

The synthesis and crystal structure of the first metal-bound stannatrane complex $\text{Os}(\text{Sn}[\text{OCH}_2\text{CH}_2]_3\text{N})(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$: structural comparisons with the analogous silatrane complex $\text{Os}(\text{Si}[\text{OCH}_2\text{CH}_2]_3\text{N})(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$

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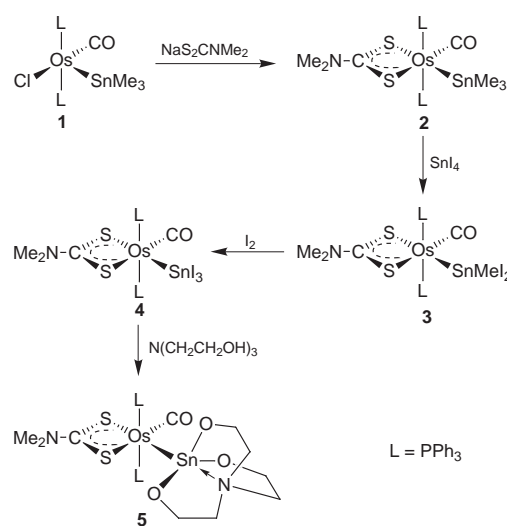
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The first metal substituted stannatrane, $\text{Os}(\text{Sn}[\text{OCH}_2\text{CH}_2]_3\text{N})(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$, has been synthesised by reaction between triethanolamine and the triiodostannyl osmium complex $\text{Os}(\text{SnI}_3)(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$: the transannular Sn–N distance of 2.422(4) Å indicates a bonding interaction which is not seen in the corresponding silatranyl complex $\text{Os}(\text{Si}[\text{OCH}_2\text{CH}_2]_3\text{N})(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ which has a Si–N distance of 3.176(6) Å.

Silatrane, cyclic organosilicon ethers of tris(2-oxyalkyl)amine, have been the subject of intense study since their discovery in 1961.¹ Perhaps the most intriguing aspect of these hypervalent silicon compounds is the nature of the silicon–nitrogen interaction and the variation in the transannular Si–N distance as a function of change in the axial silicon substituent.^{2–5} Although many structurally characterised examples of silatrane have been reported,⁶ only two bear metal atoms as axial substituents, and both of these feature strikingly long Si–N distances.^{7,8} In contrast to silatrane, reports of the analogous tin compounds, stannatrane, are sparse, with only two crystallographically characterised examples.^{9,10} Our recent work has focused on the synthesis of triiodostannyl osmium complexes because these complexes are amenable to further derivatisation at the tin centre. Here, we report the synthesis and structural characterisation of the first metal-substituted stannatrane, $\text{Os}(\text{Sn}[\text{OCH}_2\text{CH}_2]_3\text{N})(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$, which is formed by a ligand reaction of the triiodostannyl osmium complex, $\text{Os}(\text{SnI}_3)(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$, with triethanolamine. In order to compare the properties of stannatranyl and silatranyl ligands, particularly with respect to the transannular interaction, the structure of the analogous silatranyl complex, $\text{Os}(\text{Si}[\text{OCH}_2\text{CH}_2]_3\text{N})(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$, has also been determined.

The coordinatively unsaturated complex, $\text{Os}(\text{SnMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ **1**,¹¹ may be converted easily to the six coordinate dithiocarbamate complex, $\text{Os}(\text{SnMe}_3)(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ **2**, by treatment with $\text{NaS}_2\text{CNMe}_2$ at 0 °C (Scheme 1). Reaction of **2** with an excess of tin(IV) iodide in benzene provides $\text{Os}(\text{SnMeI}_2)(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ **3** in high yield. Although such redistribution reactions are common for $\text{R}_x\text{SnX}_{4-x}$ systems we believe this represents the first example of such a reaction for a metal stannyl complex. All attempts to remove the last methyl substituent with an excess of SnI_4 failed, even at elevated temperatures. However, treatment of **3** with one equivalent of I_2 in dichloromethane smoothly cleaves the remaining Sn–Me bond to yield yellow $\text{Os}(\text{SnI}_3)(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ **4**. It should be noted here that direct addition of I_2 to **2** results mainly in the cleavage of the osmium–tin bond.

