Journal of Organometallic Chemistry, *447* (1993) 9–13

JOM 23095

The first authenticated example of triorganotin(IV) perchlorate complexes of some heterocyclic bases

I. Synthesis, characterization and assessment of bonding and structure

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(Received April 13, 1992; in revised form July 8, 1992)

Abstract

A convenient method is reported for the synthesis of some novel complexes of composition (R_3SnL_2) ClO_4 where L represents pyridine, γ-picoline, 2,2′-bipyridine and 1,10-phenanthroline; and R = ^{n}Bu or Ph. All of the new ionic complexes have been characterized by elemental analysis, molar conductance, infrared, multinuclear nuclear magnetic resonance (^{1}H, ^{13}C and ^{119}Sn) and ^{119}Sn Mössbauer spectroscopies. The complexes of composition $(R_3SnL_2)ClO_4$ exist both in solution and in the solid state with *trans*-trigonal bipyramidal structure where the R-groups occupy the equatorial positions while the ligands are in the axial position.

1. Introduction

The proclivity of diorganotin(IV) dihalides to form six-coordinated complexes typically with heterocyclic α-diimine ligands such as 2,2′-bipyridine and 1,10-phenanthroline, has been well documented [1]. Accumulated Mössbauer results [2,3] provide proper understanding of their structure and isomerism; and triorganotin(IV) derivatives appear to possess diminished acceptor strengths [4]. In contrast to the work on diorganotin(IV) complexes, there have been very few investigations of trialkyltin(IV) derivatives of such heterocyclic ligands as pyridine, as five coordinated complexes [5]. Meanwhile, triaryltin(IV) derivatives of heterocyclic α-diimine ligands have been reported as outer-sphere complexes [6].

In spite of there being many types of organotin(IV) halide complexes of the above mentioned ligands, the chemistry of known organotin(IV) perchlorates [7] with such systems have not been investigated presumably owing to the highly hygroscopic and explosive nature of organotin perchlorates. We report here the first successful synthesis in high yield of the complexes of composition $(R_3SnL_2)ClO_4$.

2. Experimental details

The starting materials $(AgPy_2)ClO_4$ and (Ag γ-$Pico_2)ClO_4$ [8], $(AgBipy_2)ClO_4$ [9] and $(AgPhen_2)ClO_4$

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0022-328X/93/$6.00

[10] were prepared as previously reported and the purities were established by their analytical data, m.p. (where possible), IR and ^{1}H NMR spectra after recrystallization. Ph_3SnCl (Fluka AG) was purified as described by Gilman *et al.* [11] while Bu_3SnCl (Alfa) was used as received.

Stringent precautions were taken to exclude moisture from the system. Perchlorate was used as a counterion with a number of triorganotin(IV) complexes without incident. Care in handling the perchlorate complexes must be exercised.

Physical measurements were carried out as previously described [12]. Multinuclear NMR (^{1}H, ^{13}C and ^{119}Sn) spectra were recorded on a Bruker AMX-400 at frequencies of 400.13, 100.61 and 149.12, respectively.

2.1. Preparation of complexes

Typical preparative details are given below.

2.1.1. (i) $(Ph_3Sn\ Py_2)ClO_4$ (1)

(a) To a stirred solution of the $(Ag\ Py_2)ClO_4$ (0.5 g, 1.37 mmol) was added Ph_3SnCl (0.53 g, 1.37 mmol) in hot anhydrous benzene (20 cm^3). Stirring was continued for 1 h during which time a white solid (AgCl) separated out. The heterogeneous reaction mixture was refluxed for a further 2 h. The contents were then cooled and filtered. The filtrate was concentrated slowly on a hot plate. On cooling, a resinous substance was obtained. This was triturated with petroleum ether several times until fine crystals were obtained. Finally the product was recrystallized from benzene-petroleum ether mixture and dried *in vacuo*.

(b) A freshly prepared solution of Ph_3SnClO_4 (0.5 g, 1.11 mmol) in anhydrous methanol–benzene (1:1, 30 cm^3) was added to freshly distilled pyridine (0.17 g, 2.22 mmol) dropwise and with constant stirring. Then the reaction mixture was refluxed for 5 h and slowly concentrated on a hot plate. The product was obtained on cooling, purified as described above and dried *in vacuo*.

