SYNTHESIS, LITHIATION AND PREFERRED CONFORMATIONS OF SOME α-SILYLATED AND α-STANNYLATED PHOSPHINES

Bernd Kowall* and Joachim Heinicke*

Department of Chemistry, Ernst-Moritz-Arndt-University of Greifswald,
Soldtmannstr. 16, D-17487 Greifswald, Germany

Abstract

Several phenyl substituted functional methylphosphines bearing a silyl or a stannyl residue in α-position, $PhP(R)CH_2EMe_3$ **1-4**, $PhP(CH_2EMe_3)_2$ **5,6**, $Ph_2PCH(SiMe_3)(SnMe_3)$ 7, the stannylene-bridged *rac/meso*-$(Ph_2PCHSiMe_3)_2(SnMe_2)$ **8** and the α-silylated silylphosphine $PhP(SiMe_3)CH_2SiMe_3$ **9**, are prepared by the reaction of lithio phosphides with halomethylsilanes and -stannanes. The tin compounds offer an efficient synthetic access to α-lithiated phosphines which have a broad potential for the synthesis of α- and β-functional phosphines. Multinuclear NMR analysis of the silyl-, stannyl- and the mixed silylstannyl derivative indicates preferred conformations with strongly different $^2J(^{31}P,^{29}Si)$ and $^2J(^{119}Sn,^{31}P)$, respectively.

Introduction

Organostannanes with a phosphino or a $P(0)R_2$ substituent in ω-position have been studied extensively because of the reactivity at both the organotin and the organophosphorus group, and because of their interesting structural properties [1]. Moreover, they have been used for the preparation of transition metal stannyl complexes [2]. While much work has been focussed on β- or γ-P-substituted organostannanes which are useful for the synthesis of heterocycles or studies of intramolecular interactions, less attention has been paid to stannanes with an organophosphorus group in an α-position [3]. Nevertheless, these compounds offer access to several ways of lithiation and may therefore be considered as precursors for mono- or dilithiated phosphorus species. Thus, they have a great potential for the synthesis of α- and, by reaction with carbonyl compounds, β-functionalized phosphines which are of major interest in complex chemistry and homogenous catalysis [4,5]. Lithiation is made possible either by lithio-destannylation, or by the enhancement of CH-acidity due to the presence of geminal phosphino and silyl groups. Moreover, preparation of secondary, α-metallated phosphines allows lithiation on phosphorus as a competing process. Furthermore, the plethora of NMR active nuclei makes this class of compounds attractive for multinuclear NMR analysis and discussion of conformational behaviour. Here, we report on the synthesis of α-stannylated phosphines and analogous silicon compounds and discuss NMR data which indicate in some compounds preferred conformations.

Materials and Methods

All reactions were carried out under argon in dried solvents. Ph_2PH [6], $PhPH_2$ [7] and Me_3SnCH_2I [8] were prepared as previously described. NMR spectra were recorded using a Bruker ARX300 spectrometer operating at 75.43 MHz (^{13}C), 59.63 MHz (^{29}Si), 121.44 MHz (^{31}P) and 111.82 MHz (^{119}Sn). The references used were internal TMS, external 85% H_3PO_4 and external Me_4Sn respectively. Coupling constants with tin refer to the ^{119}Sn nucleus. All compounds were measured as solutions in C_6D_6.

Procedure, representative for the preparation of compounds **1 - 6** :

41.0 ml (50 mmol, 1.22 M) *n*BuLi in hexane were slowly added to 5.50 ml (50 mmol, 5.50g) $PhPH_2$ in 40 ml of THF at 0°C. The orange solution was brought to room temperature and stirred for 3h. After cooling to -15°C, 7.0 ml (50 mmol, 6.13g) Me_3SiCH_2Cl in 20 ml THF were added dropwise to the solution within 10 min. producing a colourless solution. Stirring was continued for 3h, THF removed in vacuo, 50 ml pentane were added and LiCl filtered off. After removal of pentane, 9.4 g (96%) of pure $PhP(H)CH_2SiMe_3$ **3** were

obtained. Upon distillation at 85°C/ 3 Torr partial decomposition took place yielding 6.0g (61%) of a colourless liquid.

