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The structural behaviour of 2,2-functionally disubstituted triorganotin chlorides

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Abstract

A series of 13 2,2-difunctional triorganotin chlorides of the general formula $Me_2(Cl)SnCH_2CH(X{=}O)Y{=}O$ (X=O, Y=O = $P(O)R_2$, C(O)R; R = O^iPr, OEt, Ph) has been synthesized by chlorination of the corresponding tetraorganotin compounds $Me_3SnCH_2CH(X{=}O)Y{=}O$ with HCl in diethyl ether. The crystal structure determination of $Me_2(Cl)SnCH_2CH[P(O)(O^iPr)_2]_2$ (VIII), IR spectroscopic data and NMR studies reveal, for the title compounds, molecular structures in which the tin atom, approaches a trigonal-bipyramidal pentacoordinated ligand arrangement as result of an intramolecular Sn · · · O interaction of one of the two functional groups X=O or Y=O respectively. In solution the compounds undergo a ligand exchange process which has been investigated by NMR. A mechanism of this process is suggested.

Keywords: Organotin; Diphosphorylmethanes; Pentacoordination; Crystal structure; NMR; IR

1. Introduction

Recently, we reported on the synthesis and chemical behaviour of stannylmethylated diphosphorylmethanes [1] of the general type $Me_3SnCH_2CH[P(O)R_2]_2$ (R = O^iPr, Ph) and some related derivatives bearing C(O)OR and C(O)R groups in the functional substituent [1]. These compounds are of biological interest because methylenebisphosphonates and various of their derivatives are used as therapeutics and diagnostics in bone diseases and calcium metabolism abnormalities [2].

Furthermore, the presence of two P=O donor groups and the tin atom as a potential Lewis-acidic centre within the molecule leads one to expect a rich structural chemistry. Investigations on the alkyldihalostannylmethyl-methylenebisphosphonates $RX_2SnCH_2CH[P(O)(O^iPr)_2]_2$ (R = Me, ^{t}Bu; X = Cl, Br) show that these compounds exist as dimers in the solid state with hexacoordinated tin resulting from intramolecular P=O · · · Sn coordination of one P=O group as well as an intermolecular P=O · · · Sn interaction of the second P=O group with the tin atom of a neighbouring molecule [3]. However, if the proton of the central CH group is substituted by a methyl group, as in $MeBr_2SnCH_2C(Me)[P(O)(O^iPr)_2]_2$, both P=O groups are intramolecularly coordinated and the 2,2-difunctionally substituted propyl group acts as a tridentate ligand in a facial position in the octahedral ligand arrangement at the tin atom [4].

In the case of the compounds $RX_2SnCH_2CH[P(O)(O^iPr)_2]_2$, a concentration and temperature dependent equilibrium exists in solution between dimeric and monomeric species [3a], whereas the solid state structure of $Me(Br)_2SnCH_2C(Me)[P(O)(O^iPr)_2]_2$ remains unchanged in solution [4].

In continuation of our investigations on 2,2-functionally disubstituted organotin compounds, we report here the structural behaviour of triorganotin chlorides of the type $Me_2Sn(Cl)CH_2CH(X{=}O)Y{=}O$ (X=O, Y=O = $P(O)R_2$ or C(O)R; R = O^iPr, OEt, Ph).

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[1] The term "phosphoryl" includes all species containing the P=O group (phosphonates, phosphinates and phosphine oxides).

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Table 2
Selected bond lengths, bond angles and torsion angles of VIII

Bond lengths (Å)		*Bond angles* (°)	
Sn(1)–Cl(1)	2.482(3)	C(1)–Sn(1)–Cl(1)	95.2(2)
Sn(1)–O(6)	2.444(6)	C(15)–Sn(1)–Cl(1)	97.5(3)
Sn(1)–C(1)	2.154(8)	C(16)–Sn(1)–Cl(1)	95.8(4)
Sn(1)–C(15)	2.14(1)	C(1)–Sn(1)–C(15)	120.2(3)
Sn(1)–C(16)	2.11(1)	C(1)–Sn(1)–C(16)	116.7(4)
P(1)–O(3)	1.458(6)	C(15)–Sn(1)–C(16)	119.6(4)
P(2)–O(6)	1.475(6)	Cl(1)–Sn(1)–O(6)	174.2(1)
Torsion angles in the five-membered ring (°)			
Sn(1)–C(1)–C(2)–P(2)	40.7(6)		
C(1)–C(2)–P(2)–O(6)	−31.1(6)		
C(2)–P(2)–O(6)–Sn(1)	8.9(4)		
P(2)–O(6)–Sn(1)–C(1)	8.9(4)		
O(6)–Sn(1)–C(1)–C(2)	−28.0(5)		
C–H · · · O hydrogen bond			
O(3′) · · · C(2)	3.237(9)	O(3′) · · · H(21)–C(2)	157.7(6)
O(3′) · · · H(21)	2.236(9)		

