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Dichlorosilylene and dichlorogermylene transfer to alkylidenephosphanes

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Abstract

The detection of $Me_3GeSiCl_3$, a product from the Si_2Cl_6 cleavage of trimethylgermylphosphanes, as a useful new source of $SiCl_2$ moieties, as well as new trapping reactions of $SiCl_2$ and $GeCl_2$ with functional alkylidenephosphanes $(Me_3Si)_2C{=}PX$ (X = halide or dialkylphosphanyl [PRR′; R = *i*-propyl, R′ = *t*-butyl]) are reviewed. In the primary step of the reactions, insertion into the P–X bond is competing with addition to the P=C bond. $SiCl_2$ and $GeCl_2$ insertions are followed by dimerisation reactions leading to new highly functional *P*-phosphanylalkylidenephosphanes, that may rearrange to diphosphenes like $(XCl_2Si)(Me_3Si)_2C{-}P{=}P{-}C(SiMe_3)_2SiCl_2X$ (X = F, Cl, P-*i*-Pr_2) or $(Cl_3Ge)(Me_3Si)_2C{-}P{=}P{-}C(SiMe_3)_2GeCl_2PRR'$ or/and react further with $SiCl_2$ or $GeCl_2$. Reaction of $(Me_3Si)_2C{=}P{-}PRR'$ (R = *i*-propyl, R′ = *t*-butyl) with $Me_3GeSiCl_3$ leads in a very selective fashion to a complete P=C double bond cleavage by unique double $SiCl_2$ addition with formation of a stable *P*-phosphanylphosphadisiletane.

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1. Introduction

Among the dichlorides of group 14 elements, $SiCl_2$ is the synthetically least available compound: the reactive intermediate CCl_2 is easily available by a number of α-elimination reactions like those of $HCCl_3$ or of $PhHgCCl_3$ (Seyferth's reagent), $GeCl_2$ can be stored as a dioxane or as a phosphane complex, and $SnCl_2$ as well as $PbCl_2$ are commercially available stable compounds [1].

2. Dichlorosilylene equivalents

Early work on $SiCl_2$ revealed, that solid materials of this composition are polysilanes (with Si–Si bonds) implying silicon in its tetracoordinated state [2]. Recently, polymeric *trans*-chain-like $SiCl_2$ has been characterised after attempted sublimation of the tetramer Si_4Cl_8 [3]. Pure monomeric carbene-analogous $SiCl_2$, however, is only available by high-temperature methods that limit its availability in organic and organometallic chemistry [4].

“Hidden $SiCl_2$ functions” (Scheme 1) are present in trichlorosilylmetal compounds (when they would undergo α-elimination of metal chloride, related to *Seyferth*s CCl_2 source), in trichlorosilane (when it undergoes – thermodynamically unfavourable – α-elimination of hydrogen chloride), and in hexachlorodisilane (when it undergoes α-elimination of silicon tetrachloride).

Catalysis by weak nucleophiles (amines, phosphanes) leads to elimination of $SiCl_4$ from Si_2Cl_6 with formation of highly branched polysilanes. The exact mechanism of this disproportionation is not known; two alternatives were proposed by Urry [5], 4-center mechanism A and silylene mechanism B (Scheme 2). In way A, $SiCl_3$ groups would be transferred from Si_2Cl_6 to nucleophile-coordinated di- and oligosilane substituting Cl atoms from “most branched Si atoms”; way B involves the α-elimination of $SiCl_4$ leading to nucleophile-coordinated $SiCl_2$ that inserts into Si–Cl bonds of the “most