$Ph_2PCH_2SiMe_3$ **1**: colourless liquid, b.p. 120°C / 0.3 Torr, yield 68 %.

$Ph_2PCH_2SnMe_3$ **2**: colourless liquid, crystallizing slowly, b.p. 130°C / 0.01 Torr, yield 27 %.

$PhP(H)CH_2SnMe_3$ **4**: colourless liquid, decomposition upon distillation, NMR yield >95 %.

$PhP(CH_2SiMe_3)_2$ **5**: colourless liquid, b.p. 105°C / 0.05 Torr, yield 50 %.

$PhP(CH_2SnMe_3)_2$ **6**: slightly yellow liquid, b.p. 100°C / 0.02 Torr, yield 59 %.

Procedure, representative for the preparation of **7** *and* **8**.

7.0 ml (10.0 mmol, 1.43 M) *n*BuLi in hexane were added dropwise over 10 min. to a solution of 2.7g (10.0 mmol) $Ph_2PCH_2SiMe_3$ **1** and 1.49 ml (1.16 g, 10 mmol) TMEDA in 10 ml pentane at 0°C. After 20 min. the solution was brought to room temperature and stirred for another 45 min. 2.2g (11.0 mmol) Me_3SnCl in 15 ml pentane were added slowly at 0°C. After stirring 2h at room temperature, LiCl was filtered off, and the solvents were removed. The remaining colourless solid was distilled at 150°C / 0.02 Torr to give 2.0g (4.6 mmol) 46%) $PhPCH(SiMe_3)SnMe_3$ **7** .

rac, meso-$[Ph_2PCH(SiMe_3)]_2SnMe_2$ **8** . The reaction product was contaminated by unreacted Me_2SnBr_2 and $Ph_2PCH_2SiMe_3$ (NMR yield 75%).

rac-**8** : ^{31}P NMR: δ -12.8 ppm. ^{119}Sn NMR: δ 7.5 ppm (t, ^2J(SnP) = 108.5 Hz). ^{1}H NMR: δ -0.05 (^4J(PH) = 0.65 Hz, 18H, $SiMe_3$), 0.62 (^2J(SnH) = 51.0, ^4J(PH) = 0.75 Hz, 6H, $SnMe_2$), 1.71 (^2J(SnH) = 65.4 Hz, 2H, C*H*), 6.96 - 7.20 (12H, Ph), 7.42 - 7.72 ppm (8H, Ph).

meso-**8** : ^{31}P NMR: δ -12.1 ppm. ^{119}Sn NMR: δ 5.5 ppm (t, ^2J(SnP) = 57 Hz). ^{1}H NMR: δ - 0.04 (^4J(PH) = 0.75 Hz, 18H, $SiMe_3$), 0.64 (^2J(SnH) = 49.8, 6H, $SnMe_2$), 1.71 (^2J(SnH) = 65.4 Hz, 2H, C*H*), 6.96 - 7.20 (12H, Ph), 7.42 - 7.72 ppm (8H, Ph).

^{13}C NMR data could not be assigned unequivocally due to impurities and due to the presence of two pairs of diastereotopic phenyl rings.

$PhP(SiMe_3)CH_2SiMe_3$ **9** : To a solution of 2.46 g (12.5 mmol) $PhP(H)CH_2SiMe_3$ **3** in 10 ml of THF were added slowly 11.5 ml (12.5 mmol, 1.09 M) *n*BuLi in hexane at 0°C. The orange reaction mixture was stirred for 2h. 1.89 ml (1.62g, 15.0 mmol) Me_3SiCl in 5 ml THF were added within 10 min, and the solution turned colourless. After stirring for 30 min THF was removed and 20 ml pentane were added. After filtration the crude product was distilled, b.p. 62°C / 0.1 Torr, yield 1.5 g (5.6 mmol, 49%). Repetition of the reaction with a 2.1 fold excess of *n*BuLi and Me_3SiCl gave an identical product.

