The more nearly statistical distributions with chlorine and hydrogen are consistent with the decreased tendency of second-row elements to form π-bonds[12]. The comparison of bond lengths[13,14] and dipole moments[15] certainly suggests a much stronger π interaction in fluorosilanes than with chloro- or bromosilanes. The change in direction of these deviations from a random distribution on proceeding from oxygen or fluorine to chlorine, in fact, suggests a different controlling factor for the second-row ligands. Either electrostatic or steric interactions between the halogen atoms would favor the silane with dissimilar ligands.

The generality of the above considerations, which suggest that first row, π-bonding ligands should prefer the most electron deficient silicon, is being explored.

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Chelation and isomerism in organotin oxinates

A variety of studies[1-3] have provided uniformly strong support for the suggestion of Holmes and Kaesz[4] that changes in the hybridisation of the tin bonding orbitals in methyltin compounds will be reflected in variations in the tin–proton spin coupling constants. In particular, as the *s*-character of the bonding orbitals of tin increases, so do the proton–tin coupling constants and a change from 67–70 c.p.s. to *ca.* 100–110 cps seems to ordinarily accompany the presumed orbital re-organisation from sp^3 to sp. We have used this criterion to probe the geometries of some organotin oxinates (Oxine = 8-hydroxy quinoline), and comparisons of the spectra of chloroform solutions of $(CH_3)_2SnCl_2$, $(CH_3)_2SnOxCl$[5] and $(CH_3)_2SnOx_2$[6] are particularly illuminating[*]. The values of $J(^{119}Sn–CH_3)$ for the three cases are 70 cps, 77 cps and 71 cps[7] respectively. The electronic spectra[8] of $(CH_3)_2SnOx_2$ and $(CH_3)_2SnOxCl$ both exhibit an absorption maximum at *ca.* 374 mμ[5] and such behaviour appears to reliably indicate a chelating oxinate ligand[8]. On this assumption, the ligand geometry about tin would alter from tetrahedral [$(CH_3)_2SnCl_2$], through trigonal bipyramidal [$(CH_3)_2SnOxCl$] to octahedral [$(CH_3)_2SnOx_2$][**]. In other words, there is no systematic variation in $J(^{119}Sn–CH_3)$, although there appears little question that the hybridisation of the tin bonding orbitals must be different in the three cases.

These results find a rationale in the suggestion that R_2SnOx_2 complexes are not chelated, but that tin is essentially tetrahedral with a covalent Sn–O bond[7]. This would appear to be inconsistent with the UV spectral data for the closely related $(C_6H_5)_2SnOx_2$ and $(C_6H_5)_3SnOx$ systems[8]. What we consider to be strong evidence that the oxinate ligands are in fact chelating in $(CH_3)_2SnOx_2$ is now presented. We have recently shown[3] that dissolution of $(CH_3)_2SnCl_2$ (and other R_2SnCl_2 types) in DMSO is accompanied by a large increase in $J(^{119}Sn–CH_3)$, the change observed being from *ca.* 70 cps to 113 cps. The isolation of stable complexes of the type $R_2SnX_2 \cdot 2DMSO$ and $R_3SnX \cdot DMSO$[3,9] indicates DMSO to possess fair donor tendencies towards tin. If $(CH_3)_2SnOx_2$ were four-coordinate, *i.e.* non-chelating oxinate, dissolution in DMSO could reasonably be expected to change $J(^{119}Sn–CH_3)$ in the manner described for other four-coordinate $(CH_3)_2Sn^{++}$ species. In fact, there is no change. Even at 160° in DMSO, $J(^{119}Sn–CH_3)$ for $(CH_3)_2SnOx_2$ is *ca.* 71–72 cps and the complex can be crystallised unchanged (m.p. and NMR spectrum). Moreover, the electronic spectrum of a DMSO solution is essentially the same as that of a chloroform solution. In particular, the lowest energy band at 375 mμ has suffered no detectable perturbation. These observations strongly suggest that all six coordination positions are occupied in $(CH_3)_2SnOx_2$ and that DMSO has no success in rupturing this chelate network. Consequently the Sn–O and Sn–N bonds are relatively strong.

