CRYSTAL STRUCTURE AND COORDINATION CHEMISTRY OF (2-CARBOMETHOXYETHYL)IODODIPHENYLSTANNANE, IPh₂SnCH₂CH₂CO₂Me

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Abstract—The crystal structure of IPh₂SnCH₂CH₂CO₂Me: $C_{16}H_{17}IO_2Sn$ (10; X = I) has been determined; the tin atom adopts a distorted trigonal bipyramidal geometry, with iodine and the internal carbonyl oxygen in axial sites. The chelated structure of 10 (X = I) [ν (CO) 1684 cm⁻¹] persists in such solvents as dichloromethane, chloroform, tetrahydrofuran and acetonitrile. Pyridine is able to compete with the intramolecular ester coordination in CH₂Cl₂ solution with the formation of unchelated IPh₂Sn(py)CH₂CH₂CO₂Me (11) [ν (CO) 1734 cm⁻¹]; the formation constant of 11 is 0.07 ± 0.01 1 mol⁻¹ at 25°C.

Ester groups are generally weak donors towards organotin acceptors. However, when sited intramolecularly, for example as in Cl₂Sn(CH₂CH₂ CO₂Me)₂ (1),¹ Cl₃SnCH₂CH₂CO₂R (2), (R = Me;¹ R = Pr^{i 2}) and Cl₃SnCH₂CH₂CH₂CO₂Et (3),³ they are able to complex strongly to tin centres.⁴ Crystal structure determinations¹⁻³ and spectral data⁴⁻⁶ for 1–3 and related compounds show that RO₂C(CH₂)_n groups do act as chelating ligands in the solid state. Similar conclusions are obtained in non-coordinating solvents.^{2.3} However in coordinating solvents such as MeCN^{2.3} or in the presence of nitrogen donors, e.g. pyridine or 2,2'- bipyridine, the coordination by the ester groups, e.g. in 2 and 3, can be broken.^{2,3} From comparison of stability constants, the five-membered chelate ring in 2 is found to be stronger than the six-membered ring in 3.

The chelating abilities of $RO_2CCH_2CH_2$ and other groups (Me₂NCS₂ and 8-quinolinato) have been compared in appropriate compounds, e.g. [MeO₂CCH₂CH₂SnCl_{3-n}(S₂CNMe₂)_n] (4; n=1-3),^{7,8} [MeO₂CCH₂CH₂)₂Sn(S₂CNMe₂)₂] (5)⁹ and [(MeO₂CCH₂CH₂)₂SnCl(8-quinolinate)] (6):¹⁰ structural studies indicate that the MeO₂CCH₂CH₂ group has the weakest chelating ability of these three groups. The sulphido compounds, [MeO₂ CCH₂CH₂)₂SnS]₃ (7)¹¹ and [MeO₂CCH₂CH₂Sn (S)(S₂CNMe₂)]₃ (8),¹¹ in the solid state, both

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contain monodentate $RO_2CCH_2CH_2$ units as does [($RO_2CCH_2CH_2$)(Me_2NCS_2)Sn(XCH_2CH_2)₂Y] (9 R = Me, X = S, Y = O; R = Et, X = O, Y = NMe).¹²

The Lewis acidity of organotin halides generally decreases in the sequence: $RSnX_3 > R_2SnX_2 >$ R_3SnX . Thus it is anticipated that the tin atom in XPh₂SnCH₂CH₂CO₂Me (10) would be a poorer acceptor centre than that in X₃SnCH₂CH₂CO₂Me (X = halide) towards both the internal ester group and external donors. In order to investigate the coordination chemistry of 10, we have determined the crystal structure of 10 (X = I) and have studied its coordination by donor molecules. We now wish to report our results.

