Synthesis of the First Hydroxomonoaryltin(IV) Complexes. Crystal and Molecular Structure of [{Sn[C_6H_3(N=NC_6H_4-Me-4')-2,Me-5]Cl_2(μ-OH)}$_2$]†

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Tin(II) chloride reacts in refluxing xylene with [HgLCl] [L = C_6H_3(N=NC_6H_4R-4')-2,R-5; R = Me (mpap) or MeO (mopap)] to give metallic mercury and [$SnLCl_3$] (L = mpap **1** or mopap **2**). Complex **1** reacts with Cl^-, dimethyl sulfoxide or [Hg(dmap)$_2$] (dmap = $C_6H_4CH_2NMe_2$-2) to give, respectively, [Sn(mpap)Cl_4]$^-$ **3**, [Sn(mpap)Cl_3($OSMe_2$)] **4** or [Sn(mpap)(dmap)Cl_2] **5**. Several types of hydrolytic process occur when **1**, **2** or [Sn(mpap)Ph_2Cl] react with various ligands. Thus, [Hg(dmap)Cl] reacts with **1** or **2** as a base to give [{$SnLCl_2$(μ-OH)}$_2$] (L = mpap **6** or mopap **7**) and Hg(Hdmap)Cl_2. Similarly, $PhCH_2NMe_2$ (bdma) reacts with **1** (1:1) to give the hydrolysis product [Hbdma][Sn(mpap)Cl_3(OH)] **8**. By treating **6** with excess of NaBr, [{Sn(mpap)Br_2(μ-OH)}$_2$] **9** can be obtained. Acetic anhydride reacts with complex **6** to give [Sn(mpap)Cl_2(O_2CMe)] **10**, but not with **8**. The complex [Sn(mpap)Ph_2Cl] reacts with Tl(acac) (acac = acetylacetonate), NaH or Ag_2O to give the hydrolysis product [Sn(mpap)Ph_2(OH)] **11**. The crystal structure of **6** was determined at −95 °C; the dimeric doubly bridged nature of the compound was confirmed. The Sn–O bridges are asymmetric, the bond lengths depending on the nature of the *trans* ligand. Two molecules of diethyl ether form hydrogen bonds to the bridging OH groups; another diethyl ether molecule is disordered over a symmetry centre. The structure of compound **7** was also determined; it too is dimeric with two hydroxo bridges, but the refinement was unsatisfactory, probably because of twinning effects.

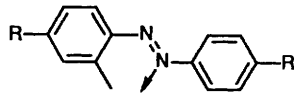
Whereas the hydrolysis of halogenoorganotin(IV) complexes to hydroxo-, oxo- and oxohydroxo-organotin(IV) complexes is a well known process, well characterized hydroxoorganotin(IV) complexes are very rare because they are usually in equilibrium with the corresponding oxo-derivatives and water.[1] As far as we are aware, only a few such complexes have been studied by X-ray diffraction, *viz.* [{$SnMe_3$(OH)}$_n$],[2] [{$SnPh_3$(OH)}$_n$],[3] [{$SnRCl_2(H_2O)$(μ-OH)}$_2$] (R = Et[4] or Bu^n[5]), [{$SnBu^t_2$X-(OH)}$_2$] (X = F, Cl or Br)[6] and [$Sn_2Ph_4(NO_3)_4$(μ-$OH)_2$]$^{2-}$.[7]

We are currently investigating the synthesis of aryltin(IV) complexes as part of a wider project involving the use of organomercury compounds as transmetallating agents. In particular, we have developed several methods of synthesising (phenylazo)phenyltin(IV) complexes.[8]

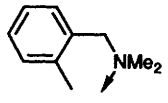
In this paper we report the synthesis of some derivatives of [$SnLCl_3$] and [$SnLPh_2Cl$], where L is a *p*-Me- or *p*-OMe-substituted 2-(phenylazo)phenyl chelating ligand. Some of these derivatives are the first hydroxomonoaryltin(IV) complexes reported.[1] We also report the crystal structure of one of them, and a partial crystal structure determination of another.

Results and Discussion

Synthesis.—Tin(II) chloride reacts in refluxing xylene with [HgLCl] [L = C_6H_3(N=NC_6H_4R-4')-2,R-5; R = Me (mpap) or MeO (mopap)] to give metallic mercury and [$SnLCl_3$] (L = mpap **1** or mopap **2**) (see formula diagram and Scheme 1). Complex **1** reacts with NMe_4Cl or dimethyl sulfoxide to give [NMe_4][Sn(mpap)Cl_4] **3** or [Sn(mpap)Cl_3($OSMe_2$)] **4**, respectively. A second aryl group can be transmetallated from mercury to tin by treating [Hg(dmap)$_2$] (dmap = $C_6H_4CH_2$-NMe_2-2) with **1** to give the mixed-ligand complex [Sn(mpap)-(dmap)Cl_2] **5**. We have previously used analogous methods to prepare complexes [$SnL(Ph)Cl_2$] and [$SnLPh_2Cl$] (L = C_6H_4N=NPh-2 or mpap).[8]



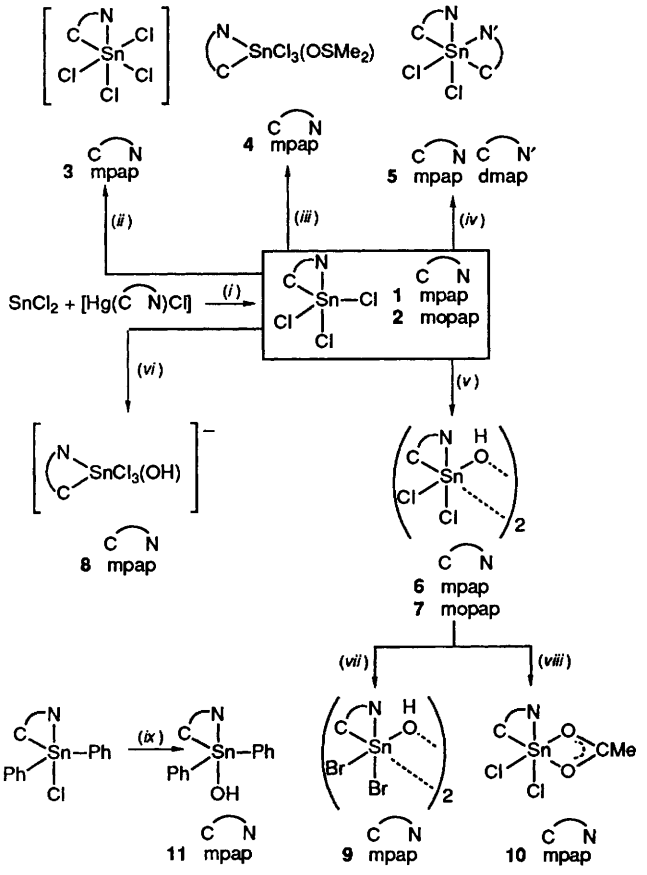
mpap (R = Me), mopap (R = OMe)



