. These coupling constants vary widely in magnitude but are always less than the corresponding

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

<i>Bond lengths</i>	
Os–C(1)	1.862(6)
Os–P(2)	2.3699(15)
Os–P(1)	2.3771(15)
Os–S(1)	2.4662(15)
Os–S(2)	2.4772(15)
Os–Sn(1)	2.6928(5)
Sn(1)–C(5)	2.188(7)
Sn(1)–C(6)	2.198(7)
Sn(1)–Sn(2)	2.8236(6)
S(1)–C(2)	1.719(6)
S(2)–C(2)	1.711(7)
N(1)–C(2)	1.339(8)
N(1)–C(4)	1.447(10)
N(1)–C(3)	1.469(9)
O(1)–C(1)	1.161(7)
<i>Bond angles</i>	
C(1)–Os–P(2)	90.09(19)
C(1)–Os–P(1)	88.46(19)
P(2)–Os–P(1)	173.15(5)
C(1)–Os–S(1)	177.4(2)
P(2)–Os–S(1)	90.39(5)
P(1)–Os–S(1)	90.76(5)
C(1)–Os–S(2)	106.5(2)
P(2)–Os–S(2)	86.99(5)
P(1)–Os–S(2)	87.00(5)
S(1)–Os–S(2)	70.94(5)
C(1)–Os–Sn(1)	98.29(19)
P(2)–Os–Sn(1)	93.55(4)
P(1)–Os–Sn(1)	93.29(4)
S(1)–Os–Sn(1)	84.26(4)
S(2)–Os–Sn(1)	155.19(4)
C(5)–Sn(1)–C(6)	93.7(3)
C(5)–Sn(1)–Os	114.74(18)
C(6)–Sn(1)–Os	116.4(2)
C(5)–Sn(1)–Sn(2)	100.1(2)
C(6)–Sn(1)–Sn(2)	95.0(2)
Os–Sn(1)–Sn(2)	129.816(18)

coupling constants for simple hexa-organoditin compounds. The methyl groups on the α -Sn atoms in each of the three distannyl complexes, **1**, **3**, and **7**, are unusually reactive and selective functionalisation at the α -Sn atom by reaction with SnCl_2Me_2 gives $\text{Os}(\text{SnClMeSnMe}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (**2**), $\text{Os}(\text{SnClMeSnPh}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (**4**), and $\text{Os}(\text{SnClMeSnPh}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ (**8**), respectively. Likewise, treatment of compounds **3** or **7** with iodine also cleaves one α -methyl group, selectively, to give $\text{Os}(\text{SnImeSnPh}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (**5**), or $\text{Os}(\text{SnImeSnPh}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ (**9**).

4. Experimental

4.1. General procedures and instruments

Standard laboratory procedures were followed as have been described previously [22]. The compounds $\text{Os}(\text{SnClMe}_2)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ [14], $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})_2$ -

Table 3
Selected bond lengths (Å) and angles (°) for **7**

<i>Bond lengths</i>	
Os–C(2)	1.882(3)
Os–C(1)	1.928(3)
Os–P(1)	2.4113(6)
Os–P(2)	2.4156(6)
Os–Cl	2.4565(6)
Os–Sn(1)	2.7925(2)
Sn(1)–C(3)	2.169(3)
Sn(1)–C(4)	2.171(3)
Sn(1)–Sn(2)	2.8367(2)
O(1)–C(1)	1.138(3)
O(2)–C(2)	1.134(3)
<i>Bond angles</i>	
C(2)–Os–C(1)	94.77(11)
C(2)–Os–P(1)	91.26(8)
C(1)–Os–P(1)	85.74(7)
C(2)–Os–P(2)	91.66(8)
C(1)–Os–P(2)	86.82(7)
P(1)–Os–P(2)	172.21(2)
C(2)–Os–Cl	170.69(8)
C(1)–Os–Cl	94.54(8)
P(1)–Os–Cl	89.69(2)
P(2)–Os–Cl	88.60(2)
C(2)–Os–Sn(1)	77.37(8)
C(1)–Os–Sn(1)	172.09(7)
P(1)–Os–Sn(1)	93.524(16)
P(2)–Os–Sn(1)	94.160(16)
Cl–Os–Sn(1)	93.330(16)
C(3)–Sn(1)–C(4)	102.38(11)
C(3)–Sn(1)–Os	112.46(8)
C(4)–Sn(1)–Os	114.10(8)
C(3)–Sn(1)–Sn(2)	98.32(8)
C(4)–Sn(1)–Sn(2)	97.16(8)
Os–Sn(1)–Sn(2)	128.496(8)

(PPh_3)₂ [23], LiSnMe_3 [24], and KSnPh_3 [25] were prepared according to the literature methods.

