Osmium nitrosyl complexes with osmium–tin bonds
Crystal structure of Os[Sn(p-tolyl)₃](NO)(CO)₂(PPh₃)

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Abstract

Oxidative addition of the tin–hydride bond of (p-tolyl)₃SnH to the formal osmium(0) nitrosyl complexes, OsCl(NO)(PPh₃)₃ and "OsH(NO)(PPh₃)₂", affords the osmium(II) stannyl complexes, Os[Sn(p-tolyl)₃]HCl(NO)(PPh₃)₂ (1), and Os[Sn(p-tolyl)₃]H₂(NO)PPh₃)₂ (2) respectively. "OsH(NO)(PPh₃)₂" was generated in situ by thermal elimination of H₂ from OsH₃(NO)(PPh₃)₂ (5). It was established from ¹H and ³¹P NMR evidence that 1 has two cis phosphine ligands, one of which is trans to the hydride ligand and the other trans to the stannyl ligand. The high trans influence of the hydride ligands confers lability on one phosphine ligand, which can be readily replaced by reaction with sodium dimethyldithiocarbamate forming OsH[Sn(p-tolyl)₃](S₂CNMe₂)(NO)(PPh₃) (3), and reaction with carbon monoxide gives eventually, after displacement of one triphenylphosphine and loss of HCl, Os[Sn(p-tolyl)₃](NO)(CO)₂(PPh₃) (4), a formal osmium(0) stannyl complex. The crystal structure of this five-coordinate osmium–tin complex, 4, has been determined. © 1997 Elsevier Science S.A.

Keywords: Osmium nitrosyl complexes; Thermal elimination; Osmium-tin bonds

1. Introduction

Oxidative addition of organo-tin hydrides to low oxidation state complexes of the platinum group metals is a versatile and widely used method of preparing compounds containing metal–tin bonds [1]. We have previously reported the addition of tri(p-tolyl)tin hydride to Os(CO)₂(PPh₃)₃ [2]. In this paper we describe the oxidative addition of tri(p-tolyl)tin hydride to two nitrosyl-containing complexes of osmium related to Os(CO)₂(PPh₃)₃, namely OsCl(NO)(PPh₃)₃ [3] and "OsH(NO)(PPh₃)₂". The latter complex is produced by thermal elimination of H₂ from OsH₃(NO)(PPh₃)₂ which is in turn produced by the action of NaBH₄ on OsHCl₂(NO)(PPh₃)₂. Addition of HCl to OsCl(NO)(PPh₃)₃ is the most direct route to OsHCl₂(NO)(PPh₃)₂.

2. Results and discussion

2.1. Oxidative addition of (p-tolyl)₃SnH to osmium(0) nitrosyl complexes

Tri(p-tolyl)tin hydride is known to undergo oxidative addition to Os(CO)₂(PPh₃)₃ forming OsH[Sn(p-tolyl)₃](CO)₂(PPh₃)₂ [2]. The reactions of OsCl(NO)(PPh₃)₃ and "OsH(NO)(PPh₃)₂" with this same reagent provided complexes which are structurally and electronically related (see Fig. 1).

OsCl(NO)(PPh₃)₃ was prepared in situ by heating a solution of the precursor peroxycarbonyl complex, Os(O₂CO)Cl(NO)(PPh₃)₂ [3] with 2 equiv. of triphenylphosphine. On addition of (p-tolyl)₃SnH at room
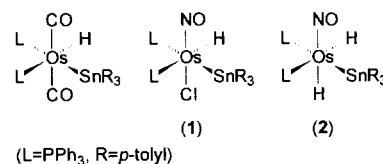

(L=PPh₃, R=p-tolyl)

Fig. 1. Structures of osmium–stannyl complexes.

