

Reversible methyl group migration between osmium and tin in reactions of osmium trimethylstannyl complexes

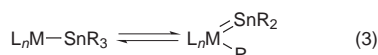
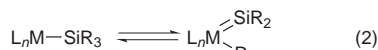
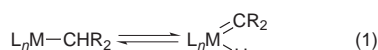
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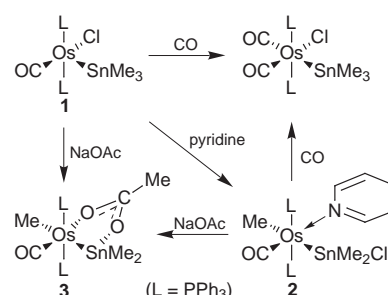
Treatment of the coordinatively unsaturated osmium trimethylstannyl complex, $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ **1**, with either pyridine (py) or sodium acetate results in methyl migration from tin to osmium, giving the structurally characterised complexes, $\text{Os}(\text{Me})(\text{SnClMe}_2)(\text{py})(\text{CO})(\text{PPh}_3)_2$ **2** or $\text{Os}(\text{Me})(\text{SnMe}_2\text{OC}[\text{Me}]\text{O})(\text{CO})(\text{PPh}_3)_2$ **3**, respectively: the methyl migration is reversible and treatment of $\text{Os}(\text{Me})(\text{SnClMe}_2)(\text{py})(\text{CO})(\text{PPh}_3)_2$ with CO gives the trimethylstannyl complex, $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$.

α -Migration, as shown in eqn. (1), is an established feature of organometallic chemistry.¹ In the closely related metal silyl complex chemistry many transformations have been observed which imply the intermediacy of metal silylene complexes generated by 1,2-migration of an R group as in eqn. (2).² In one instance, when R = H, reversible 1,2-migration has been reported for a platinum silyl complex.³ Since there is a substantial number of well characterised stannylene complexes⁴ it can be envisaged that the type of interconversion represented in eqn. (3) might play a part in understanding the reactions



undergone by metal stannyl and metal stannylene complexes. Indeed, free, stable stannylenes have been inserted into metal-halogen bonds.⁴ A further observation relevant to this idea is that $\text{Ru}[\text{Sn}(\text{C}_6\text{H}_4\text{Me-}p)_3]\text{Cl}(\text{CO})(\text{PPh}_3)_2$ readily decomposes in solution to $\text{Ru}(\text{C}_6\text{H}_4\text{Me-}p)\text{Cl}(\text{CO})(\text{PPh}_3)_2$.⁵ We describe herein new reactions undergone by the osmium trimethylstannyl complex, $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ **1**, in which (i) a methyl group migrates to osmium and this is accompanied by either a chloride transfer to tin forming a chlorodimethylstannyl ligand, or by formation of a bridging acetatodimethylstannyl ligand, (ii) an example of reverse migration of a methyl group from osmium to tin to reform the trimethylstannyl ligand, and (iii) the crystal structures of the two products of methyl migration to osmium, $\text{Os}(\text{Me})(\text{SnClMe}_2)(\text{py})(\text{CO})(\text{PPh}_3)_2$ **2** (py = pyridine) and $\text{Os}(\text{Me})(\text{SnMe}_2\text{OC}[\text{Me}]\text{O})(\text{CO})(\text{PPh}_3)_2$ **3**.

$\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ **1**, when treated with CO, $\text{CNC}_6\text{H}_4\text{Me-}p$, or sodium dimethyldithiocarbamate, gives the expected six coordinate trimethylstannyl complexes, $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$, $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})(\text{CNC}_6\text{H}_4\text{Me-}p)(\text{PPh}_3)_2$, or $\text{Os}(\text{SnMe}_3)(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$.^{6,7} We now report that reaction of **1** with pyridine (Scheme 1) leads not to the expected six-coordinate complex, ' $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{py})(\text{CO})(\text{PPh}_3)_2$ ', but rather to the colourless, methyl-migrated product, $\text{Os}(\text{Me})(\text{SnClMe}_2)(\text{py})(\text{CO})(\text{PPh}_3)_2$ **2** in 64% isolated yield. That methyl group migration has occurred in the formation of **2** is revealed by the ¹H NMR spectrum which shows the osmium-bound methyl group as a triplet at δ 0.15 (³J_{HP} 6.62 Hz) (syntheses and other data for **2** and **3** are given in footnote †). This structural assignment was fully confirmed



Scheme 1

by a crystal structure determination.‡ The structure of **2** is shown in Fig. 1, along with selected bond lengths and angles. The osmium–tin bond distance of 2.6741(4) Å does not differ substantially from the corresponding distances found in other osmium stannyl complexes. The osmium–bound methyl group is found to lie *trans* to the tin atom, with the angle C–Os–Sn at 175.30(12)°. The osmium–methyl bond length of 2.249(5) Å is similar to that observed in both $\text{Os}(\text{Me})(\text{H})(\text{CO})_2(\text{PPr}_3)_2$ [2.198(17) Å]⁸ and $\text{Os}(\text{Me})(\text{I})(\text{CO})_2(\text{PMe}_3)_2$ [2.174(15) Å].⁹ The geometry around the tin centre is quite symmetrical with the angles Os–Sn–C(3), Os–Sn–C(4) and Os–Sn–Cl(1), all close to 120°.

