Tris(trimethylsilyl)methyltin Oxinates and their Conversion into Bis(trimethylsilyl)methyltin Oxinates

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8-Hydroxyquinoline reacts in ethanol with organotin halides $SnRX_3$, $SnR'RX_2$, SnR'_2RX [where R' = Me or Ph; R = $(Me_3Si)_3C$; X = halide] to yield oxinate complexes $[SnR(ox)_3]$, $[Sn(OEt)R(ox)_2]$, $[SnR'R(ox)_2]$, and $[SnR'_2R(ox)]$. The $[SnR'R(ox)_2]$ complexes exist in two *cis* isomeric forms. When the di- or tri-oxinates are heated in ethanol nucleophilic cleavage of one trimethylsilyl group occurs yielding the bis(trimethylsilyl)methyl compounds, $[Sn(OEt)\{CH(SiMe_3)_2\}(ox)_2]$ and $[SnR'\{CH(SiMe_3)_2\}(ox)_2]$. The methyl complex has the structure *cis*-$[SnMe\{CH(SiMe_3)_2\}(ox)_2]$ with nitrogen *trans* to both Sn–C bonds. Hydrobromic acid readily converts these oxinates into the corresponding bromides.

MONO-, di-, and tri-organotin compounds form complexes with 8-hydroxyquinoline having the compositions $[SnR(ox)_3]$,[1,2] $[SnRX(ox)_2]$,[2] $[SnR_2X(ox)]$,[3] $[SnR_2(ox)_2]$,[4-8] and $[SnR_3(ox)]$,[8] where R = an alkyl or aryl group, X = an anionic ligand, and ox = $C_9H_6NO^-$. Mössbauer parameters for $[SnBu(ox)_3]$ suggest a seven-co-ordinate bipyramidal structure[1] whilst for $[SnClMe_2(ox)]$ a trigonal-bipyramidal structure has been proposed.[3] Absorption near 380—400 nm is evidently definitive of chelate formation, and this band is absent from the spectrum of $[SnPh_3(ox)]$.[8] Many compounds of the type $[SnR_2(ox)_2]$ have been reported: the crystal structure of $[SnMe_2(ox)_2]$ has established the *cis*-$SnMe_2$ configuration with nitrogen *trans* to each methyl group in a highly distorted octahedral complex[4] in which $^2J(SnCH_3)$ is *ca.* 70 Hz. By contrast in various related β-diketonato-complexes, believed on the basis of their vibrational spectra to have *trans*-$SnMe_2$ groups, typical values of $^2J(SnCH_3)$ are ≈95 Hz. An unsuccessful attempt to resolve $[SnPh_2(ox)_2]$ into optically active forms by absorption on D-lactose has been reported.[9]

In this paper we report on the formation and properties of various organotin oxinate complexes (Table 1), each containing the ligand R = $(Me_3Si)_3C$ bonded to tin. Earlier work with this ligand had demonstrated the low reactivity of Sn–R compounds towards both electrophiles and nucleophiles, due to the large steric effect of the tris(trimethylsilyl)methyl group,[10,11] and in no case has fragmentation of the R group been observed. It was therefore of interest to see if the reactivity of the R group was influenced in six-co-ordinate complexes, and to examine the stereochemistry of these compounds.

The reactions of $[SnBr_2MeR]$ and $[SnBr_2PhR]$ with 8-hydroxyquinoline under conditions previously described[5] gave yellow crystalline complexes analysing as $[SnMeR(ox)_2]$ and $[SnPhR(ox)_2]$. If the chelating ligands are non-labile in solution then six isomers are possible for these octahedral complexes: two with *trans* alkyl/aryl groups and four in which the alkyl/aryl groups are *cis*, each form being disymmetric.