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Table 1
IR data [a] for osmium stannyl complexes

Complex	ν(NO) [b]	ν(OsH) [c]	Other bands
OsH[Sn(p-tolyl)$_3$]Cl(NO)(PPh$_3$)$_2$ (1)	1764	2048	795m (p-tolyl)
OsH$_2$[Sn(p-tolyl)$_3$](NO)(PPh$_3$)$_2$ (2)	1698	1935	
OsH[Sn(p-tolyl)$_3$](S$_2$CNMe$_2$)(NO)(PPh$_3$) (3)	1713	2038	1542w (dithiocarbamate)
			800 m (p-tolyl)
Os[Sn(p-tolyl)$_3$](NO)(CO)$_2$(PPh$_3$) (4)	1683	—	1931s, 1990s (ν(CO))
OsH$_3$(NO)(PPh$_3$)$_2$ (5)	1700	1981, 1859	823 m (δ(OsH))
OsHCl$_2$(NO)(PPh$_3$)$_2$ (6)	1789	2149	

[a] In wavenumbers. Intensity of bands described as s, strong; m, medium; w, weak.
[b] All ν(NO) bands are strong.
[c] All ν(Os–H) bands are medium.

temperature, oxidative addition took place immediately. The intermediate "OsH(NO)(PPh$_3$)$_2$" was generated in situ by heating a solution of OsH$_3$(NO)(PPh$_3$)$_2$ (5). This was done in the presence of (p-tolyl)$_3$SnH, to facilitate immediate oxidative addition following dehydrogenation. Both reactions gave high yields and single products.

Infrared data showed strong bands for ν(NO) and medium–weak bands for ν(Os–H) stretching vibrations (see Table 1). ^{1}H and ^{31}P NMR spectra were compatible with the formulations above. For 1, values for ^3J(H–Os–P$_{cis}$), ^3J(H–Os–P$_{trans}$) and ^3J(H–Os–Sn$_{cis}$)

were all determined. The observation of two (H–P) coupling constants and their relative magnitudes (see Table 2) requires that the hydride ligand is trans to one phosphorus ligand and cis to the other. ^{31}P NMR spectrum of 1 reveals two (P–Sn) coupling constants and again their relative magnitudes (see Table 2) require that the stannyl ligand is trans to one phosphorus ligand and cis to the other. It follows that the geometry must be as depicted in Fig. 1.

The geometry for 2 can likewise be deduced by NMR spectroscopy. Two sets of signals are seen in the ^{1}H NMR spectrum and the observed coupling constants

Table 2
^{1}H and ^{31}P NMR data [a] for osmium stannyl complexes

Complex	^{1}H NMR data	^{31}P NMR data
OsH[Sn(p-tolyl)$_3$]-Cl(NO)(PPh$_3$)$_2$ (1)	−0.27 (dd [c], 1 H, Os–H, ^2J(HP$_{cis}$) = 18.4, ^2J(HP$_{trans}$) = 116.4, ^2J(HSn) [b] = 74.4); 2.31 (s, 9 H, CH_3); 6.9–7.7 (m, 42 H, ArH).	−5.17 (d [c], P(trans to Sn), ^2J(PP) = 12.8 (sc, ^2J(P^{117}Sn$_{trans}$) = 1063.8, ^2J(P^{119}Sn$_{trans}$) = 1113.2); −13.11 (d [c], P(cis to Sn), ^2J(PP) = 12.8, ^2J(P$^{117/119}$Sn$_{cis}$) = 60.8).
OsH$_2$[Sn(p-toly)]$_3$]-(NO)(PPh$_3$)$_2$ (2)	−6.85 (dd, 1 H, Os–H, ^2J(HP$_{cis}$) = 17.6, ^2J(HP$_{cis}$) = 28.8); −4.96 (dd, 1 H, Os–H, ^2J(HP$_{trans}$) = 61.2, ^2J(HP$_{cis}$) = 21.2); 2.25 (s, 9 H, CH_3); 6.80–7.35 (m, 42 H, ArH).	11.60 (s [c], ^2J(P$^{117/119}$Sn$_{trans}$) = 653.0); 2.06 (s [c], ^2J(P$^{117/119}$Sn$_{cis}$) ≈ 50).
OsH[Sn(p-tolyl)$_3$]-(S$_2$CNMe$_2$)(NO)(PPh$_3$) (3)	−0.86 (d [c], 1 H, Os–H, ^2J(HP$_{cis}$) = 28.6, ^2J(HS$_{cis}$) = 97.0); 2.28 (s, 9 H, CH_3); 3.10 (s, 3 H, N(CH_3)); 3.11 (s, 3 H, N(CH_3)); 6.94–7.33 (m, 27 H, ArH).	7.45 (s [c], ^2J(P$^{117/119}$Sn$_{cis}$) = 66.4).
Os[Sn(p-tolyl)$_3$]-(NO)(CO)$_2$(PPh$_3$) (4)	2.34 (s, 9 H, CH_3); 7.18–7.54 (m, 27 H, ArH).	2.58 (s [c], ^2J(P^{117}Sn$_{trans}$) = 276.2, ^2J(P^{119}Sn$_{trans}$) = 289.1).
OsH$_3$(NO)(PPh$_3$)$_2$ (5)	−5.78 (dt, 2 H, Os–H, ^2J(HP$_{cis}$) = 16.9, ^2J(HH) = 4.3); −6.77 (tt, 1 H, Os–H, ^2J(HP$_{cis}$) = 26.2, ^2J(HH) = 4.3); 6.95–7.59 (m, 30 H, PhH).	
OsHCl$_2$(NO)(PPh$_3$)$_2$ (6)	−4.64 (t, 1 H, Os–H, ^2J(HP$_{cis}$) = 14.8); 7.34–7.79 (m, 30 H, PhH).	

