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NOTE

PHOSPHINE, ARSINE AND AMINE OXIDE COMPLEXES OF SOME ORGANOTIN AND ORGANOLEAD HALIDES

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INTRODUCTION

Recently, we extended the organotin coordination area by actually isolating complexes of the types $[(CH_3)_2SnL_4]^{2+}$ and $[(CH_3)_3SnL_2]^+$ (where L=DMSO, DMF, DMA, and in one case H_2O)[1]. These complexes appeared to us to be important in that they confirmed suspicions that two[2] and four[3] neutral oxygen donors could be accommodated in the first coordination spheres of the trimethyltin(IV) and dimethyltin(IV) cations, respectively. In a continuation of this program, we deemed it desirable to extend our studies on organotin and -lead chemistry by studying complexes with phosphine, arsine and amine oxide ligands, thus providing several series of related complexes for comparative study.

EXPERIMENTAL

Dimethyltin dichloride was purchased from Alfa Inorganics, and trimethyltin bromide was prepared by redistribution of tetramethyltin with stannic bromide[4]. Trimethyllead chloride was provided by the International Lead Zinc Research Organization, Inc., New York.

Triphenylphosphine oxide was supplied by the Aldrich Chemical Co. and was used without further purification. Triphenylarsine oxide was prepared in high yield by the peroxide oxidation of triphenylarsine[5].

Pyridine *N*-oxide and the substituted *N*-oxides were synthesised by the procedures of Ochiai[6], and had m.p.'s, PMR and IR spectra in satisfactory agreement with published data.

The complexes were in general prepared by mixing the requisite amounts of the organometal halide and ligand in either dichloromethane or chloroform, and allowing crystallisation to occur. In the case of dimethyltin dichloride and 4-chloropyridine *N*-oxide, precipitation occurred on mixing. For the dibenzyltin dichloride complexes, methanol was employed as the solvent. None of the complexes is appreciably hygroscopic, and appear to have no serious survival problems. Complex formation was confirmed in almost all cases by elemental analysis. IR and PMR spectra (Varian A-60) (see text).

Analyses were performed by the Micro-analytical Department of the University of Melbourne and by Mr. J. Kent of the Micro-analytical laboratory of the University of Queensland.

RESULTS AND DISCUSSION

The analytical data and decomposition points of the organotin and -lead complexes with triphenylphosphine oxide, triphenylarsine oxide and pyridine *N*-oxide are assembled in Table 1. The complexes are stable, white and crystalline.

TABLE 1

ANALYTICAL DATA AND DECOMPOSITION POINTS OF ORGANOTIN AND -LEAD COMPLEXES

Complex	Calcd. (%)		Found (%)		Dec. point (°C)
	C	H	C	H	
L=Ph$_3$PO					
$Me_3SnBr \cdot L$	48.37	4.60	47.93	4.37	150–152
$Me_2SnCl_2 \cdot 2L$	58.84	4.65	58.51	4.76	135–136
$Ph_3SnCl \cdot L$	65.21	4.53	65.34	4.65	163–164
$Ph_2SnCl_2 \cdot 2L$	64.06	4.45	63.78	4.43	135–136
$(PhCH_2)_2SnCl_2 \cdot 2L$	64.73	4.75	64.31	4.73	94–95
$Me_3PbCl \cdot L$	44,57	4.25	44.63	4.29	137–138
L=Ph$_3$AsO					
$Me_3SnBr \cdot L$	44.61	4.25	44.70	4.37	156–158
$Me_2SnCl_2 \cdot 2L$	52.85	4.17	52.74	4.27	206–208
$Ph_3SnCl \cdot L$	61.16	4.24	60.87	4.29	200–202
$Ph_2SnCl_2 \cdot 2L$	58.35	4.05	57.10	4.06	183
L=PyO					
$Me_3SnBr \cdot L$	28.40	4.14	28.42	4.24	86–88
$Me_2SnCl_2 \cdot 2L$	35.20	3.91	35.53	3.94	132–133
$Ph_3SnCl \cdot L$	57.56	4.17	57.56	4.14	135–136
$Ph_2SnCl_2 \cdot 2L$	49.50	3.75	49.25	3.75	162–163
$(PhCH_2)_2SnCl_2 \cdot 2L$	51.14	4.24	51.00	4.35	104–107
$SnCl_4 \cdot 2L$	51.50	4.27	51.00	4.35	235–

The gross compositions of these complexes were confirmed by the integrated proton resonance spectra and it is apparent that the R_3MX compounds complex one and the R_2MX_2 compounds, two molecules of the oxides. The proton NMR and IR data in the P–O, As–O and N–O stretching regions are assembled in Table 2.