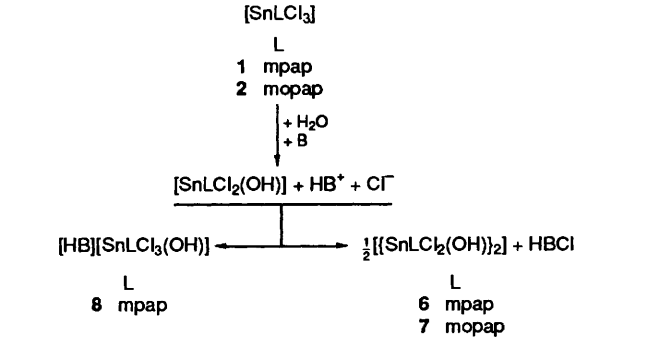
dmap

Complex **1** is stable to atmospheric moisture in solution and in the solid state. It also resists 10 h of refluxing in an acetone–water mixture. However, treatment with various ligands (except for the three mentioned above) led to the formation of hydroxo-complexes. Even the mercurial reagent [Hg(dmap)Cl] reacts with **1** or **2** as a base, removing a proton from water and substituting Cl by OH to give [{$SnLCl_2$(μ-OH)}$_2$] (L = mpap **6** or mopap **7**), instead of transmetallating the aryl group. The

† *Supplementary data available:* further details of the structure determination (complete bond lengths and angles, H-atom coordinates, structure factors, thermal parameters) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany. Any request for this material sould quote a full literature citation and the reference number CSD 56083.



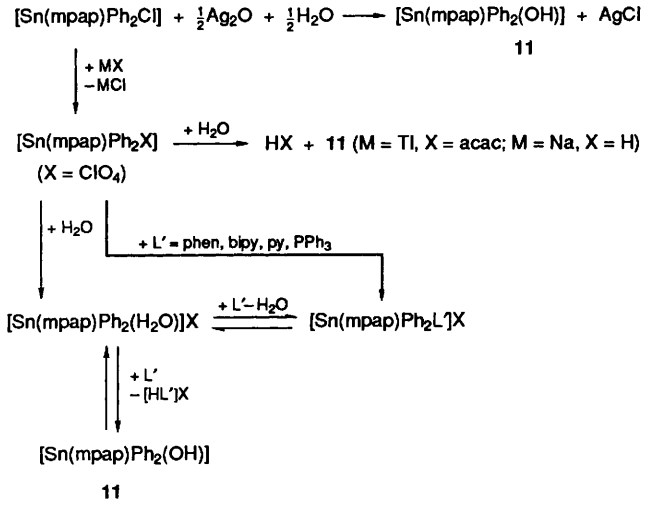
Scheme 1 Synthesis of complexes **1**–**11**. (*i*) −Hg; (*ii*) $+Cl^-$; (*iii*) + Me_2SO; (*iv*) $+[Hg(dmap)_2]$ − [Hg(dmap)Cl]; (*v*) $+H_2O$ + [Hg(dmap)Cl] − $Hg(Hdmap)Cl_2$; (*vi*) $+H_2O$ + $PhCH_2NMe_2$ − $PhCH_2NHMe_2^+$; (*vii*) +2NaBr − 2NaCl; (*viii*) $+(MeCO)_2O$ − $MeCO_2H$; (*ix*) $+\frac{1}{2}Ag_2O + \frac{1}{2}H_2O$ − AgCl or +MX + H_2O − MCl − HX (M = Tl, X = acac; M = Na, X = H)



Scheme 2 Proposed pathway for the synthesis of the hydroxo-complexes **6**–**8** (B = base)

by-product of this reaction is the unusual protonated organomercurial, $Hg(Hdmap)Cl_2$, which precipitates from the acetone solution; it can also be obtained by treating [Hg(dmap)Cl] with HCl. The basic character shown by the dmap ligand in [Hg(dmap)Cl] is also observed in the non-metallated precursor amine $PhCH_2NMe_2$ (bdma), which reacts with **1** (1:1) to give [Hbdma][$Sn(mpap)Cl_3(OH)$] **8**. However, these results indicate that the insolubility of $Hg(Hdmap)Cl_2$ is responsible for the different nature of complexes **6** and **8**.

The synthesis of complexes **6**–**8** can be rationalized assuming that the hydrolyses lead to $[SnLCl_2(OH)]$ and that this is the final product because of the insolubility of $Hg(Hdmap)Cl_2$; otherwise, complex **8**, the product of the reaction between $[SnLCl_2(OH)]$ and Cl^-, is obtained (see Scheme 2).



Scheme 3 Proposed pathways for the synthesis of complex **11**

Addition of excess of NaBr to complex **6** gives [{Sn(mpap)-$Br_2(\mu\text{-}OH)\}_2$] **9**. Complex **6** reacts with acetic anhydride to give $[Sn(mpap)Cl_2(O_2CMe)]$ **10**, whereas **8** does not react.

The complex $[Sn(mpap)Ph_2Cl]$ does not react with 1,10-phenanthroline (phen·H_2O), 2,2′-bipyridine (bipy), pyridine (py) or PPh_3.[8c] In an attempt to prepare cationic derivatives with such ligands, $[Sn(mpap)Ph_2Cl]$ was treated with $AgClO_4$. After removing AgCl, addition of the above ligands (L′) (1:1) gave mixtures which seemed to contain the expected complexes, $[Sn(mpap)Ph_2L']ClO_4$, along with some hydrolysis product(s) that could not be separated. When the reaction with phen·H_2O was carried out in 1:2 molar ratio (Sn:phen), the complex $[Sn(mpap)Ph_2(OH)]$ **11** was obtained along with $[Hphen]ClO_4$ and some excess of phen·H_2O. We interpret these results (see Scheme 3) assuming that the complex $[Sn(mpap)Ph_2(OClO_3)]$, formed first in solution, reacts with the added ligand and with water (adventitious or added with the ligand in the case of phen·H_2O) giving the cationic complexes $[Sn(mpap)Ph_2L']^+$. The aqua-complex, L′ = H_2O, is an acid, the dissociation equilibrium of which can be shifted by the added (basic) ligand to give **11**. Upon addition of a second mole of phen·H_2O, not only is this last equilibrium displaced forming **11**, but the simultaneous addition of 1 mol of water also shifts the equilibrium system $[Sn(mpap)Ph_2(H_2O)]^+$/$[Sn(mpap)Ph_2$-$(phen)]^+$ in favour of the former (see Scheme 3).

A more direct and convenient preparation of complex **11** is the reaction of $[Sn(mpap)Ph_2Cl]$ with Tl(acac) (acac = acetylacetonate), or NaH (1:1) or Ag_2O (2:1); the by-products of these reactions HX (X = acac or H) and MCl (M = Ag, Tl or Na) are easily separated from **11**.

Structure and Spectroscopic Properties of Complexes **1**–**11**.— Repeated attempts to grow crystals of complexes **1**–**11** were, except for **6** and **7** (see below), unsuccessful. Our proposals of six-co-ordination for complexes **3**–**5**, **8** and **10** and five-co-ordination for **1**, **2** and **11** (see Scheme 1) are thus based on solution data and previous reports of similar complexes. Complexes related to **1** and **2**, such as $[Sn\{C_6H_4C(Ph)=NMe\}$-$Cl_3]$[9] or $[Sn\{CH_2CH_2C(O)OPr^i\}Cl_3]$[10] have trigonal-bipyramidal structures with axial nitrogen or oxygen atoms, respectively. Complexes **1** and **2** should adopt the same type of structure because the small bite of the 2-(phenylazo)phenyl ligand (*ca.* 70°)[8] requires its location in a vertical plane and the more electronegative donor atom N should be axial.