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 proteoimpurity in the solvent (7.25 ppm for CHCl_3). ^{13}C NMR spectra were referenced to CDCl_3 (77.0 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 $\text{Os}(\text{SnMe}_2\text{SnMe}_3)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (**1**)

To a stirred pale yellow suspension of $\text{Os}(\text{SnClMe}_2)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ (0.362 g, 0.346 mmol) in thf (5 mL) was added a 0.10 mol L^{-1} solution of LiSnMe_3 in

thf (13.8 mL, 1.383 mmol). After stirring at room temperature for ca. 10 min, the initial green suspension had cleared and become green/orange in colour. Stirring was continued at room temperature for a further 50 min after which time the volume of the solution was reduced to ca. 10 mL, in vacuo. EtOH (30 mL) was added and further concentration of the now green solution gave a colourless precipitate. The solid was collected and recrystallised from toluene/heptane by slow solvent diffusion at low temperature. This afforded pure **1** as colourless crystals (yield 0.312 g, 77%). Anal. Calc. for $C_{45}H_{51}NOOsP_2S_2Sn_2 \cdot 0.5C_7H_8$: C, 47.69; H, 4.54; N, 1.15. Found: C, 47.64; H, 4.91; N, 1.17%. IR (cm^{-1}): 1907 $\nu(CO)$; 1521 (S_2CNMe_2). 1H NMR (C_6D_6 , δ): 0.12 (s with Sn satellites, 6H, $^2J_{Sn(117/119)H} = 33.2$, $^3J_{Sn(117/119)H} = 25.0$ Hz, Sn Me_2 Sn Me_3), 0.47 (s with Sn satellites, 9H, $^2J_{Sn(117/119)H} = 40.0$, $^3J_{Sn(117/119)H} = 8.8$ Hz, Sn Me_2 Sn Me_3), 1.61 (s, 3H, S_2CNMe_2), 1.78 (s, 3H, S_2CNMe_2), 7.04 (m, 18H, PPh $_3$), 7.97 (m, 12H, PPh $_3$). ^{13}C NMR (C_6D_6 , δ): -9.2 (s with Sn satellites, $^1J_{Sn(117/119)C} = 125.8$, $^2J_{Sn(117/119)C} = 52.9$ Hz, Sn Me_2 Sn Me_3), -8.6 (s with Sn satellites, $^1J_{Sn(119)C} = 166.1$, $^1J_{Sn(117)C} = 159.3$, $^2J_{Sn(117/119)C} = 30.1$ Hz, Sn Me_2 Sn Me_3), 35.6 (s, S_2CNMe_2), 36.2 (s, S_2CNMe_2), 127.6 (t [22], $^{2,4}J_{PC} = 8.0$ Hz, *o*-PPh $_3$), 129.5 (s, *p*-PPh $_3$), 135.2 (t', $^{3,5}J_{PC} = 9.1$ Hz, *m*-PPh $_3$), 189.2 (t, $^2J_{PC} = 12.1$ Hz, CO), 211.2 (s, S_2CNMe_2). $^{31}P\{^1H\}$ NMR (C_6D_6/C_6H_6 , δ): 7.2 (s with Sn satellites, $^2J_{Sn(119)P} = 87.5$, $^2J_{Sn(117)P} = 84.7$, $^3J_{Sn(117/119)P} = 7.8$ Hz). $^{119}Sn\{^1H\}$ NMR (C_6D_6/C_6H_6 , δ): -170.8 (t with Sn satellites, $^3J_{Sn(119)P} = 9$, $^1J_{Sn(117)Sn(119)} = 2332$, $^1J_{Sn(119)Sn(119)} = 2441$ Hz, Sn Me_2 Sn Me_3), -283.3 (t with Sn satellites, $^2J_{Sn(119)P} = 88$, $^1J_{Sn(117)Sn(119)} = 2333$, $^1J_{Sn(119)Sn(119)} = 2442$ Hz, Sn Me_2 Sn Me_3).