[a] Spectra recorded in CDCl$_3$ at 25 °C. Chemical shifts (δ) are given in ppm and are referenced to (CH$_3$)$_4$Si (internal standard, δ = 0.00) for ^{1}H spectra or 85% H$_3$PO$_4$ (external standard, δ = 0.00) for ^{31}P spectra. Splitting patterns are indicated thus: s, singlet; d, doublet; t, triplet; m, multiplet. Coupling constants J are in Hz.
[b] For the known structural analogue, OsH[Sn(p-tolyl)$_3$](CO)$_2$(PPh$_3$)$_2$, ^2J(HSn) = 84.26 Hz.
[c] Satellite signals arising from coupling to $^{117/119}$Sn were observed.

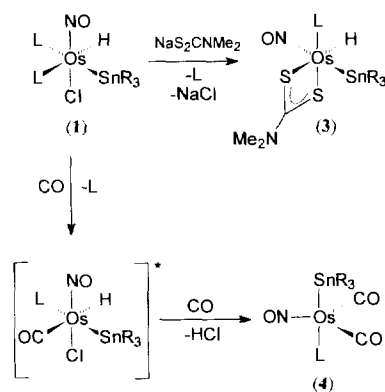(L=PPh$_3$, R=p-tolyl, *designates a postulated intermediate)
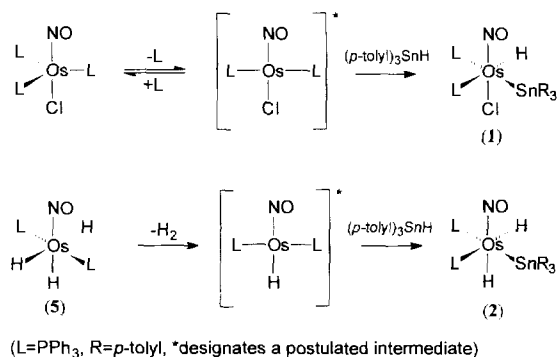
Scheme 1. L = PPh$_3$, R = p-tolyl; * designates a postulated intermediate.

to phosphorus indicate that one hydride is again trans to one PPh$_3$ and cis to the other, while the other hydride is cis to both PPh$_3$ ligands. The ^{31}P NMR spectrum shows two phosphorus signals, one of which has Sn satellites indicative of coupling to a trans tin. This fixes the geometry as shown in Fig. 1 and Scheme 1.

The determined geometries of 1 and 2 are compatible with a cis addition of stannyl and hydride ligands to planar four-coordinate intermediates as presented in Scheme 1.

2.2. Derivatisation of OsH[Sn(p-tolyl)$_3$]Cl(NO)(PPh$_3$)$_2$ (1)

The reactions to be discussed are shown in Scheme 2. One triphenylphosphine ligand in 1 is labile and substitution reactions presumably proceed via initial replacement of the triphenylphosphine ligand trans to the hydride. This lability is undoubtedly enhanced by the steric pressures associated with the presence of two bulky cis ligands, triphenylphosphine and the tri(p-tolyl)stannyl group. Substitution reactions involving both dimethyldithiocarbamate and CO have been examined.

Treatment of 1 with NaS$_2$CNMe$_2$ under mild conditions gave 3 in modest yield. The values of the (H–P) and the (H–Sn) coupling constants indicate that the hydride ligand is cis to both PPh$_3$ and Sn(p-tolyl)$_3$. The small value of the (P–Sn) coupling shows that the bulky PPh$_3$ and stannyl ligand are mutually cis. With the three ligands H, PPh$_3$, Sn(p-tolyl)$_3$ in a facial arrangement there are three possible isomers for this compound, one of which is depicted in Scheme 2.