Lithiodestannylation of $PhP(CH_2SnMe_3)_2$ **6** *and subsequent reaction with Me_3SiCl.*

2.0 g (4.31 mmol) $PhP(CH_2SnMe_3)_2$ **6** were dissolved in 10 ml THF at -70°C and 7.75 ml (9.46 mmol, 1.22 M) *n*BuLi in hexane were added within 10 min.The solution turned dark yellow and was stirred for 4h at -78°C. 1.23 ml (1.06 g, 9.8 mmol) Me_3SiCl were added, and the reaction mixture was allowed to come to room temperature overnight. After removal of THF, 20 ml pentane was added, LiCl filtered off, and the solvents were removed in vacuo. ^{1}H and ^{31}P NMR spectra indicated complete formation of $PhP(CH_2SiMe_3)_2$ **5** . $Ph_2PCH_2SnMe_3$ was converted to $Ph_2PCH_2SiMe_3$ in an analogous manner.

Results and discussion

We investigated several methods for the preparation of α-stannylated and α-silylated phosphines. Two procedures (eq. 1 and 2) were found to be suitable for preparative purposes. Lithiation of primary or secondary phenyl phosphines with BuLi and subsequent reaction with halotrimethylsilane or stannane gives the α-metallated secondary or tertiary phosphines **1** - **6** in almost quantitative NMR yields (eq. 1). In a similar method reported by Wolfsberger, Ph_2PNa is used as starting material for the preparation of $Ph_2PCH_2SiMe_3$ **1**. The latter is, however, contaminated with Ph_2PCH_3 (7%) [9]. The bis(trimethylsilyl-methyl)phosphine **5** can also be obtained by a Grignard procedure [10] .

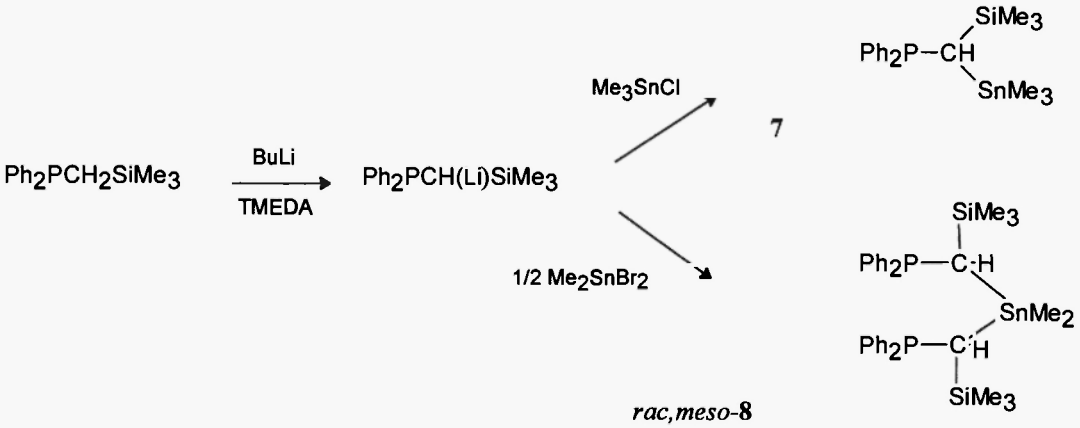
$$PhP(R)H \xrightarrow{BuLi} PhP(R)Li \xrightarrow{Me_3ECH_2X} PhP(R)CH_2EMe_3 \qquad (1a)$$

R = Ph, E = Si: **1**; E = Sn: **2**
R = H, E = Si: **3**; E = Sn: **4**

$$PhPH_2 \xrightarrow{2\ BuLi} PhPLi_2 \xrightarrow{2\ Me_3ECH_2X} PhP(CH_2EMe_3)_2$$

R = Ph, E = Si: **5**; E = Sn: **6** (1b)

A second method (eq. 2) benefits from the increased CH-acidity of **1** [11] obtained according to equ. 1(a). Two diastereomers of compound **8** are formed in a *rac/meso* ratio of ca. 1.4 / 1 (cf. NMR discussion below).