Whereas the anionic complex **3** behaves in nitromethane solutions as a 1:1 electrolyte, with $B = 247\ \Omega^{-1}\ cm^{\frac{3}{2}}\ mol^{-\frac{3}{2}}$ in the Onsager equation ($\Lambda = A - Bc^{\frac{1}{2}}$) in the range 2×10^{-3} to 10^{-4} mol dm^{-3},[11] complex **8** shows an anomalous negative value

$B = -49\ \Omega^{-1}\ cm^{\frac{3}{2}}\ mol^{-\frac{3}{2}}$ in the same range. The ^1H NMR spectrum of **8** in chloroform changes with concentration. With increased concentration the NH signal at δ *ca.* 10 shifts to high field (δ *ca.* 9.5) and the CH_2 and Me singlets (at δ 4.23 and 2.81) change to an apparent doublet (at δ 4.24 and 4.26, which should be an AB system) and two singlets (at δ 2.82 and 2.84). All these data point to the formation of a hydrogen bond RNH ··· O(H)M when the concentration rises, which could be responsible for the non-ideal electrolyte behaviour of **8**.

Complex **5** is assumed to be octahedral by analogy to the related $[Sn(mpap)_2Cl_2]$[12] and $[Sn(dmap)_2Cl_2]$;[13] in all reported structures of organotin(IV) complexes containing potential C,N ligands a N–Sn bond is indeed observed.[1,8] Furthermore, the IR spectrum of **5** gives bands assignable to ν(SnCl) modes at 300 and 280 cm^{-1}, *cf.* $[Sn(dmap)_2Cl_2]$ at 320 and 295 cm^{-1}.

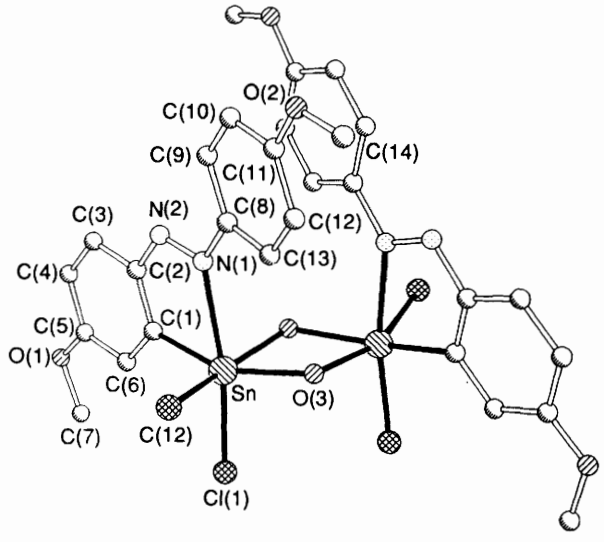


Fig. 1 The molecule of compound **7** in the crystal. The numbering scheme of the asymmetric unit is indicated. Radii are arbitrary; H atoms were not located (see Experimental section)

Complex **11** is monomeric in chloroform solution (*M* found 499, calc. 501). Although a dimeric structure in the solid state *via* bridging OH groups cannot be ruled out, an octahedral structure for this triaryl complex seems unlikely. Complex **9** is dimeric and **10** monomeric in chloroform solution (*M* found 1084 and 508, calc. 1010 and 458, respectively).

Infrared spectra show that the Me_2SO ligand of complex **4** is bonded through the oxygen atom [ν(SO) 930 cm^{-1}] and that the $MeCO_2$ ligand of **10** is chelating [$\nu_{asym}(CO_2)$ 1530 cm^{-1}]. Bands corresponding to ν(SnCl)[8] and ν(OH)[7] are observed in the regions 360–280 and 3500–3240 cm^{-1} (see Experimental section).

The peak with highest *m/z* of the mass spectra of complexes **1**, **2**, **5** and **10** corresponds to the molecular ion; otherwise for **4** $M^+ - OSMe_2$, for **6** and **7** $SnLCl_2(OH)_2^+$, for **9** $Sn(mpap)Br_2^+$ and for **11** $M^+ - OH$.

Crystal Structures of Complexes **6** *and* **7**.—Initially, single crystals of complex **7** were studied. The structure was established as a doubly bridged dimer with crystallographic two-fold symmetry (Fig. 1), but problems with the refinement (see Experimental section) rendered the structure unsatisfactory; the H atoms were not located and estimated standard deviations (e.s.d.s) were high. Furthermore, a region of electron density identified as a diethyl ether molecule (giving a ratio Sn:ether = 1:1) could not be successfully refined. We prefer not to discuss quantitative aspects of this structure.

The structure of complex **6** presented no such difficulties. It too consists of dimers with two bridging OH groups (see Fig. 2) leading to a distorted octahedral co-ordination for both tin atoms. Diethyl ether of solvation is also observed (Sn:ether = 4:5). The Sn_2OH bridges are asymmetric, with Sn–O bonds *trans* to the chloro ligands longer [2.193(3), 2.188(3) Å] than those *trans* to the phenyl groups [2.027(3), 2.015(3) Å]. In octahedral complexes containing the $Sn(\mu\text{-}OH)_2Sn$ moiety the bridge is symmetric if the other ligands in the Sn_2O_2 plane are identical or similar.[14] These Sn–O bond lengths lie in the range 2.09–2.04 Å when chloro ligands are *trans* to the OH groups. However, where the ligands are different, as in **6**, the bridge is asymmetric. Thus, in $[\{SnRCl_2(H_2O)(\mu\text{-}OH)\}_2]$ (R = Et[4] or

