

Synthesis, Reactivity & Spectral Studies of Some Pentacoordinate Tin(IV) Complexes Derived from Triphenyltin Trifluoroacetate

T N SRIVASTAVA* & JAI DEO-SINGH

Department of Chemistry, University of Lucknow, Lucknow 226 007

Received 23 August 1984; revised and accepted 3 January 1985

Triphenyltin methoxide/ethoxide prepared *in situ* reacts with trifluoroacetic acid, yielding triphenyltin trifluoroacetate in quantitative yield. The reactions of $\text{Ph}_3\text{SnOCOCF}_3$ with tetraalkylammonium salts (R_4NX) give pentacoordinated Sn(IV) complex anions of the general formulae $[\text{R}_4\text{N}]^+[(\text{C}_6\text{H}_5)_3\text{SnOCOCF}_3(\text{X})]^-$ [where $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_4\text{H}_9, \text{C}_5\text{H}_{11}, \text{C}_6\text{H}_5$ and $\text{X} = \text{Cl}, \text{Br}$ and I]. $\text{Ph}_3\text{SnOCOCF}_3$ undergoes cleavage with electrophilic reagents such as $\text{ICl}, \text{IBr}, \text{HgCl}_2, \text{Hg}(\text{SCN})_2$, yielding $\text{Ph}_2\text{Sn}(\text{OCOCF}_3)_2$. $\text{X}(\text{X} = \text{Cl}, \text{Br}, \text{SCN})$. These compounds like the parent $\text{Ph}_3\text{SnOCOCF}_3$ are polymeric in nature with five coordinated Sn(IV) atoms and bridging trifluoroacetate groups. These undergo nucleophilic substitution of (X) with other electronegative groups and form 1:1 molecular adducts with common Lewis bases. All these compounds have been characterized by elemental analyses, and IR and PMR data.

Triphenyltin trifluoroacetate $[(\text{C}_6\text{H}_5)_3\text{SnOCOCF}_3]$ is reported¹ to have been obtained in low yield by dissolving triphenyltin hydroxide in trifluoroacetic acid. In continuation of our interest in the synthesis and reactivity of organotin haloacetates^{2,3} we now report an improved method for the preparation of triphenyltin trifluoroacetate in almost quantitative yield. Its reactions with electrophilic reagents and tetraalkylammonium halides have been studied and the pentacoordinated complexes obtained characterized on the basis of elemental analyses and IR and PMR spectral data.

Materials and Methods

Triphenyltin chloride and iodine monobromide were prepared by established procedures^{4,5}. Trifluoroacetic acid (Koch-Light) was distilled before use. Iodine monochloride was procured commercially (Fluka). All operations were carried out under dry nitrogen atmosphere and physicochemical studies were made as described earlier⁶.

Preparation of $(\text{C}_6\text{H}_5)_3\text{SnOCOCF}_3$

To a solution of Ph_3SnCl (7.70 g; 20 mmol) in anhydrous ethanol (~15 ml) was added dropwise a freshly prepared solution of sodium ethoxide (20 mmol) with constant stirring and the mixture further stirred for 1 hr at 0°C and treated dropwise with trifluoroacetic acid (2.28 g; 20 mmol) suspended in ethanol (~10 ml). The mixture was stirred for 1 hr at the same temperature, filtered, filtrate concentrated under reduced pressure and the solid obtained recrystallized from chloroform; yield 9 g (97%); m.p. 122° (lit.¹ 121-23°C). The IR spectrum of the product was identical with the reported² spectrum of $(\text{C}_6\text{H}_5)_3\text{SnOCOCF}_3$.

Reactions of $(\text{C}_6\text{H}_5)_3\text{SnOCOCF}_3$:

(a) With tetraalkylammonium salts

A mixture of $(\text{C}_6\text{H}_5)_3\text{SnOCOCF}_3$ (4.63 g; 10 mmol) and $(\text{CH}_3)_4\text{NI}$ (2.01 g; 10 mmol) in absolute methanol (30 ml) was refluxed for 4 hr. The solution was concentrated under reduced pressure and the white crystals obtained washed with ether/pet. ether (40-60°) and dried *in vacuo*.