Treatment of **4** with an excess of triethanolamine in benzene over 30 min provides the colourless, air stable, stannatranyl compound, $\text{Os}(\text{Sn}[\text{OCH}_2\text{CH}_2]_3\text{N})(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ **5**, in good yield.† A single crystal X-ray structure determination of this product has been carried out‡ and the molecular structure is depicted in Fig. 1.



Scheme 1

The geometry about the osmium centre can be best described as distorted octahedral with the main cause of distortion arising from the necessarily constricted bite angle of the dithiocarbamate ligand. The Os–Sn bond distance of 2.6119(3) Å is at the low end of the range of previously reported values the mean of which is 2.721 Å.¹² The most arresting aspect of the structure lies in the stannatranyl moiety where the Sn–N distance of 2.422(4) Å is only slightly longer than those found in

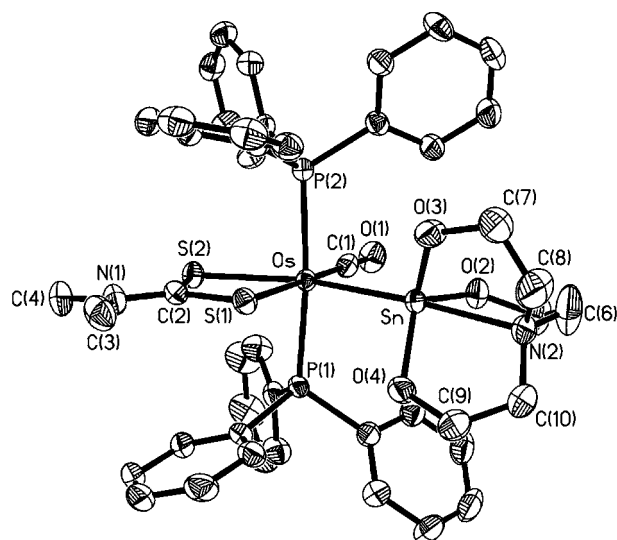


Fig. 1 Crystal structure of **5**. Selected bond lengths (Å) and angles (°): Os–Sn 2.6119(3), Sn–N(2) 2.422(4), C(8)–N(2)–C(6) 110.8(6), C(10)–N(2)–C(6) 114.4(5), C(10)–N(2)–C(8) 114.0(5), Sn–Os–S(2) 160.62(3).

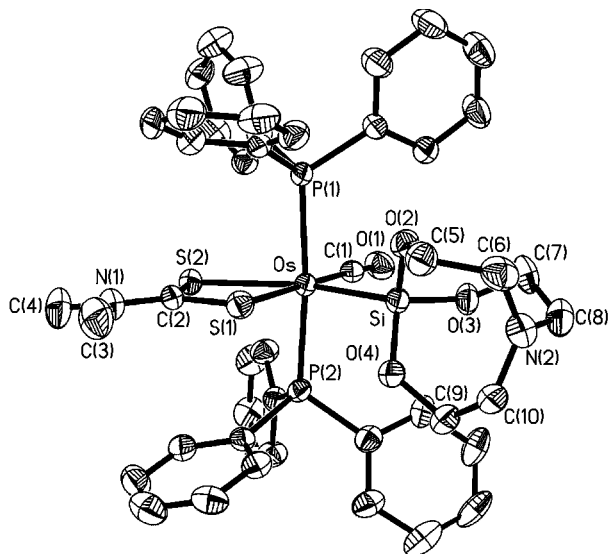


Fig. 2 Crystal structure of **6**. Selected bond lengths (Å) and angles (°): Os–Si 2.3783(17), Si–N(2) 3.176(6), C(8)–N(2)–C(6) 120.3(6), C(10)–N(2)–C(6) 120.0(6), C(10)–N(2)–C(8) 118.6(7), Si–Os–S(2) 154.98(6).

