THE STRUCTURAL BEHAVIOR OF TETRAISOPROPYL ALKYLDIHALOSTANNYLMETHYLMETHYLENEBISPHOSPHONATES $R(\text{Hal})_2\text{SnCH}_2\text{CH}[\text{P}(\text{O})(\text{O}-i\text{-Pr})_2]_2$

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Abstract

The structure of tetraisopropyl 2-(alkyl-dihalostannyl)ethane 1,1-diphosphonates $R(\text{Br})(\text{X})\text{SnCH}_2\text{CH}[\text{P}(\text{O})(\text{O}^i\text{Pr})_2]_2$ (1: $R = \text{Me}$, $\text{X} = \text{Cl}$; 2: $R = \text{Me}$, $\text{X} = \text{Br}$; 3: $R = ^i\text{Bu}$, $\text{X} = \text{Br}$) has been investigated in solution and in case of 3 also in the solid state. 3 crystallizes in the monoclinic space group $P2_1/n$ ($a = 11.909(1)$, $b = 16.089(2)$, $c = 15.473(2)$ Å; $\beta = 104.395$ (9)°; $V = 2871.6$ (6) Å³; $Z = 4$; $R = 0.063$). In the solid state 3 is dimeric as result of intermolecular interaction of one phosphonyl group with a tin atom of a neighboring molecule. The other phosphonyl group in 3 is intramolecularly coordinated to the tin. As shown by ¹¹⁹Sn, ³¹P, and ¹H NMR spectroscopy in nonpolar solvents 1 - 3 exhibit a temperature and concentration dependent monomer-dimer equilibrium.

Introduction

Methylenediphosphonates are very efficient coordinating ligands. Whereas the coordination chemistry of methylenediphosphonic acids with both main group and transition metals is well-known¹⁻⁵ only a few structures of complexes with methylenediphosphonic acid esters are described. In the octahedral copper complex $\{\text{Cu}\{\text{CH}_2[\text{P}(\text{O})(\text{O}^i\text{Pr})_2]_2\}_3\}(\text{ClO}_4)_2$ the diphosphonate is coordinated as a chelating ligand via $\text{P}=\text{O}$ groups.⁶ Between the main group Lewis acid Me_2SnCl_2 and $\text{Me}_2\text{NCH}[\text{P}(\text{O})(\text{OEt})_2]_2$ the formation of a dimeric 1 : 1 complex with the diphosphonate bridging two hexacoordinated tin atoms has been observed.⁷ Finally, in the lanthanide series an iondiameter dependent structural change from monomeric bis-chelate complexes $\text{LnL}_2(\text{NO}_3)_3$ ($\text{Ln} = \text{La-Tb}$) to complexes $[\text{Ln}_2\text{L}_3](\text{NO}_3)_6$ ($\text{Ln} = \text{Dy-Yb}$) containing two chelating and one bridging diphosphonate ligand ($\text{L} = \text{CH}_2[\text{P}(\text{O})(\text{O}^i\text{Pr})_2]_2$) is discussed.⁸

In our investigations on β-difunctional organotin compounds of the type $\text{R}_3\text{SnCH}_2\text{CH}[\text{P}(\text{O})(\text{O}^i\text{Pr})_2]_2$ ⁹ we became interested in the complexation mode of the diphosphonate group in analogous compounds with halogenated tin in which the bidentate $\text{P}=\text{O}$ ligand and the acidic tin atom are part of the same molecule. The monohalogenated species $\text{R}_2\text{Sn}(\text{X})\text{CH}_2\text{CH}[\text{P}(\text{O})(\text{O}^i\text{Pr})_2]_2$ ($\text{X} = \text{Cl, Br}$) always show a pentacoordinated ligand arrangement with only one intramolecularly coordinated $\text{P}=\text{O}$ group. There are no intermolecular $\text{P}=\text{O} \cdots \text{Sn}$ contacts at all.^{9a, b} Obviously,

the simultaneous coordination of both $\text{P}=\text{O}$ groups requires enhanced Lewis acidity of the tin atom which can be achieved by further halogenation.

