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NEW BIS- AND TETRAKIS-COMPLEXES OF TRIMETHYL- AND DIMETHYLTIN(IV) CATIONS: $Me_3SnL_2BPh_4$ AND $Me_2SnL_4(BPh_4)_2$

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SUMMARY

New examples of complexes of types $Me_2SnL_4(BPh_4)_2$ and $Me_3SnL_2BPh_4$ are reported where $L = Ph_3PO$, Ph_3AsO and $(p\text{-}CH_3C_6H_4)_3AsO$. Consideration of proton magnetic resonance data confirms that, in solution, phenyl group transfer from boron to tin occurs so that Me_2SnPh_2 and $Me_3SnC_6H_5$ may be formed, thus accounting for some puzzling features in previous spectra of complexes of these types. Some vibrational spectral data are also presented and shown to be consistent with molecular structures previously suggested.

Some time ago we reported[1] the isolation and characterisation of complexes of the types $[Me_3SnL_2]^+[BPh_4]^-$ and $[Me_2SnL_4]^{2+}[BPh_4]_2^-$ where L was a neutral oxygen donor ligand such as H_2O, DMSO, DMF or DMA. We considered these complexes important since they demonstrated that two and four neutral oxygen donors could be accommodated in the primary coordination spheres of the Me_3Sn^{IV} and Me_2Sn^{IV} cations respectively. However, some aspects of their spectral behaviour warranted further study, and we now describe similar complexes with diethyl sulfoxide, triphenylphosphine oxide, triphenylarsine oxide and tri-*p*-tolylarsine oxide as the oxygen donors, and comment further on their vibrational and particularly their proton NMR spectra.

The new complexes (other than the diethyl sulfoxide complex, which was prepared by the previously reported method) were prepared by dissolving Me_2SnCl_2 or Me_3SnCl in warm absolute alcohol containing the calculated amount of ligand and adding an alcohol solution of the appropriate amount of sodium tetraphenylborate. Generally the white crystalline complexes separated readily, but occasionally the addition of water was necessary to induce crystallisation. The analytical data for the new complexes are given in Table 1. Analyses indicated the absence of halogens in each case.

The PMR data in the $SnCH_3$ region for these new complexes are assembled in Table 2, and that for the previously reported complexes is included for comparison. We indicated previously[1] that a surprising feature of the spectra was the presence of more than one $SnCH_3$ resonance, and we attempted to account for this in terms of isomer co-existence in solution and/or ion-pair effects. With the availability of the more extensive series of complexes, we sought to probe these suggestions more fully.

TABLE 1

ANALYTICAL DATA AND DECOMPOSITION POINT OF THE NEW COMPLEXES

L	Calcd. (%)		Found (%)		Decompn. point (°C)
	C	H	C	H	
$Me_3SnL_2BPh_4$					
Ph_3PO	72.72	5.47	72.57	5.77	86–87
Ph_3AsO	67.14	5.23	67.12	5.23	112–113
$(p\text{-}CH_3C_6H_4)_3AsO$	68.41	5.86	68.29	6.01	162
Et_2SO	60.48	7.06	60.11	7.36	98
$Me_2SnL_4(BPh_4)_2$					
Ph_3PO	77.05	5.75	76.75	5.79	110–112
Ph_3AsO	70.62	5.11	70.54	5.11	172–173
$(p\text{-}CH_3C_6H_4)_3AsO$	71.7	5.8	71.05	5.90	202
Et_2SO	65.44	7.11	64.92	7.21	93–94

TABLE 2

PMR DATA OF THE NEW COMPLEXES[a]

System	Ligand	$Me_3SnL_2BPh_4$ (a)		$Me_2SnL_4(BPh_4)_2$ (b)	
		$\tau(SnCH_3)$	$J(^{119}Sn\text{–}CH_3)$	$\tau(SnCH_3)$	$J(^{119}Sn\text{–}CH_3)$
1	H_2O	9.71, 9.74	62, 56		
2	DMSO	9.50, 9.71	66, 56	9.17, 9.47	65, 57
3	DMF	9.35, 9.70	62, 56	, 9.47	56
4	DMA	9.39, 9.71	64, 56	9.06, 9.40	57
5	Ph_3PO	9.53, 9.67	68, 56	9.18, 9.40	72, 57
6	Ph_3AsO	9.67, 9.70	70, 56	9.97	112
7	$(p\text{-}CH_3C_6H_4)_3AsO$	9.68	70	9.18 (broad)	?
8	$(CH_3CH_2)_2SO$	9.33	70	9.13, 9.40[b]	68, 56

[a] CH_2Cl_2 or $CDCl_3$ media. [b] Broad immediately, after dissolution; pertains to one hour after dissolution.

Inspection of Table 2 shows that the second $SnCH_3$ resonance, when present, for both series of complexes deviates little from τ 9.70 and 9.40 ppm respectively, and also the J values remain constant at *ca.* 56–57 Hz. These uniformities seemed odd in terms of the original suggestions, since the first mentioned resonances in Table 2 exhibit considerable variation (as do the J values) and somewhat similar behaviour would be expected for isomers or closely related species. Furthermore the J values of 56–57 Hz are consistent with a tetraorganotin compound, particularly of the type Me_2SnR_2 or Me_3SnR, and we suspected that one of the $SnCH_3$ resonances was due to a common species generated when the $Me_3SnL_2BPh_4$ [and likewise for $Me_2SnL_4(BPh_4)_2$] complexes were in solution. By comparisons of PMR and VPC characteristics, it was demonstrated that the resonances at τ *ca.* 9.70 and 9.40 ppm were due to phenyltrimethylstannane and diphenyldimethylstannane respectively.