[MeSn(OCH₂CH₂)₃N]₃ [2.28(1) Å]⁹ or Bu^tSn(OCH₂CH₂)₃N (2.324 Å).¹⁰ However, is still considerably shorter than the sum of the van der Waals radii, and must surely constitute a significant interaction. The tin atom displays a very distorted trigonal bipyramidal arrangement, with the osmium and nitrogen atoms axial, and the oxygen atoms equatorial. The tin lies out of a plane taken through O(2), O(3) and O(4) by 0.533(2) Å in the direction of the osmium atom. The geometry at the nitrogen can be seen as tetrahedral, with the nitrogen atom lying out of the plane defined by C(8), C(6) and C(10) by 0.388(5) Å towards osmium.

In order to compare the structural features of this stannatranne with the corresponding silatranne, Os(Si[OCH₂CH₂]₃N)(η²-S₂CNMe₂)(CO)(PPh₃)₂ **6** was prepared in high yield by the addition of NaS₂CNMe₂ to Os(Si[OCH₂CH₂]₃N)Cl(CO)(PPh₃)₂.⁸ Crystals were grown from dichloromethane–ethanol and a single crystal diffraction study performed.† The structure of **6** is shown in Fig. 2, along with selected bond lengths and angles. It is immediately apparent that the silatranne moiety has a very different cage geometry. In this case the Si–N distance is 3.176(6) Å, whereas typical silatranne structures feature values in the range 2.00–2.26 Å. The Si–N distance in **6** is even longer than the distances found in either Os(Si[OCH₂CH₂]₃N)Cl(CO)(PPh₃)₂ [3.000(7) Å]⁸ or *trans*-Pt(Si{OCH₂CH₂]₃N)Cl(CO)(PMe₂Ph)₂ [2.89(1) Å].⁷ The bonds about the nitrogen atom are almost perfectly trigonal planar with the sum of angles at N being 358.9°. The nitrogen atom is displaced 0.088(7) Å from the plane defined by C(6), C(8) and C(10) in the direction away from the metal atom. The silicon atom has approximately tetrahedral geometry. The geometry about the osmium atom does not differ markedly from that found in compound **5**, except that the Os–S(2) distance is significantly longer for **6** [2.5431(15) Å] compared to the corresponding distance in compound **5** [2.4805(10) Å]. This disparity is presumably a reflection of a greater *trans* influence exerted by the silicon atom over that of the tin atom.

The structural comparison of these two analogous metal substituted atrane systems reveals marked differences. Whereas the stannatranne retains the Sn–N interaction to a large extent, in the silatranne the Si–N interaction is almost totally absent. This is most likely a reflection on the greater ability of tin to form hypervalent compounds when compared to silicon.

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Notes and references

† *Synthesis and selected data for* Os(Sn[OCH₂CH₂]₃N)(η²-S₂CNMe₂)(CO)(PPh₃)₂ **5**: triethanolamine (1.10 g, 1.09 mmol) was added dropwise to