Symmetry code 0.5 − *x*, −0.5 − *y*, −*z*

2. Results and discussion

2.1. Preparative aspects

A series of the title compounds $Me_2(Cl)SnCH_2CH(X{=}O)Y{=}O$ [2] (Table 1) with (i) X=O = Y=O = P(O)R_2 (R = O^{i}Pr, Ph), (ii) X=O = P(O)R_2, Y=O = C(O)R (R = O^{i}Pr, Ph) and (iii) X=O = Y=O = C(O)R (R = OEt, Ph) was obtained by chlorination of $Me_3SnCH_2CH(X{=}O)Y{=}O$ [1] with HCl in diethyl ether:

$$Me_3SnCH_2CH(X{=}O)Y{=}O + HCl \xrightarrow{\text{ether}} Me_2(Cl)SnCH_2CH(X{=}O)Y{=}O + CH_4 \quad (1)$$

I–XIII

Besides **VII**, **X** and **XIII**, which are oils, the title compounds are obtained as colourless, crystalline solids. The reaction yields exclusively the monochlorides, even if an excess of HCl is used. **I–XIII** can also be prepared by a redistribution reaction of $Me_3SnCH_2CH(X{=}O)Y{=}O$ with dimethyltin dichloride.

II and **IV–VII** exist as mixtures of isomers. In the case of **IV** we succeeded in separating one of the two *meso*-forms.

[2] If X=O and Y=O are different, X=O stands for the group with the higher donor strength.

2.2. Structure of I–XIII in the solid state

As indicated by IR spectroscopy (**I**, **IV**, **VIII** and **XI** in KBr, **XIII** as film), solid state ^{31}P NMR (**VIII**) and X-ray crystal structure determination (**VIII**), the symmetrically substituted compounds (X=O = Y=O) contain one intramolecularly tin-coordinated functional substituent resulting in pentacoordination of the metal, whereas the other donor group remains uncoordinated in the solid state.

In the IR spectra of **I**, **IV**, **VIII**, **XI** and **XIII** (Table 1), the valence vibration band of the uncoordinated P=O and C=O group appears at 1216–1244 cm^{-1} and 1670–1736 cm^{-1} respectively. The bathochromic shift of these absorptions for the groups in the coordinated state amounts to 38–76 cm^{-1} for the P=O and 43–45 cm^{-1} for the C=O group. The bands for the coordinated and uncoordinated groups have the same intensity.

The solid state ^{31}P NMR spectrum of **VIII** shows one singlet at 34.6 ppm for the coordinated and another one at 20.1 ppm for the uncoordinated P=O group. The assignment of the signals is in agreement with the low temperature ^{31}P NMR spectrum of **VIII** in solution (vide infra).

The interpretation of the spectroscopic data of the symmetrically substituted compounds **I–XIII** in the solid state is confirmed by the crystal structure determination of **VIII**. The molecular structure of **VIII** is shown in Fig. 1; the most important structural data are

Table 1
^{31}P [a], ^{119}Sn [a] NMR, selected ^{1}H [b] NMR and IR [c] data of $Me_2(Cl)SnCH_2CH(X{=}O)Y{=}O$(I–XIII)

Compound	X=O	Y=O	$\delta^1H(SnCH_3)$ (ppm)	$^2J(^{119}SnC^1H_3)$ (Hz)	$\delta^{119}Sn$ (ppm)	$\delta^{31}P_{X=O}$ (ppm)	$\delta^{31}P_{Y=O}$ (ppm)	$J(Sn,P_{X=O})$ (Hz)	$J(Sn,P_{Y=O})$ (Hz)	$^2J(P,P)$ (Hz)	$\nu(P{=}O)$ (cm^{-1})	$\nu(C{=}O)$ (cm^{-1})
I	$P(O)Ph_2$	$P(O)Ph_2$	0.77	71.0	−17.9(t)	38.5		117.5			1216	
											1178	
II	$P(O)Ph_2$	$P(O)(O^iPr)Ph$	0.57	70.3	−16.8(d/d)	40.7	35.9	64.6	235.6		1209	
			0.63	70.5	−17.2(d/d)	39.6(d)	40.3(d)	34.4	258.7	3.5	1113	
III	$P(O)Ph_2$	$P(O)(O^iPr)_2$	0.77	67.4	−14.7(d/d)	39.5(d)	22.0(d)	35.7	290.1	8.9	1245	
											1126	
IV [d,e]	$P(O)(O^iPr)Ph$	$P(O)(O^iPr)Ph$	0.78	69.4	−17.0(t)	199		41.5			1225	
											1171	
V	$P(O)(O^iPr)Ph$	$P(O)(O^iPr)_2$	0.76	70.0	−13.3(d/d)	43.3	23.9	110.0	238.7		1248	
			0.74	70.0	−12.0(d/d)	42.6(d)	24.6(d)	117.0	192.0	10.0	1156	
VI	$P(O)(O^iPr)Ph$	C(O)Ph	0.85	67.0	16.3(d)	43.3		36.3			1164	1672
			0.82	68.3		46.3		45.9				
VII	$P(O)(O^iPr)Ph$	$C(O)O^iPr$	0.60, 0.69 [f]	(Satell. not	4.7(d)	46.2		51.1			1181	1726
			0.56, 0.66	resolved)	−0.1(d)	44.9		37.2				
VIII	$P(O)(O^iPr)_2$	$P(O)(O^iPr)_2$	0.67	69.7	−9.3(t)	26.5		183.0			1244	
											1168	
IX	$P(O)(O^iPr)_2$	C(O)Ph	0.75	68.2	24.2(d)	26.7		42.0			1184	1686
X	$P(O)(O^iPr)_2$	$C(O)O^iPr$	0.71 [f]	70.6	18.1(d)	28.4		46.8			1185	1740
			0.68	67.4								
XI	C(O)Ph	C(O)Ph	0.69	65.9	65.3							1670
												1627
XII	C(O)Ph	C(O)OEt	0.74	66.1	67.5							1629
												1718
XIII	C(O)OEt	C(O)OEt	0.70	66.0	69.2							1736
												1691
Me_3SnCl			0.69	57.2	164.0							[7,8]

