Bull Soc Chim Fr (1994) 131, 674-682

Multinuclear magnetic resonance study of sterically crowded stannylphosphines and stannylamines : stereochemical influences on chemical shielding and spin-spin couplings

Armin Dörr, Dietrich Gudat*, Dieter Hänssgen, Heribert Hens, Edith Stahlhut

Anorganisch Chemisches Institut der Universität Bonn, Gerhard Domagk Str 1, D-53121 Bonn, Germany

(received 25 November 1993, accepted 31 March 1994)

Summary – Multinuclear (^{1}H, ^{15}N, ^{29}Si, ^{31}P, ^{119}Sn) NMR data of sterically crowded acyclic stannylphosphines tBu$_3$SnPHY (Y = H, SnMe$_3$, SntBu$_3$, SiMe$_3$; **1-3, 10**), (tBu$_2$RSn)$_2$PH (R = Me, Cl; **4, 5**), tBu$_3$SnPY$_2$ (Y = SnMe$_3$, SiMe$_3$; **6, 11**), PH(SntBu$_2$PHSntBu$_3$)$_2$ (**7**), SntBu$_2$(PY$_2$)$_2$ (Y = H, SiMe$_3$, PHSntBu$_3$; **8, 9, 12**), cyclic stannylphosphines (tBu$_2$SnPY)$_n$ (n = 2, Y = H, C$_3$H$_6$Cl, tBu, SnMe$_3$; **13-16**; n = **3**, Y = H; **18**), (Me$_2$SnPSntBu$_3$)$_2$ (**17**), and stannylamines tBu$_3$SnNHY (Y = H, SnMe$_3$, SntBu$_3$; **19-21**) were obtained by various 1D- and 2D-techniques. ^{31}P- and ^{15}N-shieldings may be explained qualitatively in terms of two counteracting influences, *viz* electronegativity differences and steric requirements of the substituents. In a similar manner, the trends in one-bond coupling $^1K_{SnP}$ and $^1K_{SnM}$ may be rationalized using a simple model based on the deformation of bond angles by sterically demanding substituents. The signs of long-range couplings $^2K_{SnPH}$ and $^1K_{PSnCCH}$ could be determined, which may be useful for future structural studies. Temperature-dependent effects in the spectra of **13, 18** allow conclusions about the conformational dynamics of the molecules.

tin-phosphorus compounds / tin-nitrogen compounds / ^{31}P chemical shifts / ^{15}N chemical shifts / ^{119}Sn chemical shifts / trends in $^1K_{SnP}$ and $^1K_{SnN}$ / ^{119}Sn^{119}Sn and ^{119}Sn^{31}P long-range couplings / phosphorus inversion

Introduction

Organotin compounds with direct bonds between tin and the group 15 elements phosphorus and nitrogen have attracted considerable interest because of the intriguing reactivity of the tin-element bond, which makes these derivatives useful synthetic intermediates and starting materials in organic and element-organic chemistry [1]. In addition to the application of NMR as an analytical tool to determine constitution or purity, information about the nature of the tin-nitrogen bond was gained from analysis of trends in chemical shifts and couplings for various tin-nitrogen compounds [2]. Even if the NMR investigation of tin-phosphorus compounds is much easier, systematic studies have been confined to trimethylstannylphosphines (Me$_3$Sn)$_n$PR$_{3-n}$ (R = H, alkyl, Ph) [2-4]. Recently, by following a familiar concept in element organic chemistry, as yet unknown structural types of stannylphosphines with tin-phosphorus chain or ring structures, respectively, were made accessible via kinetic stabilization by sterically demanding -Sn(tBu)$_2$- and -Sn(tBu)$_3$ groups [5-8]. Initial investigations of the chemical reactivities of these compounds [7, 8] gave evidence for a promising synthetic potential due to the presence of highly reactive phosphorus-hydrogen, phosphorus-tin, or phosphorus-silicon bonds.

In this work, a systematic multinuclear (^{1}H, ^{31}P, ^{119}Sn, ^{29}Si, ^{15}N) NMR study of these novel, sterically crowded stannylphosphines and some related stannylamines is presented. The data give evidence for a marked influence of sterically induced bond deformations and dynamic processes (pyramidal inversion at phosphorus) on the NMR parameters, thus enabling a qualitative discussion of trends in structure and bonding.

Experimental section

Compounds **1, 15** [5], **2-4, 6-8, 14, 16-18** [9], **5** [8], **9, 11, 12** [7], **10** [10], **13** [6], **19** [11], and **20, 21** [12] were prepared following literature procedures. NMR spectra were recorded on Varian FT80 A (^{31}P) and Bruker AMX 300 spectrometers (^{1}H, ^{15}N, ^{29}Si, ^{31}P, ^{119}Sn) equipped with multinuclear units. Samples were measured in C$_6$D$_6$ (5-25% solutions) in 5 mm o.d. tubes at 30°C if not stated otherwise. The spectra of **13** were recorded at 10°C and those of **14, 18** at 70°C, respectively, in order to reduce dynamic broadening effects. Chemical shifts δ^1H [δ^1H(C$_6$D$_5$H 7.15)] and δ^{29}Si (Ξ^{29}Si = 19.867184 MHz) are given relative to

