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

MICHAEL VEITH*, MARYSE GOUYGOU* and ASTRID DETEMPLE*
*Institut für Anorganische Chemie, Universität des Saarlandes, D-6600 Saarbrücken, Germany
**Laboratoire de Chimie des Métaux de Transition, 4 Place Jussieu, F-75252 Paris, France

Abstract The bis(amino)germylenes and -stannylenes 1-4 (Me₂Si(N'Bu)₂M, M=Ge(1), Sn(2); (MeSi)₂(N'Bu)₄M, M=Ge(3), Sn(4) insert into the P-Cl bonds of arylidichlorophosphine R-PCl₂ (R=Ph, Mes). While 1 may insert into one or two P-Cl bonds, depending on the molar ratios of 1 to R-PCl₂, forming Me₂Si(N'Bu)₂Ge(Cl)P(Cl)R (5) or [Me₂Si(N'Bu)₂Ge(Cl)]₂P-R (6), 2 gives exclusively the diinsertion product [Me₂Si(N'Bu)₂Sn(Cl)]₂P-R (7). The sterically more hindered stannylene 4 inserts only into one P-Cl bond forming (MeSi)₂(N'Bu)₄Sn(Cl)P(Cl)R (8). With the exception of 6 all insertion products, 5-8, are unstable and decompose via different intermediates which can be identified by 'H- and ³¹P-NMR to cyclic phosphines (RP)ₙ (n = 4, 5, 6), Me₂Si(N'Bu)₂MCl₂ or (MeSi)₂(N'Bu)₄MCl₂, respectively.

INTRODUCTION

The carbene analogues Me₂Si(N'Bu)₂Ge (1), Me₂Si(N'Bu)₂Sn (2) and Me₂Si(N'Bu)₂Pb react differently with PCl₃ (equations (1)-(3)).

\[3 \text{Me}_2\text{Si(N'Bu)}_2\text{Ge} + \text{PCl}_3 \rightarrow [\text{Me}_2\text{Si(N'Bu)}_2\text{Ge(Cl)}]_2\text{P} \quad (1)\]

\[\text{Me}_2\text{Si(N'Bu)}_2\text{Sn} + \text{PCl}_3 \rightarrow \text{Me}_2\text{Si(N'Bu)}_2\text{SnCl}_2 + 1/x\{\text{PCl}\}_x \quad (2)\]

\[\text{Me}_2\text{Si(N'Bu)}_2\text{Pb} + \text{PCl}_3 \rightarrow \text{Me}_2\text{Si(N'Bu)}_2\text{PCl} + \text{PbCl}_2 \quad (3)\]

Whereas 1 forms exclusively the triple insertion product, 2 abstracts two chlorine atoms from PCl₃ and the lead derivative gives rise to the phosphanitrogen cycle Me₂Si(N'Bu)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 2 with sterically demanding arylidichlorophosphines, like 2,4,6-tri(tert-butyl)phenyl². We have been interested to see through which intermediates these reactions proceed and have treated 1 and 2 with phenyldichlorophosphine and
mesityldichlorophosphine. We also have used the sterically more hindered gemmylene and stannylene \((\text{MeSi}_2(\text{N}^\text{Bu})_4\text{Ge})\)\(^3\) and \((\text{MeSi}_2(\text{N}^\text{Bu})_4\text{Sn})\)\(^4\).

**INSERTION OF 1 AND 2 INTO THE P-Cl BONDS OF ARYLDICHLOORPHOSPHINES**

1 and 2 react at \(-70^\circ\text{C}\) in toluene with R-PCl\(_2\) (R = Ph or Mes) to yield the insertion products 5\(^a\), 5\(b\), 6\(a\), 6\(b\), 7\(a\) and 7\(b\).

\[
\begin{align*}
\text{Me}_2\text{Si}(\text{N}^\text{Bu})_2\text{Ge} + R-\text{PCl}_2 & \rightarrow \text{Me}_2\text{Si}(\text{N}^\text{Bu})_2\text{Ge(Cl)}-\text{P(Cl)}-R \\
R & = \text{Ph}(5a), \text{Mes}(5b) \\
2 \text{Me}_2\text{Si}(\text{N}^\text{Bu})_2\text{M} + R-\text{PCl}_2 & \rightarrow [\text{Me}_2\text{Si}(\text{N}^\text{Bu})_2\text{M(Cl)}]_2\text{P-R} \\
M & = \text{Ge}(1), \text{Sn}(2) \quad M = \text{Ge}, R = \text{Ph}(6a), R = \text{Mes}(6b) \quad M = \text{Sn}, R = \text{Ph}(7a), R = \text{Mes}(7b)
\end{align*}
\]

The formation of the products 5 and 6 can be easily controlled by the molar ratios of 1 to R-PCl\(_2\), whereas in the reaction of 2 with R-PCl\(_2\) only the diinsertion product 7 is formed. The quantitative reactions can easily be followed by \(^1\text{H}-\) and \(^3\text{P}-\text{NMR}\) 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 6\(a\) and 6\(b\) are stable. They can be isolated and fully characterized, whereas the other compounds 5\(a\), 5\(b\), 7\(a\) and 7\(b\) decompose forming Me\(_2\)Si(\(\text{N}^\text{Bu})_2\text{GeCl}_2\) or Me\(_2\)Si(\(\text{N}^\text{Bu})_2\text{SnCl}_2\) and the cyclic polyphosphines \((\text{RP})_n\) \((n = 4, 5, 6)\) as major products identified by their \(^1\text{H}-\) and \(^3\text{P}-\text{NMR}\) spectra \(^4,5,6\).