4.3. Preparation of $Os(SnClMeSnMe_3)(\kappa^2-S_2CNMe_2)(CO)(PPh_3)_2$ (**2**)

$Os(SnMe_2SnMe_3)(\kappa^2-S_2CNMe_2)(CO)(PPh_3)_2$ (**1**) (0.081 g, 0.069 mmol) and $SnMe_2Cl_2$ (0.015 g, 0.069 mmol) were codissolved in CH_2Cl_2 (5 mL) and the resulting pale yellow solution stirred at room temperature for ca. 16 h. All volatiles were removed in vacuo and the residual pale yellow solution recrystallised from CH_2Cl_2 /EtOH to afford pure **2** as similarly coloured microcrystals (yield 0.067 g, 98%). Anal. Calc. for $C_{44}H_{48}ClNOOsP_2S_2Sn_2$: C, 44.19; H, 4.05; N, 1.17. Found: C, 44.27; H, 3.37; N, 1.25%. IR (cm^{-1}): 1908 $\nu(CO)$; 1530 (S_2CNMe_2). 1H NMR (CD_2Cl_2 , δ): -0.01 (s with Sn satellites, 3H, $^2J_{Sn(117/119)H} = 27.2$, $^3J_{Sn(117/119)H} = 18.8$ Hz, Sn $MeClSnMe_3$), 0.16 (s with Sn satellites, 9H, $^2J_{Sn(117/119)H} = 45.6$, $^3J_{Sn(117/119)H} = 12.4$ Hz, Sn $MeClSnMe_3$), 2.00 (s, 3H, S_2CNMe_2), 2.27 (s, 3H, S_2CNMe_2), 7.36 (m, 18H, PPh $_3$), 7.59 (m, 6H, PPh $_3$), 7.78 (m, 6H, PPh $_3$). ^{13}C NMR (CD_2Cl_2 , δ): -8.0 (s, Sn satellites not observed, Sn $MeClSnMe_3$), 0.8 (s, Sn satellites not observed, Sn $MeClSnMe_3$), 35.6 (s, S_2CNMe_2), 36.2 (s, S_2CNMe_2), 127.7, 128.1, 129.8, 130.2, 134.7, 135.1, (PPh $_3$), 187.6 (s, CO), 209.7 (s, S_2CNMe_2). $^{31}P\{^1H\}$ NMR (C_6D_6/C_6H_6 , δ): 4.6 (s, $^2J_{Sn(117/119)P} = 76.7$,

$^3J_{Sn(117/119)P} = 10.9$ Hz). $^{119}Sn\{^1H\}$ NMR (C_6D_6/C_6H_6 , δ): 11.0 (t with Sn satellites, $^2J_{Sn(119)P} = 78$, $^1J_{Sn(117)Sn(119)} = 1906$, $^1J_{Sn(119)Sn(119)} = 2002$ Hz, Sn $MeClSnPh_3$), -116.4 (t with Sn satellites, $^3J_{Sn(119)P} = 11$, $^1J_{Sn(117)Sn(119)} = 1913$, $^1J_{Sn(119)Sn(119)} = 2002$ Hz, Sn $MeClSnPh_3$).