Although in the crystalline state the methyltin compound $[SnMeR(ox)_2]$ might be a single isomer two forms

TABLE 1

Hydrogen-1 n.m.r. data for the complexes

Complex	θ_c/°C	Solvent	δ($SiMe_3$)	δ(SnMe)	δ(SnCH)	^2J(SnMe)	^2J(SnCH)	Isomer (%)
cis-$[SnMe_2(ox)_2]$	35	$CDCl_3$		0.44		67.0, 70.0		
$[SnClMe_2(ox)]$	35	$CDCl_3$		1.06		74.6, 78.2		
$[SnMeR(ox)_2]$ (2 isomers)	35	$CDCl_3$	0.21	0.72		69.4, 74.6		63
	35	$CDCl_3$	0.35	0.77		67.8, 71.2		37
$[SnMeR(ox)_2]$ (2 isomers)	35	C_6D_6	0.50	0.94		72.5, 76.4		85
	35	C_6D_6	0.54	0.79		*a*		15
$[SnMeR(ox)_2]$ (2 isomers)	50	C_6D_6	0.49	0.95		72.5, 76.4		82
			0.52	0.81		*a*		18
$[SnMeR(ox)_2]$ (2 isomers)	100	C_6D_6	0.48	0.98		72.5, 76.4		81
			0.51	0.74		*a*		19
$[SnMe_2R(ox)]$	35	$CDCl_3$	0.31	0.71		55.6, 58.4		
$[SnMe\{CH(SiMe_3)_2\}(ox)_2]$	35	$CDCl_3$	0.11	0.48	−0.35	67.5, 70.4	126.0, 131.5	
$[SnMe\{CH(SiMe_3)_2\}(ox)_2]$	35	$(CD_3)_2CO$	0.13	0.44	−0.26	68.1, 71.6	124.6, 130.5	
$[SnMe\{CH(SiMe_3)_2\}(ox)_2]$	35	C_6D_6	0.26	0.63	−0.22	67.5, 70.5	124.6, 129.4	
$[SnPhR(ox)_2]$ (2 isomers)	35	$CDCl_3$	0.16					35
			0.33					65
$[SnPh\{CH(SiMe_3)_2\}(ox)_2]$	35	$CDCl_3$	0.03		−0.25		*a*	
$[SnPh_2R(ox)]$	35	$CDCl_3$	0.24					
$[Sn(OH)R(ox)_2]$	35	$CDCl_3$	0.25					
$[Sn(OEt)R(ox)_2]$ [b]	35	$CDCl_3$	0.25					
$[SnR(ox)_3]$	35	C_6D_6	0.69					
$[Sn(OEt)\{CH(SiMe_3)_2\}(ox)_2]$ [c]	35	$CDCl_3$	0.13		−0.16		*a*	
$[SnBr_2Me\{CH(SiMe_3)_2\}]$	35	$CDCl_3$	0.26	1.36	0.70	59.0, 61.6	*a*	
$[SnBr_3\{CH(SiMe_3)_2\}]$	35	$CDCl_3$	0.34		1.45		148.4, 155.8	

[a] Not observed. [b] δ(CH_3) 1.22, δ(CH_2) 3.69 p.p.m. [c] δ(CH_3) 0.93, δ(CH_2) 3.39 p.p.m.

were present in $CDCl_3$ and C_6D_6 solution (Table 1) whilst the ^1H n.m.r. signals observed in C_2D_5OD suggest the presence of three isomers. Proton–tin coupling constants, $^2J(SnCH_3)$, of *ca.* 70 Hz for both isomers are somewhat larger than values for four-co-ordinate tin compounds of the type $[SnMeRX_2]$ (where X is an electronegative anionic ligand), but close to the value for *cis*-$[SnMe_2(ox)_2]$.[7] The isomer ratio changed with solvent (and with time in $CDCl_3$), but was essentially independent of temperature in C_6D_6 solution. Interconversion of the isomers was slow: for example crystallisation from cyclohexane gave a solid with a 1 : 3 isomer ratio [$\delta(SiMe_3) = 0.21$ and 0.35 p.p.m. respectively] whilst the mother-liquors yielded material with a 9 : 1 ratio, both measured in $CDCl_3$ solution. Slow vacuum sublimation of the mixture at 160—170 °C concentrated the isomer with $\delta(SiMe_3) = 0.21$ p.p.m. in $CDCl_3$, but this procedure did not produce a single isomer as judged by the ^1H n.m.r. spectra. The ^{13}C n.m.r. spectra (Table 2) in $CDCl_3$ and C_6D_6 confirmed the presence of two isomers. The $^1J(Sn-^{13}CH_3)$ coupling constants (*ca.* 700 Hz) were considerably larger than those reported for various $[SnMeRX_2]$ compounds and were similar to values for $[SnCl_3Me]$. The ^{119}Sn n.m.r. spectrum (74.6 MHz) (examined by Dr. T. Mitchell) showed two resonances at −262.4 (23%) and −272.9 (77%) p.p.m. from tetramethyltin in $CDCl_3$ solution *i.e.* close to values reported for $[SnEt_2(ox)_2]$. High-performance liquid chromatography (h.p.l.c.) on an ODS column using pure ethanol as the mobile phase revealed six poorly resolved components (u.v. detector at 243 nm).