[a] Solvent CH_2Cl_2(I–IX), $CHCl_3$(X–XIII). [b] Solvent $CDCl_3$. [c] I–VI, VIII, IX, XI and XII in KBr; VII, X and XIII as film. [d] Data of one isolated *meso*-form. [e] ^{31}P NMR data of the crude product of IV: racemate: δ 40.0 (d, $J(^{31}P, ^{119}Sn)$ 215, $^2J(^{31}P, ^{31}P)$ 3.4 Hz), 44.8 (d, $J(^{31}P, ^{119}Sn)$ 97.0, $^2J(^{31}P, ^{31}P)$ 3.4 Hz) ppm. *Meso*-forms: δ 41.8 (s, $J(^{31}P, ^{119}Sn)$ 131 Hz) and δ 43.4 (s, $J(^{31}P, ^{119}Sn)$ 166 Hz) ppm. [f] Below coalescence. [g] ^{31}P CP-MAS NMR: VIII: δ 20.0, 34.5 ppm. IX: δ 34.0 ppm.

collected in Table 2. The intramolecular coordination of one $P(O)(O^iPr)_2$ group gives rise to the expected distorted trigonal-bypyramidal ligand arrangement at the tin atom. The hetero atoms are situated in the apical positions, whereas the three carbon atoms and the tin centre define the equatorial plane.

An interesting detail of the structure is the small difference of only 0.017 Å between the P=O bond lengths of the coordinated and the uncoordinated $P(O)(O^iPr)_2$ groups. Apparently, this peculiarity is connected with the existence of a pair of intermolecular hydrogen bonds between the oxygen atom O(3) of the uncoordinated P=O group of a molecule and the acidic hydrogen atom H(21) of the central carbon atom of a neighbouring molecule related to the first by an inversion centre (cf. Fig. 2). Thus dimers of **VIII** are formed in the crystal. The reality of such H···O hydrogen bonds is evident from their geometric parameters given in Table 2 and their being in good agreement with the corresponding criteria developed by Taylor and Kennard [5]. The endocyclic torsion angles indicate, for the five-membered chelate ring in **VIII**, rather a twist than an envelope conformation.

The unsymmetrically substituted compounds (X=O ≠ Y=O; **II**, **III**, **V–VII**, **IX**, **X** and **XII**) exhibit, in the solid state, a similar structure to the symmetrically substituted compounds. But, whereas the two different donor groups compete in solution for the fifth coordination site at the tin atom (vide infra), in the solid state exclusively the group with the higher donor strength (X=O) is coordinated. Accordingly, in the IR spectra of these compounds, one absorption for the coordinated group X=O with the bathochromic shift mentioned above and a second one in the frequency range expected for the uncoordinated P=O or C=O group (Y=O) are observed.

In the solid state ^{31}P NMR spectrum of **IX**, the signal of the $P(O)(O^iPr)_2$ group is shown at 34 ppm. This is the same chemical shift value which has been found for

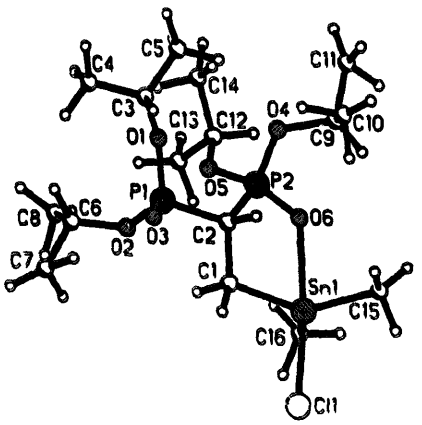


Fig. 1. Molecular structure of $Me_2(Cl)SnCH_2CH[P(O)(O^iPr)_2]_2$ (**VIII**) with atom numbering.

