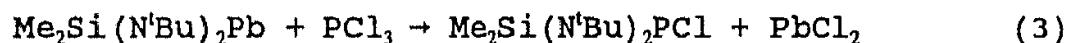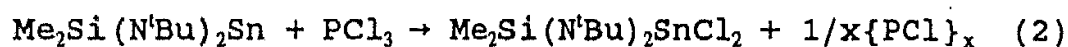# GERMA- AND STANNA-PHOSPHINES FROM THE INSERTION OF GERMYLENES AND STANNYLENES INTO P-Cl BONDS

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Abstract The bis(amino)germylenes and -stannylenes $\underline{1}$-$\underline{4}$ $(Me_2Si(N^tBu)_2M$, $M=Ge(\underline{1})$,$Sn(\underline{2})$; $(MeSi)_2(N^tBu)_4M$, $M=Ge(\underline{3})$, $Sn(\underline{4})$ insert into the P-Cl bonds of aryldichlorphosphine $R-PCl_2$ (R=Ph, Mes). While $\underline{1}$ may insert into one or two P-Cl bonds, depending on the molar ratios of $\underline{1}$ to $R-PCl_2$, forming $Me_2Si(N^tBu)_2Ge(Cl)P(Cl)R$ $(\underline{5})$ or $[Me_2Si(N^tBu)_2Ge(Cl)]_2P-R$ $(\underline{6})$, $\underline{2}$ gives exclusively the diinsertion product $[Me_2Si(N^tBu)_2Sn(Cl)]_2P-R$ $(\underline{7})$. The sterically more hindered stannylene $\underline{4}$ inserts only into one P-Cl bond forming $(MeSi)_2(N^tBu)_4Sn(Cl)P(Cl)R$ $(\underline{8})$. With the exception of $\underline{6}$ all insertion products, $\underline{5}$-$\underline{8}$, are unstable and decompose via different intermediates which can be identified by ^1H- and ^{31}P-NMR to cyclic phosphines $(RP)_n$ (n = 4, 5, 6), $Me_2Si(N^tBu)_2MCl_2$ or $(MeSi)_2(N^tBu)_4MCl_2$, respectively.

INTRODUCTION

The carbene analogues $Me_2Si(N^tBu)_2Ge$ $(\underline{1})$, $Me_2Si(N^tBu)_2Sn$ $(\underline{2})$ and $Me_2Si(N^tBu)_2Pb$ react differently with PCl_3 (equations (1)-(3)).

$$3\ Me_2Si(N^tBu)_2Ge + PCl_3 \rightarrow [Me_2Si(N^tBu)_2Ge(Cl)]_3P \qquad (1)$$

$$Me_2Si(N^tBu)_2Sn + PCl_3 \rightarrow Me_2Si(N^tBu)_2SnCl_2 + 1/x\{PCl\}_x \qquad (2)$$

$$Me_2Si(N^tBu)_2Pb + PCl_3 \rightarrow Me_2Si(N^tBu)_2PCl + PbCl_2 \qquad (3)$$
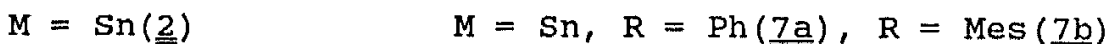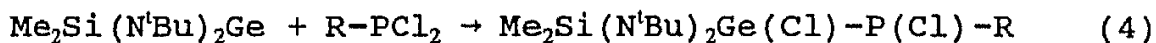
Whereas $\underline{1}$ forms exclusively the triple insertion product, $\underline{2}$ abstracts two chlorine atoms from PCl_3 and the lead derivative gives rise to the phosphanitrogen cycle $Me_2Si(N^tBu)_2PCl$ by substitution of the lead atom by phosphorus.[1] The redox type reaction (2) can be modified and used to synthesize diphosphenes R-P=P-R in good yields by treating $\underline{2}$ with sterically demanding aryldichlorphosphines, like 2,4,6-tri(tert-butyl)phenyl[2]. We have been interested to see through which intermediates these reactions proceed and have treated $\underline{1}$ and $\underline{2}$ with phenyldichlorphosphine and

mesityldichlorphosphine. We also have used the sterically more hindered germylene and stannylene $(MeSi)_2(N^tBu)_4Ge$ (<u>3</u>)[3] and $(MeSi)_2(N^tBu)_4Sn$ (<u>4</u>)[4].