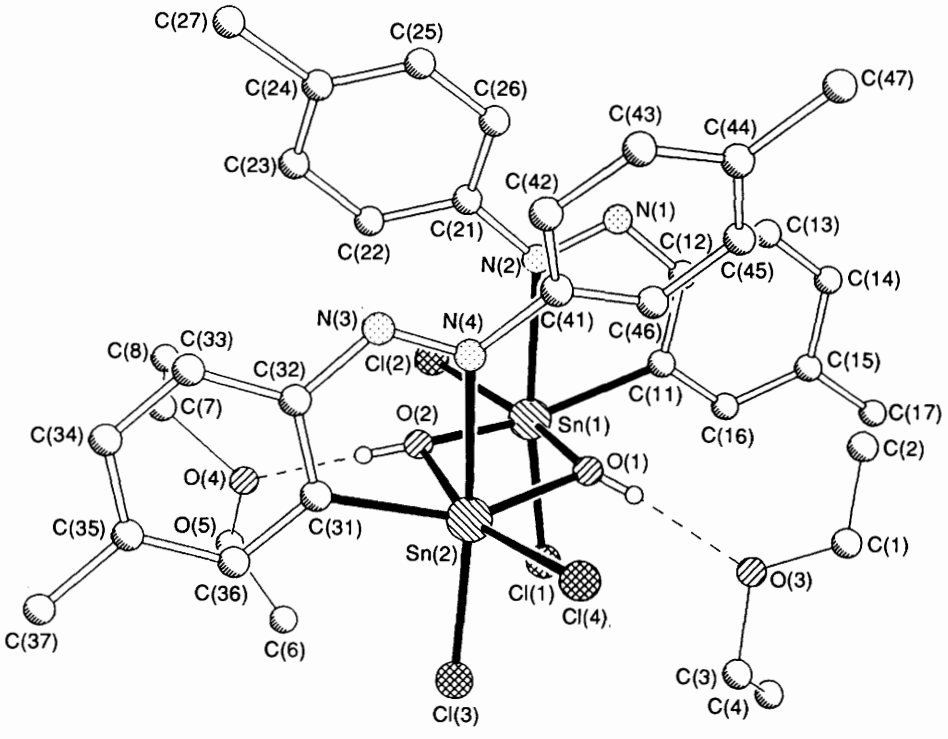


Fig. 2 The structure of compound **6** in the crystal. Radii are arbitrary; H bonds are indicated as dashed lines. The disordered solvent and the H atoms other than hydroxyl H are omitted for clarity. Symmetry operators of the ether molecules (referred to the coordinates of Table 1) are: $x, \frac{1}{2} - y, \frac{1}{2} + z$ for the molecule at O(1), $x, 1\frac{1}{2} - y, \frac{1}{2} + z$ for the molecule at O(2)

Table 1 Atomic coordinates (× 10^4) for compound **6**

Atom	x	y	z	Atom	x	y	z
Sn(1)	1484.5(1)	5272.1(3)	1610.0(1)	C(32)	4049(2)	4154(4)	1642(2)
Sn(2)	2894.4(1)	3662.5(3)	2300.4(1)	C(33)	4638(2)	4661(5)	1519(3)
Cl(1)	1202.5(6)	5721(1)	2629.7(6)	C(34)	5036(3)	5355(5)	1998(3)
Cl(2)	1402.2(6)	7326(1)	1233.3(6)	C(35)	4858(3)	5551(5)	2586(3)
Cl(3)	2845.1(6)	4219(1)	3380.3(6)	C(36)	4259(2)	5034(5)	2701(3)
Cl(4)	3041.8(6)	1559(1)	2570.4(6)	C(37)	5286(3)	6311(6)	3110(3)
O(1)	1895(1)	3487(3)	1924(2)	C(41)	2850(2)	2033(4)	821(2)
O(2)	2497(1)	5373(3)	1861(2)	C(42)	3213(3)	1441(5)	415(2)
N(1)	1143(2)	4098(4)	195(2)	C(43)	2905(3)	533(5)	15(3)
N(2)	1637(2)	4673(3)	520(2)	C(44)	2243(3)	201(5)	−9(3)
N(3)	3698(2)	3366(3)	1156(2)	C(45)	1897(3)	797(5)	398(3)
N(4)	3143(2)	2966(3)	1256(2)	C(46)	2196(3)	1700(5)	820(3)
C(11)	580(2)	4444(4)	1122(2)	C(47)	1928(4)	−793(6)	−461(3)
C(12)	586(2)	3972(4)	504(2)	O(3)	1088(2)	2828(4)	7485(2)
C(13)	27(2)	3370(4)	152(2)	C(1)	721(5)	3799(9)	7228(5)
C(14)	−533(2)	3239(5)	412(2)	C(2)	717(5)	4101(8)	6584(4)
C(15)	−560(2)	3686(4)	1036(2)	C(3)	1155(4)	2627(9)	8185(4)
C(16)	16(2)	4278(4)	1379(2)	C(4)	542(5)	2143(9)	8359(4)
C(17)	−1179(2)	3539(5)	1312(3)	O(4)	3173(2)	7581(4)	7236(2)
C(21)	2193(2)	4793(4)	201(2)	C(5)	3033(7)	6818(9)	7714(6)
C(22)	2639(2)	5740(5)	392(2)	C(6)	2795(5)	7288(10)	8220(5)
C(23)	3192(3)	5880(5)	97(3)	C(7)	3681(5)	7208(9)	6771(6)
C(24)	3308(3)	5059(6)	−363(3)	C(8)	3320(7)	6431(10)	6429(7)
C(25)	2858(3)	4136(5)	−550(3)	O(5)	5000	5000	5000
C(26)	2302(3)	3993(5)	−276(2)	C(9)	4952(9)	6247(16)	5199(9)
C(27)	3933(3)	5185(7)	−655(3)	C(10)	5132(11)	6947(20)	5600(12)
C(31)	3855(2)	4346(4)	2234(2)				

Table 2 Selected bond lengths (Å) and angles (°) for compound **6**

Sn(1)–Cl(1)	2.381(2)	Sn(1)–Cl(2)	2.402(2)
Sn(1)–O(1)	2.193(3)	Sn(1)–O(2)	2.015(3)
Sn(1)–N(2)	2.463(4)	Sn(1)–C(11)	2.118(4)
Sn(2)–Cl(3)	2.373(2)	Sn(2)–Cl(4)	2.401(2)
Sn(2)–O(1)	2.027(3)	Sn(2)–O(2)	2.188(3)
Sn(2)–N(4)	2.474(4)	Sn(2)–C(31)	2.120(5)
N(1)–N(2)	1.263(5)	N(1)–C(12)	1.420(7)
N(2)–C(21)	1.432(6)	N(3)–N(4)	1.267(5)
N(3)–C(32)	1.419(6)	N(4)–C(41)	1.425(6)
Cl(1)–Sn(1)–Cl(2)	94.9(1)	Cl(1)–Sn(1)–O(1)	93.7(1)
Cl(2)–Sn(1)–O(1)	161.5(1)	Cl(1)–Sn(1)–O(2)	99.9(1)
Cl(2)–Sn(1)–O(2)	91.8(1)	O(1)–Sn(1)–O(2)	70.6(1)
Cl(1)–Sn(1)–N(2)	172.7(1)	Cl(2)–Sn(1)–N(2)	87.8(1)
O(1)–Sn(1)–N(2)	85.7(1)	O(2)–Sn(1)–N(2)	86.7(1)
Cl(1)–Sn(1)–C(11)	100.5(1)	Cl(2)–Sn(1)–C(11)	104.8(1)
O(1)–Sn(1)–C(11)	89.6(1)	O(2)–Sn(1)–C(11)	152.3(2)
N(2)–Sn(1)–C(11)	72.2(2)	Cl(3)–Sn(2)–Cl(4)	93.1(1)
Cl(3)–Sn(2)–O(1)	99.4(1)	Cl(4)–Sn(2)–O(1)	93.8(1)
Cl(3)–Sn(2)–O(2)	95.5(1)	Cl(4)–Sn(2)–O(2)	163.1(1)
O(1)–Sn(2)–O(2)	70.5(1)	Cl(3)–Sn(2)–N(4)	170.2(1)
Cl(4)–Sn(2)–N(4)	82.5(1)	O(1)–Sn(2)–N(4)	89.6(1)
O(2)–Sn(2)–N(4)	91.1(1)	Cl(3)–Sn(2)–C(31)	100.9(1)
Cl(4)–Sn(2)–C(31)	106.9(1)	O(1)–Sn(2)–C(31)	150.0(2)
O(2)–Sn(2)–C(31)	85.8(1)	N(4)–Sn(2)–C(31)	72.3(2)
Sn(1)–O(1)–Sn(2)	108.6(1)	Sn(1)–O(2)–Sn(2)	109.3(1)
N(2)–N(1)–C(12)	114.7(4)	Sn(1)–N(2)–N(1)	113.7(3)
Sn(1)–N(2)–C(21)	132.3(3)	N(1)–N(2)–C(21)	113.9(4)
N(4)–N(3)–C(32)	115.2(4)	Sn(2)–N(4)–N(3)	112.8(3)
Sn(2)–N(4)–C(41)	131.4(3)	N(3)–N(4)–C(41)	114.5(4)