4.4. Preparation of $Os(SnMe_2SnPh_3)(\kappa^2-S_2CNMe_2)(CO)(PPh_3)_2$ (**3**)

To a stirred pale yellow suspension of $Os(ClSnMe_2)(\kappa^2-S_2CNMe_2)(CO)(PPh_3)_2$ in thf (10 mL) was added a 0.13 mol L^{-1} solution of $KSnPh_3$ in thf (8.9 mL, 1.12 mmol). After continued stirring at room temperature for ca. 2 h, a slightly cloudy yellow solution resulted. The volume of the reaction mixture was reduced to ca. 10 mL, in vacuo, and EtOH (30 mL) added. Further concentration afforded a pale coloured precipitate, which was recrystallised from CH_2Cl_2 /EtOH to afford pure **3** as a pale yellow microcrystalline solid (yield 0.343 g, 65%). Crystals suitable for single crystal X-ray diffraction were grown from CH_2Cl_2 /EtOH by slow vapour diffusion at room temperature and proved to contain 2 molecules of CH_2Cl_2 of solvation. However, the bulk sample after vacuum drying returned elemental analyses figures appropriate for only partial solvation. Anal. Calc. for $C_{60}H_{57}NOOsP_2S_2Sn_2 \cdot 0.5CH_2Cl_2$: C, 51.74; H, 4.16; N, 1.00%. Found: C, 51.39; H, 4.15; N, 1.03%. IR (cm^{-1}): 1911, 1892 (1895 in CH_2Cl_2 solution) $\nu(CO)$; 1524 (S_2CNMe_2). 1H NMR ($CDCl_3$, δ): -0.21 (s with Sn satellites, 6H, $^2J_{Sn(117/119)H} = 32.4$, $^3J_{Sn(117/119)H} = 27.6$ Hz, Sn Me_2 Sn Ph_3), 2.00 (s, 3H, S_2CNMe_2), 2.26 (s, 3H, S_2CNMe_2), 7.13 (m, 18H, PPh $_3$), 7.20 (m, 9H, Sn Ph_3), 7.35 (m, 6H, Sn Ph_3), 7.63 (m, 12H, PPh $_3$). ^{13}C NMR ($CDCl_3$, δ): -7.0 (s with Sn satellites, $^1J_{Sn(117/119)C} = 128.6$, $^2J_{Sn(117/119)C} = 53.0$ Hz, Sn Me_2 Sn Ph_3), 36.2 (s, S_2CNMe_2), 36.5 (s, S_2CNMe_2), 127.1 (s, Sn Ph_3), 127.3 (s, *o*-PPh $_3$), 127.6 (s with Sn satellites, $J_{Sn(117/119)C} = 18.1$ Hz, Sn Ph_3), 129.3 (broad s, *p*-PPh $_3$), 134.2 (t', $^{1,3}J_{PC} = 50.3$ Hz, *i*-PPh $_3$), 134.7 (broad s, *m*-PPh $_3$), 138.1 (s with Sn satellites, $J_{Sn(117/119)C} = 37.2$ Hz, Sn Ph_3), 144.1 (s, Sn Ph_3), 187.9 (t, $^2J_{PC} = 12.1$ Hz, CO), 209.8 (s, S_2CNMe_2). $^{31}P\{^1H\}$ NMR ($CDCl_3/CH_2Cl_2$, δ): 5.8 (s with Sn satellites, $^2J_{Sn(117/119)P} = 90.9$ Hz). $^{119}Sn\{^1H\}$ NMR ($CDCl_3/CH_2Cl_2$, δ): -230.3 (t with Sn satellites, $^3J_{Sn(119)P} = 15$, $^1J_{Sn(117)Sn(119)} = 1061$, $^1J_{Sn(119)Sn(119)} = 1120$ Hz, Sn Me_2 Sn Ph_3), -293.6 (t with Sn satellites, $^2J_{Sn(119)P} = 90$, $^1J_{Sn(117)Sn(119)} = 1074$, $^1J_{Sn(119)Sn(119)} = 1119$ Hz, Sn Me_2 Sn Ph_3).

4.5. Preparation of $Os(SnClMeSnPh_3)(\kappa^2-S_2CNMe_2)(CO)(PPh_3)_2$ (**4**)

$Os(SnMe_2SnPh_3)(\kappa^2-S_2CNMe_2)(CO)(PPh_3)_2$ (**3**) (0.178 g, 0.131 mmol) and $SnMe_2Cl_2$ (0.028 g, 0.131 mmol) were codissolved in CH_2Cl_2 (5 mL) and the resulting pale yellow solution stirred at room temperature for ca. 16 h. All volatiles were removed in vacuo and the residual pale yellow solution recrystallised from CH_2Cl_2 /EtOH to afford pure

4 as similarly coloured microcrystals (yield 0.178 g, 98%). Anal. Calc. for $C_{59}H_{54}ClNOOsP_2S_2Sn_2$: C, 51.27; H, 3.94; N, 1.01. Found: C, 51.14; H, 3.67; N, 1.06%. IR (cm^{-1}): 1898 $\nu(CO)$; 1522 (S_2CNMe_2). 1H NMR ($CDCl_3$, δ): 0.18 (s with Sn satellites, 3H, $^2J_{Sn(117/119)H} = 26.9$, $^3J_{Sn(117/119)H} = 21.5$ Hz, $SnMeClSnPh_3$), 2.00 (s, S_2CNMe_2), 2.24 (s, S_2CNMe_2), 7.17 (m, 13H, Ph), 7.23 (m, 12H, Ph), 7.42 (m, 8H, $SnPh_3$), 7.57 (m, 6H, PPh_3), 7.74 (m, 6H, PPh_3). ^{13}C NMR ($CDCl_3$, δ): 4.59 (s, $SnMe$), 36.2 (s, S_2CNMe_2), 36.5 (s, S_2CNMe_2), 127.2 (broad m, $SnPh$ or PPh), 127.7 (broad m, $SnPh$ or PPh), 127.8 (s with Sn satellites, $J_{Sn(117/119)C} = 41.7$ Hz, $SnPh$), 129.4 (s, $SnPh$ or PPh), 129.8 (s, $SnPh$ or PPh), 134.3 (broad m, $SnPh$ or PPh), 134.8 (broad m, $SnPh$ or PPh), 138.1 (s with Sn satellites, $J_{Sn(117/119)C} = 36.9$ Hz, $SnPh$), 142.7 (s, $SnPh$ or PPh), 186.3 (s, coupling to P not observed, CO), 209.1 (s, S_2CNMe_2). $^{31}P\{^1H\}$ NMR ($CDCl_3/CH_2Cl_2$, δ): 3.9 (s with Sn satellites, $^2J_{Sn(117/119)P} = 81.5$, $^3J_{Sn(117/119)P} = 11.5$ Hz). $^{119}Sn\{^1H\}$ NMR ($CDCl_3/CH_2Cl_2$, δ): -50.1 (t with Sn satellites, $^2J_{Sn(119)P} = 84$, $^1J_{Sn(117)Sn(119)} = 807$, $^1J_{Sn(119)Sn(119)} = 836$ Hz, $SnClMeSnPh_3$), -200.2 (t with Sn satellites, $^3J_{Sn(119)P} = 15$, $^1J_{Sn(117)Sn(119)} = 791$, $^1J_{Sn(119)Sn(119)} = 836$ Hz, $SnClMeSnPh_3$).