Addition of CO to 1 might have been expected to yield the complex shown as an intermediate in Scheme 2; however, loss of HCl occurred during the carbonylation reaction and the dicarbonyl osmium(0) stannyl–nitrosyl complex 4 was formed. Improved yields of 4 were obtained if triethylamine was added to the reaction mixture to aid in the removal of HCl. Attempts to isolate the monocarbonyl intermediate were unsuccessful.

The novel osmium(0) stannyl complex 4 is comparatively unreactive and easy to handle. Attempts to displace a carbonyl ligand by reacting with excess triphenylphosphine under forcing conditions were ineffective. Reaction with HCl and I$_2$ both caused loss of the stannyl moiety.

2.3. Crystal structure of Os[Sn(p-tolyl)$_3$](NO)(CO)$_2$(PPh$_3$) (4)

A single crystal X-ray structure determination has been made of Os[Sn(p-tolyl)$_3$](NO)(CO)$_2$(PPh$_3$) (4). The molecular geometry of 4 is depicted in Fig. 2. Selected bond lengths and bond angles are listed in Table 3. The structure is essentially trigonal bipyramidal with the two bulky ligands in the axial sites. The NO and two CO ligands in the equatorial plane are all effectively linear. The osmium–nitrosyl distance of 1.863(6) Å is at the long end of determined Os–NO

(L=PPh$_3$, R=p-tolyl, *designates a postulated intermediate. Two other isomers for 3 are compatible with observed spectral data - see text)

Scheme 2. L = PPh$_3$, R = p-tolyl; * designates a postulated intermediate. Two other isomers for 3 are compatible with observed spectral data—see text.
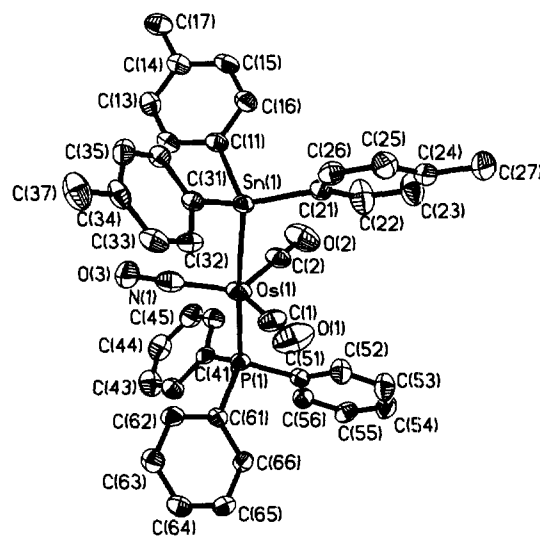

Fig. 2. Molecular structure of Os[Sn(p-tolyl)$_3$](NO)(CO)$_2$(PPh$_3$) (4).

Table 3
Selected bond lengths (Å) and angles (deg) for Os[Sn-(p-tolyl)$_3$](NO)(CO)$_2$(PPh$_3$) (4)

Os(1)–N(1)	1.863(6)
Os(1)–C(1)	1.865(6)
Os(1)–C(2)	1.866(6)
Os(1)–P(1)	2.3792(11)
Os(1)–Sn(1)	2.7147(4)
Sn(1)–C(11)	2.146(5)
Sn(1)–C(31)	2.157(5)
Sn(1)–C(21)	2.159(5)
P(1)–C(61)	1.823(5)
P(1)–C(41)	1.829(5)
P(1)–C(51)	1.831(5)
N(1)–O(3)	1.157(6)
C(1)–O(1)	1.152(7)
C(2)–O(2)	1.151(7)
N(1)–Os(1)–C(1)	121.9(3)
N(1)–Os(1)–C(2)	121.3(2)
C(1)–Os(1)–C(2)	114.7(3)
N(1)–Os(1)–P(1)	97.01(14)
C(1)–Os(1)–P(1)	94.7(2)
C(2)—-Os(1)–P(1)	92.4(2)
N(1)–Os(1)–Sn(1)	86.57(14)
C(1)–Os(1)–Sn(1)	84.8(2)
C(2)–Os(1)–Sn(1)	84.2(2)
P(1)–Os(1)–Sn(1)	176.01(3)
C(11)–Sn(1)–C(31)	103.6(2)
C(11)–Sn(1)–C(21)	110.5(2)
C(31)–Sn(1)–C(21)	106.4(2)
C(11)–Sn(1)–Os(1)	111.66(13)
C(31)–Sn(1)–Os(1)	113.71(12)
C(21)–Sn(1)–Os(1)	110.65(13)
O(3)–N(1)–Os(1)	177.5(4)
O(1)–C(1)–Os(1)	177.5(5)
O(2)–C(2)–Os(1)	179.0(5)