* Correspondence and reprints

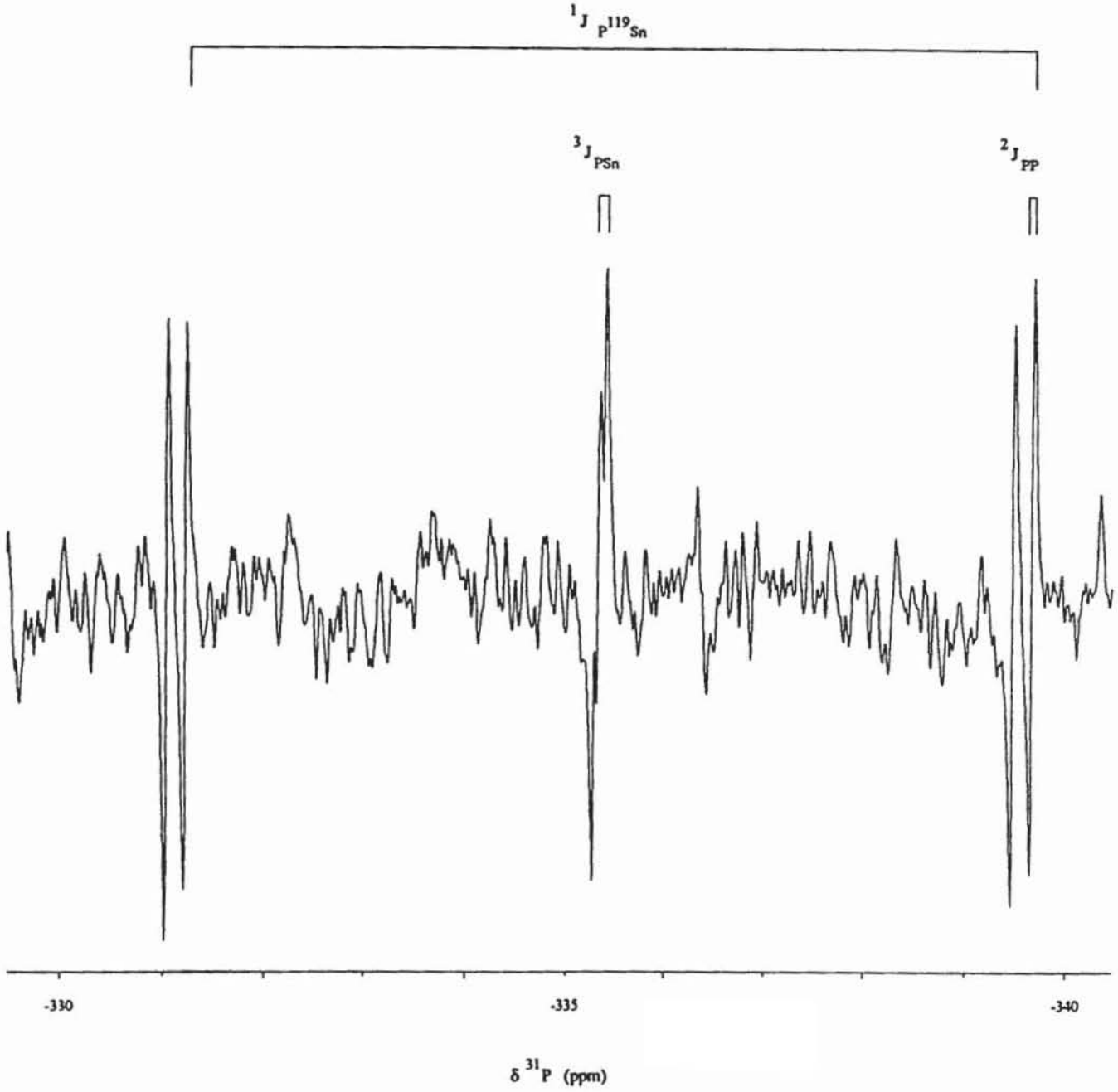

Fig 1. Double quantum filtered 121.5 MHz ^{31}P $\{^1H\}$-spectrum of $(t\mathrm{Bu_2SnPH})_3$, **18**, at 70°C (760 scans; spectral width = 3 300 Hz; 16 K data points; interpulse delays of 3 s; data processing with 3 Hz exponential line broadening). The presence of magnetically active $^{117/119}Sn$ nuclei removes the magnetic equivalence of the ^{31}P nuclei, so that the satellite spectrum may be observed. Since the parent line is suppressed by the double quantum filter, the splitting due to the ^3J (PSn) coupling becomes visible.

external Me_4Si; $\delta^{15}N$ ($\Xi^{15}N$ = 10.136767 MHz) relative to external neat $MeNO_2$; $\delta^{31}P$ ($\Xi^{31}P$ = 40.480747 MHz) relative to external 85% H_3PO_4; $\delta^{119}Sn$ ($\Xi^{119}Sn$ = 37.290665 MHz) relative to external Me_4Sn. Heteronuclear couplings were obtained from ^1H-($^nJ_{PH}$, $^nJ_{SnH}$) or ^{31}P $\{^1H\}$-spectra ($^nJ_{SnP}$). $^2J_{PP}$ between chemically equivalent nuclei was extracted from ^{119}Sn- or ^{29}Si-satellites in normal or double quantum filtered ^{31}P $\{^1H\}$-spectra (fig 1), or by analysis of the AA'XX'-pattern of the PH-resonance (**13**). $^2J_{PP}$ and $^3J_{PH}$ of **9** were calculated from the ^{31}P $\{^1H\}$-spectra of a mixture of isotopomers $H_xD_{2-x}PSn(t\mathrm{Bu})_2PH_yD_{2-y}$ (x,y = 0-2) prepared by partial deuterolysis (CD_3OD/H_2O) [7] of **12**. In order to facilitate the discussion of different heteronuclear couplings, the values of the reduced coupling constants $K_{AB} = 4\pi^2/(h\gamma_a\gamma_b)\ J_{AB}$ are also included where appropriate. All J values are given in Hz; reduced couplings are actually presented as $K \times 10^{-19}$ and are given in SI units (N $A^{-2}m^{-3}$). ^{119}Sn- and ^{29}Si-NMR spectra of phosphine derivatives were in general recorded using the DEPT-sequence based on $^3J_{SnCCH}$(62-95 Hz), $^2J_{SnCH}$ (50-55 Hz), or $^2J_{SiCH}$ (5-6 Hz), yielding the appropriate chemical shifts together with $^nJ_{SnP}$, $^1J_{PSi}$, $^2J_{^{119}Sn^{117}Sn}$ and $^2J_{SnSi}$ (fig 2). The values for $^2J_{^{119}Sn^{117}Sn}$ were converted into $^2J_{^{119}Sn^{119}Sn}$; the accuracy of the couplings is ±1 Hz for $^1J_{SnP}$ and ±0.2 Hz in the other cases. In the case of **5, 14, 18**, where line broadening resulting from dynamic effects or partially relaxed