TABLE 2

Carbon-13 n.m.r. data for the complexes

Complex	θ_c/°C	Solvent	$\delta(SiMe_3)$ [a]	δ(SnMe)	δ(SnCH)	$\delta(SnC_{quat.})$	$^1J(Sn-CH_3)$	^1J(Sn–CH)	Isomer (%)
$[SnMeR(ox)_2]$ (2 isomers)	35	$CDCl_3$	6.78	18.2		17.6	676, 709		90
			5.48	15.2		*b*	*b*		10
$[SnMeR(ox)_2]$ (2 isomers)	35	C_6D_6	7.0	18.3		17.2	683, 717		90
			5.5	16.2		*b*	*b*		10
$[SnMe\{CH(SiMe_3)_2\}(ox)_2]$	35	$CDCl_3$	3.7	11.0	16.1		629, 659	303, 318	
$[SnMe\{CH(SiMe_3)_2\}(ox)_2]$	80	C_2D_5OD	2.4	9.8			*b*	*b*	
$[SnMe_2R(ox)]$	35	$CDCl_3$	5.45	7.6		22.3	432, 452		
$[SnPh_2R(ox)]$	35	$CDCl_3$	6.08						
$[Sn(OEt)R(ox)_2]$ [c]	35	$CDCl_3$	6.58						

[a] $^1J(^{13}C-^{29}Si)$ 20.7 Hz. [b] Not observed. [c] $\delta(CH_2)$ 59.07, $\delta(CH_3)$ 19.8 Hz.

The analogous phenyl compound $[SnPhR(ox)_2]$, a yellow crystalline solid, was also a mixture of two isomers since its ^1H n.m.r. spectrum contained two $SiMe_3$ resonances at 0.16 and 0.33 p.p.m. in $CDCl_3$, with the correct ratio of aromatic to aliphatic protons. The two isomers differed in their solubility in ethanol, but complete separation was not achieved. H.p.l.c. examination in pure ethanol gave one main component (>90%) and two minor peaks (u.v. detector at 253 nm).

When the mixed isomers of $[SnMeR(ox)_2]$ were heated in ethanol in an attempt to separate pure components it was found that the intensity of all the original ^1H resonances gradually diminished [the isomer with $\delta(SiMe_3) = 0.21$ p.p.m. in $CDCl_3$ more rapidly than that with $\delta(SiMe_3) = 0.35$ p.p.m.]. After 24 h under reflux they were completely replaced by signals due to a new single compound (resonances at −0.35, 0.11, and 0.48 p.p.m. in $CDCl_3$) which was isolated as a crystalline yellow solid. On the basis of its elemental analysis, ^1H and ^{13}C n.m.r. spectra, and mass spectrum (Table 3) this material must have the structure $[SnMe\{CH(SiMe_3)_2\}(ox)_2]$, the most definitive single piece of evidence being the ^{13}C n.m.r. spectrum which showed a singlet $SiMe_3$ carbon, and singlet SnMe and SnCH carbon atoms each with tin satellites. In the off-resonance spectrum the SnCH resonance became a doublet whilst both the SnMe and $SiMe_3$ resonances appeared as quartets. In the proton spectrum $^2J(SnCH_3)$ was *ca.* 70 Hz, suggesting the grouping *cis*-$SnMe\{CH(SiMe_3)_2\}$. The chemical shift of the SnCH proton was to high field of $SiMe_4$ in contrast to the value for $Sn\{CH(SiMe_3)_2\}_2$ of 1.90 p.p.m.[12] but similar to that for tin(IV) compounds such as $[SnClH\{CH(SiMe_3)_2\}_2]$.[13] The coupling constant ^2J(Sn-CH) in $[SnMe\{CH(SiMe_3)_2\}(ox)_2]$ was remarkably high at *ca.* 130 Hz, almost twice the value of $^2J(SnCH_3)$. By contrast the ^{13}C coupling constants showed the reverse relationship. Unlike the tris(trimethylsilyl)methyl compound from which it was formed this complex gave no evidence of isomers by n.m.r., but by h.p.l.c. in ethanol two components were present in 1 : 4 ratio. Mössbauer parameters ($\delta = 0.91$ and $\Delta = 1.56$, relative to $SnO_2 = 0$) are close to values reported for $[SnMe_2(ox)_2]$. The crystal structure of this complex (P. G. Harrison and T. J. King, University of Nottingham) shows that the carbon–tin bonds are mutually *cis* with nitrogen as the *trans* ligand in each case. This is the same geometry as was found for $[SnMe_2(ox)_2]$; substitution of the bulky $(Me_3Si)_2CH$ group for methyl has very little effect on the distortions from octahedral geometry.