Bu^n [5]) the Sn–O bonds *trans* to chloro ligands [2.153, 2.169(4) Å, respectively] are longer than those *trans* to the ethyl [2.067(3) Å] or butyl [2.047(4) Å] groups. In the current structure the Sn–Cl bonds *trans* to nitrogen [2.381(2), 2.373(2) Å] are shorter than those *trans* to oxygen [2.402(2), 2.401(2) Å]. The Sn–N bond distances [2.463(4), 2.474(4) Å] are shorter than those in the octahedral complex $[Sn(mpap)_2Cl_2]$ [2.58(2), 2.51(2) Å].[12]

The narrowing of the O–Sn–O angles to *ca.* 70° in the four-membered rings may be regarded as reducing the metal–metal repulsion (Sn ··· Sn 3.429 Å); additionally, the electronegativity of the oxygen atoms decreases the repulsion of the Sn–O bonding pairs [valence shell electron pair repulsion (VSEPR) model]. The narrow C–Sn–N angles (*ca.* 72°) are probably attributable to the chelating nature of the ligand mpap. Other bond angles are correspondingly widened by 10–15° from the ideal 90°.

Two molecules of diethyl ether are involved in hydrogen bonds, each to one OH group. This type of interaction is a common feature in hydroxotin(IV) complexes.[14] The distances O(1) ··· O(3) 2.64 and O(2) ··· O(4) 2.68 Å imply strong hydrogen bonds (*cf.* O ··· O 2.59–2.79 in various hydrogen-bonded systems in ref. 14). One further molecule of diethyl ether is disordered over a centre of symmetry and is not involved in hydrogen-bonding interactions.

Experimental

The IR spectra, the C, H and N analyses, conductance measurements, melting-point determinations, and NMR spectra were recorded as described elsewhere.[15] Some spectra were recorded on a Varian Unity-300 spectrometer. The NMR spectra of **6**, **7** and **15** were measured in $(CD_3)_2CO$, those of all other complexes in $CDCl_3$, with $SiMe_4$ used as reference. The atom numbering for the ^1H and ^{13}C NMR assignments corresponds to the mpap ligand co-ordinated to Sn(1) in Fig. 2.

[Sn(mpap)Cl_3] **1**.—To a suspension of anhydrous $SnCl_2$ (500 mg, 2.64 mmol) in xylene (15 cm^3) was added [Hg(mpap)Cl] (1174.2 mg, 2.64 mmol); the suspension was refluxed for 5 h. The solvent was removed under vacuum, the residue, containing Hg, treated with dichloromethane (90 cm^3) and the resulting suspension filtered off. The filtrate was concentrated (5 cm^3) and diethyl ether (20 cm^3) added to precipitate complex **1** as a yellow solid which was recrystallized from diethyl ether. Yield 79%, m.p. 203 °C, Λ_M = 11 Ω^{-1} cm^2 mol^{-1}. Mass spectrum: *m/z* 438–432 (M^+, 1.5), 159–151 ($SnCl^+$, 10), 123–116 (Sn^+, 58), 91 ($C_7H_7^+$, 100) and 65 ($C_5H_5^+$, 19%). ν(SnCl) 355 and 325 cm^{-1}. δ(^1H) 8.18 [d, 2 H, H^{22}, $J(H^{22}H^{23})$ = 9], 8.16 [d, 1 H, H^{13}, $J(H^{13}H^{14})$ = 8], 7.92 [d, 1 H, H^{16}, $J(H^{14}H^{16})$ = 1.5 Hz], 7.64 (dd, 1 H, H^{14}), 7.35 (d, 2 H, H^{23}), 2.57 (s, 3 H, Me) and 2.46 (s, 3

H, Me); δ(^{13}C) 148.6 (C^{12}), 147.4 (C^{21}), 145.2 (C^{15}), 144.3 (C^{24}), 136.7 (C^{16}), 134.6 (C^{14}), 133.1 (C^{13}), 130.2 (C^{23}), 124.4 (C^{22}), 21.9 (Me) and 21.7 (Me) (Found: C, 39.4; H, 3.4; N, 6.5. $C_{14}H_{13}Cl_3N_2Sn$ requires C, 38.7; H, 3.0; N, 6.4%).

[Sn(mopap)Cl_3] **2**.—To a solution of anhydrous $SnCl_2$ (250 mg, 1.32 mmol) in xylene (20 cm^3) was added [Hg(mopap)Cl] (629.3 mg, 1.32 mmol); the suspension was refluxed for 5 h. The hot suspension was filtered off over $MgSO_4$ to remove Hg, the solution concentrated to 1 cm^3 and hexane (20 cm^3) added to precipitate complex **2** as a red solid, which was recrystallized from acetone–diethyl ether. Yield 67%, m.p. 171 °C, Λ_M = 0 Ω^{-1} cm^2 mol^{-1}. Mass spectrum: *m/z* 450, 448, 446 (M^+, 0.5), 161–147 ($SnCl^+$, 45), 123–116 (Sn^+, 3), 105 ($C_6H_5N_2^+$, 21.7), 92 (27), 77 (41) and 63 (21%). ν(SnCl) 360 and 310 cm^{-1}. δ(^{1}H) 8.24 [d, 2 H, H^{22}, $J(H^{22}H^{23})$ = 9], 8.14 [d, 1 H, H^{14}, $J(H^{13}H^{14})$ = 9], 7.64 [d, 1 H, H^{16}, $J(H^{14}H^{16})$ = 3 Hz], 7.26 (m, 1 H, H^{13}), 7.03 (d, 2 H, H^{23}), 4.00 (s, 3 H, OMe) and 3.92 (s, 3 H, OMe). δ(^{13}C) 165.6 (C^{15}), 163.2 (C^{24}), 144.6 (C^{12}), 141.0 (C^{21}), 134.2 (C^{13}), 126.3 (C^{22}), 121.5 (C^{16}), 118.8 (C^{14}), 114.7 (C^{23}), 56.3 (OMe) and 55.7 (OMe) (Found: C, 35.8; H, 2.8; N, 5.5. $C_{14}H_{13}Cl_3N_2O_2Sn$ requires C, 36.1; H, 2.8; N, 6.0%).