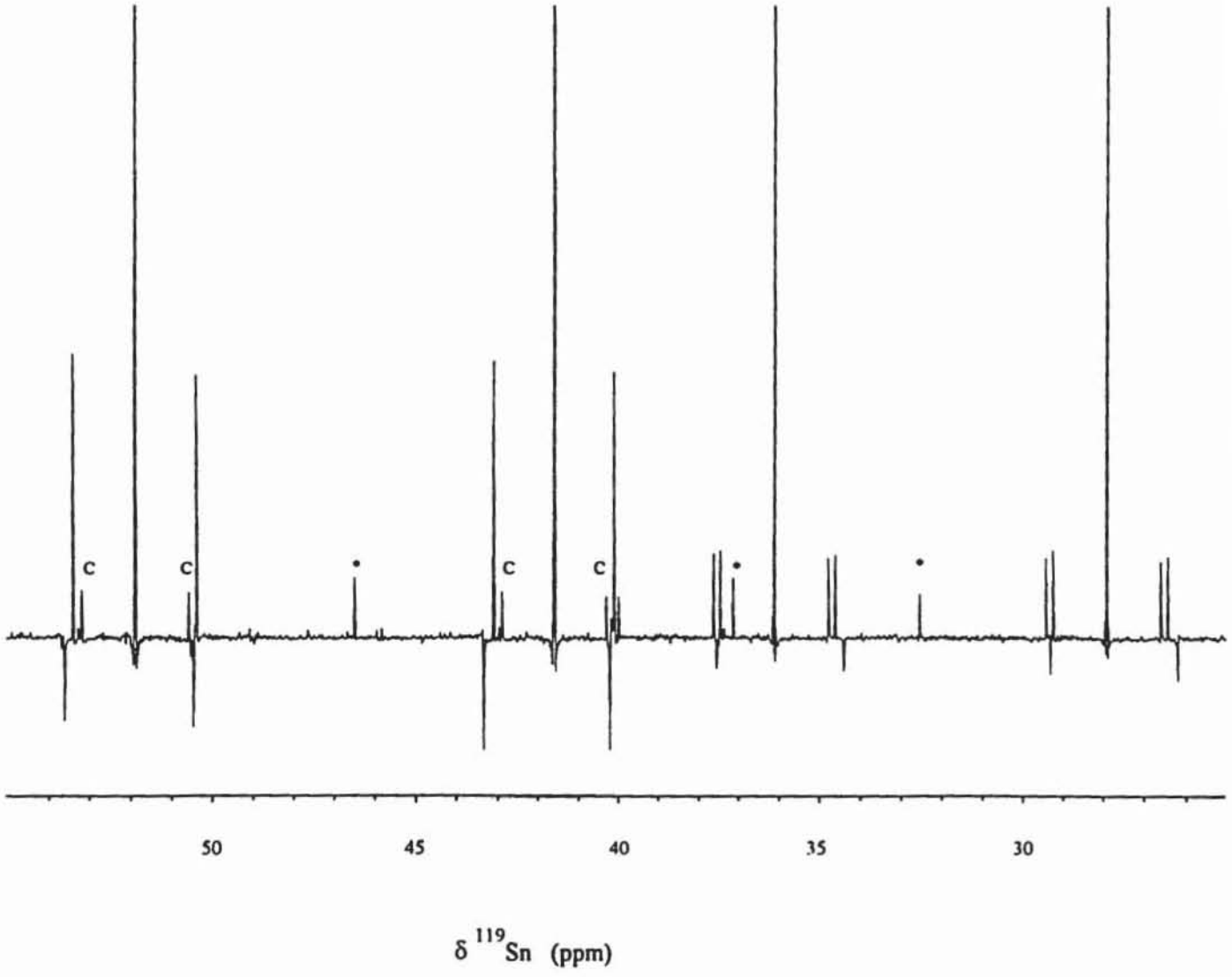

Fig 2. Vertical expansion of the 111.9 MHz ^{119}Sn {^{1}H}-DEPT spectrum of *t*-$Bu_3SnP(SnMe_3)_2$, **6** (256 scans; spectral width = 62 500 Hz; 64 K data points; interpulse delays of 4 s; defocusing delay 7 ms, 10° read pulse; data processing with zero filling to 128 K and gauss filtering). Peaks marked with an asterisk are due to an impurity; (C) denote ^{13}C satellites. $^{117/119}$Sn satellites due to coupling between chemically non-equivalent tin nuclei are present on both signals. The ^{119}Sn satellites show a characteristic phase distortion; the asymmetric appearance results from their nature of AB-type spectra. The $SnMe_3$ resonance (upfield doublet) exhibits an additional single pair of satellites arising from the isotopomer $tBu_3SnP(^{119}SnMe_3)(^{117}SnMe_3)$ where the magnetic equivalence of the $SnMe_3$ groups is removed due to the different isotopic labelling.

couplings to quadrupolar $^{35/37}$Cl-nuclei occurred, the data were obtained from ^{1}H-detected 2D-shift correlations, with couplings being accurate to ±10 Hz. In the same way, ^{15}N NMR data in natural abundance were extracted from ^{1}H-detected ^{1}H/^{15}N-correlation experiments; in addition, $^1J_{SnN}$ of **21** was obtained from the ^{119}Sn-spectrum under suppression of the signal of the ^{14}N-isotopomers with the DEPT-sequence [13].