(2)

Efforts to prepare **1** and **2** by reaction of the Ph_2PCH_2Li-TMEDA complex [12] with Me_3SiCl and Me_3SnCl, respectively, (eq. 3) lead to product mixtures. These contain the desired α-metallated compounds in yields up to 65 %, the starting phosphine Ph_2PCH_3, and small amounts of two by-products (up to 10 %) presumably resulting from lithiation of the aromatic ring [12,13]. Separation of these mixtures by distillation was not successful.

$$Ph_2PCH_3 \xrightarrow[TMEDA]{BuLi} Ph_2PCH_2Li \cdot TMEDA \xrightarrow{Me_3ECl} Ph_2PCH_2EMe_3$$

E = Si: **1**; E=Sn: **2** (3)

In an alternative procedure, an α-lithio stannane, Me_3SnCH_2Li, prepared by Kauffmann's method [14], is trapped with Ph_2PCl (eq. 4). The desired α-stannylated phosphine **2** is not detected at all in the product mixture which consists of several unidentified compounds.

$$Me_3SnCH_2I \xrightarrow{BuLi} Me_3SnCH_2Li \xrightarrow{Ph_2PCl} Ph_2PCH_2SnMe_3$$

2 (4)

***Lithiation of* 2, 3 *and* 6.**

As described above, lithiation of Ph_2PMe with *n*BuLi/TMEDA does not occur in a quantitative manner; upon reaction of the Ph_2PCH_2Li·TMEDA complex with D_2O a maximum degree of H/D-exchange of 84 % is observed [12]. An analogous investigation of $PhPMe_2$ indicates that dilithiation takes place to an extent of only 35 % [12]. However, lithiodestannylation, which is known to occur smoothly in the reaction of unsymmetrical tetraalkyl stannanes with MeLi or *n*BuLi, can also be applied to **2** and **6**, thus giving mono- or bis(lithiomethyl)phosphines in quantitative yields. Use of Me_3SiCl as a trapping reagent allows an easy identification of the products by comparison with the data of **1** and **5** (eq. 5).

$$\underset{\mathbf{2}}{Ph_2PCH_2SnMe_3} \xrightarrow{BuLi} Ph_2PCH_2Li \xrightarrow{Me_3SiCl} \underset{\mathbf{1}}{Ph_2PCH_2SiMe_3}$$

$$\underset{\mathbf{6}}{PhP(CH_2SnMe_3)_2} \xrightarrow{BuLi} Ph_2P(CH_2Li)_2 \xrightarrow{Me_3SiCl} \underset{\mathbf{5}}{PhP(CH_2SiMe_3)_2} \qquad (5)$$

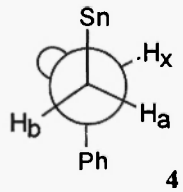
Lithiation of $PhP(H)CH_2SiMe_3$ **3** with one equivalent of BuLi could in principle take place either at the phosphorus or the carbon atom. Lithiation at -78°C and subsequent trapping with Me_3SiCl gives only the P-silylated product **9** (eq. 6).
Use of double the amounts of $BuLi/Me_3SiCl$ leads to the same result with no hints of the formation of an intermediate C- and P-dilithiated species. Results of the lithiation of $PhP(H)CH_2SnMe_3$ **4** will be reported elsewhere. The structure of all compounds, **1-9**, is elucidated by multinuclear NMR studies (Tables 1-3).

$$\underset{\mathbf{3}}{PhP(H)CH_2SiMe_3} \xrightarrow{BuLi} PhP(CH_2SiMe_3)Li \xrightarrow{Me_3SiCl} \underset{\mathbf{9}}{PhP(CH_2SiMe_3)SiMe_3} \qquad (6)$$

Discussion of NMR data.