[NMe_4][Sn(mpap)Cl_4] **3**.—To a solution of complex **1** (200 mg, 0.46 mmol) in acetone (15 cm^3) was added NMe_4Cl (50.5 mg, 0.46 mmol). The resulting suspension was stirred at room temperature for 18 h and then filtered to give complex **3** as a yellow solid. Yield 80%, m.p. 293 °C, Λ_M = 141 Ω^{-1} cm^2 mol^{-1}. ν(SnCl) 310, 275 and 250 cm^{-1}. δ(^{1}H) 8.16 [d, 2 H, H^{22}, $J(H^{22}H^{23})$ = 8], 7.96 [d, 1 H, H^{13}, $J(H^{13}H^{14})$ = 8], 7.74 [d, 1 H, H^{16}, $J(H^{16}H^{14})$ = 1 Hz], 7.36 (m, 3 H, H^{14} + H^{23}), 3.41 (s, 12 H, NMe_4^+), 2.46 (s, 3 H, Me) and 2.42 (s, 3 H, Me) (Found: C, 40.7; H, 5.00; Cl, 26.1; N, 7.9. $C_{18}H_{25}Cl_4N_3Sn$ requires C, 39.8; H, 4.6; Cl, 26.1; N, 7.7%).

[Sn(mpap)Cl_3($OSMe_2$)] **4**.—When a suspension of complex **1** (100 mg, 0.23 mmol) in diethyl ether (10 cm^3) was treated with an excess of dimethyl sulfoxide and stirred at room temperature for 4 h a new suspension was obtained. After filtration complex **4** was obtained as a yellow solid. Yield 82%, m.p. 167 °C, Λ_M = 0 Ω^{-1} cm^2 mol^{-1}. Mass spectrum: *m/z* 436–432 (M^+ − dmso, 0.1), 165 ($C_{13}H_9^+$, 19), 161–147 ($SnCl^+$, 25), 123–116 (Sn^+, 61), 91 ($C_7H_7^+$, 100) and 65 ($C_5H_5^+$, 13%). ν(SnCl) 315, 305 and 280 cm^{-1}. δ(^{1}H) 8.05 (m, 3 H, H^{13} + H^{22}), 7.78 [d, 1 H, H^{16}, $J(H^{16}H^{14})$ = 1], 7.48 [dd, 1 H, H^{14}, $J(H^{13}H^{14})$ = 7], 7.32 [d, 2 H, H^{23}, $J(H^{22}H^{23})$ = 8 Hz], 2.63 (s, 6 H, Me_2SO), 2.52 (s, 3 H, Me) and 2.45 (s, 3 H, Me). δ(^{13}C) 147.7 (C^{12}), 147.1 (C^{21}), 146.4 (C^{15}), 143.0 (C^{24}), 133.4 (C^{16}), 132.9 (C^{14}), 132.6 (C^{13}), 129.8 (C^{23}), 124.2 (C^{22}), 38.6 (Me_2SO), 22.1 (Me) and 21.7 (Me) (Found: C, 37.9; H, 4.00; N, 5.5. $C_{16}H_{19}Cl_3N_3OSSn$ requires C, 37.5; H, 3.7; N, 5.5%).

[Sn(mpap)(dmap)Cl_2] **5**.—To a dichloromethane (6 cm^3) solution of complex **1** (100 mg, 0.23 mmol) was added [Hg(dmap)$_2$] (108 mg, 0.23 mmol). The solution was stirred at room temperature for 12 h and then evaporated to dryness. The residue was extracted with diethyl ether (15 cm^3), and filtered. The filtrate was concentrated (1 cm^3) and hexane (3 cm^3) added to precipitate complex **5** as an orange solid. Yield 20%, m.p. 176 °C, Λ_M = 2 Ω^{-1} cm^2 mol^{-1}. Mass spectrum: *m/z* 537–529 (M^+, 8), 180 ($C_{14}H_{12}^+$, 22), 165 ($C_{13}H_9^+$, 15), 132 (dmap$^+$ − H_2, 100), 91 ($C_7H_7^+$, 60) and 58 ($CH_2NMe_2^+$, 26%). ν(SnCl) 300 and 280 cm^{-1}. δ(^{1}H) 8.35 (dd, 1 H, H^6 of dmap, *J* = 8 and 2), 8.14 [d, 1 H, H^{16}, $J(H^{16}H^{14})$ = 1.5], 8.10 [d, 1 H, H^{13}, $J(H^{13}H^{14})$ = 8], 7.60–7.18 [m, 6 H of H^{3-5} dmap + H^{14} + H^{22}], 7.01 [d, 2 H, H^{23}, $J(H^{22}H^{23})$ = 8.3], 3.93 (d, 1 H, NCH_2, *J* = 14.2 Hz), 3.33 (d, 1 H, NCH_2), 2.55, 2.32, 2.28 and 1.74 (s, 3 H, MeC_6H_4, MeC_6H_3, Me_2N). δ(^{13}C) 149.4, 147.9 (C^{12} and C^2 of dmap), 145.8 (C^{21}), 142.9 (C^{15}), 142.0 (C^{24}), 135.7, 134.9 (C^{16} and C^6 of dmap), 132.8 (C^{14}), 131.8 (C^{13}), 130.4 (C^4 of dmap), 129.5 (C^{23}), 128.8 (C^3 of dmap), 127.4 (C^5 of dmap), 122.9 (C^{22}), 45.9 and 44.6 (NMe_2), 22.0 (Me) and 21.7 (Me) (Found: C, 51.1; H, 5.4; N, 7.20. $C_{23}H_{25}Cl_2N_3Sn$ requires C, 51.8; H, 4.7; N, 7.9%).

[{Sn(mpap)Cl_2(μ-OH)}$_2$] **6**.—When a solution of complex **1** (250 mg, 0.58 mmol) in acetone (40 cm^3) was treated with [Hg(dmap)Cl] (213 mg, 0.58 mmol) a suspension was formed which was stirred at room temperature for 5 h and then filtered, separating Hg(Hdmap)Cl_2 as a white solid. The filtrate was evaporated to dryness and the residue stirred with diethyl ether (15 cm^3) to give complex **6** as an orange solid. Yield 90%, m.p. 145 °C, Λ_M = 15.7 Ω^{-1} cm^2 mol^{-1}. Mass spectrum: *m/z* 436–432 [Sn(mpap)$Cl_2(OH)_2^+$, 0.3], 161–147 ($SnCl^+$, 13), 123–116 (Sn^+, 53), 91 ($C_7H_7^+$, 100) and 65 ($C_5H_5^+$, 10%). ν(SnCl) 320, 300; ν(OH) 3460 cm^{-1}. δ(^{1}H) 8.00–7.12 (m, 7 H, Ph), 2.56 (s, 3 H, Me) and 2.44 (s, 3 H, Me) (Found: C, 40.4; H, 3.5; N, 6.4. $C_{28}H_{28}Cl_4N_4O_2Sn_2$ requires C, 40.4; H, 3.4; N, 6.7%).