STRUCTURES OF THE COMPLEXES

Conductivity studies (absolute ethanol solutions) on a range of the Ph_3PO, Ph_3AsO and PyO complexes showed minor conductances when compared with tetraethylammonium bromide solutions. Consequently it seems reasonable that in CH_2Cl_2 solutions (PMR measurements) where halide displacement would be less than in ethanol, the species are molecular complexes with coordinated halides. This

TABLE 2

PMR AND IR DATA OF Ph_3PO, Ph_3AsO AND PyO COMPLEXES[a]

Complex	τ(alkyl)	J^b (Hz)	J(Lewis acid)	ν^c (cm^{-1})	$\Delta\nu^d$ (cm^{-1})
L = Ph_3PO					
$Me_3SnBr\cdot L$	9.28	66	57.5	1157	−35
$Me_2SnCl_2\cdot 2L$	8.90	88	70	1153	−39
$(PhCH_2)_2SnCl_2\cdot 2L$	2.93, 6.91	104	79	1147	−45
$Me_3PbCl\cdot L$	8.54	80	69	1167	−28
$Ph_3SnCl\cdot L$				1149, 1142	−43
$Ph_2SnCl_2\cdot 2L$				1139	−53
$SnCl_4\cdot 2L$				1125	−67
L = Ph_3AsO					
$Me_3SnBr\cdot L$	9.37	70	57.5	868	−12
$Me_2SnCl_2\cdot 2L$	8.95	100	70	880	0
$Ph_3SnCl\cdot L$				860 870	−15
$Ph_2SnCl_2\cdot 2L$				860	−20
$SnCl_4\cdot 2L$				853	−27
L = PyO					
$Me_3SnBr\cdot L$	9.31	66.5	57.5	1214	−28
$Me_2SnCl_2\cdot 2L$	9.0	93	70	1204	−38
$(PhCH_2)_2SnCl_2\cdot 2L$	2.82, 6.82	105	79	1210	−32
$Me_3PbCl\cdot L$	8.56	79	69	1220	−22
$Ph_3SnCl\cdot L$				1214	−28
$Ph_2SnCl_2\cdot 2L$				1200 1209	−38
$SnCl_4\cdot 2L$				1198	−44

[a] PMR data refer to CH_2Cl_2 (τ 4.68) solutions and IR to Nujol Mulls. [b] In the case of alkyltin complexes J refers to $J(^{119}Sn-^{1}H)$ and in the lead complexes to $J(^{207}Pb-^{1}H)$. [c] ν refers to ν(P–O), ν(As–O) or ν(N–O), whatever the case may be. [d] Δν refers to the difference between ν(complex) and ν(free ligand); ν(P–O) = 1192, ν(As–O) = 880 and ν(N–O) = 1241 cm^{-1} for the respective free ligands.

implies hexa-coordination for the R_2Sn^{IV} series and penta-coordination for the R_3Sn^{IV} and R_3Pb^{IV} series.

Some information on the actual stereochemistry of these penta- and hexa-coordinate complexes was obtained by examination of the M–C stretching frequencies. In agreement with Clark and Wilkins[7], we can locate only the Sn–C asymmetric stretching frequency at 579 cm^{-1}, suggestive of a *trans* geometry for $Me_2SnCl_2\cdot 2Ph_3PO$. The observation of bands at 574 cm^{-1} for the corresponding Ph_3AsO and PyO complexes suggest similar geometries for these complexes also. No bands confidently assignable to Sn–C symmetric stretching vibration were detected. On this basis, it seems reasonable to conclude that the present complexes of type $R_2SnX_2\cdot 2L$ (L = Ph_3PO, Ph_3AsO, PyO) also adopt such a configuration, although significant distortion of the octahedral array may occur, particularly for groups with a larger steric requirement than methyl. In the case of Me_3SnBr complexes, strong Sn–C stretching frequencies were observed at 542, 543 and 550 cm^{-1} respectively, and we tentatively conclude that such complexes adopt a trigonal bipyramidal ligand geometry, with a planar Me_3Sn moiety. Similarly considerations apply to $Me_3PbCl\cdot L$.