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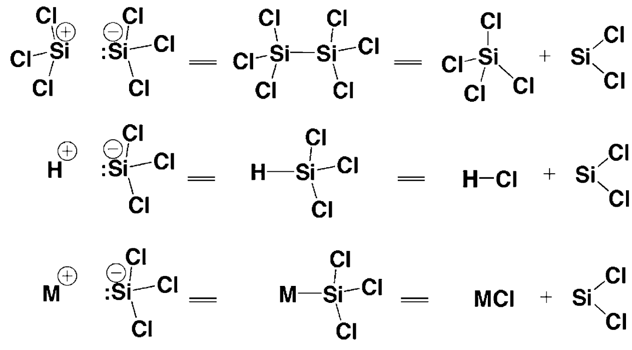


Scheme 1. $SiCl_2$ equivalents.

branched Si atoms". Cooper and Gilbert proposed, that in a similar way $SiCl_3^-$ anions give rise to the formation of new Si–Si bonds [5].

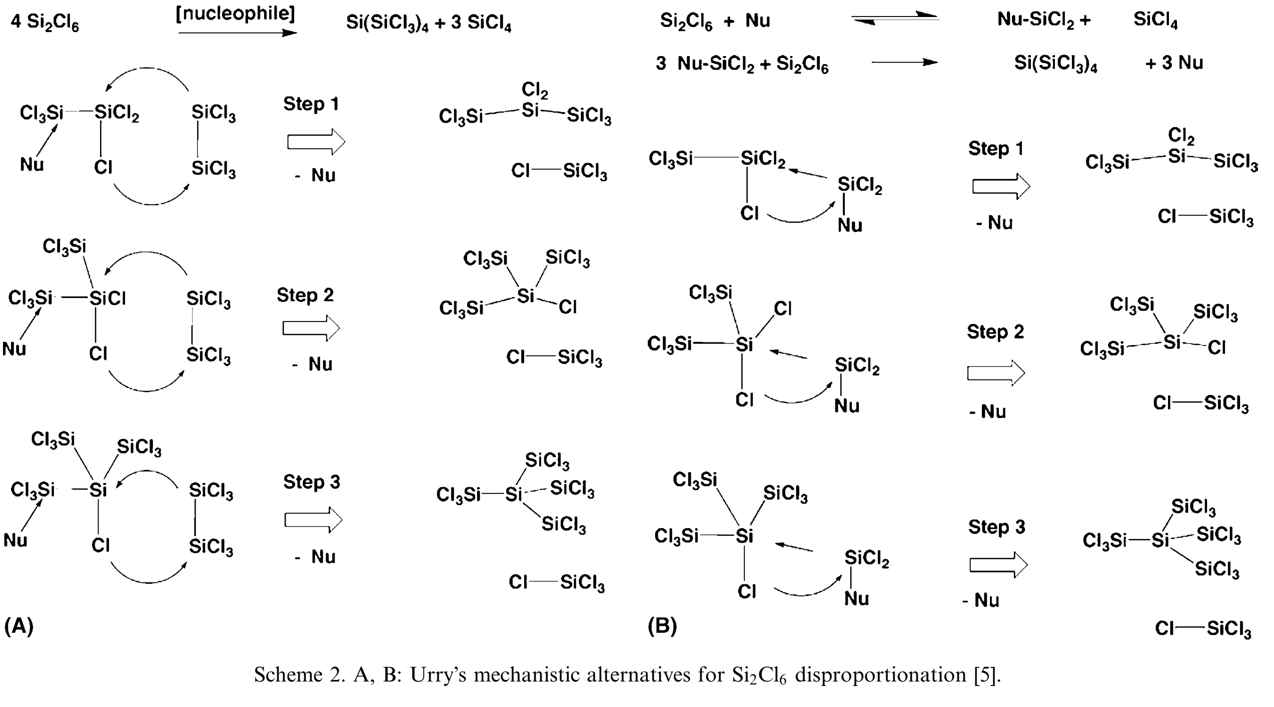
Trying to extend this scheme, Urry proposed in 1970, that related amine-catalysed reactions of $Me_3SiSiCl_3$ and of $Me_3SnSiCl_3$ should lead to $Me_3SiSi(SiCl_3)_3$ or to $Me_3SnSi(SiCl_3)_3$, both accompanied by $SiCl_4$. This hypothesis was, however, not subjected to experimental evidence at that time.