(b) With electrophiles (ICl)

A solution of ICl (1.62 g; 10 mmol) in CHCl_3 (15 ml) was added dropwise with constant stirring to a solution of $(\text{C}_6\text{H}_5)_3\text{Sn}(\text{OCOCF}_3)_3$ (4.43 g; 10 mmol) in chloroform (25 ml) at 0°C. After complete addition, the mixture was refluxed for 2 hr, the precipitated $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{OCOCF}_3)_2\text{Cl}$ filtered off and washed repeatedly with ether/pet. ether (40-60°) mixture and dried *in vacuo* (yield 2.5 g; 60%). [Identical products were obtained by the reaction of $(\text{C}_6\text{H}_5)_3\text{SnCl}$ with CF_3COOH in anhydrous benzene and also by reaction of $(\text{C}_6\text{H}_5)_3\text{SnOCOCF}_3$ with HgCl_2 . The reaction of $\text{Ph}_3\text{SnOCOCF}_3$ with IBr yielded $\text{Ph}_2\text{Sn}(\text{OCOCF}_3)_2\text{Br}$].

(c) With $\text{BF}_3 - \text{Et}_2\text{O}$

Reaction of $(\text{C}_6\text{H}_5)_3\text{SnOCOCF}_3$ (1 mol) and $\text{BF}_3 - \text{Et}_2\text{O}$ (1 mol) in anhydrous ether gave $(\text{C}_6\text{H}_5)_3\text{SnF}$. When (2 mol) of $\text{BF}_3 - \text{Et}_2\text{O}$ was used $(\text{C}_6\text{H}_5)_2\text{SnF}_2$ was isolated as the end product.

Reactions of $(\text{C}_6\text{H}_5)_3\text{Sn}(\text{OCOCF}_3)_2\text{Br}$:

(a) With Lewis bases

In a typical experiment a mixture of $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{OCOCF}_3)_2\text{Br}$ (2.32 g; 5 mmol) and *N,N*-diethylacetamide (2.3034 g; 20 mmol) was refluxed for 4 hr, in acetone (20 ml). Excess of the solvent was

Table 1—Products Obtained in Reactions of $(C_6H_5)_3SnOCOCF_3$ with Some Electrophiles and Their Characterization Data

Reagent	Product	m.p. (°C)	Found % (Calc.)		ν_{max} (cm ⁻¹)		
			Sn	(X = Cl, Br, NCS or CN)	$\nu_s OCO$	$\nu_s OCO$	$-\Delta\nu OCO$
ICI/HgCl ₂ or (C ₆ H ₅) ₃ SnCl + CF ₃ COOH	(C ₆ H ₅) ₂ Sn(OCOCF ₃)Cl	>250	27.96 (28.16)	8.14 (8.43)	1630	1430	200
IBr/Br ₂ /HgBr ₂ or (C ₆ H ₅) ₃ SnBr + CF ₃ COOH	(C ₆ H ₅) ₂ Sn(OCOCF ₃)Br	247	25.07 (25.47)	16.02 (16.18)	1645	1440	205
Hg(SCN) ₂	(C ₆ H ₅) ₃ SnOCOCF ₃ (NCS)	159(d)	26.50 (26.73)	12.84 (13.07)	1630	1420	210
Me ₄ NCl	[(C ₆ H ₅) ₃ SnOCOCF ₃ (Cl)] ⁻ [Me ₄ N] ⁺	101	20.36 (20.73)	6.18 (6.20)	1690	1400	290
Me ₄ NBr	[(C ₆ H ₅) ₃ SnOCOCF ₃ (Br)] ⁻ [Me ₄ N] ⁺	78	19.23 (19.62)	12.60 (12.97)	1700	1395	305
Et ₄ NCl	[(C ₆ H ₅) ₃ SnOCOCF ₃ (Cl)] ⁻ [Et ₄ N] ⁺	108	18.73 (18.08)	5.54 (5.65)	1700	1400	300
Et ₄ NBr	[(C ₆ H ₅) ₃ SnOCOCF ₃ (Br)] ⁻ [Et ₄ N] ⁺	139	17.27 (17.63)	11.70 (11.89)	1710	1400	310
Bu ₄ NBr	[(C ₆ H ₅) ₃ SnOCOCF ₃ (Br)] ⁻ [Bu ₄ N] ⁺	85	14.96 (15.11)	10.01 (10.19)	1690	1390	300
(Bu ₄ N)I	[(C ₆ H ₅) ₃ SnOCOCF ₃ (I)] ⁻ [(Bu ₄ N)] ⁺	93	14.13 (14.26)	15.14 (15.27)	1700	1395	305
(C ₅ H ₁₁) ₄ NBr	[(C ₆ H ₅) ₃ SnOCOCF ₃ (Br)] ⁻ [(C ₅ H ₁₁) ₄] ⁺	128	13.86 (14.10)	9.40 (9.51)	1700	1390	310
(C ₅ H ₁₁) ₄ NI	[(C ₆ H ₅) ₃ SnOCOCF ₃ (I)] ⁻ [(C ₅ H ₁₁) ₄] ⁺	143	13.20 (13.36)	14.16 (14.30)	1695	1390	315
(C ₆ H ₅) ₄ PBr	[(C ₆ H ₅) ₃ SnOCOCF ₃ (Br)] ⁻ [(C ₅ H ₅) ₄ P] ⁺	155	13.17 (13.43)	14.20 (14.38)	1700	1390	310