From Table 2 it is apparent that in essentially all of the complexes, coordination, which must be via oxygen, results in a decrease in ν(P–O), ν(As–O), ν(N–O). Such reductions seem best correlated with a decrease in the respective band orders[8,9] and Me_3PbCl appears to cause least polarisation of the P–O or N–O systems.

The observations of a single methyl or benzyl resonance indicate the complexes $R_2SnCl_2 \cdot 2L$ and $Me_3MX \cdot L$ to be isomerically homogeneous, but it cannot decide whether the R groups are *trans* or *cis*. Of most interest are the magnitudes of the coupling constants between the alkyl protons and the magnetically active metal isotopes (^{119}Sn, ^{207}Pb). In the complexes listed, a significant increase in J does occur on complexation. Such increases are usually taken to mean[10] that the metal atom now employs more *s*-character in the orbitals directed to carbon (contact interaction). The coupling constant data for $Me_2SnCl_2 \cdot 2Ph_3AsO$ and $Me_3SnBr \cdot Ph_3AsO$ are particularly illuminating, the J values of 100 and 70 Hz respectively being close to the maximum J values observed or predicted for Me_2Sn^{IV} and Me_3Sn^{IV} species[3]. Thus for the Me_2Sn^{IV} aquo system in which the Me_2Sn skeleton is linear[3], $J = 107$ Hz and for the solvated Me_3Sn^{IV} species $J = 70$ Hz. These strong agreements in coupling constants for the Ph_3AsO complexes with those for systems of known skeletal geometries, strongly suggest linear and planar geometries for the C–Sn skeletons in these complexes. Similar considerations appear to apply to the corresponding PyO complexes, although the respective J values are somewhat smaller.

Some comparisons of sulfoxide, phosphine oxide, arsine oxide and pyridine N-oxide complexes

So far in this paper, we have presented spectral data for complexes of related oxygen ligands with some alkyltin and (in some cases) methyllead systems. Previously[11,12], some data were available for DMSO complexes of alkyltin systems, and we have extended this where necessary to make the following comparisons more complete. Coupled with the previous PMR results[12] on $Me_2SnCl_2 \cdot 2DMSO$ and $(PhCH_2)_2SnCl_2 \cdot 2DMSO$ we have obtained data for $Me_3SnBr \cdot DMSO$. In addition, examination of the Sn–C stretching region for $Me_2SnCl_2 \cdot 2DMSO$ and $Me_3SnBr \cdot DMSO$ reveals strong asymmetric stretching vibrations at 574 cm^{-1}, with only very feeble and almost imperceptible bands at 509 and 512 cm^{-1} which may be the Sn–C symmetric stretching frequencies. If this latter suggestion is correct, it implies significant distortion from the regular octahedral array, which is consistent with the low $J(^{119}Sn-^{1}H)$ value (86 Hz) (*vide infra*).

These foregoing data seem nicely consistent with structure (I) and (II) respectively for the complexes $R_3MX \cdot L$ (X=Cl, Br; L=DMSO, Ph_3PO, Ph_3AsO, PyO) and $R_2SnCl_2 \cdot L_2$, and it is of some importance to inquire how the nature of L affects the spectral parameters of the complexes. Viewed most optimistically, systems (I) and (II) would allow investigation of what are formally *cis* effects, and we now demonstrate that the nature of L appears to alter properties of the *cis* ligands R, and in cases Cl, in the alkyl tin series*. We shall confine attention to the system where $R = CH_3$ and some data is set down in Table 3.