$PhP(H)CH_2SnMe_3$ **4** possessing diastereotopic protons seems suitable for a discussion of the stereochemical behaviour since two dihedral dependances from the literature can be referred to. Firstly, ^2J(PH) depends on the dihedral angle ϑ(H-C-P-lone pair) [15], secondly, a Karplus type behaviour [16] may be anticipated for ^3J(HCPH) since (averaged) ^3J(HCCH) and ^3J(HCPH) coupling constants are similar in alkyl phosphines. The preferred population of one conformation can be inferred from large differences in the respective ^2J(PH) and ^3J(HH) values of the diastereotopic hydrogens H_a and H_b. If the values of ^2J(PH) and ^3J(HH) are related to these dihedral dependances, **4** can be assumed to prefer a conformation where the lone pair is in a *gauche* position to the tin moiety (fig. 1). The signs of the coupling constants have not been determined. However, the large magnitude of $^3J(H_bH_x)$ is compatible only with large or low dihedral angles near 180° or 0°. The latter case with sterically unfavorable eclipsed positions of the stannyl and phenyl groups as well as of H_a and the lone pair at phosphorus can be excluded. A small dihedral angle ϑ(H_a-C-P-lone pair) would induce large positive $^2J(PH_a)$ coupling constants in contrast to the observed value near 0 Hz. Thus, it may be concluded that **4** adopts preferably or even almost entirely the *trans* conformation of fig. 1. Emphasis should be given to the heteronuclear coupling constant $^2J(^{119}Sn^{31}P) = 55.9$ Hz in **4**, the lowest of the α-stannylated phosphines presented in this paper. The lack of data for comparison and the dependence on different factors such as dihedral angle (Sn-C-P-lp), substituents and possibly small, sterically forced intramolecular interactions between the lone electron pair of phosphorus and the empty d-orbitals of tin, as found to contribute to ^3J(SnP) [17], does not yet allow to draw conclusions from the measured magnitude of ^2J(SnP). The above results justify, however, to assign it to a dihedral angle (Sn-C-P-lp) corresponding to a *gauche* orientation of Sn towards the lone electron pair, i.e. *trans* orientation towards the phenyl group.

Figure 1



4

$^3J_{HbHx} = 12.8$
$^3J_{HaHx} = 5.3$
$^2J_{PHb} = 6.9$
$^2J_{PHa} = 0.8$

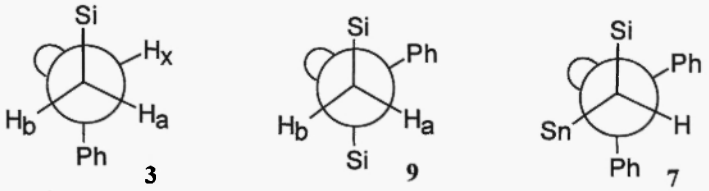
The values for ^2J(PH) and ^3J(HH) of the analogous silicon compound **3** indicate that there is a similar preferably populated *trans* conformation (fig.2). A rough comparison with the β-substituted stannyl ethane derivative $Me_3SnCH_2CH_2SiMe_3$ (CH_2 instead of P, $SiMe_3$ instead of Ph), where the preference of a *trans* conformation has been shown [18], indicates a low influence of the lone electron pair at phosphorus. From this it may be concluded that interactions with the empty d-orbitals of tin or silicon, if they exist at all, are only small.

Table 1: ^{1}H NMR data of **2** - **7** , **9**[a] (Chemical shifts in ppm, coupling constants in Hz)

No.	δ(SiCH$_3$) ^2J(SiH) ^4J(PH)	δ(SnCH$_3$) ^2J(SnH) ^4J(PH)	δ(PCH$_2$)[b] ^2J(PH) ^2J(SnH) / ^2J(SiH)	δ(PCH$_A$)[c] ^2J(PH$_A$) ^3J(H$_A$CPH) / ^2J(H$_A$H$_B$)	δ(PCH$_B$)[c] ^2J(PH$_B$) ^3J(H$_B$CPH)	δ(PH) ^1J(PH)	δ(Ph)
2	-	- 0.03 (54.6) (0)	1.28 (2.1) (57.5 / -)	-	-	-	7.25 - 7.41
3	0.13 (6.5) (0.7)	-	-	1.16 (2.8) (5.3) / (13.3)	0.88 (5.0) (12.8)	4.34 (205.7)	7.18 - 7.22 (3H) 7.51 - 7.54 (2H)
4	-	0.05 (54.5) (0)	-	1.03 (0.8) (5.3) / (11.8)	0.88 (6.9) (12.8)	4.43 (205.8) (47.7)[d]	7.06 - 7.14 (3H) 7.44 - 7.46 (2H)
5	- 0.03 (n.o.) (0)	-	-	0.83 (0) (-) / (13.7)	1.03 (1.6) (-)	-	7.11 - 7.14 (3H) 7.56 - 7.61 (2H)
6	-	0.03 (54.2) (0)	-	1.15 (0) (-) / (12.2)	1.05 (5.0) (-)	-	7.11- 7.16 (3H) 7.53 - 7.57 (2H)
7	0.04 (6.6) (0.6)	0.05 (53.1) (0)	1.42[e] (1.0) (64.1/ 6.6)	-	-	-	7.02 - 7.06 (6H) 7.54 - 7.58 (4H)
9	0.08[f] / 0.03[g] (6.5)[f] / (6.5)[g] (0.7)[f] / (4.4)[gh]	-	-	0.61 (1.9) (-) / (14.4)	1.26 (3.7) (-)	-	7.00 - 7.15 (3H) 7.38 - 7.44 (2H)