The corresponding phenyl compound $[SnPhR(ox)_2]$ behaved in a completely analogous way when refluxed in ethanol; both $SiMe_3$ resonances for the two isomers were replaced by one very close to $SiMe_4$, together with a higher field SnCH proton having tin satellites, again with a large coupling constant. This evidence, together with elemental analyses and the mass spectrum, confirms the identity of the product as $[SnPh\{CH(SiMe_3)_2\}(ox)_2]$. The ^1H n.m.r. spectrum gave no evidence for isomeric forms and h.p.l.c. in ethanol suggested one main (95%) and one minor component (5%).

A number of four-co-ordinate germanium and tin compounds containing an R group bonded to the metal have been subjected to quite severe chemical reactions (*e.g.* heating with Br_2, I_2, HCl, CF_3CO_2H, or Na[OH]) without either cleaving the metal–R bond or degrading the R group[10,11] yet in these six-co-ordinate oxine complexes displacement of one $SiMe_3$ group takes place under mild conditions. Elimination of Me_2SiCH_2 seemed improbable under these conditions yet direct nucleophilic attack by EtO^- on silicon also appeared unlikely since, for example, $[SnCl_3R]$ can be treated with strong base without degrading the R group. Moreover, the tris(trimethylsilyl)methyl oxine complex was unaffected by heating in benzene solution over a period of 1 month. Following Gillard's work[14] on the action of nucleophiles on pyridine-type metal complexes it seems probable that the first stage in the reaction is attack by EtO^- on the 2-position of a co-ordinated oxine with protonation at nitrogen. Such an intermediate might be stereochemically favourable for subsequent elimination of $SiMe_3(OEt)$ with protonation of the SnC carbon atom. The presence of four electronegative atoms bonded to tin will increase the nucleophilic character of the R group and hence augment the tendency for this reaction to occur. Where the R group is more strongly nucleophilic a similar type of substitution reaction has been reported (see reaction below).[15]

TABLE 3

Mass spectral data[a] (tin-containing ions)

$[SnMeR(ox)_2]$	$[SnMe\{CH(SiMe_3)_2\}(ox)_2]$	$[SnPhR(ox)_2]$	$[SnPh\{CH(SiMe_3)_2\}(ox)_2]$
654(vw) *P*	582(w) *P*	701(m) *P* — Me	629(m) *P* — Me
639(vs) *P* — Me	567(vs) *P* — Me	639(m) *P* — Ph	567(m) *P* — Ph
510(vvs) *P* — ox	438(vs) *P* — ox	572(vvs) *P* — ox	500 (vs) *P* — ox
423(m)[b] $[SnMe(ox)_2]$	423(vs)[b] $[SnMe(ox)_2]$	485(s)[b] $[SnPh(ox)_2]$	485(s)[b] $[SnPh(ox)_2]$
408(s)[b] $[Sn(ox)_2]$	408(s)[b] $[Sn(ox)_2]$	408(w) $[Sn(ox)_2]$	408(m) $[Sn(ox)_2]$
	294(s) $[SnMe\{CH(SiMe_3)_2\}]$		356(m) *P* — 2(ox)
264(vs) [Sn(ox)]	264(vs) [Sn(ox)]	264(vs) [Sn(ox)]	264(vs) [Sn(ox)]