The most complete set of data is for the formally octahedral $Me_2SnCl_2 \cdot 2L$

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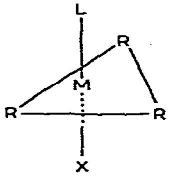
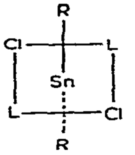
* Dr. C. H. L. Kennard and his group in this Department are currently conducting structural studies on $Me_2SnCl_2 \cdot 2DMSO$ and $Me_2SnCl_2 \cdot 2Ph_3AsO$ by X-ray diffraction techniques.

system and several interesting trends are immediately apparent. Firstly the coupling constant J appears sensitive to the nature of L in both the Me_2Sn^{IV} and Me_3Sn^{IV} series, and in the same order, *i.e.* DMSO < Ph_3PO < PyO < Ph_3AsO. The response of J would be expected to be more sensitive for the Me_2Sn^{IV} system, since a greater range in J is possible[3]. Associated with the dependence of J on L is the dependence of ν(Sn–Cl), which decreases markedly as J increases, and indicates a rather large reduction in the force constant. The J values (Table 3) for the $Me_2SnCl_2 \cdot 2L$ complexes parallel the accepted base or donor strengths of the ligands, L* and suggest increasing utilisation of the 5*s* orbital of tin in the bonds to the methyl groups, implying a shortening of these bonds, but a lengthening of the Sn–Cl bonds, which is consistent with the reduction in ν(Sn–Cl) in the series. The apparent insensitivity of ν(Sn–C) to the nature of L is somewhat surprising, although the uncertainties (± 5 cm^{-1}) may mask any trends. It is to be expected that both ν(Sn–C) and $J(^{119}Sn-^{1}H)$ will increase with increasing *s*-character of the Sn–C bond. It is gratifying to note that the J values for the $Me_3SnBr \cdot L$ complexes show the same trend, and the more limited data for the $(PhCH_2)_2SnCl_2 \cdot 2L$ complexes are not out of line.



(I)



(II)

TABLE 3

SOME NMR AND IR DATA OF METHYLTIN HALIDE COMPLEXES

System	L	J(Hz)	ν(Sn–C) (± 5 cm^{-1})	ν(Sn–Cl) (± 5 cm^{-1})
$Me_2SnCl_2 \cdot 2L$	DMSO	86	574	341
	Ph_3PO	88	579	261, 246
	PyO	93	574	ca. 230
	Ph_3AsO	100	574	[a]
$Me_3SnBr \cdot L$	DMSO	62	550	
	Ph_3PO	66.0	543	
	PyO	66.5	550	
	Ph_3AsO	70	543	

[a] A rather sharp band observed at *ca.* 225 cm^{-1} may be ν(Sn–Cl) although this is by no means certain.

A feature of some interest is that $\Delta\nu$(S–O) > $\Delta\nu$(P–O) > $\Delta\nu$(N–O) > $\Delta\nu$(As–O) with values −109, −38, −38 and 0 cm^{-1}**, respectively for the $Me_2SnCl_2 \cdot 2L$ series.

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* This trend is consistent with the fact that Ph_3AsO produces a greater ligand field when coordinated with first row transition elements than does Ph_3PO.

** At this stage, it probably should be pointed out that PyO is structurally dissimilar to DMSO, Ph_3PO and Ph_3AsO, since the oxygen is attached to a hetero-atom constituting part of a conjugated ring system.

Such reductions, as suggested by Cotton[8] and Drago[9], are consistent with a lowering of the respective bond orders as a result of complexation, which means that Ph_3AsO is best able to bring about complexation with minimal changes in the As–O bond order*. This is consistent with the proposal that a form $Ph_3As^+–O^-$, which may be viewed as significantly responsible for the base strength of Ph_3AsO, is more favourable than the corresponding form $Me_2S^+–O^-$ for DMSO, since the matching of *p* and *d* orbitals for oxygen and sulphur is probably better, favouring the $Me_2S=O$ formulation.

Further work on related complexes is currently underway and will be reported at a later date.

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* However, the real cause may not be quite so simple since in some cases ν(As–O) actually increases on coordination. Admittedly, these cases involve transition metals where σ and π bonding components must be considered. We do not envisage π-bonding effects to be at all important in the present cases.