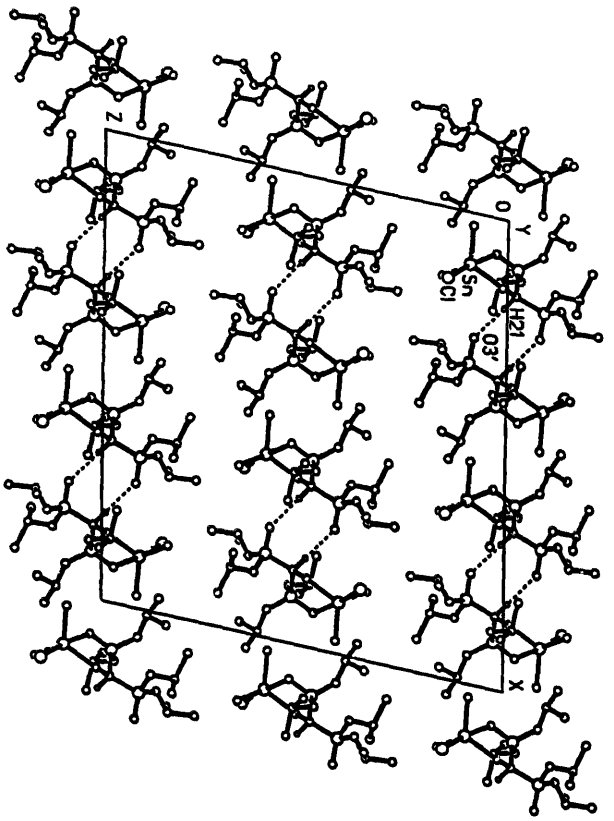


Fig. 2. Crystal packing of $Me_2(Cl)SnCH_2CH[P(O)(O^iPr)_2]_2$ (**VIII**).

the coordinated $P(O)(O^iPr)_2$ group of the bisphosphonate **VIII**.

As expected, the molecular structure of **III** reveals that the $P(O)Ph_2$ group with the higher donor strength is coordinated at the tin atom and the $P(O)(O^iPr)_2$ group remains uncoordinated [6].

The spectroscopic data and the results of the crystal determinations confirm the expected sequence of increasing donor strength for the functional groups X=O and Y=O in the solid state:

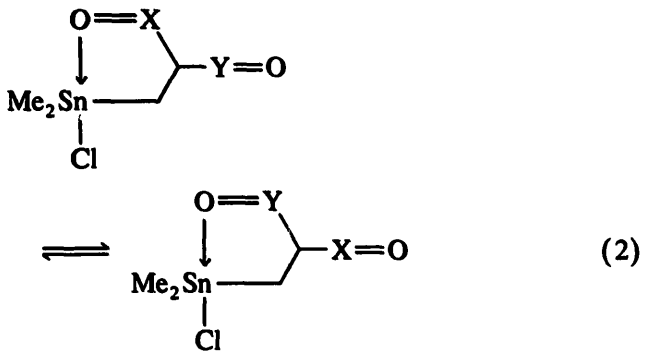
$$C(O)^iPr < C(O)Ph < P(O)(O^iPr)_2 < P(O)(O^iPr)Ph < P(O)Ph_2$$

2.3. *Structure and molecular dynamics of I–XIII in solution*

The main feature of the structures of **I–XIII** in solution is also the trigonal-bipyramidal ligand arrangement around the tin atom. This follows both from the up-field shift of the ^{119}Sn NMR resonance by 95–182 ppm and the increase of the $^2J(^{119}SnC^1H_3)$ coupling constant to 66–71 Hz compared with Me_3SnCl which is tetracoordinated in unpolar solvents ($\delta^{119}Sn = 164$ ppm [7]; $^2J(^{119}SnC^1H_3) = 57.2$ Hz [8]) (Table 1). The correlation between $\delta^{119}Sn$ and $^2J(^{119}SnC^1H_3)$ respectively

and the tin coordination number is well-known [7–10]. In agreement with the monomerism of **I–XIII** (osmometry in $CHCl_3$), the pentacoordination of the tin atom results from an intramolecular P=O or C=O · · · Sn coordination.

Refering to our previous studies on the molecular mobility of 2-phosphoryl-substituted triorganotin halides [3a,11], **I–XIII** are expected to exhibit an intramolecular ligand exchange process according to Eq. (2) in solution:



(2)

The following discussion is focussed on the influence of the functional groups X=O and Y=O on this equilibrium and the exchange mechanism.

2.3.1. Variation of X=O and Y=O

The constant of the above equilibrium is equal to 1 for X=O = Y=O and less than 1 when X=O has the higher donor strength compared with Y=O.

X=O = Y=O. If one of the donor groups is intramolecularly coordinated in **I, IV, VIII, XI** and **XIII**, as a consequence of the asymmetry of the molecules both the protons of the two tin bonded methyl groups and the ^{31}P and ^{13}C nuclei of the P=O and C=O groups respectively should absorb at different frequencies in the appropriate NMR spectra. The appearance of only one signal for the atoms/groups mentioned above in the room temperature NMR spectra of **I, IV, VIII, XI** and **XIII** indicates a fast exchange process compared with the NMR time scale between X=O and Y=O, according to Eq. (2). By recording the NMR spectra at −90°C in CD_2Cl_2 this process can be resolved (only **XIII** shows no signal splitting).