[a] Source temperature 140—160 °C. [b] Strong 2+ ions.

$$Li[C(SiMe_3)_3] \xrightarrow{O(CH_2)_2} Li[(Me_3Si)_2C(CH_2)_2OSiMe_3]$$

Supporting evidence that reaction of the mixed isomers of $[SnMeR(ox)_2]$ with ethanol is a nucleophilic substitution was obtained by using fully deuteriated ethanol as solvent. In a sealed ^{13}C n.m.r. tube signals due to the isomers of $[SnMeR(ox)_2]$ diminished with time (80 °C, 24 h) and new signals appeared due to $SiMe_3$, SnMe, and the cleaved $SiMe_3$ group (−1.9 p.p.m. in C_2D_6O). Work-up of the mixture gave $[SnMe\{CD(SiMe_3)_2\}(ox)_2]$ in which the ^{13}CD resonance appeared as a weak 1 : 1 : 1 triplet after 30 000 scans with a 10-s repetition time. Mass spectroscopic examination confirmed the presence of one deuterium atom in the complex, and characterised $Me_3SiOC_2D_5$, Me_3SiOD, and $(Me_3Si)_2O$ as volatile reaction products.

Both $[SnBrMe_2R]$ {or $[SnMe_2R(OOCCF_3)]$} and $[SnBrPh_2R]$ {or $[Sn(OH)Ph_2R]$} gave colourless crystalline mono-oxine complexes. The methyl complex, $[SnMe_2R(ox)]$, was a single isomer with $^1J(SnCH_3)$ *ca.* 450 Hz and $^2J(SnCH_3)$ *ca.* 55 Hz. If this complex has a trigonal-bipyramidal structure then six isomeric forms are possible, but by h.p.l.c. in 20% pentane–80% ethanol it appeared to be >95% of one component. Refluxing this mixture in ethanol for 3 days produced no change in the ^1H n.m.r. spectrum. This may imply that the R and N ligands are mutually *trans* and/or that with only two electronegative groups bonded to tin the R group is insufficiently reactive for elimination of an $SiMe_3$ group by the ethoxide ion.

A yellow oxine complex was formed from $[SnBr_3R]$ under similar conditions, but its analysis and spectroscopic properties corresponded to the six-co-ordinate ethoxide $[Sn(OEt)R(ox)_2]$. When heated with an excess of oxine the, presumed, seven-co-ordinate complex $[SnR(ox)_3]$ was isolated as a yellow crystalline solid. When $[Sn(OEt)R(ox)_2]$ was heated in ethanol it eliminated 1 mole of $SiMe_3(OEt)$ yielding $[Sn(OEt)\{CH(SiMe_3)_2\}(ox)_2]$ which was contaminated with the corresponding hydroxide $[Sn(OH)\{CH(SiMe_3)_2\}(ox)_2]$.

The mono-oxine complexes $[SnMe_2R(ox)]$ and $[SnPh_2R(ox)]$ were both very readily hydrolysed whereas all of the bis complexes {$[SnMeR(ox)_2]$, $[SnMe\{CH(SiMe_3)_2\}(ox)_2]$, and the phenyl analogues} were stable to water. The trioxine, $[SnR(ox)_3]$, was also extremely sensitive to the hydrolysis or alcoholysis of one oxine group. Conversion of all the oxinates into the corresponding bromides was readily accomplished by shaking for 3 days with 50% aqueous hydrogen bromide in dioxan solution.