An important application of $SiCl_2$ would be its reactions with organic chlorides leading to a variety of trichlorosilyl compounds. Trihalogenosilyl compounds are of general importance as trifunctional precursors for the synthesis of highly functionalised silicon compounds, like branched silicones and silsesquioxanes.

As a synthetic alternative to "free" $SiCl_2$, the trichlorosilylation of related organic chlorides with $HSiCl_3$ in presence of amines (*Benkeser* reaction) [6] or halide ions [7] has made available a number of alkyltrichlorosilanes and bis-trichlorosilanes. By use of trimethylsilyltriflate as starting material, the $HSiCl_3/NEt_3$ reagent has also been applied for Si–Si-bond formation [8]. This method is, however, limited to substrates that are unreactive towards HCl or organic ammonium salts which are the unavoidable byproducts from the $HSiCl_3$ method.

In phosphorus chemistry, the $HSiCl_3$ method has, apart from its application for $P^V \rightarrow P^{III}$ deoxygenation or desulfuration reactions [9], for long only been used for the hydrogenation of chlorophosphanes furnishing primary or secondary phosphanes (RPH_2 or R_2PH) [10]. Species with P–Si bonds have been proposed for long to be intermediates of these hydrogenations [10]. Later, in course of such a reaction Schmutzler et al. recognised the formation of a trichlorosilylphosphane $Ph_3CP(SiCl_3)H$ by ^{31}P NMR [11]. Subsequently we found, that under strictly anhydrous conditions, a number of alkyl- and alkyl(diorganylamino)chlorophosphanes can be transformed straightforwardly into the corresponding trichlorosilylphosphanes with help of the $HSiCl_3/NEt_3$ reagent [12].

Tetraalkyldiphosphanes cannot be reduced using the $HSiCl_3$ method; they are, however, reactive towards Si_2Cl_6. Si_2Cl_6 is a valuable reagent that can substitute $SiCl_2$ or $HSiCl_3$ on certain occasions: Its application for $P^V \rightarrow P^{III}$ deoxygenation or desulfuration reactions has been recognised for long [9,13], and the dismutation-like trichlorosilylation of Me_4P_2 with Si_2Cl_6 providing two equivalents of Me_2PSiCl_3 as well as the reduction of



Scheme 2. A, B: Urry's mechanistic alternatives for Si_2Cl_6 disproportionation [5].

$$\mathrm{RCl + HSiCl_3 + NEt_3 \longrightarrow RSiCl_3 + HNEt_3Cl} \quad (\mathrm{R = alkyl})$$
$$\mathrm{R_2PCl + HSiCl_3 + NEt_3 \longrightarrow R_2PSiCl_3 + HNEt_3Cl} \quad (\mathrm{R} = i\text{-Pr}, t\text{-Bu})$$
$$\mathrm{RPCl_2 + 2\ HSiCl_3 + 2\ NEt_3 \longrightarrow RP(SiCl_3)_2 + 2\ HNEt_3Cl} \quad (\mathrm{R} = i\text{-Pr}, t\text{-Bu}, \text{N-}i\text{Pr}_2)$$
$$\mathrm{R_3GeCl + HSiCl_3 + NEt_3 \longrightarrow R_3GeSiCl_3 + HNEt_3Cl} \quad (\mathrm{R = Me, Et})$$
$$\mathrm{R_2GeCl_2 + 2\ HSiCl_3 + 2\ NEt_3 \longrightarrow R_2Ge(SiCl_3)_2 + 2\ HNEt_3Cl} \quad (\mathrm{R = Me, Et})$$

Scheme 3. Benkeser trichlorosilylation [6] and its extension to chlorophosphanes [12] and – germanes [22].

$$\mathrm{Me_2NCl + Si_2Cl_6 \longrightarrow Me_2NSiCl_3 + SiCl_4}$$
$$\mathrm{2\ Ph_2PCl + Si_2Cl_6 \longrightarrow Ph_4P_2 + 2\ SiCl_4}$$
$$\mathrm{Me_4P_2 + Si_2Cl_6 \longrightarrow 2\ Me_2PSiCl_3}$$

Scheme 4. *MacDiarmid*'s hexachlorodisilane reactions [14].