In the low temperature ^{31}P NMR spectrum of **VIII** (Fig. 3) the low-field signal at 33.6 ppm results from the coordinated phosphonyl group, whereas the high-field signal at 21.4 ppm points to the uncoordinated one. This signal assignment is confirmed by the different $J(^{31}P, ^{119}Sn)$ coupling constants. As described for related compounds, the $J(^{31}P, ^{119}Sn)$ coupling constant in the

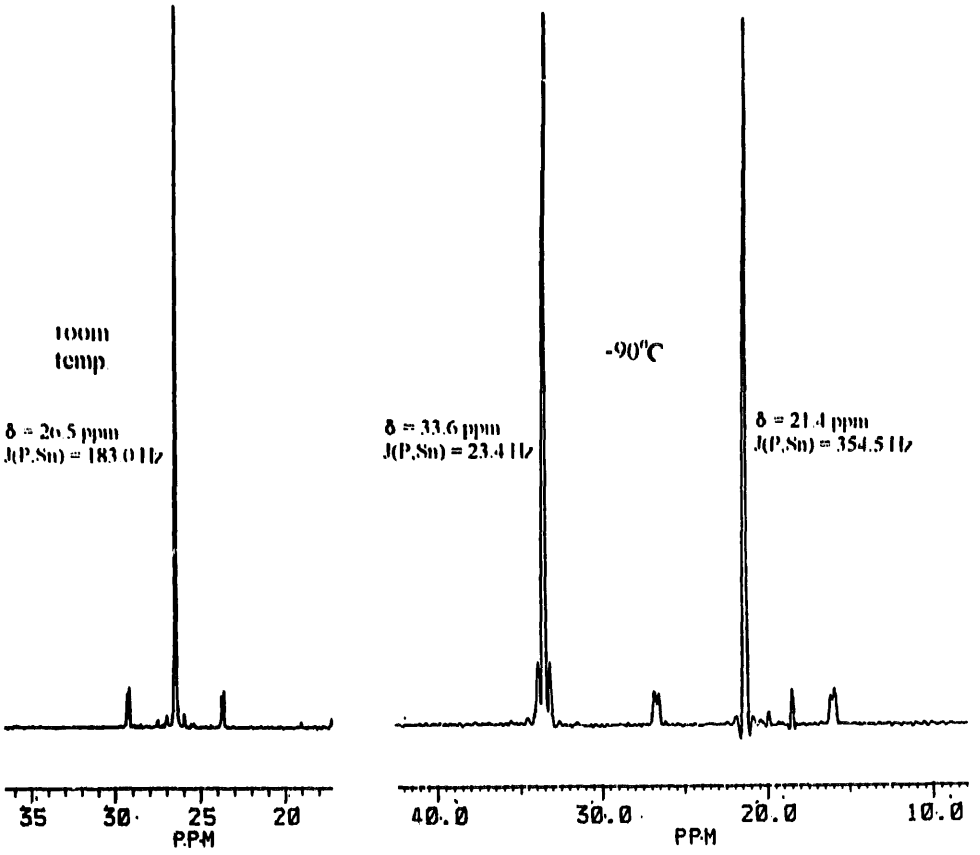


Fig. 3. ^{31}P NMR spectrum of $Me_2(Cl)SnCH_2CH[P(O)(O^iPr)_2]_2$ (**VIII**) in CD_2Cl_2 at room temperature and −90°C (32.4 MHz).

five-membered chelate ring is the sum of $^{3}J(^{31}PCC^{119}Sn)$ and $^{2}J(^{31}PO^{119}Sn)$, which have opposite signs, resulting in a very small value of the observed coupling constant [11,12]. In contrast, there is only one pathway for the coupling between the tin and phosphorus nuclei of the uncoordinated P=O group, giving rise to the observed high value for $^{2}J(^{31}PCC^{119}Sn)$ in **VIII**.

As expected, IR spectroscopy resolves the exchange process and, in the spectra of **I**, **IV**, **VIII**, **XI** and **XIII** in solution, the stretching vibration bands of both the coordinated and the free donor groups appear. As in the solid state (vide supra), the first is bathochromically shifted about 50 cm^{-1} from the latter.