4.6. Preparation of $Os(SnIMeSnPh_3)(\kappa^2-S_2CNMe_2)(CO)(PPh_3)_2$ (**5**)

To a stirred pale yellow solution of $Os(SnMe_2SnPh_3)(\kappa^2-S_2CNMe_2)(CO)(PPh_3)_2$ (**3**) (0.103 g, 0.076 mmol) in CH_2Cl_2 (5 mL), cooled in a $CO_2(s)$ /ethanol bath, was added dropwise a solution of I_2 (0.019 g, 0.076 mmol) in CH_2Cl_2 (5 mL). The purple colour of the I_2 was discharged immediately and after complete addition all volatiles were removed in vacuo from the resulting pale yellow solution. Recrystallisation of the residual yellow solid afforded pure **5** as a colourless, microcrystalline solid (0.094 g, 84%). Anal. Calc. for $C_{59}H_{54}INOOsP_2S_2Sn_2$: C, 48.09; H, 3.69; N, 0.95. Found: C, 48.51; H, 3.46; N, 1.00%. IR (cm^{-1}): 1911 $\nu(CO)$; 1528 (S_2CNMe_2). 1H NMR ($CDCl_3$, δ): 0.50 (s, 3H, $^{2/3}J_{Sn(117/119)H} = 23.0$ Hz, $SnMeI$ SnPh₃), 2.04 (s, S_2CNMe_2), 2.20 (s, S_2CNMe_2), 7.12 (m, 13H, Ph), 7.24 (m, 12H, Ph), 7.55 (m, 8H, $SnPh_3$), 7.55 (m, 6H, PPh_3), 7.71 (m, 6H, PPh_3). ^{13}C NMR ($CDCl_3$, δ): 3.9 (s, Sn satellites not observed, $SnMe$), 36.2 (s, S_2CNMe_2), 36.5 (s, S_2CNMe_2), 127.2 (m, $SnPh$ or PPh), 127.7 (m, $SnPh$ or PPh), 127.8 (s with Sn satellites, $J_{Sn(117/119)C} = 40.2$ Hz, $SnPh_3$), 129.2 (m, $SnPh$ or PPh), 129.5 (m, $SnPh$ or PPh), 129.8 (m, $SnPh$ or PPh), 130.1 (m, $SnPh$ or PPh), 134.4 (m, $SnPh$ or PPh), 135.0 (m, $SnPh$ or PPh), 138.1 (s, $SnPh_3$), 138.2 (s with Sn satellites, $J_{Sn(117/119)C} = 27.2$ Hz, $SnPh_3$), 142.3 (s, $SnPh_3$), 186.2 (s, coupling to P not observed, CO), 208.2 (s, S_2CNMe_2). $^{31}P\{^1H\}$ NMR ($CDCl_3/CH_2Cl_2$, δ): 2.3 (s with Sn satellites, $^2J_{Sn(117/119)P} = 91.6$, $^3J_{Sn(117/119)P} = 14.3$ Hz), 3.2 (see discussion) (s with Sn satellites, $^2J_{Sn(117/119)P} = 62.7$ Hz, $^3J_{Sn(117/119)P}$ not resolved). $^{119}Sn\{^1H\}$ NMR ($CDCl_3/CH_2Cl_2$, δ): -245.3 (dd with Sn satellites, $^3J_{Sn(119)P(a)} = 15$, $^3J_{Sn(119)P(b)} = 7$

(see discussion for explanation of P(a) and P(b)), $^1J_{Sn(117)Sn(119)} = 522$, $^1J_{Sn(119)Sn(119)} = 537$ Hz $SnIMeSnPh_3$), -156.4 (dd with Sn satellites, $^2J_{Sn(119)P(a)} = 93$, $^2J_{Sn(119)P(b)} = 64$, $^1J_{Sn(117)Sn(119)} = 525$, $^1J_{Sn(119)Sn(119)} = 531$ Hz, $SnIMeSnPh_3$).