Results and discussion

Relevant NMR data (^{1}H, ^{15}N, ^{29}Si, ^{31}P, ^{119}Sn) are given in tables I-III (acyclic stannylphosphines), IV (cyclic stannylphosphines), and V (stannylamines). The values of coupling constants are generally shown without a sign. In those cases where signs are explicitly included, their determination is based on the extraction of relative signs of reduced couplings from analysis of 2D-spectra (fig 3) or higher order multiplets. The assignment of absolute signs is based on the following "key couplings" : $^1K_{SnP} < 0$ [4, 14]; $^1K_{SnN} < 0$ [2, 14, 15]; $^1K_{SiP} < 0$ [14]; $^2K_{SnCH} < 0$ [14]; and $^3K_{SnCCH} > 0$ [14].

Chemical shifts

The ^{31}P and ^{15}N resonances of acyclic stannylphosphines **1-6** and stannylamines **19-21** appear at higher field than the parent hydrogen derivatives EH_3 (E = N, P) and further display a marked increase with the number of stannyl groups attached to the phosphorus or nitrogen atom, respectively. The same effects are known for the derivatives $(Me_3Sn)_nPR_{3-n}$ [2-4], and their origin has been related to a low degree of

Table I. NMR data of acyclic stannylmonophosphines $H_nP(SnR_2R')_m(SnR''_2R''')_{3-n-m}$.

		$\delta^{31}P$	$\delta^{119}Sn$	$^1J_{^{119}Sn^{31}P}$[a]	$^2J_{^{119}Sn^{119}Sn}$[a]	δ^1H (PH)	$^1J_{PH}$[a]	$^2J_{^{119}SnH}$[a]
1	tBu$_3$SnPH$_2$	−304.4	29.3	626 (343)	–	0.6	171.3 (35.18)	42.2 (9.37)
2	tBu$_3$Sn^A(Me$_3$Sn^B)PH	−316	38.7 [Sn^A] 23.0 [Sn^B]	896 (491) 755 (414)	388 (230)	nd	163.3 (33.54)	nd
3	(tBu$_2$SnMe)$_2$PH	−339.6	62.1	875 (479)	376 (223)	0.36	161.0 (33.07)	41.7 (9.26)
4	(tBu$_3$Sn)$_2$PH	−325.4	42.0	1 044 (572.0)	515 (305)	0.30	171 (35.1)	31.6 (7.02)
5	(tBu$_2$SnCl)$_2$PH	−295.8	152.1	1 119 (613.1)	236 (140)	1.31	161.4 (33.15)	45.6 (10.1)
6	tBu$_3$Sn^A(Me$_3$Sn^B)$_2$P	−326.8	46.8 [Sn^A]	1 150 (630.1)	351 (208) [$^2J_{Sn^ASn^B}$]	–	–	–
			32.1 [Sn^B]	915 (501)	312 (185) [$^2J_{Sn^BSn^B}$]			

[a] reduced couplings K (in units of 10^{19} N A^{-2} m^{-3}) in parentheses.

Table II. NMR data of acyclic stannyloligophosphines.

		$\delta^{31}P$	$^2J_{PP}$[a]	$\delta^{119}Sn$	$^1J^a_{^{119}Sn^{31}P}$	$^3J^a_{^{119}Sn^{31}P}$	$^2J^a_{^{119}Sn^{119}Sn}$	δ^1H	$^2J_{^{119}Sn^1H}$[a]	$J_{^{31}P^1H}$
7	tBu$_3$Sn^{A}P^{a}HSn^BtBu$_2$ | P^{b}H	−298.7 [P^a]	7.9 (4.0) [P^{a}P^b]	41.2 [Sn^A]	1 022 (560.0) [P^{a}Sn^A]	2.9 (1.5) [P^{a}Sn^B]	501 (297) [Sn^{A}Sn^B]	0.78 [P^{a}H]	31.8 (7.06) 37.2 (8.26)	169 [$^1J_{PA_H}$] 166 [$^1J_{Pb_H}$]
	| tBu$_3$Sn^{A}P^{a}HSn^BtBu$_2$	−272.5 [P^b]	3.2 (1.6) [$^4J_{PaPa}$]	117.1 [Sn^B]	1 107 (606.5) [P^{a}Sn^B] 1 074 (588.4) [P^{b}Sn^B]	4.0 (2.2) [P^{b}Sn^A]	489 (289) [Sn^{B}Sn^B]	1.21 [P^{b}H]	37.3 (8.28)	0.8 [$^3J_{Pa_H}$] 0.9 [$^3J_{Pb_H}$]
8	tBu$_3$Sn^A–PH | Sn^BtBu$_2$ | tBu$_3$Sn^A–PH	−298.8	7.8 (4.0)	41.1 [Sn^A] 119.6 [Sn^B]	+1 024 (−561.0) +1 113 (−609.8)	4.0 (2.2)	533 (316)	0.86	37.3 (8.28) [Sn^{A}H] 31.6 (7.02) [Sn^{B}H]	169 [$^1J_{PH}$] +0.5 [$^3J_{PH}$]
9	tBu$_2$Sn(PH$_2$)$_2$	−288.1	1.1 (0.56)	74.9	650 (356)	–	–	nd	–	174 [$^1J_{PH}$] 2.6 [$^3J_{PH}$]

[a] reduced couplings K (in units of 10^{19} N A^{-2} m^{-3}) in parentheses.

Table III. NMR data of stannyl-silyl-phosphines.

		$\delta^{31}P$	$\delta^{119}Sn$	$^{1}J_{^{119}Sn^{31}P}$[a]	$\delta^{29}Si$	$J_{^{31}P^{29}Si}$	$^{2}J_{^{119}Sn^{29}Si}$	others[a]
10	tBu$_3$SnPHSiMe$_3$	−276.9	25.6	855 (468)	5.15	36.6	37.5	δ^{1}H 0.533 [PH] $^{1}J_{^{31}P^{1}H}$ 181.4, $^{2}J_{^{119}SnH}$ 31.0, $^{2}J_{SiH}$ 5.2
11	tBu$_3$SnP(SiMe$_3$)$_2$	−271.4	30.7	1 028 (563.2)	4.65	38.8	27.9	–
12	tBu$_2$Sn[P(SiMe$_3$)$_2$]$_2$	−252.2	95.1	1 029 (563.8)	4.56	37.7 −3.2 [$^{3}J_{PSi}$]	26.3	$^{2}J_{PP}$ 38.2

[a] reduced couplings K (in units of 10^{19} N A^{-2} m^{-3}) in parentheses.