INSERTION OF <u>1</u> AND <u>2</u> INTO THE P-Cl BONDS OF ARYLDICHLOR-PHOSPHINES

<u>1</u> and <u>2</u> react at $-70°C$ in toluene with $R-PCl_2$ (R = Ph or Mes) to yield the insertion products <u>5a</u>, <u>5b</u>, <u>6a</u>, <u>6b</u>, <u>7a</u> and <u>7b</u>.

$$Me_2Si(N^tBu)_2Ge + R-PCl_2 \rightarrow Me_2Si(N^tBu)_2Ge(Cl)-P(Cl)-R \qquad (4)$$
$$\underline{1} \qquad\qquad\qquad\qquad R = Ph(\underline{5a}), \ Mes(\underline{5b})$$

$$2 \ Me_2Si(N^tBu)_2M + R-PCl_2 \rightarrow [Me_2Si(N^tBu)_2M(Cl)]_2P-R \qquad (5)$$

| M = Ge(<u>1</u>) | M = Ge, R = Ph(<u>6a</u>), R = Mes(<u>6b</u>) |
| M = Sn(<u>2</u>) | M = Sn, R = Ph(<u>7a</u>), R = Mes(<u>7b</u>) |

The formation of the products <u>5</u> and <u>6</u> can be easily controlled by the molar ratios of <u>1</u> to $R-PCl_2$, whereas in the reaction of <u>2</u> with $R-PCl_2$ only the diinsertion product <u>7</u> is formed. The quantitative reactions can easily be followed by $^1H-$ and $^{31}P-NMR$ techniques (see also table I).

When the reaction mixture is allowed to warm to ambient temperature, the spectra of the solutions change instantly. As shown by these spectra, only the diinsertion products <u>6a</u> and <u>6b</u> are stable. They can be isolated and fully characterized, whereas the other compounds <u>5a</u>, <u>5b</u>, <u>7a</u> and <u>7b</u> decompose forming $Me_2Si(N^tBu)_2GeCl_2$ or $Me_2Si(N^tBu)_2SnCl_2$ and the cyclic polyphosphines $(RP)_n$ (n = 4, 5, 6) as major products identified by their $^1H-$ and $^{31}P-NMR$ spectra [4,5,6].
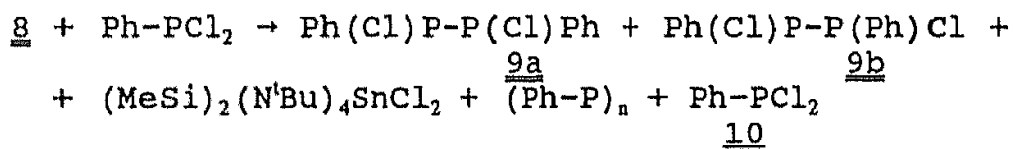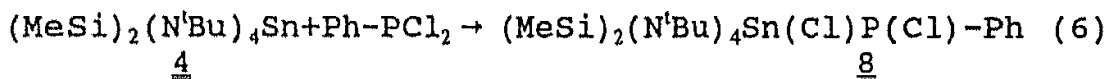
Neither the germylene <u>1</u> nor the stannylene <u>2</u> react with the crowded 2,4,6-tri(tert-butyl)phenyldichlorphosphine, Ar-PCl_2, at low temperatures. But when slightly heated reaction proceeds leading to the diphosphene Ar-P=P-Ar and $Me_2Si(N^tBu)_2GeCl_2$ or $Me_2Si(N^tBu)_2SnCl_2$. It can be seen from the spectra that in the case of the reaction of <u>1</u>, apart from the main products, the mono- and diinsertion products

$Me_2Si(N^tBu)_2Ge(Cl)-Ar$ and $[Me_2Si(N^tBu)_2Ge(Cl)]_2P-Ar$ are also produced.