Remarkably, when compound **2** is treated with CO, pyridine is displaced but the compound formed is not ' $\text{Os}(\text{Me})(\text{SnMe}_2\text{Cl})(\text{CO})_2(\text{PPh}_3)_2$ '. Instead, the trimethylstannyl complex, $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$, is obtained in 80% isolated yield, where the methyl group has migrated back to the tin atom and chloride has returned to osmium. It may be significant for this

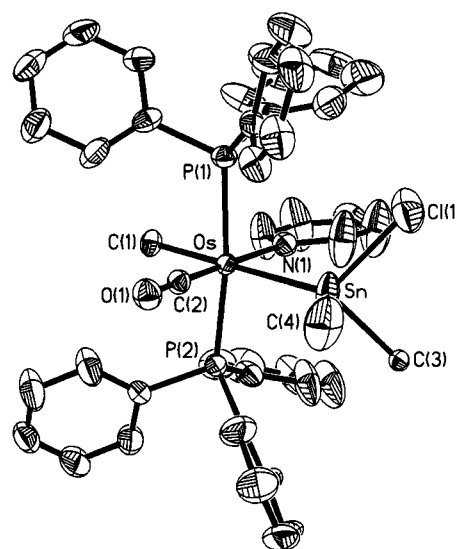


Fig. 1 Crystal structure of **2**. Selected bond lengths (Å) and angles (°): Os–Sn 2.6741(4), Os–C(1) 2.249(5), Os–N(1) 2.251(4), Sn–Cl(1) 2.422(2), Os–Sn–C(3) 123.47(11), Os–Sn–C(4) 120.9(2), Os–Sn–Cl(1) 119.17(6), C(3)–Sn–C(4) 99.5(3), C(1)–Os–Sn 175.30(12).

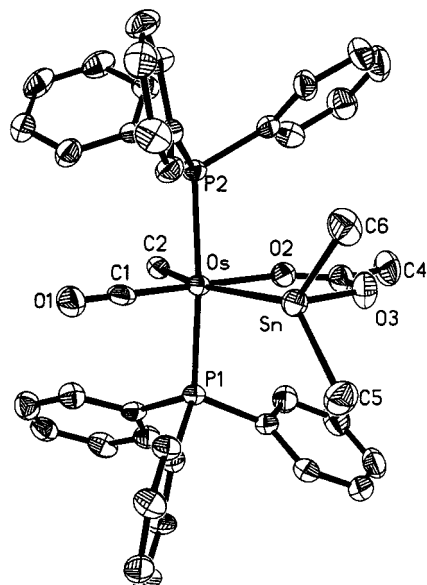


Fig. 2 Crystal structure of **3**. Selected bond lengths (Å) and angles (°): Os–Sn 2.6766(4), Os–C(2) 2.183(5), Os–O(2) 2.183(4), Sn–O(3) 2.143(4), Os–Sn–C(5) 131.22(19), Os–Sn–C(6) 129.70(18), C(5)–Sn–C(6) 98.2(3), C(2)–Os–Sn 158.77(15).

transformation that solutions of **2** are red suggesting that partial pyridine dissociation occurs to give a coordinatively unsaturated species in solution.

Treatment of **1** with sodium acetate also gives a methyl-migrated product, $\text{Os}(\text{Me})(\text{SnMe}_2\text{OC}[\text{Me}]\text{O})(\text{CO})(\text{PPh}_3)_2$ **3** (Scheme 1). The same compound is accessible from a reaction between **2** and sodium acetate. The ^1H NMR spectrum of **3** shows the osmium-bound methyl group as a triplet at δ 0.25 ($^3J_{\text{HP}}$ 7.12 Hz). The structure was confirmed by a crystal structure determination.[‡] The molecular geometry of **3** is shown in Fig. 2, along with selected bond lengths and angles. The acetate bridges across the osmium–tin bond forming a five-membered chelate ring. The osmium–tin bond distance of 2.6766(4) Å does not differ substantially from the corresponding distances found in other osmium stannyl complexes. The osmium–methyl bond length is 2.183(5) Å, and the osmium-bound methyl group is found to lie *trans* to the tin atom, with the angle C–Os–Sn at 158.77(15)°. This considerable deviation from linearity is no doubt a consequence of the small O–Os–Sn angle required by the bridging acetate ligand. The osmium atom, the osmium-bound methyl, the carbonyl, the tin atom and the acetate ligand are all coplanar. The geometry around the tin centre is far from tetrahedral with C(5), C(6), Sn, and Os almost coplanar. The sum of the angles made by the two methyl groups and the osmium atom about tin is 359.1°, with the tin atom lying only 0.127(3) Å from the plane through C(5), C(6) and Os. The acetate oxygen, O(3), is bound to tin at a distance of 2.143(4) Å and the O(3)–Sn bond is perpendicular to the Os, Sn, C(5), C(6) plane. These structural parameters are compatible with some base-stabilised stannylene character in the bonding of the tin ligand. The tin resonance found in the ^{119}Sn NMR spectrum of **3** is a triplet signal at δ 392.94 ($^2J_{\text{SnP}}$ 119.4 Hz).