Neither the germmylene 1 nor the stannylene 2 react with the crowded 2,4,6-tri(tert-butyl)phenyldichlorophosphine, Ar-PCl\(_2\), at low temperatures. But when slightly heated reaction proceeds leading to the diphosphene Ar-P=P-Ar and Me\(_2\)Si(\(\text{N}^\text{Bu})_2\text{GeCl}_2\) or Me\(_2\)Si(\(\text{N}^\text{Bu})_2\text{SnCl}_2\). It can be seen from the spectra that in the case of the reaction of 1, apart from the main products, the mono- and diinsertion products
\[ \text{Me}_2\text{Si(N'Bu)_2Ge(Cl)-Ar and } [\text{Me}_2\text{Si(N'Bu)_2Ge(Cl)}]_2\text{P-Ar are also produced.} \]

### Table I \( ^1\text{H-NMR and } ^3\text{P-NMR Data} \)

\( (\delta\text{-values in ppm}) \)

<table>
<thead>
<tr>
<th>( R_2 = \text{Me}_2\text{Si(N'Bu)_2} )</th>
<th>( ^1\text{H-NMR} )</th>
<th>( ^3\text{P NMR (J in Hz)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>([R_2\text{Ge(Cl)}]_2\text{P(Cl)}\text{Ph(5a)})</td>
<td>0.26, 0.35</td>
<td>1.00, 1.20</td>
</tr>
<tr>
<td>([R_2\text{Ge(Cl)}]_2\text{P(Cl)}\text{Mes(5b)})</td>
<td>0.32, 0.39</td>
<td>1.07, 1.21</td>
</tr>
<tr>
<td>([1.94(p, Me); 2.66(o, Me); 2.95(o, Me)])</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([R_2\text{Ge(Cl)}]_2\text{PPh(5a)})</td>
<td>0.37, 0.43</td>
<td>1.28</td>
</tr>
<tr>
<td>([R_2\text{Ge(Cl)}]_2\text{PMes(5b)})</td>
<td>0.33, 0.42</td>
<td>1.29</td>
</tr>
<tr>
<td>([1.98(p, Me); 2.89(o, Me)])</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([R_2\text{Sn(Cl)}]_2\text{PPh(7a)})</td>
<td>0.34, 0.42</td>
<td>1.22</td>
</tr>
<tr>
<td>([R_2\text{Sn(Cl)}]_2\text{PMes(7b)})</td>
<td>0.33, 0.43</td>
<td>1.21</td>
</tr>
<tr>
<td>([1.93(p, Me); 2.81(o, Me)])</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The bulky stannylene 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 \(^1\text{H-} \text{and } ^3\text{P-NMR.}\)

\[
(\text{MeSi})_2(N'^{Bu})_4\text{Sn} + \text{Ph-PCl}_2 \rightarrow (\text{MeSi})_2(N'^{Bu})_4\text{Sn(Cl)} \text{P(Cl)} - \text{Ph} \quad (6)
\]

\[8 + \text{Ph-PCl}_2 \rightarrow \text{Ph(Cl)} \text{P-P(Cl)} \text{Ph} + \text{Ph(Cl)} \text{P-P(Ph)} \text{Cl} +
\]

\[+ (\text{MeSi})_2(N'^{Bu})_4\text{SnCl}_2 + (\text{Ph-P})_8 + \text{Ph-PCl}_2 \]

The mono insertion compound 8 is found first as main product; the P-Sn satellite intensities \( ^1\text{J}[^{31}\text{P-}^{117/119}\text{Sn}) = 1636, 1714 \text{ Hz} \) show that only one tin atom is bonded to phosphorus. 8 decomposes slowly, forming \((\text{MeSi})_2(N'^{Bu})_4\text{SnCl}_2 \) and the diphosphines 9a and 9b. The products are identified by their \( ^3\text{P-signals} \).

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 9a and 9b in the NMR-spectra, leaving only those of \((\text{PhP})_8, 10 \) and \((\text{MeSi})_2(N'^{Bu})_4\text{SnCl}_2 \).

**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 \( (J^{31P-19Sn} = 2295 \text{ Hz})^{10} \) 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 around 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 \([\text{Me}_2\text{Si(NBu)}_2\text{Ge(Cl)}]_3\text{P}\) 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.

REFERENCES