2.1.2. $(Ph_3Sn\ Bipy_2)\ ClO_4$ (4)

This complex was prepared by mixing stoichiometric amounts of the freshly prepared Ph_3SnClO_4 (0.5 g, 1.11 mmol) and 2,2′-bipyridine (0.34 g, 2.17 mmol) in an anhydrous methanol–benzene mixture under reflux. The product was purified as described above.

3. Results and discussion

3.1. Synthesis and formulation

The triorganotin perchlorates of composition $(R_3SnL_2)ClO_4$ can be prepared by allowing stoichiometric amounts of R_3SnClO_4 and ligand or of $(AgL_2)ClO_4$ and R_3SnCl to react in hot methanol-benzene mixture at reflux temperature. Under the same conditions, R_3SnCl does not react with $(AgPhen_2)ClO_4$, owing to the insolubility of the latter in common organic solvents. However, this reaction was tried using nitrobenzene as a solvent but the resulting product was a complex mixture which could not be separated nor identified. In general, the reaction of Ph_3SnCl with Ag-complexes proceeded smoothly and essentially quantitatively, while the Bu_3SnCl substrate proved extremely difficult to isolate and purify; the yield of the resulting product was also lower.

The complexes are white crystalline solids. They are non-hygroscopic and non-explosive, at least at ordinary temperature. The complexes were characterized by elemental analyses which confirmed that there were two

TABLE 1. Analytical and molar conductance data for the complexes **1–6**

Complex [a]	Yield (%)	Analysis (Found (calcd.) (%))				M [b]
		C	H	N	Sn	
$(Ph_3SnPy_2)ClO_4$	75	55.01	4.10	4.50	19.30	176.46
(1)		(55.33)	(4.12)	(4.61)	(19.55)	
$(Bu_3SnPy_2)ClO_4$	50	47.85	6.50	5.10	21.50	190.40
(2)		(48.25)	(6.76)	(5.12)	(21.69)	
$(Ph_3SnPico_2)ClO_4$	52	56.50	4.50	4.40	18.50	181.47
(3)		(56.67)	(4.56)	(4.41)	(18.69)	
$(Ph_3SnBipy_2)ClO_4$	80	59.60	4.05	7.40	15.42	170.60
(4)		(59.88)	(4.07)	(7.35)	(15.59)	
$(Bu_3SnBipy_2)ClO_4$	51	54.52	6.01	7.63	16.70	172.65
(5)		(54.76)	(6.13)	(7.98)	(16.93)	
$(Ph_3SnPhen_2)ClO_4$	85	62.10	3.48	6.90	14.35	168.46
(6)		(62.28)	(3.83)	(6.92)	(14.65)	

[a] Abbreviation used for each complexes are listed immediately after the complexes; m.p. not determined because of unknown nature of perchlorate complexes.

[b] In 10^{-3} M acetonitrile (Ω^{-1} cm^2 mol^{-1}) at 18°C.

ligands per tin atom. The molar conductance of the complexes in acetonitrile was between 168 and 190 Ω^{-1} cm^2 mol^{-1} (Table 1), suggesting a 1 : 1 electrolyte [13]. These results collectively confirm the formulation of the complexes as $(R_3SnL_2)ClO_4$.

3.2. *IR spectra*

Diagnostically useful infrared results are summarized in Table 2.

The ligand ν(C=N) band is shifted to the higher frequency at *ca.* 1618 cm^{-1} in the complexes **1–3**, suggesting coordination through the pyridine nitrogen atom [12] while other absorptions due to pyridine have not been identified because of the interferences from the R_3Sn and perchlorate vibrations. In the case of 2,2′-bipyridine, characteristic frequencies associated with ν(C=C), ν(C=N) and ring stretching appear at *ca.* 1581, 1552 and 1532 cm^{-1}, respectively. Positive shifts of these bands to respectively *ca.* 1595, 1581 and 1560 cm^{-1} in the complexes (**4** and **5**), are consistent with the coordination of bipyridine nitrogen to metal atom [10,14]. In phenanthroline [15], the bands at 1588, 1503 and 1450 cm^{-1} are expected to be sensitive on coordination and in complex **6** were shifted to 1618, 1555 and 1480 cm^{-1}.