EXPERIMENTAL

The compound Ph₃SnCH₂CH₂CO₂Me (11) was prepared from Ph₃SnH and CH₂=CHCO₂Me by a published procedure.¹³ The reaction of 11 (4.37 g 0.01 mol) and I₂ (2.54 g, 0.01 mol) in CCl₄ (50 ml) gave IPh₂SnCH₂CH₂CO₂Me. The reaction residue, after removal of all volatiles, was recrystallized from EtOH to give a solid; melting point 77°C (ref. 13, 76°C). Found: C, 39.3; H, 3.5; I, 26.2. Calc. for C₁₆H₁₇IO₂Sn: C, 39.5, H, 3.5; I, 26.1%. ¹¹⁹Sn NMR (CDCl₃, 33.35 MHz): δ –92.07 ppm (relative to Me₄Sn).

 $Cl_3SnCH_2CH_2CO_2Me$ was a recrystallized sample from a previous study.⁶

Solvents and donor molecules

MeCN was purified by a standard procedure;¹⁴ CH_2Cl_2 and THF were dried over CaH_2 and distilled prior to use. Donor molecules were either redistilled or recrystallized prior to use.

The compound $Cl_2Pt(COD)$ (COD = 1,5-cyclooctadiene) was obtained by a literature procedure.¹⁵

Formation constants

These were determined from IR data, from the carbonyl region, at $25 \pm 1^{\circ}$ C in CH₂Cl₂ solution as previously described.⁶

Reaction between **11** *and* Cl₂Pt(COD)

Solutions of 11 (0.0437 g, 1 mmol) and $Cl_2Pt(COD)$ (0.0374 g, 1 mmol) in CD_2Cl_2 (total volume 1 cm³) were mixed and the reaction monitored by ¹H NMR spectroscopy (220 MHz) at 30°C. The successive formations of $ClPh_2SnCH_2CH_2$ CO₂Me and $Cl_2PhSnCH_2CH_2CO_2Me$ were indicated (see Table 1 for ¹H NMR details).

The platinum products—ClPhPt(COD) and $Ph_2Pt(COD)$ —were also detected by NMR.

ClPhPt(COD). δ ¹H 2.46 (m, 8H, CH₂), 4.55 (t, 2H, J^{119} Pt–¹H 75 Hz, CH), 5.70 (t, 2H, 34 Hz, CH), 6.7–7.4 (m, 5H, phenyl).

Ph₂Pt(COD). δ^{1} H 2.5 (m, 8H, CH₂), 5.02 (t, 4H, J^{119} Pt⁻¹H, 40 Hz, CH), 6.6-7.5 (m, 10H, phenyl).

Crystal structure determination

Crystal data. $C_{16}H_{17}IO_2Sn$, M = 486.91, monoclinic, space group $P2_{1/n}$, a = 10.073(8), b = 17.721(14), c = 10.427(10) Å, $\beta = 112.11(7)^{\circ}$, V = 1725(2) Å³, Z = 4, $D_c = 1.875$ g cm⁻³, $D_m = 1.88$ g cm⁻³, F(000) = 928, $\mu(Mo-K_{\alpha}) = 3.26$ mm⁻¹, $\lambda = 0.71069$ Å, T = room temperature.

Compound	$\operatorname{CH}_2^a \alpha$	CH_2^a β	OMe	Ph ^b		
				m+p	0	
Ph ₃ SnCH ₂ CH ₂ CO ₂ Me	1.61	2.65	3.43	7.35	7.53	
<i>y</i> z <i>z z</i>	(55)	(68)				
IPh ₂ SnCH ₂ CH ₂ CO ₂ Me	1.96	2.82	3.73	7.35	7.76	
ClPh ₂ SnCH ₂ CH ₂ CO ₂ Me	1.73	2.82	3.78	7.38	7.77	
Cl ₂ PhSnCH ₂ CH ₂ CO ₂ Me	1.96	2.92	3.86	7.46	7.90	
Cl ₃ SnCH ₂ CH ₂ CO ₂ Me	2.23	2.96	3.97			
	(108)	(191)				

Table 1. ¹H NMR spectra (220 MHz) for Ph_nX_{3-n}SnCH₂CH₂CO₂Me in CD₂Cl₂ $\delta(J^{119}Sn^{-1}H Hz)$

^{*a*} Triplet J_{H,H} 8 Hz.

^b Multiplets.