We report here the structural behavior of 2-(alkyl-dihalostannyl)ethane 1,1-diphosphonates $R(\text{X})_2\text{SnCH}_2\text{CH}[\text{P}(\text{O})(\text{O}^i\text{Pr})_2]_2$ ($R = \text{Me}, ^i\text{Bu}$; $\text{X} = \text{Cl}, \text{Br}$) both in the solid state and in solution.

Materials and Methods

The solvents were dried by standard methods and freshly distilled before use. NMR spectroscopy at ambient temperature in solution was performed at the following frequencies [MHz]: ^1H : 80.1, ^{31}P : 32.4, ^{119}Sn : 29.8. ^{31}P CP-MAS NMR spectra were recorded at 161.9 MHz using spinning frequencies of about 5 kHz. ^{31}P and ^{119}Sn NMR spectroscopy at low temperature was performed in CD_2Cl_2 solutions at 121.4 and 111.9 MHz, respectively. Infrared spectra were obtained in KBr. Syntheses and physical and spectroscopic data of 2 and 3 we have reported previously.^{9c}

Synthesis of $\text{Me}(\text{Cl})(\text{Br})\text{SnCH}_2\text{CH}[\text{P}(\text{O})(\text{O}^i\text{Pr})_2]_2$ (1). To a cooled (-30°C) solution of $\text{Me}_2(\text{Cl})\text{SnCH}_2\text{CH}[\text{P}(\text{O})(\text{O}^i\text{Pr})_2]_2$ ^{9a} (5.4 g, 10 mmol) in 30 ml of dry CH_2Cl_2 were added dropwise with magnetic stirring 1.6 g (10 mmol) of Br_2 , dissolved in 20 ml of dry CH_2Cl_2 . The mixture was kept overnight at ambient temperature and the volatile material was evaporated *in vacuo* (0.01 mm Hg). The solid residue was recrystallized from *n*-hexane to give 1 as colorless crystals: yield 5.6 g (92%); mp $138\text{--}139^\circ\text{C}$. IR $\nu(\text{P}=\text{O})$: $1215/1189\text{ cm}^{-1}$. Anal. Calcd for $\text{C}_{15}\text{H}_{34}\text{P}_2\text{O}_6\text{ClBrSn}$: C, 29.71; H, 5.65. Found: C, 29.68; H, 5.72.

Structure Determination of 3. Suitable single crystals of 3 for X-ray analysis were obtained by recrystallization of the compound from CH_2Cl_2 /*n*-hexane. A summary of crystal data and details of the structure determination are given in Table 1. Lattice constants were obtained by a least-squares treatment of the setting angles of 88 reflections. An approximately linear decrease of the intensity of the standard reflections indicating a deterioration of the crystal quality was observed during the data collection. An appropriate correction for this effect including Lorentz and polarization corrections was applied during the data reduction. An empirical absorption correction based on ψ -scan measurements was performed with maximum and minimum transmission factors of 0.326 and 0.252, respectively. The structure of 3 was solved by the Patterson method (SHELXS-86²⁰). Fullmatrix least-squares refinement on F including all non-H atoms gives anomalously high U_{iso} -values for the terminal C atoms of the isopropoxy groups and the *tert*-butyl group as well as unsatisfactory bond lengths and angles for these groups. Both effects point to disorder phenomena. Consequently, in difference Fourier maps two alternative positions A and B for the two terminal C atoms of one O^iPr -group and for the three terminal C atoms of one ^iBu -group could be detected. The described positional disorder was taken into consideration by relative site occupation factors for the atoms in question refined to 0.55(1) and 0.51(3) (the numbers refer to the position A of the O^iPr - and the ^iBu -group, respectively). The disordered atoms (labeled in Fig. 1 with A and B, respectively) were refined isotropically with group displacement parameters and individual ones were assigned to the C atoms of the remaining O^iPr -groups. All other non-H atoms of 3 were subjected to an anisotropic refinement. H atoms were positioned by geometric calculations and were included using the riding model according to SHELXS-76²¹. Final non-H atomic parameters are summarized in Table 2.