The NMR spectroscopic behaviour of **IV** is more complex. In addition to the two chiral phosphorus atoms, the bridging carbon atom is a centre of pseudoasymmetry [1b,13]. Therefore, the compound exists as the four diastereomers P(*R*)CP(*R*), P(*S*)CP(*S*), P(*R*)C(*r*)P(*S*) and P(*R*)C(*s*)P(*S*), which form a racemate (P(*R*)CP(*R*)/P(*S*)CP(*S*)) and two *meso*-compounds. The phosphorus atoms in the racemate are not equivalent and give rise to an ABX (A,B = P; X = ^{119}Sn) spin system. Each of the two *meso*-compounds appears as an A_2X spin system because here the phosphorus atoms are equivalent [1b,13c]. Therefore, in the ^{31}P NMR spectrum of the crude product of **IV** the two doublet splitted signals (AB part of the ABX spectrum) at 44.8 and 40 ppm ($^{2}J(^{31}P, ^{31}P) = 3.4$ Hz) are indicative of the racemate. The two *meso*-compounds cause singlets (A_2 part of the A_2X spectrum) at 41.8 and 43.4 ppm. One of the *meso*-forms could be isolated as a crystalline compound (for NMR data see Table 3). It is unexpected that the chemical shift difference between the ^{31}P signals in the racemate of **IV** amounts to 4.8 ppm and that the $J(^{31}P, ^{119}Sn)$ coupling constant for the low-field signal is much smaller (97 Hz) compared with that of the high-field resonance (215 Hz). It seems that, on average, one of the phosphinate groups in the racemate of **IV** is favoured for the intramolecular interaction with the tin atom.

X = O ≠ Y = O. For the unsymmetrically substituted compounds **II**, **III**, **V–VII**, **IX**, **X** and **XII** a shift of the exchange equilibrium according to Eq. (2) to the left side (X=O is the group with the higher donor strength) is expected. If both donor groups X=O and Y=O take place in the exchange process the ν(P=O) and ν(C=O)

Table 3
Physical and analytical data of **I–XIII**

Compound	M.p. (°C)	Yield (%)	Formula (M_r)	Analysis Found (Calc.)		
				C	H	Cl
I	253–54	92.3	$C_{28}H_{29}O_2P_2SnCl$ (613.6)	53.31 (54.81)	4.64 (4.75)	6.23 (5.78)
II	153–61 172–82	89.8	$C_{25}H_{31}O_3P_2SnCl$ (595.6)	51.30 (50.41)	5.62 (5.25)	6.21 (5.95)
III	153–54	96.8	$C_{22}H_{33}O_4P_2SnCl$ (577.6)	46.88 (45.75)	5.83 (5.76)	5.80 (6.14)
IV [a]	163–67	95.6	$C_{22}H_{33}O_4P_2SnCl$ (577.6)	44.38 (45.75)	6.01 (5.76)	6.22 (6.14)
V	73–75 98–102	98.2	$C_{19}H_{35}O_5P_2SnCl$ (559.6)	40.72 (40.78)	6.40 (6.30)	6.32 (6.33)
VI	92–94 101–02	87.6	$C_{20}H_{26}O_3PSnCl$ (499.5)	48.28 (48.09)	5.38 (5.25)	7.22 (7.10)
VII	67–72 78–81	98.9	$C_{17}H_{28}O_4PSnCl$ (481.5)	42.38 (42.40)	5.74 (5.86)	7.28 (7.36)
VIII	81–83	90.2	$C_{16}H_{37}O_6P_2SnCl$ (541.6)	35.40 (35.49)	7.15 (6.89)	6.61 (6.55)
IX	85	96.3	$C_{17}H_{28}O_4PSnCl$ (481.5)	42.06 (42.40)	5.80 (5.86)	7.70 (7.36)
X [b]	—	87.6	$C_{14}H_{30}O_5PSnCl$ (463.5)	35.75 (36.28)	6.58 (6.52)	7.62 (7.65)
XI	140	85.3	$C_{18}C_{19}O_2SnCl$ (421.5)	51.57 (51.29)	4.60 (4.54)	8.78 (8.41)
XII	61–64	98.5	$C_{14}H_{19}O_3SnCl$ (389.4)	42.98 (43.18)	4.87 (4.92)	8.79 (9.10)
XIII [c]	—	97.8	$C_{10}H_{19}O_4SnCl$ (357.4)	33.55 (33.61)	5.40 (5.36)	9.87 (9.92)

[a] One *meso*-form; yield corresponds to the oily crude product.
[b] B.p. 130–40°C/0.01 Torr; n_D^{20}: 1.4750. [c] Oil.

bands, for both the coordinated and uncoordinated functional groups, should be detectable in the IR spectra of the compounds in solution. The ratio of the extinctions of these bands should serve as an estimate for the equilibrium shift.

For the mixed P=O, C=O substituted compounds **VI**, **VII**, **IX** and **X**, owing to the lower donor strength of the C=O group, the absorption for the uncoordinated C=O group is stronger than that of the coordinated one. Accordingly, the reverse situation has been found for the P=O bands. Furthermore, the intensity ratio of the absorption of the free to that of the coordinated C=O group is higher for the C(O)O^{i}Pr group in **VII** and **X** than for the C(O)Ph group in **VI** and **IX**, since the latter is the stronger donor. These findings, together with analogous considerations for **II**, **III**, **V** and **XII**, point to the same sequence of increasing donor strength for the functional groups X=O and Y=O as has been found for the solid state:

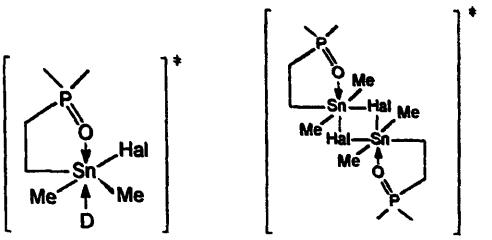
$$C(O)^iPr < C(O)Ph < P(O)(O^iPr)_2 < P(O)(O^iPr)Ph < P(O)Ph_2$$

According to this, in **III** and **VII** with the largest differences of the donor strength between X=O and Y=O also in solution, no detectable absorption for the coordinated group with the lower donor strength ($P(O)(O^iPr)_2$ in **III** and C(O)O^{i}Pr in **VII** respectively) has been found.