EXPERIMENTAL

$[SnMeR(ox)_2]$.—8-Hydroxyquinoline (0.7 g) was added to $[SnBr_2MeR]$ (1.0 g) in ethanol (150 cm^3) and diethyl ether (50 cm^3). Removal of ether from the yellow solution followed by addition of $Na[O_2CMe]$ (0.1 g) and ammonia (1 cm^3) gave, after stirring overnight and crystallising from ethanol, the *complex* $[SnMeR(ox)_2]\cdot 4H_2O$ (Found: C, 48.3; H, 6.8; N, 4.2. $C_{29}H_{50}N_2O_6Si_3Sn$ requires C, 48.0; H, 6.9; N, 3.9%). The *anhydrous* complex was obtained after 1 day *in vacuo* over P_2O_5 (Found: C, 53.2; H, 6.5; N, 4.3. $C_{29}H_{42}N_2O_2Si_3Sn$ requires C, 53.3; H, 6.5; N, 4.3%). Its ^1H n.m.r. spectrum in $CDCl_3$ showed the presence of two isomers, ratio 1 : 1.73 [$\delta(Me_3Si)$ = 0.21 and 0.35 p.p.m. respectively] with the correct ratio of aromatic to aliphatic protons. In C_2D_5OD the aliphatic proton signals suggested the presence of three isomers: δ(R/Me) at 0.26, 0.81; 0.29, 0.69; 0.35, 0.94, though SnMe couplings were obscured.

$[SnMe\{CH(SiMe_3)_2\}(ox)_2]$ *and* $[SnMe\{CD(SiMe_3)_2\}(ox)_2]$.—The mixed isomers of $[SnMeR(ox)_2]$ (1.0 g) were heated under reflux with ethanol (200 cm^3). Samples taken at intervals for ^1H n.m.r. examination showed that the isomer with $\delta(SiMe_3) = 0.21$ diminished in intensity more rapidly than the isomer with $\delta(SiMe_3) = 0.35$ p.p.m. After 24 h under reflux, conversion to $[SnMe\{CH(SiMe_3)_2\}(ox)_2]$ was complete: it separated from ethanol as large yellow crystals (0.9 g) (Found: C, 53.7; H, 5.8; N, 4.7. $C_{26}H_{34}N_2O_2Si_2Sn$ requires C, 53.9; H, 5.9; N, 4.8%).

A similar reaction using C_2D_5OD in a sealed ^{13}C n.m.r. tube gave the corresponding deuteride $[SnMe\{CD(SiMe_3)_2\}(ox)_2]$ (^{13}C n.m.r. and mass spectroscopically characterised). When the volatile components were examined mass spectroscopically the following ions were identified at high resolution: $Me_2SiOC_2D_5^+$, Me_2SiOD^+, and $Me_5Si_2O^+$.

$[SnMe_2R(ox)]$.—The compound $[SnMe_2R(OOCCF_3)]$ (1 mol) and 8-hydroxyquinoline (1.5 mol) in ethanol gave, by the procedure previously described, the *complex* as white crystals (Found: C, 47.7; H, 7.4; N, 2.5. $C_{21}H_{39}NOSi_3Sn$ requires C, 48.0; H, 7.5; N, 2.8%. Proton ratio, SiMe : SnMe : ox, 4.8 : 1.0 : 1.2 Calc. 4.5 : 1 : 1). Its mass spectrum showed the following tin-containing ions: P^+, 525(vw); $(P - Me)^+$, 510(vs); $(P - ox)^+$, 381(vs); $SnCH_2R^+$, 365(vs); $(P - R)^+$, 294(vs); $[Sn(ox)]^+$, 264(vs). This mono-oxine was unaffected by 3 days refluxing in ethanol; in moist $CDCl_3$ it partially hydrolysed to $[Sn(OH)Me_2R]$.

$[SnPhR(ox)_2]$.—The compound $[SnBr_2PhR]$ (1.0 g) was treated with 8-hydroxyquinoline (0.6 g) as described for the preparation of $[SnMeR(ox)_2]$, yielding the *complex* $[SnPhR(ox)_2]$ as a yellow solid (Found: C, 57.5; H, 6.3; N, 3.9. $C_{34}H_{44}N_2O_2Si_3Sn$ requires C, 57.0; H, 6.2; N, 3.9%). Its ^1H n.m.r. spectrum in $CDCl_3$ contained two $SiMe_3$ resonances at 0.16 and 0.33 p.p.m. (ratio 1 : 1.87), indicating the presence of two isomers. The overall proton ratio, $SiMe_3$: aromatic was 1.64 : 1 (calc. 1.59 : 1).