We have as yet no mechanistic information regarding these methyl group migrations. However, from the observations depicted in Scheme 1 and discussed herein, it is clear that methyl migration occurs only when a coordinatively unsaturated osmium stannyl species is accessible. It is possible that such a species is in an equilibrium of the type shown in eqn. (3).

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Notes and references

[‡] *Synthesis of* $\text{Os}(\text{Me})(\text{SnClMe}_2)(\text{py})(\text{CO})(\text{PPh}_3)_2$ **2**: $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$ (1.00 g, 0.960 mmol) was added directly to a solution of trimethylvinyltin

(1.00 g, 5.23 mmol) in a mixture of benzene (18 mL) and toluene (18 mL) and heated to reflux under nitrogen. The mixture was then photolysed with a 1000 W tungsten/halogen lamp held 10 cm from the flask, the heat of the lamp being sufficient to maintain reflux. After 7 min the photolysis was stopped. The resulting red solution of $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ **1** was cooled to 0 °C in an ice bath and pyridine (2 mL) was added. The red colour changed rapidly to pale yellow. The reaction was maintained at room temperature for 30 min and then the solvent was removed *in vacuo*. Recrystallisation from dichloromethane–ethanol gave **2** as a white microcrystalline solid in 63.8% yield. $\nu_{\text{max}}(\text{Nujol mull})/\text{cm}^{-1}$: 1878 (CO); $\delta_{\text{H}}(\text{CDCl}_3, 400.133 \text{ MHz}, 300 \text{ K})$ 0.15 [t, 3H, OsCH_3 , $^3J(\text{PH})$ 6.62 Hz], 0.24 [s, 6H, SnCH_3 , $^2J(\text{SnH})$ 21.0 Hz], 6.95–7.60 (m, 35H, PPh_3 and pyridine); $\delta_{\text{Sn}}(\text{CDCl}_3, 149.144 \text{ MHz}, 300 \text{ K})$ 186.63 [t, $^2J(\text{SnP})$ 110.4 Hz]. Calc. for $\text{C}_{45}\text{H}_{44}\text{NOClP}_2\text{OsSn}$: C, 52.93; H, 4.34; N, 1.37. Found: C, 53.52; H, 4.32; N, 1.26%.

Synthesis of $\text{Os}(\text{Me})(\text{SnMe}_2\text{OC}[\text{Me}]\text{O})(\text{CO})(\text{PPh}_3)_2$ **3**: to the red solution of $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ **1** produced as described above but cooled only to 40 °C, was added NaO_2CMe (0.080 g, 0.975 mmol) dissolved in a mixture of ethanol (10 mL) and water (5 mL). The colour of the solution changed from deep red to pale yellow over 10 s. The reaction mixture was then stirred at room temp. for 30 min. Solvent removal *in vacuo* provided a pale yellow solid which was recrystallised from dichloromethane–ethanol to give colourless microcrystals of **3** in 76.4% yield, mp 167–171 °C. $\nu_{\text{max}}(\text{Nujol mull})/\text{cm}^{-1}$: 1881 (CO), 1535 (O_2CMe); $\delta_{\text{H}}(\text{CDCl}_3, 400.133 \text{ MHz}, 300 \text{ K})$ –0.19 [s, 6H, Sn-CH_3 , $^2J(\text{SnH})$ 21.4 Hz], 0.25 [t, 3H, OsCH_3 , $^3J(\text{PH})$ 7.12 Hz], 0.71 [s, 3H, O_2CCH_3], 7.25–7.70 (m, 30H, PPh_3); $\delta_{\text{Sn}}(\text{CDCl}_3, 149.144 \text{ MHz}, 300 \text{ K})$ 392.94 [t, $^2J(\text{SnP})$ 119.4 Hz]. Calc. for $\text{C}_{42}\text{H}_{42}\text{O}_3\text{P}_2\text{SnOs}$: C, 52.24; H, 4.38%. Found: C, 53.53; H, 4.38%.