Table I ¹H-NMR and ³¹P-NMR Data
(δ-values in ppm)

$R_2 = Me_2Si(N^tBu)_2$	¹H-NMR			³¹P NMR (J in Hz)
	Me	ᵗBu		
$[R_2Ge(Cl)]P(Cl)Ph(\underline{5a})$	0.26,0.35	1.00,1.20		55.1
$[R_2Ge(Cl)]P(Cl)Mes(\underline{5b})$	0.32,0.39	1.07,1.21		69.8
	[1.94(p.Me);2.66(o.Me);2.95(o.Me)]			
$[R_2Ge(Cl)]_2PPh(\underline{6a})$	0.37,0.43	1.28		-6.88
$[R_2Ge(Cl)]_2PMes(\underline{6b})$	0.33,0.42	1.29		-40.35
	[1.98(p-Me); 2.89(o-Me)]			
$[R_2Sn(Cl)]_2PPh(\underline{7a})$	0.34,0.42	1.22		-58.6 $^1J^{31}P^{117,119}Sn=1525;145$
$[R_2Sn(Cl)]_2PMes(\underline{7b})$	0.33,0.43	1.21		-61.98 $^1J^{31}P^{117,119}Sn=1764;1684$
	[1.93(p-Me);2.81(o.Me)]			

The bulky stannylene $\underline{4}$ reacts with $Ph-PCl_2$ in a very interesting reaction sequence. Equation (6) sums up all the products formed which have been detected by ¹H- and ³¹P-NMR.

$$(MeSi)_2(N^tBu)_4Sn + Ph-PCl_2 \rightarrow (MeSi)_2(N^tBu)_4Sn(Cl)P(Cl)-Ph \quad (6)$$
$$\underline{4} \qquad\qquad\qquad\qquad\qquad\qquad \underline{8}$$

$$\underline{8} + Ph-PCl_2 \rightarrow Ph(Cl)P-P(Cl)Ph + Ph(Cl)P-P(Ph)Cl +$$
$$\underline{9a} \qquad\qquad\qquad \underline{9b}$$
$$+ (MeSi)_2(N^tBu)_4SnCl_2 + (Ph-P)_n + Ph-PCl_2$$
$$\underline{10}$$

The mono insertion compound $\underline{8}$ is found first as main product; the P-Sn satellite intensities $^1J(^{31}P-^{117/119}Sn)= 1636$, 1714 Hz show that only one tin atom is bonded to phosphorus. $\underline{8}$ decomposes slowly, forming $(MeSi)_2(N^tBu)_4SnCl_2$ and the diphosphines $\underline{9a}$ and $\underline{9b}$. The products are identified by their ³¹P-signals[8,9]. Simultaneously the signals for the cyclo-phosphines as well as two singlets characteristic for transient species in their formation[7] show up and disappear after a while together with the signals of $\underline{9a}$ and $\underline{9b}$ in the NMR-spectra, leaving only those of $(PhP)_n$, $\underline{10}$ and $(MeSi)_2(N^tBu)_4SnCl_2$.

CHEMICAL AND STRUCTURAL CONSEQUENCES

From these findings a radical pathway in these insertion reactions (4)-(6) cannot be ruled out. As far as the NMR-spectra of 5-7 are concerned (table I), two phenomena are worth pointing out: firstly the very high coupling constants for P-Sn around 1500 Hz in 7a and 7b, comparable to P=Sn double bonds $(^{1}J(^{31}P-^{119}Sn) = 2295$ Hz$)^{10}$ and secondly the appearance of two signals for the tert-butyl group in compounds 3 in contrast to the single resonance in 4. When compound 4a is allowed to cool in the NMR-tube, the singlet is transformed to two new signals, the coalescence point being 243 K. From these values a free activation enthalpy of 11,5 kcal/mol can be deduced. It can be shown by molecular mechanics[11] that rotation arround a P-Ge bond cannot account for this phenomenon. Instead it must be assumed, that the pyramidal angle at the central phosphorus is very large (in $[Me_{2}Si(N^{t}Bu)_{2}Ge(Cl)]_{3}P$ it is 115°) and that the energy calculated corresponds to the inversion barrier at phosphorus. Following these ideas it is clear that a mono-insertion product 5 is sterically less hindered than a diinsertion product 6. The pyramidal angle is smaller, the activation energy thus higher and two resonance lines appear for the tert-butyl groups. Again it can be shown by molecular mechanics[11] that a rotation arround the P-Ge bond is considerably hindered in the derivatives 5.

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