[a] For data of **1** cf. [4]. [b] PCH_2 protons not diastereotopic. [c] PCH_2 protons diastereotopic. [d] ^3J(HSn). [e] $Ph_2PC\underline{H}$. [f] CH_2SiCH_3. [g] $PSiCH_3$. [h] ^3J(PH).

Figure 2



3 **9** **7**

	3	**9**	**7**
$^2J_{PHa}$	– 2.8	1.9	1,0
$^2J_{PHb}$	= 5.0	3.7	-
$^3J_{SiP}$	= 8.3	1.8	13.9

When the P-bonded hydrogen in **4** (or **3**) is replaced by a substituent, an eclipsed conformation with the tin (silicon) atom close to the lone pair of phosphorus may be preferred relative to other orientations. This is supported by the much greater $^2J(^{119}Sn^{31}P)$ = 93.9 Hz of **2** compared to that of **4** (^2J(SnP)(**2**) : ^2J(SnP)(**4**) = 1.7). A similar ratio, ^2J(PSi)(**1**) : ^2J(PSi)(**3**) = 1.8, is observed for the silicon compounds. Although of limited value for comparison, it should be mentioned that a large $^2J(^{119}Sn^{31}P)$ = 352.5 Hz (negative sign) was recently reported for a 2-stannylphosphabenzene with unambiguous eclipsed orientation of the $SnMe_3$ group and the lone-pair at phosphorus (being perpendicular to the π-plane) [19]. The large difference towards ^2J(SnP)(4) may be due to the different hybridization at the carbon and phosphorus atoms which has a strong impact on the magnitude (and eventually also the sign).

Table 2: ^{13}C NMR data of **2** - **7** , **9**[a] (Chemical shifts in ppm, coupling constants in Hz)

No.	$\delta(SiCH_3)$ $^1J(SiC)$ $^3J(PC)$	$\delta(SnCH_3)$ $^1J(SnC)$ $^3J(PC)$	$\delta(PCH_2)$ $^1J(PC)$ $^1J(SiC)$ / $^1J(SnC)$	$\delta(C_{ipso})$ $^1J(PC)$	$\delta(C_o)$ $^2J(PC)$	$\delta(C_m)$ $^3J(PC)$	$\delta(C_p)$ $^4J(PC)$
2	-	- 8.3 (339) (4.3)	+ 8.4 (33.1) (- / n.o.)	143.6 (15.6)	133.5 (20.6)	129.1 (3.2)	129.2 (0)
3	- 0.8 (51.8) (3.8)	-	+ 9.2 (26.0) (n.o. / -)	138.6 (15.0)	132.7 (16.5)	128.3 (5.6)	127.8 (0)
4	-	- 8.6 (339) (3.4)	1.2 (28.0) (- / 231.4)	140.6 [b] (15.0)	133.3 (16)	129.3 (6)	128.7 (0)
5	- 0.1 (n.o.) (n.o.)	-	20.8 (31.1) (n.o. / -)	143.0 (16.2)	132.9 (22.3)	128.2 (7.8)	129.1 (0)
6	-	- 8.0 (335.7) (3.9)	15.5[c] (34.3) (- / 282.2)	144.7 (22.9)	133.0 (21.2)	129.2 (8.0)	129.8 (0)
7	1.7 (n.o.) (5.1)	- 6.1 (333) (4.9)	8.8 [h] (50.8) (n.o. / 202)	142.1 / 143.0 [d] (15.1) / (19.7)	133.1 / 133.4 [d] (16.9) / (17.0)	128.4 / 128.5 / 128.6/128.7 [d]	
9	- 0.2[e] / - 2.8[f] (51.2)[e] / (48.0)[f] (5.1)[e] / (11.4)[fg]	-	3.6 (33.2) (n.o. / -)	137.4 (20)	132.5 (19)	127.7 (8)	126.9 (0)