Table 1 Crystallographic data and structure determination details for $t\text{Bu}(\text{Br})_2\text{SnCH}_2\text{CH}[\text{P}(\text{O})(\text{O}^i\text{Pr})_2]_2$ (**3**)

formula unit	$\text{C}_{18}\text{H}_{40}\text{O}_6\text{P}_2\text{Br}_2\text{Sn}$
formula weight	693.0
crystal system	monoclinic
space group	$\text{P}2_1/\text{n}$
$a(\text{\AA})$	11.909(1)
$b(\text{\AA})$	16.089(2)
$c(\text{\AA})$	15.473(2)
$\beta(\text{deg})$	104.395(9)
$V(\text{\AA}^3)$	2871.6(6)
Z	4
F(000)	1384
$D_{\text{calc}} (\text{g} \cdot \text{cm}^{-3})$	1.603
$\mu(\text{Mo K}\alpha) (\text{cm}^{-1})$	37.9
crystal dimensions (mm)	0.38 x 0.46 x 0.40
diffractometer	Stoe Stadi4
temperature (K)	293
check reflections	004, 202, 042
intensity decrease	12.7%, 8.2%, 21.7%
intensity variation	$\pm 6.8\%$, $\pm 4.3\%$, $\pm 12.2\%$
unique reflections	4073
range of measurement (deg)	$3 \leq 2\theta \leq 50$
min. h,k,l/ max. h,k,l	-14, 0, 0/13, 19, 18
reflections observed	2307($I \geq 1.96\sigma(I)$)
reflections/parameter	10.4
weighting scheme	$w = 2.63/(\sigma^2(F_o) + 0.0006F_o^2)$
max. shift/ σ (last l.s. cycle)	0.013
max./ min. $\Delta\rho$ in dimap ($\text{e} \cdot \text{\AA}^{-3}$)	0.71/ -0.72
R (wR)	0.063 (0.068)
goodness of fit (S)	2.99

Results and Discussion

As described earlier^{9c} for **2** and **3** the title compounds are synthesized according to eq.(1).

(1)

1: R = Me, X = Cl

2: R = Me, X = Br

3: R = ^tBu, X = Br

1-3 form air-stable, colorless crystals.

Structure of 3 in the solid state. The mixed halogenated methyltin derivative 1 and the *tert*-butyl compound 3 have been investigated by X-ray crystal structure analysis (the crystal structure of 1 will be published elsewhere¹⁰). Single crystals of 2 were not available. However, the identical ³¹P CP-MAS NMR spectra of 1 and 2 indicate analogous structures for both compounds (Fig.2d; for discussion see next chapter).

Figure 1 Molecular structure of ^tBu(Br)₂SnCH₂CH[P(O)(OⁱPr)₂]₂ (3) with atom numbering

Fig.1 shows the molecular structure of 3 with the adopted labelling scheme. Final atomic coordinates are listed in Table 2. Selected bond distances and bond angles are collected in Table

Table 2 Fractional coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for the non-hydrogen atoms of $\text{tBu}(\text{Br})_2\text{SnCH}_2\text{CH}[\text{P}(\text{O})(\text{O}^i\text{Pr})_2]_2$ (3)