All the complexes show a very intense broad band due to the perchlorate anion [16,17] in the region *ca.* 1081–1144 cm^{-1}, which can be assigned to the asymmetric stretch (ν_3). However, the only band that can be associated with ClO_4^- is observed at *ca.* 625 cm^{-1}, may be assigned to the asymmetric bend (ν_4). The band at *ca.* 900 cm^{-1} corresponding to symmetric stretch is also absent. These results also suggest the presence of an undistorted ClO_4^- ion in solid state.

In the low frequency infrared region, the appearance of the medium intensity bands at *ca.* 270 and 235 cm^{-1} in the complexes **1**, **3**, **4** and **6** may be assigned to the ν_{as} (Sn–C(Ph)) and ν_s (Sn–C(Ph)), respectively [4,18,19]. The complexes **2** and **5** also show ν_{as} and ν_s (Sn–C(Bu)) bands [20] at 603 and 511 cm^{-1}, respectively. The presence of the $\nu(\text{Sn–C})_{as,s}$ bands in all the complexes excludes the possibility of an exactly planar arrangement of three Sn–C bonds around the tin atom [21].

TABLE 2. Characteristic IR (cm^{-1}) data for the complexes **1–6**

Complex	$\nu(ClO_4^-)$		ν(Sn–C)	
	$\nu3$ [b]	$\nu4$	νas	νs
1 [a]	1083–1144	625	266	232
2 [a]	1077–1149	626	603	511
3 [a]	1093–1144	624	271	235
4	1082–1128	625	268	232
5	1085–1143	626	602	509
6	1090–1150	623	268	230

[a] Sample reacts with KBr when spectra were attempted in the range 4000–600 cm^{-1}. Finally, the spectra were recorded in Nujol mull squeezed between transparent polyethylene cells (4000–180 cm^{-1}).

[b] Very broad band.

TABLE 3. ^{1}H NMR data (δ ppm) of the complexes **1–6**

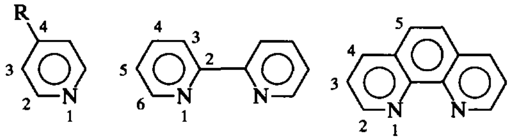
Proton [a] No.	Complex (solvent used)					
	1 (b)	**2** (c)	**3** (c)	**4** (b)	**5** (d)	**6** (b)
1 *	–	1.12	–	–	1.20	–
2 *	7.84	1.50	7.43–7.80 [e]	7.83	1.58	7.89
3 *	7.62	1.24	7.43–7.80 [e]	7.65	1.24	7.58
4 *	7.57	0.90	7.43–7.80 [e]	7.53	0.90	7.50
2	8.69	8.93	8.50	–	–	9.43
3	7.58	8.00	7.43–7.80 [e]	8.41	8.46	8.27
4	7.99	8.48	2.50	7.96	8.17	9.14
5	–	–	–	7.47	7.67	8.40
6	–	–	–	8.70	8.81	–

[a] Proton numbers as shown below:

(i) Sn–R protons

4 * 3 * 2 * 1 *
CH_3 CH_2 CH_2 CH_2

(ii) Ligand protons



(R = H, CH_3)

[b] In DMSO.

[c] In acetone.

[d] In chloroform.

[e] Cannot be identified because of unresolved complex multiplicity.

3.3. *NMR spectral data*

In recording NMR spectra of organotin(IV) complexes in solution, non-coordinating solvents are preferable to coordinating ones to preclude possible changes in the coordination number of the tin atom. In the present case, solubility considerations led to the choice of coordinating solvents. The chemical shifts and the coupling constants of the complexes studied showed no concentration dependence, within experimental error.