4.7. Preparation of $Os(SnClMe_2)Cl(CO)_2(PPh_3)_2$ (**6**)

$Os(SnMe_3)Cl(CO)_2(PPh_3)_2$ (0.464 g, 0.478 mmol) and $SnMe_2Cl_2$ (0.104 g, 0.478 mmol) were codissolved in dichloromethane (10 mL) and the resulting colourless solution stirred at room temperature for ca. 16 h. All volatiles were removed in vacuo and the residual colourless solid recrystallised from dichloromethane–ethanol to afford pure **6** as a colourless microcrystalline solid (0.416 g, 88%). Anal. Calc. for $C_{40}H_{36}Cl_2O_2OsP_2Sn$: C, 48.50; H, 3.66. Found: C, 48.15; H, 3.79%. IR (cm^{-1}): 2025, 1966 $\nu(CO)$. 1H NMR ($CDCl_3$, δ): 0.21 (s with Sn satellites, 6H, $^2J_{Sn(117/119)H} = 35.6$ Hz, $SnMe_2$), 7.40 (m, 18H, PPh_3), 7.82 (m, 12H, PPh_3). ^{13}C NMR ($CDCl_3$, δ): 1.8 (s with Sn satellites, $^1J_{Sn(117/119)C} = 176.1$ Hz, $SnMe_2$), 128.5 (t', $^{2,4}J_{PC} = 10.4$ Hz, $o-PPh_3$), 130.8 (s, $p-PPh_3$), 133.6 (t', $^{3,5}J_{PC} = 10.6$ Hz, $m-PPh_3$), 133.7 (t', $^{1,3}J_{PC} = 54.6$ Hz, $i-PPh_3$), 175.1 (t, $^2J_{PC} = 6.0$ Hz, CO), 177.6 (t, $^2J_{PC} = 9.4$ Hz, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3/CH_2Cl_2$, δ): 3.9 (s with Sn satellites, $^2J_{Sn(117/119)P} = 147.6$ Hz). $^{119}Sn\{^1H\}$ NMR ($CDCl_3/CH_2Cl_2$, δ): 114.4 (t, $^2J_{Sn(119)P} = 150$ Hz).

4.8. Preparation of $Os(SnMe_2SnPh_3)Cl(CO)_2(PPh_3)_2$ (**7**)

To a stirred, colourless solution of $Os(SnClMe_2)Cl(CO)_2(PPh_3)_2$ (**6**) (0.514 g, 0.519 mmol) in thf (5 mL) was added a 0.36 mol L^{-1} solution of $KSnPh_3$ in thf (4.3 mL, 1.557 mmol). After continued stirring at room temperature for ca. 1.5 h, a slightly cloudy, yellow solution resulted. EtOH (20 mL) was added and concentration of the mixture, in vacuo, afforded a pale coloured precipitate. Analysis of this material by tlc on silica gel, eluting with 1:1 dichloromethane–hexane, indicated a mixture containing two components (Sn_2Ph_6 : $R_F = 0.6$ and **7**: $R_F = 0.3$), and these could not be separated by recrystallisation. Purification by flash chromatography, under the above conditions, afforded pure **7** as a colourless crystalline solid (0.432 g, 62%). Anal. Calc. for $C_{57}H_{51}ClO_2OsP_2Sn_2$: C, 52.95; H, 3.98. Found: C, 52.63; H, 3.70%. IR (cm^{-1}): 2017, 1958 $\nu(CO)$. 1H NMR ($CDCl_3$, δ): -0.12 (s with Sn satellites, 6H, $^2J_{Sn(117/119)H} = 32.4$, $^3J_{Sn(117/119)H} = 26.8$ Hz, $SnMe_2SnPh_3$), 7.25 (m, 26H, Ph), 7.45 (m, 7H, $SnPh_3$), 7.76 (m, 12H, PPh_3). ^{13}C NMR ($CDCl_3$, δ): -5.7 (s, Sn satellites not observed, $SnMe_2$), 127.4 (s, $SnPh_3$), 127.8 (s with Sn satellites, $J_{Sn(117/119)C} = 38.2$ Hz, $SnPh_3$), 128.3 (t', $^{2,4}J_{PC} = 10.1$ Hz, $o-PPh_3$), 130.5 (s, $p-PPh_3$), 133.6 (t', $^{1,3}J_{PC} = 56.3$ Hz, $i-PPh_3$), 133.7 (t', $^{3,5}J_{PC} = 10.0$ Hz, $m-PPh_3$), 138.0 (s with Sn satellites, $J_{Sn(117/119)C} = 37.2$ Hz, $SnPh_3$), 143.5 (s, $SnPh_3$), 177.5 (s, coupling to P not observed, CO), 178.0 (s, coupling to P not observed, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3/CH_2Cl_2$, δ): -10.4 (s with Sn satellites,