 Table 2—Products Obtained in the Reaction $(C_6H_5)_2Sn(OCOCF_3)_2.X$ with Silver Halides/Lewis Bases and Their Characterization Data

Reagent	Product	m.p. (°C)	Found (%) (Calc.)		ν_{max} in (cm ⁻¹)		
			Sn	X = Br, CN, or SCN	$\nu_s OCO$	$\nu_s OCO$	$-\Delta\nu OCO$
AgSCN	(C ₆ H ₅) ₂ Sn(OCOCF ₃)(SCN)	159(d)	26.50 (26.73)	12.84 (13.07)	1630	1420	210
AgCN	(C ₆ H ₅) ₂ Sn(OCOCF ₃)(CN)	196(d)	28.40 (28.81)	6.17 (6.31)	1640	1445	195
AgOCOCH ₃	(C ₆ H ₅) ₂ Sn(OCOCF ₃)(OCOCH ₃)	192(d)	26.07 (26.43)	—	1660 1560	1440 1400	220 160
Ag ₂ O/CF ₃ COOH	(C ₆ H ₅) ₂ Sn(OCOCF ₃) ₂	250	23.50 (23.78)	—	1620	1425	195
[Me ₂ N] ₂ CO	(C ₆ H ₅) ₂ Sn(OCOCF ₃).Cl.OC[Me ₂ N] ₂	127	21.70 (22.08)	6.42 (6.60)	1695	1400	295
[Me ₂ N] ₂ CO	(C ₆ H ₅) ₂ Sn(OCOCF ₃)(NCS).OC[Me ₂ N] ₂	178(d)	21.02 (21.19)	—	1690	1400	290
(C ₂ H ₅) ₂ N.CH ₃ CO	(C ₆ H ₅) ₂ Sn(OCOCF ₃).Br.OCOCH ₃ N(C ₂ H ₅) ₂	88	20.17 (20.42)	13.65 (13.77)	1695	1405	290
(CH ₃) ₂ .C ₅ H ₃ .NO	(C ₆ H ₅) ₂ Sn(OCOCF ₃) ₂ ONC ₅ H ₃ (CH ₃) ₂	92	18.96 (19.07)	—	1690	1395	295

distilled off and the concentrate kept overnight in a freezer. The separated molecular adduct $(C_6H_5)_2Sn(OCOCH_3)Br \cdot OCNCH_3(C_2H_5)_2$ that separated out as light yellow solid was dried *in vacuo*.

(e) With AgX ($X = SCN, CN, OCOCH_3$ or $OCOCH_3$)

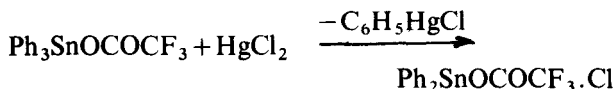
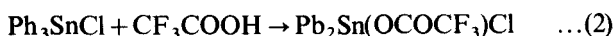
In a typical reaction, a mixture of $(C_6H_5)_2Sn(OCOCH_3) \cdot Br$ (4.64 g; 10 mmol) and CH_3COOAg (3.34 g; 10 mmol) was stirred at room temperature in dry acetone. Filtration followed by evaporation of the solvent gave $(C_6H_5)_2Sn(OCOCH_3)(OCOCH_3)$.

Results and Discussion

The analytical data of the products obtained in the reactions of $Ph_3SnOCOCH_3$ and $Ph_2SnOCOCH_3 \cdot Br$ are summarised in Tables 1 and 2 respectively.

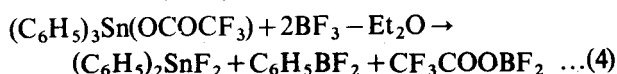
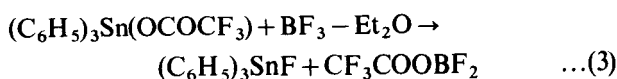
Triphenyltin trifluoroacetate is thermally stable at room temperature. It is recovered unchanged from refluxing toluene indicating absence of decarboxylation. This is in contrast to the behaviour of the corresponding trichloroacetate species which undergoes decarboxylation in refluxing toluene to give Ph_3SnCl .