Table IV. NMR data of cyclic stannylphosphines [tBu$_2$Sn-PR′]$_n$.

		$\delta^{31}P$	$^{2}J_{PP}$[a]	$\delta^{119}Sn$	$^{1}J^{a}_{^{119}Sn^{31}P}$	$^{3}J_{^{119}Sn^{31}P}$	$^{2}J^{a}_{^{119}Sn^{119}Sn}$	δ^{1}H (PH)	$^{2}J_{^{119}SnH}$[a]	$^{n}J_{PH}$
13	*cis*-[tBu$_2$Sn-PH]$_2$	−259.1	39.2 (19.9)	50.1	571 (313)	–	382 (226)	1.87	47.2 (10.5)	144.5 [$^{1}J_{PH}$] 144.5 [$^{1}J_{PH}$]
	trans-[tBu$_2$Sn-PH]$_2$	−263.0	30.5 (15.5)	48.1	584 (320)	–	380 (225)	1.99	47.9 (10.6)	+1.4 [$^{3}J_{PH}$]
14	[tBu$_2$Sn-P(CH$_2$)$_3$Cl]$_2$	−122.7	nd	8.1	763 (418)	–	325 (192)	–	–	–
15	[tBu$_2$Sn-PtBu]$_2$	−50.1	nd	51.3	941 (516)	–	325 (192)	–	–	–
16	*trans*-[tBu$_2$Sn^{A}PSn^{B}Me$_3$]$_2$	−264.8	48.4 (24.5)	108.1 [Sn^{A}]	876 (480)		234 (139) [Sn^{A}Sn^{A}]	–	–	–
				16.3 [Sn^{B}]	1 065 (583.5)	12.6 [Sn^{B}P]	415 (246) [Sn^{A}Sn^{B}]			
17	*trans*-[Me$_2$Sn^{A}PSn^{B}tBu$_3$]$_2$	−223.6	nd	84.3 [Sn^{A}]	789 (432)		688 (407) [Sn^{A}Sn^{A}]	–	–	–
				32.1 [Sn^{B}]	1 209 (662.4)	12.0 [Sn^{B}P]	418 (247) [Sn^{A}Sn^{B}]			
18	[tBu$_2$Sn-PH]$_3$	−335.6	6.0 (3.0)	55.2	1 048 (574.2)	7.0	357 (211)	0.38	−41.9 (+9.30)	160.6 [$^{1}J_{PH}$] 0.6 [$^{3}J_{PH}$]

[a] reduced couplings K (in units of 10^{19} N A^{-2} m^{-3}) in parentheses.

Table V. NMR data of stannylamines.

		δ^{119}Sn	$^2J_{^{119}Sn^{119}Sn}$ [a]	δ^{15}N	$^1J_{^{119}Sn^{15}N}$ [a]	δ^1H (NH)	$^1J_{^{15}N^1H}$	$^2J_{^{119}Sn^1H}$ [a]
19	tBu$_3$SnNH$_2$	−27.9	–	−402.5	113.3 (248.0)	−0.65	62.8	16.5 (3.66)
20	tBu$_3$Sn^{A}NHSn^{B}Me$_3$	−15.7 [Sn^A] 74.5 [Sn^B]	430 (255)	−408.7	nd[b]	−1.50	60.2	18 (4.0) 11 (2.4)
21	(tBu$_3$Sn)$_2$NH	−16.1	381 (226)	−419.3	138.5 (303.2)	−1.87	55.1	+35 (−7.8)

[a] reduced couplings K (in units of 10^{19} N A^{-2} m^{-3}) in parentheses. [b] no unequivocal assignment possible because of low S/N level.

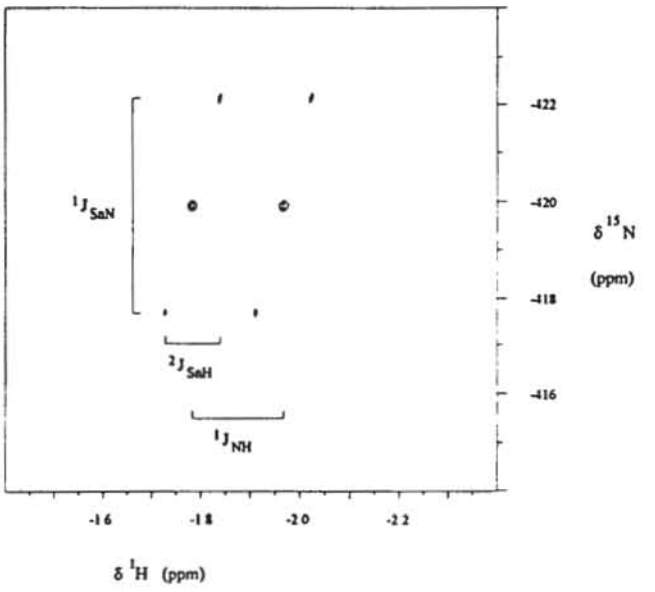

Fig 3. 300.13 MHz ^{1}H-detected ^{1}H/^{15}N heteronuclear HMQC-shift correlation of (tBu$_3$Sn)NH, **21**. 256 experiments of 48 scans and 2K data points were collected; spectral width 1 200 Hz in F2 and 608 Hz in F1; zero-filling to 512 W in F1, shifted sine multiplication in both dimensions. The spectrum is displayed in magnitude mode. The tilt of the cross peaks attributable to the $^{117/119}$Sn satellites gives $^2K(^{117/119}Sn^1H)/^1K(^{117/119}Sn^{15}N) > 0$). Since ^1K ($^{119}Sn^{15}N) < 0$ [2, 14], it follows that ^2K ($^{117/119}Sn^1H) < 0$ and $^2J(^{117/119}Sn^1H) > 0$.