Data collection and processing. Colourless crystal, $0.31 \times 0.14 \times 0.25$ mm. The cell dimensions were obtained from setting angles of 14 independent reflections with $2\theta \approx 20^{\circ}$ on a Nicolet P3 4-circle diffractometer using monochromatic Mo- K_{α} radiation. 3059 unique intensities were measured with $\theta \leq 25^{\circ}$ as $\theta/2\theta$ scans; 1958 reflections had $F > 5\sigma(F)$. Range of $h \ k \ l: \ 0 \leq h \leq 11; \ 0 \leq k \leq 21; \ -11 \leq l \leq 11.$

The data were corrected for Lorentz and polarization effects but absorption was ignored. Two reference reflections, monitored periodically, showed no significant variation in intensity.

Structure analysis and refinement

The structure was determined by the heavy-atom method (Patterson function), which revealed the approximate positions of the tin and iodine atoms. The remaining non-hydrogen atoms were located from successive Fourier difference maps using SHELX 76.¹⁶ The hydrogen atoms were placed in calculated positions and refined relative to their bonded carbons. Full-matrix least squares calculations on F with unit weights and anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms converged at R=0.052. Atomic scattering factors for carbon, hydrogen, oxygen and tin were taken¹⁶ from SHELX 76. Data for iodine was taken from the International Tables for X-ray Crystallography.¹⁷ Final $\Delta \rho_{\text{max}} = +0.76$ eÅ⁻³, $\Delta \rho_{\rm min} = -0.66 \ {\rm e}{\rm \AA}^{-3}$. Molecular geometries were generated by the GX package.¹⁸

RESULTS AND DISCUSSION

Compound 10 (X=I) was obtained by the reaction of 11 with I₂; this cleavage reaction occurs particularly readily, due to the nucleophilic assistance afforded by the ester group in the rate-determining step. Other reactions of 11 with electrophilic reagents are facile, e.g. even the weakly electrophilic, Me₃SiX, is able to cleave a Ph—Sn bond¹⁹ in 11 to give 10 (X=Cl, Br or I); Cl₂Pt(COD) can cause cleavage of two Ph—Sn bonds to give successively 10 (X=Cl) and Cl₂PhSnCH₂CH₂CO₂Me, as shown in this study. ¹H NMR spectral data for Ph_nX_{3-n}SnCH₂CH₂CO₂Me compounds are given in Table 1.

Crystal structure of 10 (X = I)

The atomic arrangements are shown in Fig. 1. Bond lengths are given in Table 2 and bond angles



Fig. 1. Molecular structure of 10 (X = I).

in Table 3. Compound 10 (X=I) exists as discrete molecules, containing five-membered chelate rings.

The geometry about tin is that of a distorted trigonal bipyramid, the axial atoms being I [Sn-I 2.811(2) Å] and the carbonyl oxygen [Sn-O 2.55(2) Å] with the valence angle, I-Sn-O, equal to $170.5(3)^{\circ}$. The three carbon units are in equatorial sites [Sn-C=2.10(2)-2.16(2) Å]: the sum of the C-Sn-C valence angles is 353.8° .

Intramolecular Sn—O distances in other $RO_2(CH_2)_n$ —Sn compounds are given in Table 4. It can be seen in Table 3 that the Sn—O distance in **10** (X = I) is comparable with those in **1** (Sn—O 2.52), but is appreciably greater than in **2** [Sn—O 2.337(5)–2.357(5) Å]. The sum of the covalent radii of tin and oxygen is 2.13 Å, while the sum of the van der Waals' radii is 3.70 Å. The Sn—I bond distance is relatively long, cf. the value of 2.764(2) Å in the five-coordinate tin compound,²⁰ 3-C-(IBu₂SnCH₂)-1,2:5,6-di-O-isopropylidene- α -D-allo-furanose, in which the intramolecular Sn—O distance is 2.68(2) Å. Sn—I bond lengths in a number of tetrahedral tin compounds range²¹ from 2.69(3) to 2.729(3) Å.