Ph_2PCl furnishing Ph_4P_2 have long ago been reported by MacDiarmid et al. in a single short paper [14]. (Scheme 4).

Extending this *MacDiarmid* trichlorosilylation concept to other tetraalkyldiphosphanes and to a number of chloro- and dichlorophosphanes (Scheme 5) allowed the reductive $SiCl_3$ transfer to phosphorus compounds under aprotic conditions [15]. From these reactions, no evidence for a role of Si_2Cl_6 as source of $SiCl_2$ was provided; the reaction of Si_2Cl_6 with dipyridyl that allowed to prepare the coloured [dipy$SiCl_2$] complex remains a single example [16]. Formally, however, the chlorophosphane trichlorosilylation with Si_2Cl_6 is related to the $GeCl_2$ insertion into P–Cl bonds furnishing trichlorogermylphosphanes [17]. This holds for a *P*-chloroalkylidenephosphane: Attempted *MacDiarmid* trichlorosilylation of the alkylidenephosphane $(Me_3Si)_2C{=}PCl$ with Si_2Cl_6 gave not a simple dismutation-like trichlorosilylation, but two different dimers of $(Me_3Si)_2C{=}PSiCl_3$ were identified, a *P*-phosphanylphosphaalkene intermediate and the stable product (a diphosphene!) of this reaction (Scheme 6) [18]. With $GeCl_2$-dioxane, the related diphosphene was isolated [18].

$$\mathrm{R_2PCl + Si_2Cl_6 \longrightarrow R_2PSiCl_3 + SiCl_4} \quad (\mathrm{R} = i\text{-Pr}, t\text{-Bu})$$
$$\mathrm{R(R'_2N)PCl + Si_2Cl_6 \longrightarrow R(R'_2N)PSiCl_3 + SiCl_4} \quad (\mathrm{R} = i\text{-Pr}, t\text{-Bu};\ \mathrm{R'} = \mathrm{Et}, i\text{-Pr}, \mathrm{Ph})$$
$$\mathrm{RPCl_2 + 2\ Si_2Cl_6 \longrightarrow RP(SiCl_3)_2 + 2\ SiCl_4} \quad (\mathrm{R} = t\text{-Bu}, \text{N-}i\text{-Pr}_2)$$

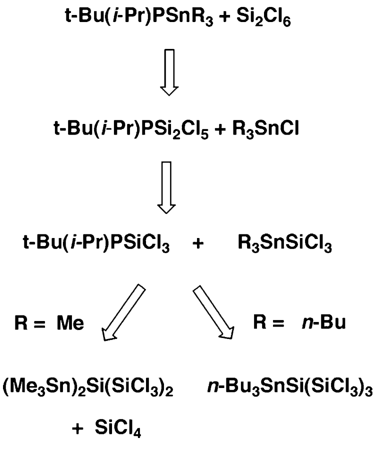
Scheme 5. Extension of *MacDiarmid*'s reaction to alkyl- and aminochlorophosphanes [12,15].

The fact, that Si_2Cl_6 "dismutates" with tetraalkyldiphosphenes [14,15] like i-Pr_4P_2 straightforwardly to i-Pr_2PSiCl_3 [(i-$Pr_2P)_2SiCl_2$ is not observed in the reaction mixture] stimulated us to evaluate, if related dismutations of P–Si–, P–Ge–, and P–Sn– bonds with the Si–Si bond from Si_2Cl_6 would open a further way to trichlorosilylphosphanes, now accompanied by new species with Si–Si-, Si–Ge– or Si–Sn–bonds [15,19].