The interaction of $(C_6H_5)_3SnOCOCH_3$ with tetraalkylammonium salts yields anionic complexes of the general formulae $[R_4N]^+ [(C_6H_5)_3SnOCOCH_3(X)]^-$ [$R = CH_3, C_2H_5, C_4H_9, C_5H_{11}; X = Cl, Br$ or I]. These complexes are soluble in polar solvents and behave as 1:1 electrolytes in methanol, ethanol, nitrobenzene and methyl cyanide. The reactions of $Ph_3SnOCOCH_3$ with electrophiles ($IBr, ICl, HgCl_2$) readily cleave the weaker $Sn-C$ bond in preference to $Sn-O$. Even in the presence of excess of electrophiles the second $Sn-C$ bond is not cleaved (see Eqs 1 and 2).



The compounds $(C_6H_5)_2Sn(OCOCH_3) \cdot X$, are partially soluble in common organic solvents. Their molar conductances in methanol and nitrobenzene show their non-electrolytic nature.

The reactions of $BF_3 - Et_2O$ with $Ph_3SnOCOCH_3$, in 1:1 and 1:2 molar ratios can be expressed by Eqs (3) and (4) respectively.



The products were characterized by analytical data and IR spectra¹⁸. Such reactions have also been reported with other organotin compounds^{7,8}.

IR Spectra

Infrared spectra have been recorded in the region $4000-200 \text{ cm}^{-1}$ in CsI and $4000-650 \text{ cm}^{-1}$ in KBr .

The $\nu_{as}(Sn-C)$ and $\nu_s(Sn-C)$ modes appear in the range 265 ± 5 and $230 \pm 5 \text{ cm}^{-1}$ respectively and are not significantly affected by the nature of the halide group attached to the metal atom in the anionic complexes. The occurrence of $\nu_{as}OCO$ and ν_sOCO modes in the anionic complex species and their separation value ($\Delta\nu_{OCO} = \nu_{as}OCO - \nu_sOCO$) of $300 \pm 10 \text{ cm}^{-1}$ in contrast to that in triphenyltin trifluoroacetate (Table 1), shows unidentate bonding of the CF_3COO group. In compounds $(C_6H_5)_2Sn(OCOCH_3) \cdot X$ ($X = Cl, Br, CN, NCS$) the $\nu_{as}OCO$ and ν_sOCO modes and their separation values compare favourably with those of triphenyltin trifluoroacetate, indicating trigonal bipyramidal geometry, and five-coordinated polymeric structure with $O-C-O$ bridges between the Sn atoms in the solid state^{1,2}. The spectra of $(C_6H_5)_2Sn(OCOCH_3) \cdot X$ ($X = CN$ and NCS) are consistent with the iso structure^{9,10}. The ν_{Sn-O} and ν_{Sn-Cl} modes in $(C_6H_5)_2Sn(OCOCH_3) \cdot Cl$ appear at 340 and 285 cm^{-1} respectively.

In the IR spectra of the compounds $(C_6H_5)_2Sn(OCOCH_3)_2$ and $(C_6H_5)_2Sn(OCOCH_3)(OCOCH_3)$, the $\Delta\nu_{OCO}$ values (Table 2) correspond to the bridging bidentate nature of OCO groups^{2,11,12}. Thus, these compounds are hexacoordinated in which the apical positions are occupied by the two phenyl groups and the other positions are held by carboxylate groups in bridging bidentate manner. The ν_{Sn-O} modes are identified at 325 cm^{-1} . In the complexes $(C_6H_5)_2Sn(OCOCH_3) \cdot X \cdot L$ [$X = Cl, Br, NCS$ and $L = OC(Me_2N)_2, OC \cdot CH_3N(C_2H_5)_2, ONC_5H_3(CH_3)_2$] shifts in diagnostic absorptions of the ligands (see Table 2) indicate the presence of coordinated bases¹³⁻¹⁵. The nature of $-OCOCH_3$ group is unidentate and the complexes have pentacoordinated structure.