[a] Data of **1** see [4]. [b] $^3J(SnC) = 41$ Hz. [c] $^3J(SnC) = 37.4$ Hz. [d] Phenyl rings diastereotopic. [e] $CH_2Si(\underline{C}H_3)$. [f] $PSi\underline{C}H_3$. [g] $^2J(PC)$. [h] $Ph_2P\underline{C}HSiSn$.

Table 3: ^{29}Si, ^{31}P and ^{119}Sn NMR data of $PhPRR'$ **1** - **7** , **9**
(Chemical shifts in ppm, coupling constants in Hz)

No.	R	R'	$\delta(^{31}P)$	$\delta(^{29}Si)$	$\delta(^{119}Sn)$	$^2J(PSi)/^2J(SnP)$
1 [4]	Ph	CH_2SiMe_3	- 21.9	1.3	-	15.0 / -
2	Ph	CH_2SnMe_3	- 17.5	-	3.6	- / 93.9
3	H	CH_2SiMe_3	- 65.4	1.5	-	8.3 / -
4	H	CH_2SnMe_3	- 57.6	-	5.8	- / 55.9
5	CH_2SiMe_3	CH_2SiMe_3	- 35.2	0.2	-	14.2 / -
6	CH_2SnMe_3	CH_2SnMe_3	- 25.2	-	4.1[a]	- / 82.3
7	Ph	$CH(SiMe_3)SnMe_3$	- 14.6	2.0	6.5	13.9 / 73.0
9	$SiMe_3$	CH_2SiMe_3	- 95.9	2.9 ($PS\underline{i}$) 3.2 ($PC\underline{Si}$)	-	1.8 / - [b]

[a] $^4J(SnSn) = 49.9$ Hz. [b] $^1J(PSi) = 11.1$ Hz.

If the surroundings of the phosphorus atom are asymmetric or enantiotopic with respect to the methylene protons, the eclipsed conformation might be less optimal. In spite of this the ^2J(PH) coupling constants of the diastereotopic protons H_a and H_b in 9 and in **5**, bearing a (second) CH_2SiMe_3 substituent, are nearly equal and also the magnitude of ^2J(PSi) of **5** is close to the value of **1** (ratio 1.05). The sterical repulsion is more pronounced in the analogous distannyl derivative **6** and causes a Δ^2J(PH) of 5 Hz and a slightly increased ratio ^2J(SnP)(**2**) : ^2J(SnP)(6) = 1.14. The low value ^2J(PSi) of **9** cannot be compared because of the impact of the enhanced electron density at phosphorus of silylphosphines ($P^{\delta-}$-$Si^{\delta+}$). Also bonding contributions from the phosphorus lone pair of electrons with empty d orbitals of the directly bonded Si atom have been discussed [20]. In the case of 7, it appears that the heteroatoms are in *gauche* and the hydrogen atom, in agreement with the small value of ^2J(PH) [15], in *trans* position of the lone pair. The two diastereomers **8** formed according to eq. (2) display a large difference in the absolute magnitude of ^2J(SnP). The smaller value, 57 Hz, is tentatively assigned to the *meso* form with opposite configuration of the asymmetrical carbon atoms, the larger value, 108 Hz, to the *rac* isomers.

In summary, a convenient method for the preparation of α-silyl and α-stannyl phosphines is presented. We expect that it can be extended to the preparation of more complex structures and via $Ph_2PCHRLi$ to the introduction of other metals. Due to the large number of NMR active nuclei, the preferred imaginary orientation of the phosphorus lone pair of electrons with respect to the silyl or stannyl groups can be deduced from coupling constants. α-Metalated phosphines are of potential interest for the preparation of functionalized phosphines which are useful in coordination chemistry and catalysis.

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