3.3.1. *^{1}H NMR spectra*

As shown in Table 3, which lists the ^{1}H chemical shifts for complexes **1–6**, coordination to tin induces a considerable differentiation of the signals from the aromatic protons. The ligands *ortho*-protons were sensitive to coordination and shifted downfield by 0.27 ppm in comparison with those in the free ligand. This observation is in good agreement with the weak Sn–N interaction.

3.3.2. ^{13}C NMR spectra

In the ^{13}C NMR spectra of the complexes studied (Table 4), the number of the signals found correspond with the presence of magnetically non-equivalent carbon atoms. The values of carbon atoms in the *ipso*-position of the phenyl groups $\delta(^{13}\mathrm{C1}^{*})$ also support the conclusions about the coordination and configuration of complexes. The signal for the *ipso*-carbon (the carbon atom attached to tin) of the Ph_3Sn group is shifted upfield by *ca.* 3.5 ppm when compared with the $Ph_3SnCl \cdot DMSO$ complex [22] in the same solvent owing to increased coordination of tin atom. This observation is also in good agreement with the weak Sn–N interaction [23]. The ligand carbon atoms were not very sensitive to coordination. In the pyridine ring of the complex **1**, the resonances due to carbons 3 and 4 shifted downfield relative to those of the free ligand (pyridine), whereas those of C2 exhibit an upfield shift. Such behaviour further confirms the coordination of pyridine rings [24]. A substantially smaller change of ligand δ(C) values observed in the complexes in DMSO-d_6 may be due to a fast reversible displacement reaction [25].

3.3.3. ^{119}Sn NMR spectra

In order to obtain additional support for our conclusion, we recorded the ^{119}Sn NMR spectra of some representative complexes **1** and **4** in DMSO-d_6 solution (Table 4) since the ^{119}Sn chemical shift is very sensitive to complexation, and is usually shifted upfield on bonding to a Lewis base [1,26]. The observed upfield shifts are *ca.* 10.8 ppm in the complexes when compared with the free Ph_3SnCl values in the same solvent. Thus, this shift may be attributed to five coordinate triorganotin(IV) complexes. In the structurally characterized five-coordinated ionic complex, $[(CH_3)_3Sn \cdot Bipy]^+[B(C_6H_5)_4]^-$ a low field shift is observed in contrast to its anionic counterpart $[(CH_3)_3SnCl_2]^-[(C_2H_5)_4N]^+$ and the $\delta(^{119}\mathrm{Sn})$ values were 18 (in saturated CH_2Cl_2 solution) and 53 ppm (in saturated $(CH_3)_2CO$ solution), respectively. The observed $\delta(^{119}\mathrm{Sn})$ values in complexes **1** and **4** are around −237.6 ppm (in DMSO-d_6) when compared with the complexed, anionic triphenyltin species $[Ph_3SnCl_2]^-[(C_2H_5)_4N]^+$ (−257.2 ppm in CD_3NO_2) [22]. However, the precise interpretation and the extent of the chemical shifts $\delta(^{119}\mathrm{Sn})$ of the complexes studied is very difficult since the shift depends primarily on the type of substituent in the triorganotin(IV) group (butyl or phenyl), on the concentration, on the type of solvent, on the character of the group bonded to tin atom through nitrogen (pyridine or bipyridine), and on the nature of complexes (neutral or ionic). The observed $\delta(^{119}\mathrm{Sn})$ chemical shifts for the complexes with two monodentate ligands **1** and two bidentate ligands **4**, are of the same order of magnitude (see Table 4) which further leads us to conclude that the complexes are isostructural, five coordinated ionic species at least in the NMR time scale.