The changes of the ^{31}P chemical shifts, as well as the values of the $J(^{119}Sn, ^{31}P)$ coupling constants of the unsymmetrically substituted species **II**, **III**, **V–VII**, **IX** and **X**, in comparison with their parent tetraorganotin compounds $Me_3SnCH_2CH(X{=}O)Y{=}O$ [1b] are in agreement with the results of the IR spectroscopy. In general, the intramolecular interaction of a P=O group with the tin atom in these compounds is accompanied by a down-field shift of the ^{31}P NMR resonance and a decrease of the $^3J(^{119}Sn, ^{31}P)$ value, while a more weakly coordinated or even free P=O group respectively absorbs at about the same frequency as in the parent tetraorganotin derivative and the $^3J(^{119}Sn, ^{31}P)$ coupling constant increases.

Mechanism of the exchange process. Monofunctional triorganotin halides of the type $Me_2(Hal)SnCH_2CH_2P$ (P = P(O)(OEt)$_2$, P(O)(OEt)Ph, P(O)Ph^{t}Bu) undergo a ligand exchange process whose energy barrier decreases dramatically on lowering the donor strength of the P=O group [14]. It has been postulated that the course of this stereoisomerization process depends on the polarity of the solvent. In donor solvents hexacoordinated intermediates of type A are expected (D = solvent molecule), whereas in unpolar solvents the process runs via dimeric species like B.

For **I–XIII** the reverse situation is observed! The configurational stability of these compounds increases

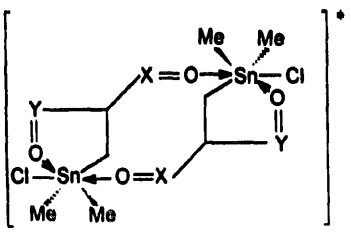


(A) (B)

with decreasing donor strength of the functional groups X=O and Y=O. For example, the $\Delta G^{\ddagger}_{coal}$ value of the exchange process determined by ^{31}P NMR (81 MHz) in CD_2Cl_2 is higher for **VIII** (40.2 kJ mol^{-1}; T_c = 216 K) than for **I** (34.8 kJ mol^{-1}; T_c = 192 K). Furthermore, the ligand exchange for **VIII–X** was investigated by ^1H NMR (200 MHz; $SnCH_3$) in $CDCl_3$ with the following results. **VIII**: above coalescence at room temperature, no change of the spectrum up to 180 K. **IX**: $\Delta G^{\ddagger}_{coal}$ = 60.8 kJ mol^{-1}, K_c = 261 K. **X**: below coalescence at room temperature. Finally, for **IX** a reaction entropy of $\Delta S^{\ddagger} = -150.9$ J mol^{-1} K^{-1} (^1H NMR at 100 MHz in $CDCl_2$) was found, which indicates a transition state with limited mobility and high symmetry.

These results indicate that the uncoordinated donor group of a molecule of **I–XIII** induces the ligand exchange in a neighbouring molecule by intermolecular O ··· Sn interactions via hexacoordinated dimeric species of the type C. Therefore, the ability to induce this exchange process enhances with increasing donor strength of the intramocularly uncoordinated group. Dimers of the type C could be proved by us to be stable also in the ground state for the disubstituted organotin dihalides $RX_2SnCH_2CH[P(O)(O^iPr)_2]_2$ in the solid state and in solution at low temperature [3a].

The decrease of the configurational stability of **I–XIII** with increasing concentration of the compounds in nonpolar solvents or in the presence of donor solvents is in agreement with the suggested mechanism for the ligand exchange in **I–XIII**.



(C)

3. Experimental details

3.1. General comments

The preparation of the starting compounds Me_3Sn-$CH_2CH(X{=}O)Y{=}O$ is described elsewhere [1b].

The NMR spectra were recorded on Bruker AC 80, WP 100, WP 200 and AM 400 spectrometers with TMS (^1H), 85% H_3PO_4 (^{31}P) and Me_4Sn (^{119}Sn) as references. ^{31}P CP-MAS NMR spectra were recorded at 161.9 MHz using spinning frequencies of about 5 kHz.

IR spectra were obtained on a Carl Zeiss Specord 75 IR instrument.

Microanalyses of all compounds were carried out with a Carlo Erba elemental analyser.