$[SnPh\{CH(SiMe_3)_2\}(ox)_2]$.—The mixed isomers of $[SnPhR(ox)_2]$ (1.0 g) were refluxed in ethanol (400 cm^3) for 24 h yielding the *product* (0.9 g) as a yellow crystalline solid (Found: C, 57.5; H, 5.8; N, 4.2. $C_{31}H_{36}N_2O_2Si_2Sn$ requires C, 57.9; H, 5.6; N, 4.3%). Its ^1H n.m.r. spectrum in $CDCl_3$ gave the proton ratio $SiMe_3$: SnCH as 16.9 : 1 (calc. 18 : 1) and the ratio $SiMe_3$: aromatic as 1.1 : 1 (calc. 1.1 : 1).

$[SnPh_2R(ox)]$.—8-Hydroxyquinoline (1.45 g) and $[Sn(OH)Ph_2R]$ (3.9 g) were stirred in ethanol (200 cm^3) for 2 days at 20 °C when the ethanol was replaced by $CHCl_3$ (100 cm^3) and the mixture refluxed for 2 h. Removal of solvent and vacuum sublimation of excess of oxine left the *complex* as a pale yellow solid (4.9 g), contaminated with C_9H_7NO and $[Sn(OH)Ph_2R]$ (Found: C, 57.2; H, 6.3; N, 2.0. $C_{31}H_{33}NOSi_3Sn$ requires C, 57.3; H, 5.1; N, 2.2%). Its mass spectrum contained ions due to $P -$ Me(m), $P -$ Ph(m), and $P -$ R(s).

$[Sn(OEt)R(ox)_2]$, $[Sn(OH)R(ox)_2]$, *and* $[SnR(ox)_3]$.—8-Hydroxyquinoline (4.5 g) and $[SnBr_3R]$ (5.6 g) were dissolved in diethyl ether (150 cm^3) forming a yellow solution. Ethanol (100 cm^3), sodium acetate (0.3 g), and ammonia solution (3 cm^3) were then added. Normal work-up after 1 week at 20 °C gave $[Sn(OEt)R(ox)_2]$ as a bright yellow solid (Found: C, 52.0; H, 6.5; N, 3.9. $C_{30}H_{44}N_2O_3Si_3Sn$ requires C, 52.6; H, 6.4; N, 4.1%). Its mass spectrum included ions due to $P -$ Me(w), $P -$ OEt(m), $P -$ ox(s), and $P -$ R(m). Treatment with Na[OH] (0.1 mol dm^{-3}) gave $[Sn(OH)R(ox)_2]$ as yellow crystals (Found: C, 51.2; H, 6.2; N, 4.3. $C_{28}H_{40}N_2O_3Si_3Sn$ requires C, 51.2; H, 6.1; N, 4.3%). The complex $[Sn(OEt)R(ox)_2]$ (50 mg) and 8-hydroxyquinoline (10 mg) were heated under N_2 at 100 °C overnight in a ^1H n.m.r. tube followed by vacuum sublimation of the excess of the oxine. The ^1H n.m.r. spectrum of the product in C_6D_6 showed a $SiMe_3$ resonance due to $[SnR(ox)_3]$ at 0.69 p.p.m. together with 15% of $[Sn(OH)R(ox)_2]$. The mass spectrum contained ions due to $P -$ Me(w) at 768 and $P -$ ox (vs) at 639.

$[Sn(OEt)\{CH(SiMe_3)_2\}(ox)_2]$.—The complex $[Sn(OEt)R(ox)_2]$ (0.4 g) was refluxed in ethanol for 3 days. Concentration of the solution gave the *product* contaminated with $[Sn(OH)\{CH(SiMe_3)_2\}(ox)_2]$ as a yellow solid (Found: C, 50.9; H, 5.6; N, 4.4. $C_{27}H_{36}N_2O_3Si_2Sn$ requires C, 52.9; H, 5.8; N, 4.5%). Its mass spectrum contained ions due to $P -$ Me(m) and $P -$ OEt(s).

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