[{Sn(mopap)Cl_2(μ-OH)}$_2$] **7**.—To a solution of complex **2** (300 mg, 0.64 mmol) in acetone (15 cm^3) was added [Hg(dmap)Cl] (238.2 mg, 0.64 mmol); the resulting suspension was stirred at room temperature for 1 h and then filtered to separate Hg(Hdmap)Cl_2. The filtrate was concentrated (1 cm^3) and diethyl ether (10 cm^3) added to precipitate complex **7** as a brick-red solid. Yield 85%, m.p. 125 °C, Λ_M = 0 Ω^{-1} cm^2 mol^{-1}. Mass spectrum: *m/z* 467–463 [Sn(mopap)$Cl_2(OH)_2^+$, 0.1], 433–432 [Sn(mopap)Cl_2^+, 0.1), 242 ($C_{14}H_{13}O_2^+$, 5), 186–180 ($SnCl_2^+$, 21), 156–149 ($SnCl^+$, 7), 123–116 (Sn^+, 12), 107 ($C_7H_7O^+$, 18.5), 91 ($C_7H_7^+$, 100), 77 ($C_6H_5^+$, 21), 65 ($C_5H_5^+$, 11) and 51 ($C_4H_3^+$, 15%). ν(SnCl) 320, 300; ν(OH) 3240 cm^{-1}. δ(^{1}H) 8.03 [d, 1 H, H^{13}, $J(H^{13}H^{14})$ = 8.7], 7.84 (m, 2 H, H^{22}), 7.49 [d, 1 H, H^{16}, $J(H^{16}H^{14})$ = 2.4 Hz], 7.33 (m, 1 H, H^{14}), 6.75 (m, 2 H, H^{23}), 4.02 (s, 3 H, OMe) and 3.94 (s, 3 H, OMe). δ(^{13}C) 166.3 (C^{15}), 163.3 (C^{24}), 134.7 (C^{13}), 127.5 (C^{23}), 114.4 (C^{22}), 56.6 (OMe) and 56.2 (OMe) (Found: C, 37.8; H, 3.3; N, 5.6. $C_{28}H_{28}Cl_4N_4O_6Sn_2$ requires C, 37.5; H, 3.2; N, 6.2%).

[Hbdma][Sn(mpap)Cl_3(OH)] **8**.—To a solution of complex **1** (300 mg, 0.69 mmol) in diethyl ether (30 cm^3) was added liquid $PhCH_2NMe_2$ (89.5 mg, 0.66 mmol); the resulting suspension was stirred at room temperature for 5 min and then filtered to give complex **8** as a yellow solid. Yield 69%, m.p. 131 °C, Λ_M = 93 Ω^{-1} cm^2 mol^{-1}. ν(SnCl) 330, 310, 280; ν(OH) 3500 cm^{-1}. δ(^{1}H) (concentrated solution) 9.39 (br s, 1 H, NH), 8.09 [m, 3 H, H^{22} + H^{13}], 7.82 [d, 1 H, H^{16} $J(H^{16}H^{14})$ = 1], 7.50–6.93 [m, 8 H, Hbdma + H^{14} + H^{23}], 4.26 (s, 1 H, CH_2), 4.24 (s, 1 H, CH_2), 2.84 (s, 3 H, Me of Hbdma), 2.82 (s, 3 H, Me of Hbdma), 2.50 (s, 3 H, Me) and 2.44 (s, 3 H, Me); (dilute solution) 10.0 (br s, 1 H, NH), 8.11 (m, 3 H, H^{22} + H^{13}), 7.84 [d, 1 H, H^{16}, $J(H^{16}H^{14})$ = 1], 7.50–7.36 [m, 6 H, Hbdma + H^{14}], 7.32 [d, 2 H, H^{23}, $J(H^{22}H^{23})$ = 8 Hz], 4.23 (s, 2 H, CH_2), 2.81 (s, 6 H, Me_2), 2.51 (s, 3 H, Me) and 2.44 (s, 3 H, Me). δ(^{13}C) 147.4 (C^{12} + C^{21}), 142.4 (C^{24} + C^{15}), 132.9 (C^{16}), 132.1 and 132.0 (C^{14} + C^{13}), 131.2 and 130.3 (*o*-, *p*-C of Hbdma), 129.5 (C^{23}), 129.3 (*m*-C of Hbdma), 124.3 (C^{22}), 61.6 (CH_2), 42.9 (2 Me of Hbdma), 22.0 (Me) and 21.5 (Me) (Found: C, 46.9; H, 4.8; Cl, 20.3; N, 7.0. $C_{23}H_{28}Cl_3N_3OSn$ requires C, 47.0: H, 4.8; Cl, 18.1; N, 7.2%).

[{Sn(mpap)Br_2(μ-OH)}$_2$] **9**.—To a suspension of complex **6** (200 mg, 0.22 mmol) in acetone (10 cm^3) was added NaBr (125 mg, 1.21 mmol); the resulting suspension was stirred for 72 h and then filtered. The solution was evaporated to dryness and the residue washed with diethyl ether (5 cm^3) and filtered off to give complex **9** as an orange solid. Yield 77%, m.p. 169 °C, Λ_M = 5 Ω^{-1} cm^2 mol^{-1}, *M* found (calc.) 1084 (1010). Mass spectrum: *m/z* 490–485 [Sn(mpap)Br_2^+, 31], 205–191 ($SnBr^+$, 21), 165 ($C_{13}H_9^+$, 19), 122–116 (Sn^+, 16), 91 ($C_7H_7^+$, 100) and 65 ($C_5H_5^+$, 18%). ν(OH) 3410 cm^{-1}. δ(^{1}H) 8.22–7.25 (m, 7 H, Ph), 2.57 (s, 3 H, Me) and 2.46 (s, 3 H, Me) (Found: C, 32.9; H, 2.8; N, 5.4. $C_{28}H_{28}Br_4N_4O_2Sn_2$ requires C, 33.3; H, 2.8; N, 5.6%).

Table 3 Atomic coordinates ($\times 10^4$) for c ıpound **7**

Atom	*x*	*y*	*z*
Sn	4392	1634	3572
Cl(1)	4332	632	3654
Cl(2)	2786	1752	3814
N(1)	4482	2640	3778
N(2)	4846	2789	4566
O(1)	6086	1142	7072
O(2)	2936	4407	1678
O(3)	4258	1687	2088
C(1)	5045	1799	4936
C(2)	5213	2350	5167
C(3)	5642	2497	6060
C(4)	5888	2066	6685
C(5)	5752	1522	6449
C(6)	5344	1391	5607
C(7)	6059	567	6815
C(8)	4128	3119	3208
C(9)	4258	3673	3496
C(10)	3859	4121	2934
C(11)	3319	3987	2146
C(12)	3194	3395	1866
C(13)	3611	2988	2386
C(14)	2339	4322	835