atom	x/a	y/b	z/c	U_{eq}^a
Sn	0.08124(7)	0.19330(5)	0.45345(6)	0.0715(3)
Br1	0.02327(15)	0.26425(10)	0.29790(10)	0.1180(8)
Br2	-0.05212(13)	0.28683(10)	0.52315(11)	0.1071(7)
P1	-0.1223(3)	-0.0478(2)	0.3177(3)	0.084(2)
P2	0.1243(3)	0.0249(2)	0.3417(2)	0.073(1)
O1	-0.1184(7)	-0.1002(5)	0.3955(5)	0.089(4)
O2	-0.0961(8)	-0.0917(6)	0.2369(5)	0.104(4)
O3	-0.2409(8)	0.0003(7)	0.2804(7)	0.132(5)
O4	0.1906(6)	0.0966(5)	0.3892(5)	0.081(3)
O5	0.1570(7)	-0.0614(5)	0.3865(6)	0.096(4)
O6	0.1410(8)	0.0110(6)	0.2469(6)	0.096(4)
C1	0.2504(11)	0.2513(8)	0.5147(9)	0.097(6)
C2	-0.0435(9)	0.0947(7)	0.4158(7)	0.069(5)
C3	-0.0270(9)	0.0431(7)	0.3367(8)	0.074(5)
C4	-0.072(1)	-0.178(1)	0.232(1)	0.134(9)
C5	0.014(2)	-0.189(2)	0.175(1)	0.24(1) ^b
C6	-0.178(2)	-0.231(1)	0.195(1)	0.22(1) ^b
C7	-0.346(2)	-0.040(1)	0.242(1)	0.21(2)
C8	-0.383(2)	-0.007(2)	0.147(1)	0.204(10) ^h
C9	-0.433(2)	-0.014(2)	0.295(2)	0.27(1) ^b
C10	0.288(1)	-0.087(1)	0.409(1)	0.143(10)
C11A	0.315(3)	-0.112(3)	0.507(1)	0.140(6) ^b
C11B	0.344(3)	-0.058(3)	0.505(2)	0.140(6) ^b
C12A	0.285(3)	-0.160(2)	0.345(2)	0.140(6) ^b
C12B	0.288(4)	-0.182(1)	0.401(3)	0.140(6) ^b
C13	0.156(1)	0.080(1)	0.1929(9)	0.117(8)
C14	0.279(1)	0.081(1)	0.181(1)	0.208(10) ^h
C15	0.075(2)	0.068(1)	0.101(1)	0.193(9) ^b
C16A	0.335(3)	0.184(2)	0.562(2)	0.151(6) ^b
C16B	0.351(2)	0.205(2)	0.491(3)	0.151(6) ^b
C17A	0.249(3)	0.319(2)	0.584(2)	0.151(6) ^b
C17B	0.260(3)	0.258(2)	0.615(1)	0.151(6) ^b
C18A	0.298(3)	0.281(2)	0.436(2)	0.151(6) ^b
C18B	0.234(3)	0.340(1)	0.476(2)	0.151(6) ^b

^a $U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^*$; $a_i \cdot a_j$. ^b Isotropic displacement parameters.

3. The large standard deviations obtained for the geometric parameters of 3 can be explained by the slight worsening of the crystal quality during the data collection.

Table 3 Selected bond lengths, bond angles, and torsion angles for $t\text{Bu}(\text{Br})_2\text{SnCH}_2\text{CH}[\text{P}(\text{O})(\text{O}^i\text{Pr})_2]_2$ (3) with standard deviations in parentheses

bond lengths (Å)			
Sn-Br1	2.597(2)	P1-O3	1.588(10)
Sn-Br2	2.608(2)	P1-C3	1.830(11)
Sn...O1'	2.718(9)	P2-O4	1.486(9)
Sn-O4	2.397(8)	P2-O5	1.557(9)
Sn-C1	2.209(9)	P2-O6	1.545(10)
Sn-C2	2.152(11)	P2-C3	1.808(11)
P1-O1	1.460(9)	C2-C3	1.532(17)
P1-O2	1.535(10)		
bond angles (deg)			
C1-Sn-Br1	102.5(4)	P1-O1...Sn'	172.6(4)
C1-Sn-Br2	99.4(3)	C3-P1-O1	116.0(5)
C1-Sn-O4	85.4(4)	C3-P1-O2	104.7(6)
C1-Sn-O1'	85.8(4)	C3-P1-O3	97.4(5)
C2-Sn-Br1	93.8(3)	O1-P1-O2	115.8(5)
C2-Sn-Br2	95.0(3)	O1-P1-O3	115.1(6)
C2-Sn-O4	79.6(4)	O2-P1-O3	105.7(6)
C2-Sn-O1'	77.3(4)	C2-C3-P1	111.3(7)
O4-Sn-Br1	87.0(2)	P2-C3-C2	112.2(7)
O4-Sn-O1'	90.6(3)	P2-C3-P1	116.8(5)
Br2-Sn-Br1	94.6(6)	C3-P2-O4	107.2(5)
Br2-Sn-O1'	87.0(2)	C3-P2-O5	107.4(5)
C1-Sn-C2	157.2(4)	C3-P2-O6	110.2(5)
Br1-Sn-O1'	171.1(2)	O4-P2-O5	115.4(4)
Br2-Sn-O4	174.4(2)	O4-P2-O6	113.9(5)
Sn-C2-C3	113.5(7)	O5-P2-O6	102.6(5)
Sn-O4-P2	115.7(4)		
torsion angles in the five-membered ring (deg)			
Sn-C2-C3-P2	39.3(8)	C2-C3-P2-O4	-29.3(8)
C3-P2-O4-Sn	7.3(5)	P2-O4-Sn-C2	9.6(5)
O4-Sn-C2-C3	-27.2(7)		