$^2J_{\text{Sn}(117/119)\text{P}} = 140.6$ Hz, $^3J_{\text{Sn}(117/119)\text{P}}$ poorly resolved and not measured). $^{119}\text{Sn}\{^1\text{H}\}$ NMR ($\text{CDCl}_3/\text{CH}_2\text{Cl}_2$, δ): -203.5 (t with Sn satellites, $^2J_{\text{Sn}(119)\text{P}} = 149$, $^1J_{\text{Sn}(117)\text{Sn}(119)} = 1298$, $^1J_{\text{Sn}(119)\text{Sn}(119)} = 1358$ Hz, $\text{SnMe}_2\text{SnPh}_3$), -163.3 (s, P-coupling not resolved but with Sn satellites, $^1J_{\text{Sn}(117)\text{Sn}(119)} = 1268$, $^1J_{\text{Sn}(119)\text{Sn}(119)} = 1343$ Hz, $\text{SnMe}_2\text{SnPh}_3$).

4.9. Preparation of $\text{Os}(\text{SnClMeSnPh}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ (**8**)

$\text{Os}(\text{SnMe}_2\text{SnPh}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ (0.201 g, 0.154 mmol) and SnMe_2Cl_2 (0.169 g, 0.770 mmol) were codissolved in CH_2Cl_2 (5 mL) and the resulting colourless solution stirred at room temperature for ca. 16 h. All volatiles were then removed in vacuo and the residual colourless solid recrystallised from dichloromethane–ethanol to afford pure **8** as a colourless microcrystalline solid (0.176 g, 86%). Anal. Calc. for $\text{C}_{57}\text{H}_{48}\text{Cl}_2\text{O}_2\text{OsP}_2\text{Sn}_2$: C, 51.65; H, 3.65. Found: C, 51.85; H, 3.43%. IR (cm^{-1}): 2019, 1958 $\nu(\text{CO})$. ^1H NMR (CDCl_3 , δ): 0.22 (s with Sn satellites, 3H, $^2J_{\text{Sn}(117/119)\text{H}} = 23.3$, $^3J_{\text{Sn}(117/119)\text{H}} = 21.4$ Hz, SnMeClSnPh_3), 7.16 (m, 13H, *Ph*), 7.26 (m, 12H, *Ph*), 7.50 (m, 8H, SnPh_3), 7.71 (m, 6H, PPh_3), 7.86 (m, 6H, PPh_3). ^{13}C NMR (CDCl_3 , δ): 5.8 (s, coupling to Sn not observed, SnMe), 128.0 (s, *Ph*), 128.1 (s with Sn satellites, $J_{\text{Sn}(117/119)\text{C}} = 43.5$ Hz, SnPh), 128.3 (m, *o-PPh}_3), 128.8 (m, *o-PPh}_3), 130.5 (s, *p-PPh}_3*), 131.0 (s, *p-PPh}_3*), 133.1 (m, *m-PPh}_3*), 133.6 (m, *m-PPh}_3*), 138.1 (s with Sn satellites, $J_{\text{Sn}(117/119)\text{C}} = 37.8$ Hz, SnPh_3), 142.1 (s, SnPh_3), 174.9 (m, CO), 176.9 (m, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{CDCl}_3/\text{CH}_2\text{Cl}_2$, δ): -10.7 (s with Sn satellites, $^2J_{\text{Sn}(117/119)\text{P}} = 142.4$ Hz), -10.5 (s with Sn satellites, $^2J_{\text{Sn}(117/119)\text{P}} = 136.0$ Hz). $^{119}\text{Sn}\{^1\text{H}\}$ NMR ($\text{CDCl}_3/\text{CH}_2\text{Cl}_2$, δ): -140.7 (apparent t with Sn satellites, $^3J_{\text{Sn}(119)\text{P}} = 15$, $^1J_{\text{Sn}(117)\text{Sn}(119)} = 910$, $^1J_{\text{Sn}(119)\text{Sn}(119)} = 946$ Hz, SnClMeSnPh_3), 35.9 (apparent t with Sn satellites, $^2J_{\text{Sn}(119)\text{P}} = 144$, $^1J_{\text{Sn}(117)\text{Sn}(119)} = 910$, $^1J_{\text{Sn}(119)\text{Sn}(119)} = 940$ Hz, SnClMeSnPh_3).**