[Sn(mpap)$Cl_2(O_2CMe)$] **10**.—To a suspension of complex **6** (100 mg, 0.11 mmol) in dichloromethane (20 cm^3) was added $(MeCO)_2O$ (62 mg, 0.61 mmol); the suspension was stirred for 5 h and then filtered. The solution was evaporated under vacuum (1 cm^3) and hexane added to precipitate complex **10** as a yellow solid. Yield 68%, m.p. 105 °C, $\Lambda_M = 2\ \Omega^{-1}\ cm^2\ mol^{-1}$, *M* found (calc.) 508 (458). Mass spectrum: *m*/*z* 460–456 (M^+, 0.4), 183–175 [$Sn(O_2CMe)^+$, 4], 161–147 ($SnCl^+$, 14), 123–116 (Sn^+, 46), 91 ($C_7H_7^+$, 100) and 65 ($C_5H_5^+$, 51%). ν(SnCl) 320 and 310 cm^{-1}. δ(^{1}H) 8.12 (m, 3 H, H^{13} + H^{22}), 7.83 (s, 1 H, H^{16}), 7.57 [d, 1 H, H^{14}, $J(H^{13}H^{14})$ = 8], 7.37 [d, 2 H, H^{23}, $J(H^{22}H^{23})$ = 8 Hz], 2.57 (s, 3 H, Me), 2.49 (s, 3 H, Me) and 1.98 (s, 3 H, $MeCO_2$). δ(^{13}C) 147.9 (C^{12} + C^{21}), 145.7 (C^{15}), 143.9 (C^{24}), 134.6 (C^{16}), 133.4 (C^{14}), 132.6 (C^{13}), 130.2 (C^{23}), 124.3 (C^{22}), 22.1 (Me), 21.7 (Me) and 18.0 ($MeCO_2$) (Found: C, 41.3; H, 3.6; N, 6.0. $C_{16}H_{16}Cl_2N_2O_2Sn$ requires C, 42.0; H, 3.5; N, 6.1%).

[Sn(mpap)Ph_2(OH)] **11**.—(*a*) To a solution of [Sn(mpap)Ph_2Cl][8c] (80 mg, 0.15 mmol) in dichloromethane (7 cm^3) was added Tl(acac) (47 mg, 0.15 mmol); the resulting suspension was stirred at room temperature for 4 h and filtered over Celite. The filtrate was concentrated to dryness and the residue stirred with hexane (3 cm^3) to give complex **11** as an orange solid. Yield 53%.

(*b*) To a solution of [Sn(mpap)Ph_2Cl] (80 mg, 0.15 mmol) in dichloromethane (5 cm^3) was added NaH (7.02 mg, 0.29 mmol) under a nitrogen atmosphere. The resulting suspension was stirred under nitrogen for 14 h and then filtered over $MgSO_4$. The filtrate was concentrated (1 cm^3) and hexane (5 cm^3) added to precipitate complex **11**. Yield 56%.

(*c*) To a solution of [Sn(mpap)Ph_2Cl] (100 mg, 0.19 mmol) in dichloromethane (6 cm^3) was added Ag_2O (44.8 mg, 0.19 mmol); the resulting suspension was stirred at room temperature for 38 h and then filtered. The filtrate was concentrated (1 cm^3) and hexane (3 cm^3) added to precipitate complex **11**. Yield 37%, m.p. 176 °C, $\Lambda_M = 0\ \Omega^{-1}\ cm^2\ mol^{-1}$, *M* found (calc.) 501 (499). Mass spectrum: *m*/*z* 483 (M^+ − OH, 0.6), 165 ($C_{13}H_9^+$, 31), 152 ($C_{12}H_8^+$, 36), 122–116 (Sn^+, 9), 91 ($C_7H_7^+$, 100), 77 ($C_6H_5^+$, 15), 65 ($C_5H_5^+$, 68) and 51 ($C_4H_3^+$, 31%). ν(OH) 3360 cm^{-1}. δ(^{1}H) 8.14 [d, 1 H, H^{13}, $J(H^{13}H^{14})$ = 8], 8.00 [d, 1 H, H^{16}, $J(H^{14}H^{16})$ = 2], 7.46 (m, 7 H, H^{22} + H^{14} + *o*-H of Ph), 7.3 (m, 6 H, *m*- and *p*-H of Ph), 7.02 [d, 2 H, H^{23}, $J(H^{22}H^{23})$ = 8 Hz], 2.47 (s, 3 H, Me) and 2.27 (s, 3 H, Me). δ(^{13}C) 153.7 (C^{12}), 144.1 (C^{21}), 143.9 (C^{15}), 142.3 (C^{24}), 138.8 (C^{16}), 136.0 (*o*-C of Ph), 132.6 (C^{14}), 131.6 (C^{13}), 129.6 and 129.2 (C^{23} + *p*-C of Ph), 128.6 (*m*-C of Ph), 122.9 (C^{22}), 21.6 (Me) and 21.3 (Me) (Found: C, 62.9; H, 4.6; N, 5.8. $C_{26}H_{24}N_2OSn$ requires C, 62.6; H, 4.8; N, 5.6%).

X-Ray Structure Determination of Compound **6** *(Diethyl Ether Solvate).—Crystal data.* $C_{28}H_{28}Cl_4N_4O_2Sn_2 \cdot 2.5C_4H_{10}O$, *M* = 1017.0, monoclinic, space group $P2_1/c$, *a* = 20.278(7), *b* = 11.073(4), *c* = 21.016(7) Å, β = 101.82(3)°, *U* = 4619(3) $Å^3$, *Z* = 4, D_c = 1.46 Mg m^{-3}, λ(Mo-Kα) = 0.710 69 Å, μ = 1.36 mm^{-1}, *F*(000) = 2052, *T* = −95 °C.

Data collection and reduction. A yellow prism *ca.* 0.6 × 0.35 × 0.3 mm was mounted in inert oil on a glass fibre and transferred to the cold gas stream of the diffractometer (Siemens R3 with LT-2 low-temperature attachment). A total of 9372 reflections were measured to $2\theta_{max}$ 50°, of which 8119 were unique (R_{int} 0.025) and 6588 considered observed [$F > 4\sigma(F)$]. An absorption correction based on ψ scans was applied, with transmission factors 0.61–0.89. Cell constants were refined from diffractometer angles of 50 reflections in the 2θ range 20–22°.

Structure solution and refinement. The structure was solved by direct methods (to locate the tin atoms) and subsequent tangent recycling. Two ordered molecules of diethyl ether, hydrogen bonded to the complex, were located, and another molecule was found to be disordered over a symmetry centre. Hydrogen atoms were included in the refinement using a riding model, except for the disordered solvent H (not included) and the hydroxyl H, which were refined subject to the O–H bond length restraint 0.85 ± 0.02 Å. Anisotropic refinement on *F* led to a final *R* value of 0.039, *R'* 0.048. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.000\ 35\ F^2$. 466 Parameters; *S* 1.7; maximum Δ/σ 0.1; maximum Δρ 1.5 e $Å^{-3}$. The crystallographic program system Siemens SHELXTL PLUS was used. Final atom coordinates are given in Table 1, selected bond lengths and angles in Table 2.

X-Ray Structure Determination of Compound **7** *(Diethyl Ether Solvate).*—Compound **7** crystallizes in the orthorhombic space group $C222_1$ with *a* = 14.644(5), *b* = 23.840(7), *c* = 13.640(7) Å (at −95 °C), *Z* = 4. Data were collected as above. The structure was refined to *R* 0.09. A region of unidentified electron density was tentatively identified as an ether molecule, but two large difference peaks were impossibly close to ring carbon atoms. Attempts to refine the structure in a transformed cell of lower symmetry, $P2_1$ with *a* = *c*, were similarly unsuccessful (such structures can falsely simulate space group $C222_1$[16]). It is probable that the crystal was twinned. In view of these difficulties the bond lengths and angles must be unreliable, and we do not present them. The atom coordinates are given, without e.s.d.s, in Table 3.

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