distances probably because of the two other strongly π-accepting ligands in the equatorial plane. [2] There have been three previous determinations of a triorgano-stannyl–osmium distance and all are very close to the value found in **4** [4]. The Os–P distance at 2.379(1) Å is normal.

3. Experimental details

The general experimental conditions were as described previously [2]. Tri(p-tolyl)tin hydride was prepared as described in Ref. [5]. Infrared spectra were measured on a Perkin Elmer Paragon 1000 series FTIR spectrometer as nujol mulls between potassium bromide plates. 200 MHz ^{1}H NMR spectra were measured using a Bruker AC 200 instrument and other NMR data measured using a Bruker DRX 400.

[2] Cambridge X-ray Crystallographic Data Base.

3.1. OsH[Sn(p-tolyl)$_3$]Cl(NO)(PPh$_3$)$_2$ (1)

To dry, degassed benzene (10 ml) was added Os(OCO$_2$)Cl(NO)(PPh$_3$)$_2$ [3] (200 mg) with PPh$_3$ (200 mg). The mixture was heated under reflux for several minutes to ensure complete decomposition of the peroxycarbonyl substrate and formation of OsCl(NO)(PPh$_3$)$_3$, then the solution was cooled to room temperature. (p-Tolyl)$_3$SnH (100 mg) was added with stirring, and the solution became deep orange almost immediately. After precipitation with heptane, an orange microcrystalline sample of pure **1** was obtained (184 mg, 66%). Melting point: 132–135 °C. Anal. Found: C, 57.23; H, 4.18; N, 1.15. C$_{57}$H$_{52}$NOOsP$_2$Sn · $\frac{1}{2}$CH$_2$Cl$_2$. Calc.: C, 56.80; H, 4.40; N, 1.15%.

3.2. OsH$_2$(Sn[p-tolyl]$_3$)(NO)(PPh$_3$)$_2$ (2)

To dry, degassed benzene (10 ml) was added OsH$_3$(NO)(PPh$_3$)$_2$ (150 mg) and (p-tolyl)$_3$SnH (95 mg). The solution was heated under reflux for 1 h. On precipitation with heptane, a yellow microcrystalline sample of **2** (132 mg, 58%) was obtained. Anal. Found: C 57.07; H, 5.05; N, 1.00. C$_{57}$H$_{53}$NOOsP$_2$Sn · $\frac{1}{2}$CH$_2$Cl$_2$ Calc.: C, 56.95; H, 4.87; N, 1.15%.

3.3. OsH(Sn[p-tolyl]$_3$)(S$_2$CNMe$_2$)(NO)(PPh$_3$) (3)

1 (100 mg) was added to CH$_2$Cl$_2$ (10 ml) NaS$_2$CNMe$_2$ (16 mg) was dissolved in MeOH (5 ml) and several drops of water. These solutions were combined and heated under reflux under a nitrogen atmosphere for 30 min. Removal of solvent under reduced pressure gave yellow microcrystals of **3**, (33 mg, 39%). Melting point: 184–188 °C. Anal. Found: C, 48.32; H, 4.30; N, 2.55. C$_{42}$H$_{43}$N$_2$OOsPS$_2$Sn · CH$_2$Cl$_2$. Calc.: C, 47.76; H, 4.20; N, 2.59%.

3.4. Os(Sn[p-tolyl]$_3$)(NO)(CO)$_2$(PPh$_3$) (4)

1 (300 mg) was placed in a Fisher–Porter bottle. Dry benzene (15 ml) and triethylamine (1 ml) were added. A carbonylation head was fitted and 4–5 atm CO pressure was applied, while the reaction tube was heated to ca. 50–60 °C. After 40 min the pressure was released and the contents of the bottle transferred to a flask. Heptane was added and the benzene removed in vacuo. A terra-cotta-coloured powder was obtained (190 mg, 80%) which, on recrystallisation from CH$_2$Cl$_2$–EtOH, yielded analytically pure bright orange microcrystals of **4**. Melting point: 202–212 °C. Anal. Found; C, 52.54; H, 3.95; N, 1.41. C$_{41}$R$_{36}$NO$_3$OsPSn. Calc.: C, 52.89, H, 3.90, N, 1.51%.