Solution study

Compound 10 (X = I) remains completely chelated in chlorocarbon solvents (CH₂Cl₂ and CCl₄) [ν (CO) 1684 cm⁻¹] as well as in MeCN and THF solutions: the values of ν (CO) for 10 (X = I) in a KBr disc is 1670 cm⁻¹, while ν (CO) for Ph₃SnCH₂ CH₂CO₂Me in KBr is 1740 cm⁻¹. Similar findings are obtained for 10 (X = Cl). As can be seen from the ¹H NMR spectral data given in Table 1, complexation of the MeO₂C group to tin [in Ph_nX_{3-n}SnCH₂CH₂CO₂Me (n=0, 1 or 2)] results in shifts for δ Me and in β -CH₂, from values in Ph₃SnCH₂CH₂CO₂Me.

Sn—I	2.811(2)	SnO(1)	2.55(2)
SnC(1)	2.14(2)	SnC(7)	2.16(2)
Sn-C(13)	2.10(2)	C(13)-C(14)	1.45(4)
C(14)—C(15)	1.48(3)	C(15)—O(1)	1.20(2)
C(15)—O(2)	1.30(3)	C(16)O(2)	1.47(3)
C(1)C(2)	1.38(3)	C(7)—C(12)	1.33(3)
C(2) - C(3)	1.39(3)	C(11)—C(12)	1.37(3)
C(3)-C(4)	1.35(4)	C(10)—C(12)	1.34(4)
C(4)C(5)	1.35(4)	C(9)—C(10)	1.35(3)
C(5)-C(6)	1.38(3)	C(8)C(9)	1.40(3)
C(6)—C(1)	1.37(3)	C(7)C(8)	1.39(3)

Table 2. Bond lengths (Å) for 10 (X=I) with ESDs in parentheses

In CH₂Cl₂ solution, pyridine is able to compete with the intramolecular ester coordination in **10** (X = I) and equilibrium (1) is set up. The value of the formation constant, K_1 , at 25°C was calculated to be 0.07 ± 0.01 dm³ mol⁻¹. Only one pyridine molecule is able to coordinate to **10**. The value of K_1 indicates the difficulty of opening the chelate ring; even in pyridine as solvent, only *ca* 40% has the open structure. One molar equivalents of such donors as 2,2'-bipyridine, acridine and Ph₃P, had no impact on the spectrum of **10** (X = I) in CH₂Cl₂ solution.



The compound $Cl_3SnCH_2CH_2CO_2Me$ has been previously shown to take part in equilibria with pyridine in CH_2Cl_2 solution (Scheme 1).⁶ With $Cl_3SnCH_2CH_2CO_2Me$ 2 (R = Me), both one and two molecules of pyridine could be coordinated; however only on coordination of the second molecule of pyridine is the chelate ring broken.

From comparison of values of K_1 and K_3 , it can be seen that the chelate ring in 10 (X = I) is considerably more resistant to opening than in 13; in other words, the intramolecular ester coordination in 10 (X = I) is surprisingly stronger than that in 13. The relative strengths of the chelate rings in 10 (X = I) and 2 are also borne out by the effects of MeCN on the opening of the chelates.

Formation constants for 1:1 R₃SnCl-py complexes have also been reported :^{22,23} values obtained are 1.9 dm³ mol⁻¹ for R = Me in CCl₄ at 27°C (and also in C₆H₆ at 30°C) and 1.1 dm³ mol⁻¹ for R = Ph