A corollary of the Holmes–Kaesz treatment is that as the equatorial bonds about tin rival the axial bonds in strength, then $J(^{119}Sn–CH_3)$ should decrease since now the 5*s* character has been largely re-distributed. The observed *J* value of 71–72 cps indicates appreciable re-distribution, since this is the value considered to indicate[4] sp^3 hybridisation (25% *s*). Clearly sp^3 hybridisation cannot provide six bonds of roughly equivalent strength and we believe extensive *d*-orbital participation is involved and hybridisation approaching d^2sp^3 may be employed[***]. ($d_{x^2-y^2}, d_{z^2}, s, p_x, p_y, p_z$). Since the *s*-character in such a scheme is *ca.* 17%, the value of $J(^{119}Sn–CH_3)$ may have been

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[*] These compounds had satisfactory elemental analyses and had melting-points, proton resonance spectra and electronic spectra essentially identical with those previously reported. The tin–proton coupling constants were not significantly concentration dependent.

[**] These geometries would be anticipated to satisfactorily represent the gross ligand dispositions, but significant distortions from these basic patterns may occur for a variety of reasons.

[***] A question of some importance relates to the nature of the 5*s* orbital as a result of the perturbing effect of nitrogen co-ordination. Expansion of the 5*s* orbital, with a reduction in $\psi_{5s}(o)$ merits consideration. Such effects would be accommodated by a change in the radial dependence of the wave function.

lower. However, it is not at all clear that the Kaesz treatment can tolerate extensive *d*-involvement, though one could anticipate *p* or *d* character to have effects in the same direction. Also the d^2sp^3 scheme may be an extreme one. The actual status of *d*-involvement in five and six coordinate complexes of the $(CH_3)_2Sn^{++}$(IV) cation is far from clear, however.

Results so far reported[1,5,6] on the stereochemistry of complexes of $(CH_3)_2Sn^{++}$ have been rationalised in terms of *trans* methyl groups. Two strong carbon–tin bonds and four relatively weak polar Sn–ligand bonds have been envisaged and held to be consistent with the observed $J(^{119}Sn\text{-}CH_3)$ values[1]. In the $(CH_3)_2SnOx_2$ case, since the clear distinction between bond types appears no longer to hold to the same extent, the $J(^{119}Sn\text{-}CH_3)$ is not inconsistent with *cis* methyl groups. However, attempts to resolve $(CH_3)_2SnOx_2$ into isomers have failed[5], and provided problems centering about isomer lability could be safely dismissed, this could be consistent with *trans* methyl groups*. Infra-red studies by Martin[5] seem to indicate *trans* methyl groups, in so far as no band assignable to an Sn–C symmetric vibration was observed. However, such a band would apparently arise in a region complicated by ligand absorptions[6]. The observation of a single sharp methyl resonance in the proton NMR spectrum could be consistent with either a *cis* or *trans* arrangement (*vide infra*).

The proton NMR spectrum of $(CH_3)_2SnOx_2$ shows a single sharp methyl resonance at 9.57 τ, *ca.* 0.60 ppm to higher field than the major signal for $(CH_3)_2SnCl_2$. $(CH_3)_2Sn(acac)_2$ and $(CH_3)_2Sn(pic)_2$ show CH_3–Sn resonance at 9.51 τ and 9.40 τ[7]. Electron withdrawing substituents in the acetylacetone ring markedly deshield the CH_3–Sn protons. Thus resonance positions of 8.91 τ and 9.07 τ are found for $(CH_3)_2Sn(hfacac)_2$ (Hhfacac = 1,1,1,5,5,5 hexafluoroacetylacetone) and $(CH_3)_2Sn(Hdbzm)_2$ (Hdbzm = 1,3 diphenyl-1,3-propanedione) respectively[7]. Since σ-transmission of inductive effects falls off rapidly with distance, it appears that the Π-networks of the chelates are in some way responsible. The fluctuations in τ values may be a reflection of the location of the methyl hydrogens (the methyl groups are presumably freely rotating) where ring current effects are operative, *i.e.* a location above the face of the aromatic or quasi-aromatic chelate rings. This may imply some tilting of the rings towards the methyl groups.

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* The failure to achieve resolution under only apparently one set of chromatographic conditions cannot be considered to adequately answer this question.