As a result of its high Lewis acidity in **3** the tin is hexacoordinated and situated in an octahedral ligand polyhedron. Obviously, for steric reasons only one phosphonyl group of the functional substituent is intramolecularly coordinated whereas the other one interacts with the tin atom of a neighboring molecule resulting in the formation of centrosymmetric dimers. The crystallographically imposed inversion center of the structure coincides with the midpoint of the ten-membered macrocycle formed by the dimerization of **3**.

As for most hexacoordinated diorganotin dihalides reported¹¹ the two alkyl groups in the ligand polyhedron of the tin atom in **3** are *trans*. The two halogen and the oxygen atoms of the two phosphonyl groups, respectively, are *cis*. The deviation of the ligand arrangement from the ideal octahedron is particularly reflected by the small values for the C-Sn-C angle (157,2°) and the two C2-Sn-O angles (77.3 and 79.6°) instead of 180° and 90°, respectively.

The significant difference of 0.32 Å between the two Sn...O distances in **3** points to a remarkably weaker strength of the intermolecular P=O...Sn interaction compared with the intramolecular one (see the behavior of **3** in solution). The P=O bond lengths are not remarkably affected by the interaction of the oxygen with the tin atom and are close to those found in two other methanediphosphonates (twice 1,453(3) Å for Cl₂C[P(O)(O'Pr)₂]₂; 1,472(6) and 1,438(9) Å for Br₂C[P(O)(OMe)₂]₂¹²).

Another interesting detail in the structure of **3** is the nearly linearity of the intermolecular P=O...Sn bridge (P-O-Sn: 172,6°). In general, values between 140 - 165° have been found for this angle in noncyclic compounds.¹³ Obviously, the rigidity of the tricyclic structure of **3** allows for the P=O...Sn bridge only a linear arrangement. The same situation is found in the 4-phosphastanninane Me(Cl)Sn(CH₂-CH₂)₂P(O)Ph which also forms cyclic dimers by intermolecular P=O...Sn interactions (Sn-O-P: 173,5°).¹⁴ In contrast to this is the dimeric adduct {Me₂NCH[P(O)(OEt)₂]₂ · Me₂SnCl₂}₂ with the diphosphonate ligand bridging two hexacoordinated tin atoms. Here, in the resulting more flexible twelve-membered macrocycle the P-O-Sn angle is 150,1°.⁷

The torsion angles of **3** summarized in Table 3 show the five-membered Sn-C2-C3-P2-O4 ring to adopt a twist conformation. The ten-membered ring resulting from the dimerization shows a chair conformation.

The chloro-bromo compound **1** has, in principle, the same structure as compound **3**.¹⁰ But, in contrast to **3** the Sn...O bond distances (2.430(2), 2.497(2) Å) indicate for **1** a similar strength of the intra- and the intermolecular P=O...Sn coordination. Furthermore, for the two different kinds of halogen atoms in **1** a statistical distribution has been observed. This effect is obviously due to halogen exchange reactions in solution which have already been observed in solutions of 1:1 mixtures of diphenyl tin dibromide and -dichloride.¹⁵