PMR spectra

The 90 MHz PMR spectrum of $(Et_4N)^+ [Ph_3SnOCOCH_3 \cdot Br]^-$ in acetone- d_6 exhibits signals at δ 8.03 [$m, C_6H_5(O)$], 7.30 [$m, C_6H_5(m,p)$], 3.10 [$q, 8H, 4XCH_2, CH_3$] and 1.12 [$t, 12H, 4XCH_2CH_3$]. The 90 MHz PMR spectrum of $(Bu_4N)^+ [Ph_3SnOCOCH_3 \cdot I]^-$ in $CDCl_3$ display signals at δ 7.80 [$m, C_6H_5(O)$], 7.16 [$m, C_6H_5(m,p)$] 2.8 ($bm, 8H, 4XCH_2CH_2CH_2CH_3$) and 0.6-1.4 ($bm, 28H, 4X-CH_2CH_2CH_2CH_3$). The 60 MHz PMR spectrum of

$\text{Ph}_2\text{Sn}(\text{OCOCF}_3)\text{Br} \cdot \text{OCCH}_3\text{N}(\text{C}_2\text{H}_5)_2$ in CDCl_3 displays signals at δ 7.60 [*m*, $\text{C}_6\text{H}_5(\text{O})$], 7.13 [*m*, C_6H_5 (*m*, *p*)], 0.95 (*t*, $\text{N}-\text{CH}_2\text{CH}_3$), 3.00 (*q*, $\text{N}-\text{CH}_2$) and 1.92 (*s*, $-\text{C}-\text{CH}_3$). The signals at δ 8.03, 7.80 and

||
O

7.60; respectively are assigned to aromatic *ortho* protons while those at δ 7.30, 7.16 and 7.13 are assigned to aromatic *meta* and *para* protons. The two sets of aromatic proton signals in the PMR spectra of these complexes have relative intensity ratios of $\sim 1/1.8$. The values are given for the approximate centre of the multiplets, one of the satellite bands, due to coupling of ^{117}Sn and ^{119}Sn with the *ortho*-protons of the phenyl rings appearing 0.6-0.7 ppm downfield from the main *ortho*-proton resonances. The high field satellite band overlaps with the *meta*- and *para*-proton resonances¹⁶.

The shielding effect on α -protons of the tetraalkylammonium cation is greater than that on β - or more distant alkyl protons while protons of bulky cations (Bu_4N^+), are less shielded than those of relatively smaller ones $[\text{Et}_4\text{N}]^+$. Similar results have been reported in other aryltin compounds¹⁶. In the complex $[\text{Et}_4\text{N}]^+ [\text{C}_6\text{H}_5)_3\text{SnOCOCF}_3\text{Br}]^-$ the CH_3 protons of $[\text{Et}_4\text{N}]^+$ moiety appear as a triplet, each signal splitting into 1:1:1 (approx.) triplets. Such splitting is due to coupling with ^{14}N nucleus^{17,18}.

Acknowledgement

Financial assistance from the CSIR, New Delhi in support of the present work is gratefully acknowledged.

References

- 1 Ford B F E & Sams J R, *J organometal Chem*, **31** (1971) 47.
- 2 Srivastava T N & Singh Jai Deo, *Indian J Chem*, **22A** (1983) 128.
- 3 Srivastava T N & Singh Jai Deo, *Indian J Chem*, **22A** (1983) 674.
- 4 Kocheskov K A & Nad M M, *J Gen Chem*, **4** (1934) 1434.
- 5 Folaranmi A, Mclean R A N & Wadibia N, *J organometal Chem*, **73** (1974) 59.
- 6 Srivastava T N, Singh Jai Deo & Srivastava R C, *Synth React Inorg Met-Org Chem* (In press).
- 7 Chambers R D & Chivers T, *J chem Soc*, (1965) 3933.
- 8 Leusink A, Drenth W & Noltes J G, *Tetrahedron Lett*, (1967) 1263.
- 9 Dows D A, Haim A & Wilmarth W K, *J inorg nucl Chem*, **21** (1961) 33.
- 10 Norbury A H, *Adv Inorg Chem Radiochem*, **17** (1975) 231.
- 11 Bandoli G, Clemente D A & Panatoni C, *Chem Commun*, (1971) 311.
- 12 Garner C D & Hughes B, *Adv Inorg Chem Radio Chem*, **17** (1975) 1.
- 13 Paul R C, Gupta S K & Chadha S L, *Indian J Chem*, **8** (1970) 1020.
- 14 Schafer M & Curran C, *Inorg Chem*, **5** (1966) 265.
- 15 Karayannis N M, *Coord Chem Rev*, **11** (1973) 93.
- 16 Sau A C, Carpino L A & Holmes R R, *J organometal Chem*, **197** (1980) 181.
- 17 Anderson J N, Baldeschwieler J D, Dittmer D C & Philips W D, *J chem Phys*, **38** (1963) 1260.
- 18 Bullock E, Tuck D G & Woodhouse E J, *J chem Phys*, **38** (1963) 2318.