3.3.3.1. Coupling constants.

More conclusive information may be obtained from the values of the coupling constants $^{n}J(^{119}\mathrm{Sn},^{13}\mathrm{C})$ of the carbon atoms of the substituents R and especially from the values of $^{1}J(^{119}\mathrm{Sn}-^{13}\mathrm{C})$. The higher value of the coupling constant (810.3) in complex **1**, are close to those of $Ph_3SnCl \cdot DMSO$ complex and with other five-coordinate chelates [22]. Thus, these data support *trans*-trigonal bipyramidal geometry in which three phenyl groups lie in equatorial positions and the ligands occupy the axial positions [27] (see Mössbauer discussion for additional support). Unfortunately, the value of ^{1}J (^{119}Sn–

TABLE 4. ^{119}Sn [a] and ^{13}C [b] NMR data: δ(ppm) and $J(^{119}\mathrm{Sn}-^{13}\mathrm{C})$ (Hz) for the complexes **1** and **4** in DMSO-d_6

Complex	δ^{119}Sn	^{13}C NMR [c]								
		Sn–R				Ligand				
		(δC1 *) ^{1}J(Sn–C)	(δC2 *) ^{2}J(Sn–C)	(δC3 *) ^{3}J(Sn–C)	(δC4 *) ^{4}J(Sn–C)	(δC_2)	(δC_3)	(δC_4)	(δC_5)	(δC_6)
Ph_3SnCl(free)	−48.0 [d]	(137.3) [f]	(136.2) [f]	(129.2) [f]	(130.5) [f]	–	–	–	–	–
	−226.8 [e]	614.7	50	64.7	11.8					
1	−237.6	(140.2)	(136.1)	(129.4)	(130.4)	148.2	124.8	138.4	–	–
	(402.2)	810.3	46.8	70.3	14.1					
4	−237.7	(140.5)	(136.5)	(129.5)	(130.5)	154.7	122.2	139.2	125.3	145.5
	(405.0)	–	56.6	75.4	–					

[a] Downfield from external Me_4Sn at 300 K and values in parentheses are against reference $SnCl_4$ set at 0.0 ppm.

[b] Downfield from external Me_4Si.

[c] See Table 3 for numbering of carbon.

[d] Data (in $CDCl_3$) taken from ref. [28].

[e] In DMSO-d_6 (this work).

[f] Data (in $CDCl_3$) taken from ref. [29].

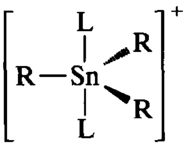


Fig. 1. The proposed configuration of triorganotin(IV) perchlorate complexes of L (L as described in the text).

TABLE 5. ^{119}Sn Mössbauer spectral data [a] (mm s^{-1}) of representative complexes

Complex	I.S.	Q.S.	$\Gamma\pm$
1	1.17	2.82	0.98
3	1.32	2.88	0.94
4	1.13	2.80	0.91
6	1.14	2.80	0.87

[a] At liquid nitrogen temperature.

^{13}C) could not be obtained in complex **4** because the poor signal to noise ratio prevented observation of the tin satellites. The $^{2/3/4}J(^{119}\text{Sn}-^{13}\text{C})$ values were not significantly affected.

3.4. ^{119}*Sn Mössbauer spectra*

In order to provide further structural evidence, the Mössbauer spectra of the representative complexes have been recorded (Table 5). The δE_Q values obtained for the complexes in the solid state are *ca.* 2.8 mm s^{-1} and thus clearly indicate *trans*-trigonal bipyramidal structure [1,30], supporting our previous assignment (*vide* NMR discussion). The observed isomer shifts are in the range 1.13–1.32 mm s^{-1}, typical of quadrivalent tin in organometallic compounds [12]. The full width of half maximum ($\Gamma\pm$) of these resonance absorptions are approximately 0.94 mm s^{-1}, further suggests the presence of a single metal atom site in the structure.

The structural inferences extracted from the various spectroscopic data in combination with elemental analysis and conductance measurements, collectively suggest the proposed configuration of the complexes as shown in Fig. 1.

Acknowledgments

The authors (T.S.B.B., D.D. and W.L.B.) thank Prof. D.T. Khathing, Head, Regional Sophisticated Instrumentation Centre, North-Eastern Hill University, Shillong for research facilities. E.R. acknowledges financial support received in the ratio 40:60 from the Progetto Finalizzato Chimica Fine e Secondaria II (CNR, Rome) and from M.U.R.S. (Italy). Thanks are also due to the Head, Sophisticated Instrument Facility, Indian Institute of Science, Bangalore, India for recording the NMR spectra.

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