3.5. OsH$_3$(NO)(PPh$_3$)$_2$ (5)

OsHCl$_2$(NO)(PPh$_3$)$_2$ (**6**) (250 mg) and NaBH$_4$ (100 mg) in a mixture of ethanol (40 ml) and 2-

Table 4
Crystal data for Os[Sn(p-tolyl)$_3$](NO)(CO)$_2$(PPh$_3$) (4)

Formula	C$_{41}$H$_{36}$NO$_3$OsPSn
Molecular weight	930.57
Crystal system	Monoclinic
Space group	P2$_1$/c
a (Å)	10.2123(3)
b (Å)	17.6716(5)
c (Å)	20.4427(7)
β (deg)	94.204(10)
V (Å^3)	3679.3(3)
Z	4
d(calc) (g cm^{-3})	1.680
F(000)	1816
μ (mm^{-1})	4.21
Radiation Mo Kα (monochromatic) λ (Å)	0.71069
Temperature (K)	203
Diffractometer	Siemens SMART
2θ (min, max) (deg)	1.5, 26.3
h,k,l range	$-12 \le h \le 11$, $-22 \le k \le 16$, $-23 \le l \le 25$
No. of reflections	21672
No. of unique reflections, R_{int}	7442, 0.0248
No. of observed reflections $I > 2\sigma(I)$	6209
Crystal size (mm^3)	0.32 × 0.20 × 0.20
A (min, max)	0.739, 1.00
Least squares weights a,b	0.017, 15.584
Goodness of fit on F^2	1.137
Function minimised	$\Sigma w(F_o^2 - F_c^2)^2$
R and $wR2$	0.0381, 0.0809
Peak height in final density map (min, max) (e$^-$ Å^{-3})	1.98, 3.08

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; weight $= 1.0/[\sigma^2(F_o^2) + aP^2 + bP]$; $P = (F_o^2 + {}^2F_c^2)/3$.

methoxyethanol (20 ml) were heated under reflux for 2 h. The solution was then cooled and reduced in volume to 10–15 ml whereupon small yellow crystals of OsH$_3$(NO)(PPh$_3$)$_2$ were formed (160 mg, 70%). Melting point: 168–171 °C. Anal. Found: C, 57.80; H, 4.40; N, 2.25. C$_{36}$H$_{33}$NOOsP$_2$. Calc.: C, 58.30; H, 4.50; N, 1.90%.

3.6. OsHCl$_2$(NO)(PPh$_3$)$_2$ (6)

OsCl(NO)(PPh$_3$)$_3$ was generated in situ from Os(OCO$_2$)Cl(NO)(PPh$_3$)$_2$ [3] (200 mg) and PPh$_3$ (200 mg) as in Section 3.1. Several drops of 35% aqueous HCl were added to this stirred solution causing an instant lightening of colour and some precipitation of 6. Addition of heptane and removal of benzene gave rise to a nearly quantitative yield of OsHCl$_2$(NO)(PPh$_3$)$_2$ as a yellow microcrystalline solid. Melting point: 220–225 °C. Anal. Found: C, 52.65; H, 4.30; N, 1.65. C$_{36}$H$_{31}$Cl$_2$NOOsP$_2$. Calc.: C, 52.90; H, 3.85; N, 1.70%.

3.7. X-ray diffraction study of Os[Sn(p-tolyl)$_3$](NO)(CO)$_2$(PPh$_3$) (4)

3.7.1. Crystal data

Details of crystal data and refinement are given in Table 4. Data collection was by Siemens SMART area