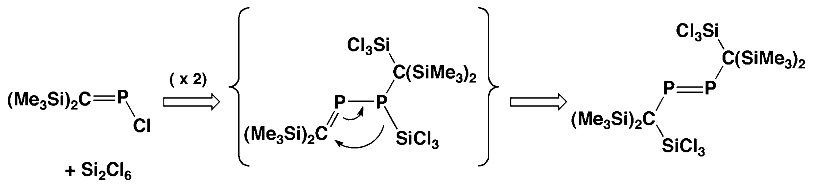
Experimentally, the hypothetic, P–Ge + Si–Si=P–Si + Ge–Si dismutation turned out to follow a more complex reaction path [15,20], because silyl-, germyl- and stannylphosphanes react with Si_2Cl_6 in the first step by formation of pentachlorodisilanylphosphanes ($R_2PSi_2Cl_5$) and chlorosilanes, germanes or stannanes (transsilylation-like reactions at phosphorus, see Scheme 7). Pentachlorodisilanylphosphanes, however, act as reductive trichlorosilylation agents towards Me_3GeCl and R_3SnCl (R = Me, Et, *n*-Bu), leading to the initially desired silylgermanes and silylstannanes R_3ESiCl_3 (E = Ge, Sn), that suffer from subsequent decomposition [19,20].

As an alternative pathway to R_3ESiCl_3 (E = Ge, Sn), *Benkeser*-type reductive trichlorosilylations of chlorogermanes and of chlorostannanes appeared to be a useful synthesis; again, however, the products suffer from decomposition under the reaction conditions. The related disilane $Me_3SiSiCl_3$ is known to decompose base-catalysed furnishing Me_3SiCl and polysilanes [21].

Only germanium derivatives ($R_3GeSiCl_3$; R = Me, Et) could be isolated as pure compounds in moderate



Scheme 7. Stannylphosphane cleavage with Si_2Cl_6 [20].



Scheme 6. Reaction of a chloroalkylidenephosphane with Si_2Cl_6 [18].

yield (Scheme 3) [22]. This stimulated our present work to study nucleophile-catalysed $SiCl_3$ or $SiCl_2$ transfer reactions involving trichlorosilyl compounds $R_3GeSiCl_3$ and $R_2Ge(SiCl_3)_2$ with the aim to exploit their potential as sources of nucleophile-coordinated $SiCl_2$ that may be as useful as the well-known complexes of $GeCl_2$ with ethers, amines and phosphanes in germylene chemistry.

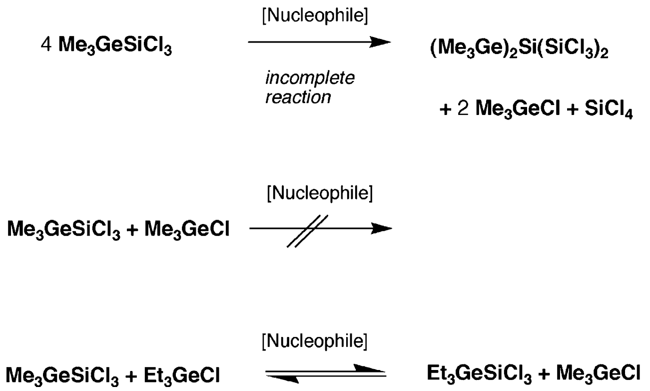
3. Dismutation behaviour of trichlorosilylgermanes $R_3GeSiCl_3$ and $R_2Ge(SiCl_3)_2$

The *Benkeser*-type synthesis of $Me_3GeSiCl_3$ (**1**) (Scheme 1) is affected by its decomposition to the branched compound $(Me_3Ge)_2Si(SiCl_3)_2$ (**2**), whereas a related decomposition of $Me_2Ge(SiCl_3)_2$ (**3**) does not take place under the reaction conditions [23].