a chilled (0 °C) and stirred solution of Os(SnI₃)(η²-S₂CNMe₂)(CO)(PPh₃)₂ (0.195 g, 0.143 mmol) in deoxygenated dichloromethane (40 cm³). The solution was stirred for 1 h, during which time the yellow colour faded completely. The organic layer was washed with water (3 × 25 cm³) and filtered. Addition of ethanol (20 cm³) and reduction of solvent volume *in vacuo* to 5 cm³ produced a white precipitate which was collected by filtration. Recrystallisation from dichloromethane–ethanol provided **5** in 76% yield. ν_{\max} (KBr)/cm⁻¹: 1896 (CO), 1535, 1155 (dithiocarbamate); δ_{H} (CDCl₃, 400.133 MHz, 300 K) 1.89 (s, 3H, NCH₃), 2.23 (t, 6H, *J* 5.34 Hz, NCH₂), 2.31 (s, 3H, NCH₃), 3.28 (t, *J* 5.34 Hz, 6H, OCH₂), 7.25–7.95 (m, 30H, PhH); δ_{C} (CDCl₃, 100.623 MHz, 300 K) 35.80 (S₂CNMe₂), 36.42 (S₂CNMe₂), 53.30 [Sn(OCH₂CH₂)₃N, ³*J*(SnC) 34.2 Hz], 57.39 [Sn(OCH₂CH₂)₃N, ²*J*(SnC) 42.4 Hz], 126.76 (*o*-PPh₃), 128.67 (*p*-PPh₃), 129.78 (*ipso*-PPh₃), 135.27 (*m*-PPh₃), 185.61 [t, CO, ²*J*(PC) 22.0 Hz], 210.59 (S₂CNMe₂); δ_{195Sn} [CDCl₃–CHCl₃ (1:3) 149.144 MHz, 300 K] –513.4 [t, ²*J*(SnP) 193.86 Hz]; Calc. for C₄₆H₄₈N₂O₄P₂S₂OsSn-2CH₂Cl₂: C, 47.72; H, 4.22; N, 2.39. Found: C, 47.54; H, 4.29; N, 2.35%.

‡ *Crystal data*: Os(Sn[OCH₂CH₂]₃N)(η²-S₂CNMe₂)(CO)(PPh₃)₂·2CH₂Cl₂ **5**: Crystals were grown from dichloromethane–ethanol. C₄₈H₅₂Cl₄N₂O₄·P₂S₂OsSn, *M* = 1295.65, monoclinic, space group *P*2₁/*c*, *a* = 12.45670(10), *b* = 19.2826(2), *c* = 21.7933(2) Å, β = 100.76(1)°, *U* = 5142.61(8) Å³, *F*(000) = 2560, *D*_c = 1.673 g cm⁻³, *Z* = 4, μ(Mo-Kα, λ = 0.71073 Å) = 3.349 mm⁻¹. Intensity data were collected to a θ limit of 27.51° on a Siemens 'SMART' diffractometer¹³ at 203(2) K and corrected for absorption.¹⁴ The structure was solved from Patterson and heavy-atom electron density maps¹⁵ and refined by full-matrix least squares analysis on *F*² employing SHELXL97.¹⁶ All non-hydrogen atoms were allowed to assume anisotropic motion. Hydrogen atoms were placed in calculated positions and refined using a riding model. Refinement converged to 0.0354 (*R*_w = 0.0982) for 10018 reflections for which *I* > 2σ(*I*).

Os(Si[OCH₂CH₂]₃N)(η²-S₂CNMe₂)(CO)(PPh₃)₂ **6**: Crystals were grown from dichloromethane–ethanol. C₄₆H₄₈N₂O₄P₂S₂OsSi, *M* = 1037.21, orthorhombic, space group *Pca*2₁/*c*, *a* = 19.939(2), *b* = 9.94490(10), *c* = 22.2254(2) Å, *U* = 4401.56(7) Å³, *F*(000) = 2088, *D*_c = 1.565 g cm⁻³, *Z* = 4, μ(Mo-Kα, λ = 0.71073 Å) = 3.137 mm⁻¹. Intensity data were collected to a θ limit of 27.49° on a Siemens 'SMART' diffractometer¹² at 203(2) K and corrected for absorption.¹³ Structure solution as above. Refinement converged to 0.0346 (*R*_w = 0.0762) for 8353 reflections for which *I* > 2σ(*I*).

CCDC 182/1207. See <http://rsc.org/suppdata/cc/1999/837/> for crystallographic files in .cif format.

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