hybridization at phosphorus [3], and low electronegativity and high nuclear polarisability of the adjacent tin nuclei [4]. In addition, the observed values of δ^{31}P (**1-6**) and δ^{15}N (**19-21**) show a strong dependence upon the nature of R in the R$_3$Sn-groups, which can be understood qualitatively on the basis of two major influences. Firstly, the group electronegativity of an R$_3$Sn-moiety is enhanced by σ-acceptor (R = Cl) and attenuated by σ-donor substituents (R = tBu, Me), leading to relative deshielding or shielding, respectively, of the adjacent phosphorus or nitrogen nuclei (see δ^{31}P for (tBu$_2$RSn)$_2$PH : −296 (R = Cl, **5**), −340 (R = Me, **4**)). In the same sense, the strong electron-releasing properties of the tBu-moieties may be held responsible for the fact that the increase in ^{31}P-shielding, which is observed as a consequence of formal replacement of hydrogens in EH$_3$, by R$_3$Sn-substituents, is significantly stronger for R = tBu than for R = Me (δ^{31}P for PH$_3$: −238 [14]; R$_3$SnPH$_2$: −304 (R = tBu, **1**), −269 (R = Me [16]); tBu$_3$Sn(R$_3$Sn)PH : −325 (R = tBu, **3**), −316 (R = Me, **2**). Secondly, intramolecular interactions between bulky stannyl ligands can force enlargement of the valence angles at the central atom, which results in a decrease of nuclear shielding. A similar relation is known for tertiary phosphines [17]. In the case of the extremely large tBu$_3$Sn-group, the effect of sterically induced distortions on the phosphorus or nitrogen shielding counteracts the electronegativity influence, which is seen as the reason for the observed sequence of chemical shifts for (tBu$_2$RSn)$_2$PH (δ^{31}P = −340 (R = Me, **4**), −326 (R = tBu, **3**). The sterically induced bond angle variation is certainly a cooperative quality which is determined by both the number and size of all non-hydrogen ligands present. Since its influence on the phosphorus shielding cannot be neglected in comparison to other effects, it was not possible to derive a simple increment system to predict chemical shifts of stannylphosphines in terms of additive substituent contributions.

Synchronism of both electronegativity and steric factors sufficiently explains the ^{31}P-deshielding in the chain-type stannylphosphines **7-9** and the silylated derivatives **10-12**, in particular, the downfield shifts observed for ^{31}P in **12** and the central ^{31}P nucleus in **7** point to a high degree of local steric hindrance. A significant influence of the ring size on phosphorus shielding is found for the heterocycles [PHSn(tBu$_2$)]$_n$ (n = 2 (**13**), 3 (**18**)). As compared to the chemical shift of the central phosphorus in **7** (δ^{31}P −272.5), which displays a very similar substitution pattern as in the cyclic derivatives, the ^{31}P resonance is shifted to lower field for the four-membered ring derivative, **13** (δ^{31}P = −261 (average)), and to higher field for the six-membered ring compound, **18** (δ^{31}P = −336). The latter suggests that the phosphorus bond angles in the six-membered heterocycle may be somewhat smaller than in the open-chain derivatives.

The observed range of ^{119}Sn chemical shifts indicates tetra-coordination of the tin nuclei in all cases. Even if a consistent theoretical discussion of ^{119}Sn shielding is extremely difficult [2], some qualitative trends emerge from the data in table I-V. The tin nuclei in the stannylamines **19-21** are slightly deshielded (δ^{119}Sn −28 to −16 ppm) with respect to comparable tetraalkylstannanes (tBu$_3$SnMe : δ^{119}Sn −25.4 [2]), reflecting the

higher electronegativity of the amino group. Phosphinyl substituents induce pronounced downfield shifts comparable to those of tin-sulfur or -selenium derivatives [2], which can be attributed to the availability of low lying σ^*(PSn) states. The rather large but non-overlapping ranges observed for the chemical shifts of ^{119}Sn nuclei in tBu$_3$SnP (δ^{119}Sn 25-50 ppm) and tBu$_2$SnP$_2$ fragments (δ^{119}Sn 75-120 ppm), respectively, indicate a sensitive dependence of the shielding on the lowering of the local symmetry [14] as well as on neighboring effects associated with variations in the second coordination sphere. The ^{119}Sn chemical shifts for compounds $(R_3Sn)_nEH_{3-n}$ increase with n for derivatives with E = P, N; however, both systems exhibit a different behavior with respect to variation of R. For stannylamines, the values of δ^{119}Sn increase upon changing from R = Me to R = tBu (see **20** and appropriate examples in [2]). The opposite effect is observed in the phosphine series : in the case of tBu$_3$SnPH$_n$(SnMe$_3$)$_{2-n}$ (n = 1 (**2**), 2 (**6**)), the ^{119}Sn resonances of the nuclei in the tBu$_3$Sn-groups appear at lower field than those of the Me$_3$Sn-group ($\Delta\delta \approx 15$ ppm). Chemical shifts for ^{119}Sn nuclei in tBu$_2$SnP$_2$ fragments are generally higher in cyclic stannylphosphines as in acyclic derivatives, irrespective of the ring size. No simple explanation is present for the unique upfield shift of **14**, however, a higher coordination number at tin resulting from weak intramolecular interactions between tin and the chlorine atoms in the side chains [18] may be of importance.

Coupling constants

Due to the dependence of the signs and values of J_{AB} on the gyromagnetic ratios (γ) of the nuclei, comparisons of couplings involving different elements or even different isotopes of the same element are best done by using the concept of reduced coupling constants $K_{AB} = 4\pi^2/(h\gamma_a\gamma_b)\, J_{AB}$ instead (values are given together with J in tables I-V where necessary). It is recognized that $^1K_{SnP}$ is generally negative [2, 4, 14]; furthermore, $^1K_{SnN}$ has been found to be negative in compounds of the type R_3SnNY_2 [13, 15]. For the following discussion it is therefore assumed that $^1K_{SnE} < 0$ (E = P, N), even if the signs were not experimentally determined for each individual case.