[‡] *Crystal data*: $2 \cdot \text{CH}_2\text{Cl}_2$; crystals were grown from dichloromethane–ethanol. $\text{C}_{45}\text{H}_{44}\text{ClN}_2\text{O}_3\text{P}_2\text{OsSn-CH}_2\text{Cl}_2$, $M = 1106.02$, triclinic, space group $P\bar{1}$, $a = 9.6249(1)$, $b = 12.5510(2)$, $c = 19.6568(3)$ Å, $\alpha = 96.708(1)$, $\beta = 97.968(1)$, $\gamma = 107.02(1)^\circ$, $U = 2217.36(5)$ Å³, $F(000) = 1088$, $D_c = 1.657 \text{ g cm}^{-3}$, $Z = 2$, $\mu(\text{Mo-K}\alpha, \lambda = 0.71073 \text{ Å}) = 3.714 \text{ mm}^{-1}$. Intensity data were collected to a θ limit of 27.45° on a Siemens ‘SMART’ diffractometer¹⁰ at 203(2) K and corrected for absorption.¹¹ The structure was solved using Patterson methods¹² and refined by full-matrix least squares analysis on F^2 employing SHELXL97.¹³ All non-hydrogen atoms were allowed to assume anisotropic motion, except C(3) which was refined isotropically. Hydrogens were placed in calculated positions and refined using a riding model. Refinement converged to 0.0384 ($R_w = 0.0944$) for 9304 reflections for which $I > 2\sigma(I)$.

3· CH_2Cl_2 : crystals were grown from dichloromethane–ethanol. $\text{C}_{42}\text{H}_{42}\text{O}_3\text{OsP}_2\text{Sn-CH}_2\text{Cl}_2$, $M = 1050.51$, triclinic, space group $P\bar{1}$, $a = 9.8487(1)$, $b = 11.9753(2)$, $c = 18.5656(3)$ Å, $\alpha = 95.559(1)$, $\beta = 101.214(1)$, $\gamma = 103.598(1)^\circ$, $U = 2064.36(5)$ Å³, $F(000) = 1032$, $D_c = 1.690 \text{ g cm}^{-3}$, $Z = 2$, $\mu(\text{Mo-K}\alpha, \lambda = 0.71073 \text{ Å}) = 3.924 \text{ mm}^{-1}$. Intensity data were collected to a θ limit of 27.40° on a Siemens ‘SMART’ diffractometer¹⁰ at 203(2) K and corrected for absorption.¹¹ The structure was solved by direct methods¹² and refined by full-matrix least-squares analysis on F^2 employing SHELXL97.¹³ All non-hydrogen atoms were allowed to assume anisotropic motion. Hydrogens were placed in calculated positions and refined using a riding model. Refinement converged to 0.0401 ($R_w = 0.0721$) for 7401 reflections for which $I > 2\sigma(I)$.

CCDC 182/1258. See <http://www.rsc.org/suppdata/cc/1999/1101/> for crystallographic files in .cif format.

- R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, Wiley, New York, 2nd edn., 1994, p. 176.
- K. H. Pannell and H. K. Sharma, *Chem. Rev.*, 1995, **95**, 1351; T. D. Tilley, *Comments Inorg. Chem.*, 1990, **10**, 37.
- G. P. Mitchell and T. D. Tilley, *J. Am. Chem. Soc.*, 1998, **120**, 7635.
- M. F. Lappert and R. S. Rowe, *Coord. Chem. Rev.*, 1990, **100**, 267.
- G. R. Clark, K. R. Flower, W. R. Roper and L. J. Wright, *Organometallics*, 1993, **12**, 259.
- P. D. Craig, K. R. Flower, W. R. Roper and L. J. Wright, *Inorg. Chim. Acta*, 1995, **240**, 385.
- C. E. F. Rickard, W. R. Roper, T. J. Woodman and L. J. Wright, *Chem. Commun.*, 1999, 837.
- M. A. Esteruelas, F. J. Lahez, J. A. Lopez, L. A. Oro, C. Schlöcken, C. Valero and H. Werner, *Organometallics*, 1992, **11**, 2034.
- G. Bellachioma, G. Cardaci, A. Macchioni and P. Zanazzi, *Inorg. Chem.*, 1993, **32**, 547.
- SMART and SAINT, Siemens Analytical Instruments Inc., Madison, WI, 1994.
- R. H. Blessing, *Acta Crystallogr., Sect. A*, 1995, **51**, 33.
- SHELXTL, Siemens Analytical Instruments Inc., Madison, WI, USA, 1994.
- G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, Universität Göttingen, Germany, 1997.