Table 3. Bond angles (°) for 10 (X = I) with ESDs in parentheses

I—Sn—C(1)	96.9(5)	O(1)— Sn — $C(1)$	85.5(6)
I-Sn-C(7)	100.3(5)	O(1)—Sn— $C(7)$	87.2(5)
I—Sn—C(13)	97.6(6)	O(1)—Sn— $C(13)$	73.4(6)
I - Sn - O(1)	170.5(3)	C(1)— Sn — $C(7)$	112.1(7)
C(1) - Sn - C(13)	119.8(7)	C(7)—Sn—C(13)	121.9(7)
Sn-C(13)-C(14)	116.6(14)	C(14)C(15)O(2)	115.4(16)
C(13)-C(14)-C(15)	119.4(19)	C(15)C(16)	116.0(15)
C(14)-C(15)-O(1)	120.0(18)	O(1)-C(15)-O(2)	124.6(16)
C(15)—O(1)—Sn	110.7(11)		
Sn—C(7)—C(12)	123.6(14)	SnC(1)C(2)	122.0(13)
C(7)C(12)-C(11)	123.3(19)	C(1) - C(2) - C(3)	118.9(17)
C(12)C(11)C(10)	120.7(19)	C(2) - C(3) - C(4)	122.1(19)
C(11)C(10)C(9)	117.7(17)	C(3) - C(4) - C(5)	119.6(20)
C(10)C(9)C(8)	122.6(20)	C(4) - C(5) - C(6)	119.2(17)
C(9)C(8)C(7)	117.9(17)	C(5) - C(6) - C(1)	122.4(18)
C(8)C(7)C(12)	117.5(16)	C(6) - C(1) - Sn	120.2(13)
C(8) - C(7) - Sn	118.8(12)	C(2)C(1)C(6)	117.8(16)

Compound	Crystal structure details	v(CO) solid (cm ⁻¹)	Reference
(MeO ₂ CCH ₂ CH ₂) ₂ SnCl ₂	Six-coordinate Sn; bothO complexed SnO 2.52 Å	1675ª	1
$(MeO_2CCH_2CH_2)_2SnCl(8-quinolinate)$	Six-coordinate Sn; one O complexed Sn-O 2.847(4) Å	1732ª 1712ª	10
$(MeO_2CCH_2CH_2)_2Sn(S_2CNMe_2)_2$	Seven-coordinate Sn; one O complexed Sn-O 2.751(5) Å	1730 ^a 1693 ^a	9
$[(MeO_2CCH_2CH_2)_2SnS]_3$	Four-coordinate Sn; noO complexed bridging S	1713	11
MeO ₂ CCH ₂ CH ₂ SnCl ₃	Five-coordinate Sn; O coordinated Sn—O 2.347(5) Å	1658	1
Pr ⁱ O ₂ CCH ₂ CH ₂ SnCl ₃	Five-coordinate Sn O coordinated Sn—O 2.337(5) Å		2
MeO ₂ CCH ₂ CH ₂ SnCl ₂ (S ₂ CNMe ₂)	Six-coordinate Sn; complexed Sn—O 2.436(6) Å	1652	7
MeO ₂ CCH ₂ CH ₂ SnCl(S ₂ CNMe ₂) ₂	Six-coordinate Sn —O not complexed	1724	8
[MeO ₂ CCH ₂ CH ₂ Sn(S)(S ₂ CNMe ₂] ₂	Five-coordinate Sn; O not complexed [Sn———O 3.19]	1730 Åj	11
MeO ₂ CCH ₂ CH ₂ Sn(S ₂ CNMe ₂) [(SCH ₂ CH ₂) ₂ O]	Six-coordinate Sn; O not complexed	-	12
EtO ₂ CCH ₂ CH ₂ Sn(S ₂ CNMe ₂) [(OCH ₂ CH ₂) ₂ NMe]	Six-coordinate Sn; O not complexed		12
EtO ₂ CCH ₂ CH ₂ CH ₂ SnCl ₃	Five-coordinate Sn; O complexed Sn-O 2.405(8) Å	1645	3
MeO ₂ CCH ₂ CH ₂ SnIPh ₂	Five-coordinate Sn; O complexed Sn—O 2.55(2) Å	1684	Ь

Table 4. Crystal structure data for RO₂C(CH₂)_n-Sn compounds

^a V. G. Kumar Das, N. S. Wang and P. J. Smith, *Inorg. Chim. Acta.* 1981, **49**, 149. ^b This study.



Scheme 1.

in C₆H₆ at 30°C. Compounds R₃SnCl and R₃SnI have similar Lewis acidities, and so the reduction of the Lewis acidity of 10 (X = I) arising from chelation can be deduced to be a factor of *ca* 20.

1:1 Complexes of Me₃SnX-py (15) have been isolated; moreover the crystal structure of 15 (X=Cl) has been determined.²⁴ As predicted by the values of the formation constants of 15, it is completely dissociated in non-polar solvents.

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