Structure of in solution. Diluted (10%) solutions of **1** - **3** in CDCl₃ show resonances in the ¹¹⁹Sn NMR spectra at about -100 ppm. In pyridine one observes a drastic upfield shift of the ¹¹⁹Sn NMR signal to about -250 ppm. Compared with the shift values of Me₂SnX₂ in nonpolar solvents where the tin atom is tetracoordinated (δ_{119Sn}(CCl₄): Me₂SnCl₂: 137,0 ; Me₂SnBr₂: 70,0 ppm¹⁶) and in agreement with the well-known upfield shift of the ¹¹⁹Sn NMR signal with increasing coordination number of the tin atom¹⁷ the data for **1** - **3** (Table 4) indicate in diluted solutions of CDCl₃ pentacoordinated tin and in pyridine hexacoordination by interaction of the strong donor pyridine with the tin atom. The ¹¹⁹Sn NMR signal of **3** in CDCl₃ is a sharp triplet, and neither the δ_{119Sn} value nor the ^aJ(¹¹⁹Sn, ³¹P) coupling constant alter on varying the concentration. On the other hand, the ¹¹⁹Sn NMR signal for **1** and **2** in the same solvent is very broad, and increasing concentration of the solution causes a significant high field shift and an increasing of the ^aJ(¹¹⁹Sn, ³¹P) coupling constant. This indicates for **1** and **2** in nonpolar solvents an equilibrium

Table 4 ^{119}Sn , ^{31}P , and selected ^1H NMR data for $R(\text{Br})(\text{X})\text{SnCH}_2\text{CH}[\text{P}(\text{O})(\text{O}^i\text{Pr})_2]_2$ (1: $R = \text{Me}$, $X = \text{Cl}$; 2: $R = \text{Me}$, $X = \text{Br}$;3: $R = t\text{Bu}$, $X = \text{Br}$)^{a,b,c}

compd	2			3
solvent	CDCl_3 (10%)	CDCl_3 (saturated)	pyridine- d_5 (10%)	CDCl_3 ^{d)} pyridine- d_5 (10%)
$\delta_{^{119}\text{Sn}}$ (ppm)	-100 (br) ^{e)}	-160 (br)	-270 (t, br)	-113.7 (t)
$\delta_{^{31}\text{P}}$ (ppm)	25.5	25.5		25.5
$\nu_{\text{J}}(^{119}\text{Sn}, ^{31}\text{P})$ (Hz) ^{f)}	205.5	262.4	330	168.6
$\delta_{\text{H}}(\text{SnCH}_3)$ (ppm)	1.37	1.27	1.96	
$2\nu_{\text{J}}(^{119}\text{SnC}^1\text{H})$ (Hz)	90.6	96.1	111.5	
$\delta_{\text{H}}(\text{SnCCCH}_3)$ (ppm)				1.46
$3\nu_{\text{J}}(^{119}\text{SnCC}^1\text{H})$ (Hz)				160.6
				179.5

a) As consequence of the Br-C-exchange in solution¹⁵⁾ at room temperature the spectra of 1 are nearly identical with those of 2. b) ^{119}Sn and ^{31}P NMR data of 1 - 3 at -95°C in CD_2Cl_2 : 1: ^{119}Sn δ -274 (v br) ppm. ^{31}P δ 17.8 (m, $^3\text{J}(\text{SnCCP}) \sim 720$ Hz), $^2\text{J}(\text{SnOP})$ not resolved; 33.5 (m, $^0\text{J}(\text{Sn}, \text{P})$ not resolved) ppm. 2: ^{119}Sn δ -264 (d br, $^3\text{J}(\text{SnCCP}) \sim 620$ Hz) ppm. ^{31}P δ 17.5 ($^3\text{J}(\text{SnCCP})$ 629, $^2\text{J}(\text{SnOP})$ 167 Hz); 33.6 ($^0\text{J}(\text{Sn}, \text{P})$ 96 Hz) ppm. 3: Monomer: ^{119}Sn δ -142 (v br) ppm. ^{31}P δ 26.5 (v br) ppm. Dimer: ^{119}Sn δ -249 (d br, $^3\text{J}(\text{SnCCP}) \sim 520$ Hz) ppm. ^{31}P δ 15.5 ($^3\text{J}(\text{SnCCP})$ 516, $^2\text{J}(\text{SnOP})$ 157 Hz); 33.8 ($^0\text{J}(\text{Sn}, \text{P})$ not resolved) ppm. c) ^{31}P CP-MAS NMR of 2: δ 17.3, 32.8 ppm (the spectrum of 1 is identical). d) The NMR data of 3 in CDCl_3 are concentration independent. e) br = broadened signal; d = doublet; m = complex pattern. f) $^0\text{J}(\text{Sn}, \text{P}) = |^3\text{J}(\text{SnCCP})| + |^2\text{J}(\text{SnOP})|$ (intra-molecular).