3.2. General procedure for the synthesis of I–XIII

To a solution of 0.01–0.1 mol of the tetraorganostannanes $Me_3SnCH_2CH(X{=}O)Y{=}O$ in 20–100 ml of CH_2Cl_2 at −30°C under stirring was added a 10% excess of a 1.5 M ethereal HCl solution. After warming to room temperature and stirring for 1 h, **I–XIII** were precipitated as crude products by slow addition of *n*-hexane. Because of its low solubility **I** partly crystallized during the reaction. **I–XIII** were purified by recrystallization from CH_2Cl_2/hexane or kugelrohr distillation (**VII**, **X** and **XIII**) respectively. The phosphinates **II** and **IV–VII** exhibit a delayed tendency to crystallize (physical and analytical data are given in Table 3).

3.3. Crystal structure determination of VIII

Crystal data: $C_{16}H_{37}ClO_6P_2Sn$, $M = 541.4$, monoclinic, space group $C2/c$, $a = 24.777(3)$, $b = 9.934(2)$, $c = 22.006(4)$ Å, $\beta = 101.70(1)°$, $V = 5304(2)$ Å^3, $Z = 8$ g mol^{-1}, μ(Cu Kα) = 96.47 cm^{-1}, $D = 1.36$ g cm^{-3}, $F(000) = 2224$.

Intensity data for 3602 unique reflections ($2\Theta_{max} = 115°$) of a crystal with approximate dimensions $0.20 \times 0.20 \times 0.25$ mm^3 were measured on a Syntex $P2_1$ diffractometer using graphite-monochromated Cu Kα radiation ($\lambda = 1.54178$ Å). Data correction was carried out in the usual way, empirical absorption and extinction corrections were applied. The structure was solved by heavy atom methods and refined on F by least-squares methods, whereas the H atom positions were geometrically calculated and not refined. For the refinement 2855 reflections with $|F_o| \geq 3.92\sigma(F)$ were used, the final R-value was 0.049 ($R_w = 0.050$). The final atomic coordinates for non-hydrogen atoms are listed in Table 4.

All calculations were carried out on an ESER 1040 computer by use of the programs SHELX-76 [15], SHELXS [16] and GEOME [17]. Figs. 1 and 2 were plotted by means of program XP/PC [18].

Table 4
Fractional atomic coordinates and equivalent isotropic thermal parameters (Å) $U_{eq} = 1/3\Sigma_i\Sigma_j\Sigma_{ij}a_i^* a_j^* a_i \cdot a_j$ for **VIII**

Atom	x	y	z	U_{eq}
Sn	0.11076(3)	−0.16345(6)	0.09309(3)	0.0676(2)
Cl	0.1494(1)	0.0434(3)	0.1486(1)	0.092(1)
P(1)	0.1788(1)	−0.2162(2)	−0.09342(9)	0.0595(8)
P(2)	0.1007(1)	−0.3742(2)	−0.0261(1)	0.0604(8)
O(1)	0.1666(2)	−0.3437(6)	−0.1359(3)	0.077(2)
O(2)	0.1347(2)	−0.1100(6)	−0.1225(2)	0.074(2)
O(3)	0.2358(2)	−0.1702(6)	−0.0826(2)	0.074(2)
O(4)	0.1226(2)	−0.5192(6)	−0.0329(2)	0.074(2)
O(5)	0.0611(2)	−0.3468(6)	−0.0890(2)	0.070(2)
O(6)	0.0764(2)	−0.3589(6)	0.0294(2)	0.074(2)
C(1)	0.1457(4)	−0.1280(8)	0.0125(3)	0.064(3)
C(2)	0.1564(3)	−0.2563(8)	−0.0221(3)	0.054(3)
C(3)	0.2064(4)	−0.413(1)	−0.1644(5)	0.084(4)
C(4)	0.2013(6)	−0.368(2)	−0.2298(5)	0.148(8)
C(5)	0.1952(7)	−0.558(1)	−0.1607(8)	0.160(8)
C(6)	0.1325(4)	−0.048(1)	−0.1819(4)	0.092(5)
C(7)	0.1636(7)	0.087(1)	−0.1747(8)	0.197(7)
C(8)	0.0713(4)	−0.043(2)	−0.2140(7)	0.165(6)
C(9)	0.1352(5)	−0.614(1)	0.0201(5)	0.109(5)
C(10)	0.1981(5)	−0.635(2)	0.0366(9)	0.215(8)
C(11)	0.1105(6)	−0.749(1)	−0.0064(7)	0.177(6)
C(12)	0.0101(4)	−0.422(1)	−0.1125(4)	0.090(5)
C(13)	−0.0316(5)	−0.323(2)	−0.1410(6)	0.148(8)
C(14)	0.0220(6)	−0.525(1)	−0.1585(6)	0.149(8)
C(15)	0.1480(4)	−0.306(1)	0.1619(4)	0.093(5)
C(16)	0.0274(4)	−0.110(1)	0.0863(6)	0.122(6)

4. Supplementary material available

Tables of anisotropic thermal parameters and hydrogen atom coordinates, complete bond lengths, angles and torsion angles for compound **VIII** are available from H.H.

Acknowledgments

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