Inspection of the data in tables I-V reveals that variation of the substituents at phosphorus and nitrogen results in similar trends for $^1K_{SnP}$ and $^1K_{SnN}$, respectively, as has been discussed for the ^{31}P and ^{15}N nuclear shieldings. Thus, $^1K_{SnE}$ in **1-12** (E = P) and **19-21** (E = N) changes continually to more negative values with increasing number of stannyl- or silyl-substituents at E. Similar behavior has been previously found for $^1K_{SnP}$ in trimethylstannyl-phosphines $(Me_3Sn)_nPR_{3-n}$ (R = H, Ph, tBu) [3, 4, 16]. Comparison of the values for $^1K_{SnP}$ between compounds with the same number of R_3Sn-substituents indicates that the reduced coupling is also notably affected by the nature of the alkyl group R : $^1K_{SnP}$ is substantially more negative in a fragment tBu$_3$SnP as compared to Me$_3$SnP. The same trend emerges when the values of $^1K_{SnN}$ in **19-21** (table V) are compared with that of $(Me_3Sn)_3N$, **22** ($^1J_{SnN}$ = −84 Hz [15], $^1K_{SnN} = -184 \times 10^{19}$ N A^{-2} m^{-3}). The value of $^1K_{SnP}$ for the common R_3SnP-fragment in $R_3SnPHSnR'_3$ (R = tBu; R′ = Me (**2**), tBu (**6**)) and $(R_3Sn)_2SnPR'$ (R = Me, R′ = Me ($^1J_{SnP}$ = +832 Hz [3, 4], $^1K_{SnP} = -457 \times 10^{19}$ N A^{-2} m^{-3}), tBu (**3**)), respectively, grows more negative when the alkyl substituents in adjacent stannyl groups are changed from R′ = Me to R′ = tBu. As has been discussed in the previous section, this neighboring-group effect strongly suggests that the variations in $^1K_{SnE}$ are to a great part attributable to steric effects which grow in importance with increasing bulk of the stannyl moieties. Again, the same situation has been found for tertiary phosphines R_3P, where $^1K_{PC}$ also adopts more negative values with increasing size of R [17, 19].

Even if it is generally recognized that a concise discussion of substituent effects on $^1K_{SnE}$ (E = P, N) is rather intricate [2, 13, 14], the observed trends indicate that sterically induced expansion of phosphorus or nitrogen valence angles is of major importance. Whereas a moderate variation of the bond angles is expected to have no effect on the hybridization (this seems appropriate at least for E = P [20]), it will result in reduced s-orbital overlap β_{SnE} and concomitantly lower bond energies (and therefore lower σ-σ^* excitation energies). In terms of the Pople-Santry model [21], both factors work to enhance the negative value of the mutual polarizability term and thus produce an overall algebraic decrease of ^1K.

In contrast to the steric influences discussed so far, the electronegativity of R in the R_3Sn ligands seems to exert rather small effects on $^1K_{SnP}$ in **1-11**. The only notable exception is **5**, where the increase of all couplings to the tin nuclei ($^1K_{SnP}$, $^2K_{SnPH}$, $^3K_{SnCCH}$) can be attributed to the presence of the electronegative chlorine atom.

The bond angle influence on $^1K_{SnP}$ is lucidly corroborated by the observed differences between endocyclic and exocyclic couplings in the four-membered ring systems **13-17**, where endocyclic Sn–P–Sn bond angles have been found to be close to 90° [5, 6]. Regarding the low degree of hybridization in the phosphorus valence shell [20], this allows maximum overlap of bonding orbitals, giving less negative values of β_{SnP} as well as higher bond energies. As a result, a net algebraic increase in ^1K is expected, which is in accord with the less negative values observed for $^1K_{SnP,endo}$ (see table IV). Since the endocyclic bonds are fixed within the rigid ring structure, any steric pressure resulting from introduction of additional bulky stannyl groups in **16, 17** is expected to be released predominantly via distortion of the exocyclic phosphorus-tin bonds; consequently, $^1K_{SnP,exo}$ is comparable to the values found for the acyclic derivatives **1-12**. The magnitude of $^1K_{SnP}$ for the six-membered ring system **18** ($^1K_{SnP}$ 574 × 10^{19} N A^{-2} m^{-3}) is only marginally smaller than for the open-chain analogues **7, 8** ($^1K_{SnP}$ 588, (−)610 × 10^{19} N A^{-2} m^{-3} in the PSn^B fragment, table II), indicating that the Sn–P–Sn bond angles in **18** are significantly larger than in four-membered ring systems and presumably come close to those in the open-chain structures.

The magnitude of the geminal couplings $^2K_{SnNSn}$ in **20, 21** (226, 255 × 10^{19} N A^{-2} m^{-3}) is in the same range

as $^2K_{SnPSn}$ in **2-18** (139-407 $\times 10^{19}$ N A^{-2} m^{-3}); no sign information is as yet available. A general correlation of the values of $^2K_{SnESn}$ with structural parameters is not immediately evident, but it appears that changes in both steric requirements and electronegativity of the substituents have effects on the coupling. Considering that quantitative understanding of structural influences upon $^2J_{SnESn}$ is generally difficult [2], no further discussion is attempted.