between monomeric units containing pentacoordinated tin and dimeric species with hexacoordinated tin. **3** does not undergo any association process in nonpolar solvents at room temperature. In agreement with a monomer-dimer equilibrium of **1** and **2** in unpolar solvents is also the concentration dependence of the $^2J(^{119}\text{Sn}^1\text{H})$ coupling constant of the methyl group protons in the ^1H NMR spectra (Table 4). In general, in methyl substituted organotin compounds the value of this coupling constant increases when the coordination number of the tin atom becomes higher.¹⁸ The values of $^2J(^{119}\text{Sn}^1\text{H})$ in pyridine also indicate hexacoordinated tin for **1** and **2**.

Figure 2 ^{31}P NMR spectra of **1** - **3** in CD_2Cl_2 (10%) at a) room temperature, b) -70°C (32.4 MHz), and c) -95°C (121.4 MHz). ^{31}P CP-MAS spectrum of **2** (d) (for spectra data see footnote in Table 4).

Further insight into the structural behavior of **1** - **3** in solution results from low-temperature NMR investigations (Fig. 2; footnote in Table 4). The appearance of only one signal in the ^{31}P NMR spectra of **1** - **3** at room temperature (Fig. 2a) is indicative for a fast intramolecular exchange of both phosphonyl groups at the tin atom, as it is described also for monohalides of the type $\text{R}_2(\text{Hal})\text{SnCH}_2\text{CH}[\text{P}(\text{O})(\text{OR}')_2]_2$.^{9b} On cooling (Fig. 2b,c) this signal splits into two signals indicating a different coordination mode for the two phosphonyl groups. ^{31}P CP-MAS spectra show the same two signals (Fig. 2d). On the basis of earlier experiences^{9b,19} the low-field resonance is assigned to an intramolecular coordinated $\text{P}=\text{O}$ group. Furthermore, the high-field ^{31}P NMR signal of **2** and **3** shows a second pair of satellites (marked with asterisks in Fig. 2c). This is assigned to the intermolecular $^2J(^{119}\text{Sn}^{31}\text{P})$ coupling resulting from the dimerization of **1** - **3** at low temperature. This interpretation is supported by the drastic upfield shift of the ^{119}Sn NMR signal of **1** - **3** on cooling (footnote in Table 4). Whereas the spectra of **1** and **2** below -50° show only the sig-

nals of the dimers, the simultaneous existence of monomeric and dimeric species is indicated by the spectrum of **3**. This means, that in the case of **1** and **2** at low temperature the dimeric form is considerably more stable than the monomeric one, whereas both forms of **3** are of comparable stability. Obviously, this is the consequence of weaker intermolecular $\text{P}=\text{O} \cdots \text{Sn}$ contacts in **3** compared with **1** and **2** as has been established already for the solid state.

The complex pattern of the signals in the low-temperature ^{31}P NMR spectrum of **1** obviously results from the frozen halogen exchange leading to the statistical halogen distribution found for the solid state.¹⁰

Acknowledgment. The authors thank the Fonds der Chemischen Industrie for financial support. F.R. gratefully acknowledges the DAAD (German Academic Exchange Service) for a grant and Professor D.Seyferth (Massachusetts Institute of Technology, Cambridge, USA) for the opportunity to carry out part of this investigations in his laboratory.

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**Received: February 28, 1994 - Accepted: March 22, 1994 - Received
in camera-ready form: April 18, 1994**