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for Os[Sn(p-tolyl)$_3$](NO)(CO)$_2$(PPh$_3$) (4)

	x	y	z	U_{eq} [a]
Os(1)	1641(1)	7435(1)	1129(1)	40(1)
Sn(1)	2786(1)	7391(1)	−28(1)	29(1)
P(1)	708(1)	7558(1)	2156(1)	27(1)
N(1)	1663(5)	6382(3)	1103(2)	46(1)
O(3)	1681(5)	5729(3)	1064(2)	61(1)
C(1)	337(6)	7998(4)	665(3)	44(1)
O(1)	−452(6)	8336(4)	358(3)	81(2)
C(2)	3131(6)	7987(3)	1419(3)	39(1)
O(2)	4054(5)	8329(3)	1588(2)	72(2)
C(11)	4699(5)	6883(3)	80(2)	30(1)
C(12)	4829(5)	6134(3)	288(2)	35(1)
C(13)	6021(5)	5767(3)	326(3)	37(1)
C(14)	7155(5)	6134(3)	165(2)	34(1)
C(15)	7046(5)	6884(3)	−32(3)	41(1)
C(16)	5845(5)	7253(3)	−72(3)	38(1)
C(17)	8460(6)	5720(4)	199(3)	47(1)
C(21)	2899(5)	8511(3)	441(2)	32(1)
C(22)	3310(8)	9137(4)	−77(3)	58(2)
C(23)	3314(S)	9553(3)	−354(3)	58(2)
C(24)	2913(6)	9977(3)	−1000(3)	40(1)
C(25)	2525(6)	9355(3)	−1375(3)	44(1)
C(26)	2509(6)	8630(3)	−1097(3)	38(1)
C(27)	2925(7)	10759(3)	−1297(3)	56(2)
C(31)	1743(5)	6701(3)	−765(2)	30(1)
C(32)	397(5)	6750(3)	−905(3)	39(1)
C(33)	−255(6)	6298(3)	−1379(3)	44(1)
C(34)	416(6)	5780(3)	−1737(3)	38(1)
C(35)	1763(6)	5733(3)	−1608(2)	37(1)
C(36)	2416(5)	6178(3)	−1129(2)	33(1)
C(37)	−302(7)	5292(4)	−2256(3)	57(2)
C(41)	1491(5)	6971(3)	2810(2)	28(1)
C(42)	759(6)	6489(3)	3182(3)	38(1)
C(43)	1389(7)	6074(4)	3693(3)	50(2)
C(44)	2714(7)	6141(3)	3838(3)	49(2)
C(45)	3449(6)	6617(3)	3464(3)	47(1)
C(46)	2839(5)	7021(3)	952(3)	39(1)
C(51)	793(5)	8510(3)	2511(2)	27(1)
C(52)	678(6)	9137(3)	2106(3)	41(1)
C(53)	649(7)	9856(3)	2375(3)	50(2)
C(54)	759(6)	9958(3)	3044(3)	43(1)
C(55)	895(5)	9339(3)	3451(3)	39(1)
C(56)	910(5)	614(3)	187(2)	34(1)
C(61)	−1029(5)	7312(3)	2137(2)	26(1)
C(62)	−1459(5)	6643(3)	1828(2)	36(1)
C(63)	−2760(6)	6435(3)	1820(3)	40(1)
C(64)	−3661(5)	6900(3)	2104(3)	38(1)
C(65)	−3249(5)	7557(3)	2407(3)	40(1)
C(66)	−1936(5)	7768(3)	2427(2)	30(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalised U_{ij} tensor.

detector system using graphite-monochromated Mo K α radiation. The data collection covered a nominal hemisphere of reciprocal space by a combination of three sets of exposures: each set had a different ϕ angle and each exposure covered 0.3° in ω. The crystal to detector distance was 5 cm and coverage of the unique data set is over 98% to at least 26° in θ. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analysing duplicate reflections; no evidence of decay being observed. Unit cell parameters were obtained by least squares fit to all data with $I > 10\sigma(I)$. Lorentz and polarisation corrections were applied and empirical absorption corrections by the method of Blessing [6] and duplicate reflections averaged to give the unique data set.

The structures were solved by Patterson [7] and difference Fourier techniques and refined by full-matrix least squares [8]. All non-hydrogen atoms were allowed to assume anisotropic motion. Hydrogen atoms were placed geometrically and refined with a riding model (including free rotation about the C–C bond for methyl groups) with U_{iso} constrained to be 20% greater than U_{eq} of the carrier atom. Atomic coordinates are given in Table 5. Supplementary data available (from C.E.F.R) comprises anisotropic thermal parameters, hydrogen atom positions, full listing of interatomic distances and angles and observed and calculated structure factors.

Acknowledgements

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