Data on further long-range couplings ($^2K_{PSnP}$, $^2K_{SnPH}$, $^3K_{PSnPH}$) are included in tables I-V. The signs of $^2K_{SnPH}$ (< 0) and $^4K_{PSnCCH}$ (> 0) were determined from 2D-spectra and may prove valuable as a base for further relative sign determinations. The values of $^2K_{PP}$ are generally small; this is not unexpected regarding the presence of highly electropositive stannyl-substituents as well as steric crowding effects which tend to increase the energies of rotamers with gauche-orientations of phosphorus lone-pairs (this would place bulky stannyl-groups in positions gauche to each other). The absolute values of both $^2K_{SnPH}$ and $^2K_{PSnP}$ show a marked increase in the four-membered ring systems as compared to acyclic derivatives and the six-membered heterocycle **18**. This effect may be attributed to changes in the bond structure discussed above, together with the presence of an additional coupling pathway. The relative magnitudes for the two isomers of **13** ($^2K_{PSnP\ cis} > {}^2K_{PSnP\ trans}$) are in accord with the different dihedral angles between the two phosphorus lone pairs [22].

Conformation and stereoisomerism

All studied substrates except **13** display a single set of NMR signals, indicating that these molecules may be described in terms of a single stereoisomer on the NMR time scale. According to their ^{1}H-spectra, the two sets of signals in the case of **13** can be assigned to stereoisomers with *cis*- or *trans*-orientation of the phosphorus substituents relative to the four-membered ring. From the integration of relative intensities, the *trans*-isomer is slightly energetically favored ($\Delta G = 0.3$ kJ mol^{-1} at 298 K). The dynamic interconversion of both isomers at elevated temperatures has been reported previously [6]. In the case of **14**, a similar isomerization process is suggested by the observed temperature dependence of the ^{31}P- and ^{119}Sn-NMR spectra which show substantial dynamically induced line broadening at ambient temperature. However, owing to the extremely low solubility at temperatures below 0°C, no spectrum in the slow exchange limit could be obtained. No evidence for dynamic changes was detected for the remaining four-membered ring systems, **15-17**, suggesting that these derivatives exist in a stable conformation. The number and multiplicity of the signals in the ^{1}H- and ^{13}C-spectra is in accord with *trans* (C_{2h})-rather than *cis* (C_{2v})-substitution, in analogy to the solid state structures of **13** and **15** [5, 6]. It may be proposed that the *cis*-isomers are in this case destabilized owing to energetically unfavorable interactions between the bulky phosphorus ligands.

Temperature-dependent line-broadening effects similar to that of **14** were also observed for the six-membered heterocycle, **18**. At the high temperature limit, only a single set of sharp signals is found for all *t*Bu- and PH-moieties, respectively, indicating an effective molecular symmetry of D_{3h}. Since no static molecular conformation of appropriate symmetry is possible to give a pyramidal coordination geometry at the phosphorus centers, the observed symmetry must be explained by dynamic averaging between different conformational isomers via configuration inversion. To be observed spectroscopically, the dynamic process must involve diastereomers with different orientation of the PH-hydrogens relative to the ring plane (*cis-trans-trans* and all-*cis* stereoisomers), but the NMR data allow no conclusion if the six-membered ring has a planar or rapidly inverting, puckered structure.

Even if different diastereomers are expected for the acyclic stannyl-phosphines **7-9** due to the presence of two chiral phosphorus centers, only a single set of NMR signals is observed, and no dynamic broadening effects are detectable in this case. This suggests that as in the cyclic systems, configuration inversion at phosphorus occurs very easily. The comparison of the extent of the dynamic effects in the spectra of cyclic (**13, 18**) and acyclic (**7, 9**) stannylphosphines indicates that the inversion process is fastest in the open chain derivatives and becomes consecutively slower with smaller ring sizes.

Acknowledgment

Financial support by the Fonds der Chemischen Industrie is gratefully acknowledged.

References

1 Schumann H, Schumann I, *Organotin Compounds*, Gmelin Handbook of Inorganic and Organometallic Chemistry, Pt 18, Springer, Berlin (1990); *ibid*, Pt 19 (1991)

2 Wrackmeyer B, in *Annual Reports on NMR Spectroscopy*, GA Webb Ed, Vol 16, Academic, London (1985) pp 73ff

3 Schumann H, Kroth HJ, *Z Naturforsch* (1977) 32b, 513; *Z Naturforsch* (1977) 32b, 876; *Z Naturforsch* (1981) 36b, 904

4 Mc Farlane W, Rycroft DS, *J Chem Soc Dalton* (1974) 1977

5 Hänssgen D, Aldenhoven H, Nieger M, *J Organomet Chem* (1989) 367, 47

6 Hänssgen D, Aldenhoven H, Nieger M, *Chem Ber* (1990) 123, 1837

7 Hänssgen D, Aldenhoven H, *Chem Ber* (1990) 123, 1833

8 Hänssgen D, Stahlhut E, Aldenhoven H, Dörr A, *J Organomet Chem* (1992) 425, 19

9 Dörr A, Dissertation, University of Bonn, 1992

10 Aldenhoven H, Dissertation, University of Bonn, 1990

11 Götze HJ, *Angew Chem* (1974) 86, 104

12 Hens H, Diploma Thesis, University of Bonn, 1992

13 Kupce E, Wrackmeyer B, *J Magn Res* (1992) 97, 568

14 Mason J, *Multinuclear NMR*, Plenum, New York, 1987

15 Wrackmeyer B, Zhou H, *Magn Res Chem* (1990) 28, 1066

16 Norman AD, *J Organomet Chem* (1971) 28, 81

17 Mann BE, *J Chem Soc Perkin Trans II* (1972) 30

18 Kober C, Kroner J, Storch W, *Angew Chem* (1993) 105, 1693

19 Quin LD, "Stereospecificity in ^{31}P-^{13}C Coupling", in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, Verkade JG, Quin LD Eds, VCH, Deerfield Beach, 1987, 391ff

20 Kutzelnigg W, *Angew Chem* (1984) 96, 262; *Angew Chem Int Ed Engl* (1984) 23, 272; Magnusson E, *J Am Chem Soc* (1984) 106, 1177, 1185

21 Pople JA, Santry DP, *Mol Phys* (1964) 8, 1

22 Gil VMS, v Philipsborn W, *Magn Res Chem* (1989) 27, 409