The formation of these compounds must involve phenyl group transfer from boron to tin, and we picture this as involving electrophilic attack by $Me_3SnL_2^+$ or $Me_2SnL_4^{2+}$ on BPh_4^- in close proximity. (These complexes would almost certainly exist as ion-pairs or aggregates in poorly ionising solvents such as CH_2Cl_2 or $CDCl_3$.)

$$Me_3SnL_2BPh_4 \rightarrow Me_3SnPh + Ph_3B + 2\,L$$

$$\begin{tikzcd} Me_2SnL_4(BPh_4)_2 \arrow[r] & {[Me_2PhSnL_2BPh_4] + Ph_3B + 2\,L} \arrow[dr] & \\ & (I) & Me_2SnPh_2 + 2\,L + Ph_3B \end{tikzcd}$$

The species (I), expected as an intermediate on the basis of stepwise transfer of phenyl groups, has not been isolated or characterised. The above explanation is supported by molecular weight measurements which are much lower than expected for the complexes, and conductivity measurements which indicated the almost complete lack of ionic species in absolute ethanol.

This phenyl group transfer would be retarded by reduced electrophilicity of the tin cation, and this would be dependent on the donor strength of L. Steric and other effects about tin would also be important, and this may explain the lack of phenyl group transfer in systems 6(b), 7(a) and 8(a). Thus in these cases the resonances shown are probably the genuine resonances of the complexes, but in the other cases it is not certain that the first mentioned resonances do correspond to the complexes, but the variations in τ and J values indicate the presence of ligands of different donor strengths on tin. For the $Me_3SnL_2BPh_4$ complexes, however J values of *ca.* 70 Hz [$L = Ph_3PO$, Ph_3AsO, $(p\text{-}CH_3\text{-}C_6H_4)_3AsO$] are appropriate for penta-coordinate Me_3Sn^{IV} complexes. This phenyl group transfer is related to two other reported observations*. Firstly the formation[2] of phenylmercurials from the reaction of Ph_4B^- and Hg^{II} salts almost certainly involves basically the same process, and the report by Clark[3] that Me_3SnBF_4 decomposes to yield $(CH_3)_3SnF$ is in line with our results, and indicates that alkyltin cations, when only marginally satisfied as regards coordination, are moderately electrophilic. When the above complexes were dissolved in donor solvents *e.g.* DMSO, no phenyl group transfer occurred, presumably because of cation solvation (and reduced electrophilicity) and ion dissociation. The role of organometal cations as electrophiles certainly requires study.

The infrared spectra (Nujol mulls) in the region 2000–250 cm^{-1} were examined but most interest attaches to observations in the Sn–C stretching regions. The configurations of the SnC_3 and SnC_2 moieties in these complexes are indicated as planar or linear by the presence of only $\nu_{as}(Sn\text{–}C)$ in the 500–600 cm^{-1} region. Twin stretching frequencies (symmetric and asymmetric modes) would imply considerable distortion from regular trigonal bipyramidal or octahedral structures. The IR bands most appropriate for $\nu(Sn\text{–}C)$ in the solid Me_2Sn^{IV} complexes are curiously weak and ill-resolved, but the possibility that these frequencies may be located in the 605–615 cm^{-1} range cannot be dismissed, and would find a precedent in the AsF_6^- and SbF_6^- complexes of Me_3Sn^{IV} reported by Clark[3]. A non-linear geometry for the SnC_2 linkage would activate the symmetric mode in the infrared, but this would have

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* A referee has kindly drawn our attention to another example of phenyl transfer from tetraphenylborate ion to a metallic cation[4].

$$cis\text{-}[PtCl_2(PEt_3)_2] + 2\,NaBPh_4 \xrightarrow[THF]{Reflux} trans\text{-}[Ph_2Pt(PEt_3)_2] + 2\,NaCl$$

This reaction is probably general for electrophilic metallic and organometallic ions, and could serve as a synthetic route for aryl metal systems.

been expected to arise 30–50 cm^{-1} below the asymmetric mode. However, the complexity in the 540–570 cm^{-1} could be occasioned by acute distortions in the octahedral framework, resulting from extensive cation–anion interactions, probably of a directional nature, in the solid. A similar situation appears to apply to $Me_2Pb(DMSO)_4(ClO_4)_2$, since no band in the IR spectrum of this complex could be assigned[5] with certainty to ν(Pb–C).

For the $Me_3SnL_2BPh_4$ complexes, the general observation of a single ν(Sn–C) in the 500–600 cm^{-1} region favors a bipyramidal structure with a planar SnC_3 unit. However, this result does not preclude strong cation–anion interactions, since these might reduce only the effective symmetry (T_d) of the Ph_4B^- counterion. Thus in Me_3SnClO_4, although the $(CH_3)_3Sn$ is planar on the basis of IR data, the symmetry of the perchlorate has been reduced from T_d to C_{2v}, apparently the result of quite intense cation–anion interaction[3].

Thus our previous suggestions relating to the possible existence of isomers in solution must be withdrawn, but the solid state structures probably approximate to those discussed.

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