4.10. Preparation of $\text{Os}(\text{SnImeSnPh}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ (**9**)

To a stirred clear, colourless solution of $\text{Os}(\text{SnMe}_2\text{SnPh}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ (0.122 g, 0.093 mmol) in CH_2Cl_2 (10 mL), cooled in a CO_2 (s)/ethanol bath, was added dropwise a solution of I_2 (0.024 g, 0.093 mmol) in CH_2Cl_2 (10 mL). The purple colour of the I_2 was discharged immediately and after complete addition all volatiles were removed in vacuo from the resulting pale yellow solution. Recrystallisation of the residual pale yellow solid afforded pure **9** as a colourless, microcrystalline solid (0.109 g, 83%). Anal. Calc. for $\text{C}_{57}\text{H}_{48}\text{ClIO}_2\text{OsP}_2\text{Sn}_2$: C, 48.32; H, 3.41. Found: C, 48.36; H, 3.24%. IR (cm^{-1}): 2026, 1969 $\nu(\text{CO})$. ^1H NMR (CDCl_3 , δ): 0.51 (s with Sn satellites, 3H, $^{2/3}J_{\text{Sn}(117/119)\text{H}} = 22.7$ Hz, $\text{SnMeI}\text{SnPh}_3$), 7.18 (m, 18H, PPh_3), 7.27 (m, 7H, SnPh_3), 7.57 (m, 8H, SnPh_3), 7.71 (m, 6H, PPh_3), 7.76 (m, 6H, PPh_3). ^{13}C NMR (CDCl_3 , δ): 3.3 (s, coupling to Sn not observed, SnMe), 128.1 (s with Sn satellites,

$J_{\text{Sn}(117/119)\text{C}} = 44.3$ Hz, SnPh), 128.3 (m, *o-PPh}_3*), 128.8 (m, *o-PPh}_3*), 130.7 (s, *p-PPh}_3*), 131.0 (s, *p-PPh}_3*), 132.4 (apparent dd, $J_{\text{PC}} = 39.2$, $J_{\text{PC}} = 15.1$ Hz, *i-PPh}_3*), 132.92 (apparent d, $J_{\text{PC}} = 15.1$ Hz, *i-PPh}_3*), 133.3 (m, *m-PPh}_3*), 134.0 (m, *m-PPh}_3*), 138.2 (s with Sn satellites, $J_{\text{Sn}(117/119)\text{C}} = 37.2$ Hz, SnPh_3), 144.8 (s with Sn satellites, $J_{\text{Sn}(117/119)\text{C}} = 36.2$ Hz, SnPh_3), 175.5 (m, CO), 175.7 (m, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{CDCl}_3/\text{CH}_2\text{Cl}_2$, δ): -10.2 (s with Sn satellites, $^2J_{\text{Sn}(117/119)\text{P}} = 133.9$ Hz), -10.4 (s with Sn satellites, $^2J_{\text{Sn}(117/119)\text{P}} = 137.8$ Hz). $^{119}\text{Sn}\{^1\text{H}\}$ NMR ($\text{CDCl}_3/\text{CH}_2\text{Cl}_2$, δ): -183.9 (apparent t, $^3J_{\text{Sn}(119)\text{P}} = 15$, $^1J_{\text{Sn}(117)\text{Sn}(119)} = 671$, $^1J_{\text{Sn}(119)\text{Sn}(119)} = 701$ Hz, $\text{SnMeI}\text{SnPh}_3$), -95.0 (apparent t, $^2J_{\text{Sn}(119)\text{P}} = 140$, $^1J_{\text{Sn}(117)\text{Sn}(119)} = 673$, $^1J_{\text{Sn}(119)\text{Sn}(119)} = 698$ Hz, $\text{SnMeI}\text{SnPh}_3$).

4.11. X-ray crystal structure determinations for complexes **3** and **7**

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 [26]. Semi-empirical absorption corrections were applied based on equivalent reflections using SADABS [27]. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares on F^2 using programs SHELXS [28] and SHELXL [29]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located geometrically and refined using a riding model. Crystal data and refinement details for both structures are given in Table 1.

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Appendix A. Supplementary material

Crystallographic data (excluding structure factors) for **3** and **7** have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publications Nos. 602840 and 602841. 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>). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.06.010.

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