Pure **1** is thermally perfectly stable; only in presence of nucleophiles disproportionation takes place. Adding triethylamine to pure samples of **1** revealed, that formation of **2** is incomplete and that **2** is accompanied by Me_3GeCl and $SiCl_4$. When about equivalent amounts of Me_3GeCl are added to samples of **1**, subsequent addition of NEt_3 as "disproportionation catalyst" (see Scheme 2) does not initiate disproportionation of **1**: "Me_3GeCl is stabilising **1**".

To evaluate if added Me_3GeCl plays a role in a dynamic equilibrium, Et_3GeCl was added instead of Me_3GeCl: again, disproportionation does not take place, but now the presence of NEt_3 induces a $Cl/SiCl_3$ exchange reaction between the two kinds of trialkylgermyl groups. Adding Me_3GeCl to $Et_3GeSiCl_3$ (**4**) and a catalytic amounts of NEt_3 leads to the same equilibrium mixture (Scheme 8).

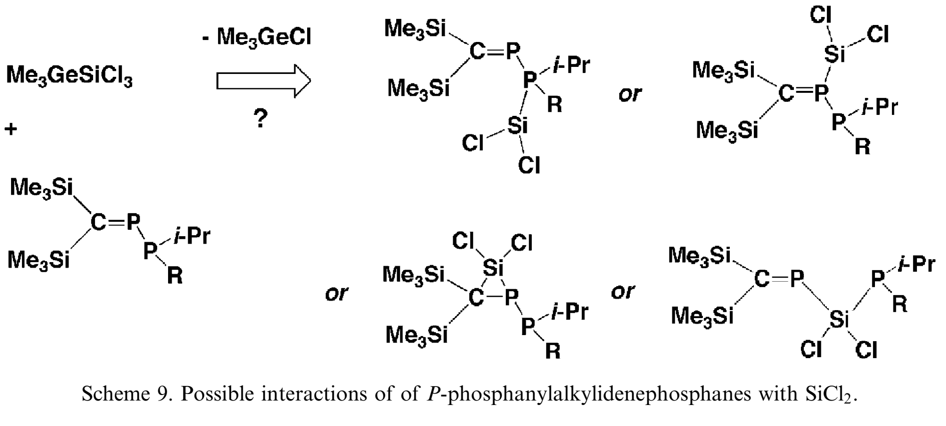
These observations allow to suggest, that trichlorosilylgermanes **1** and **4** are – similar as Si_2Cl_6 – activated by nucleophiles either through adduct formation or by α-elimination under formation of nucleophile-coordinated dichlorosilylene (Scheme 2).



Scheme 8. Nucleophile-catalysed reactions of $Me_3GeSiCl_3$ (**1**).

An experimental probe would be trapping reactions that do not involve organic organoelement halides (thus excluding S_N reactions of transient or latent $SiCl_3^-$ anions, see Scheme 2). A very useful azadiene-type trapping reagent, that would meet these requirement, had been featured by Karsch et al., who "extract" a $SiCl_2$ moitey out of the $HSiCl_3$/amine system [24]. As alternative reagents, that combine sufficient nucleophilicity and high reactivity towards carbene-analogous species, we chose a sterically tuned set of *P*-phosphanylalkylidenephosphanes [25]. Reactions of *P*-phosphanylalkylidenephosphanes with phosphinidenes and with sulfur or selenium (that are formally also to be regarded as carbene analogous moieties) are known. Phosphinidenes prefer to add to the P=C double bond [26], whereas sulfur and selenium start their reaction sequence by inserting into P–P bonds, then adding to tricoordinated phosphorus, before they add to the P=C double bond, leading to dithio- and diselenophosphinato-substituted thia- or selenaphosphiranes [25].

Related products were also to be expected from reactions of *P*-phosphanyl-alkylidenephosphanes with $SiCl_2$ or $GeCl_2$ (Scheme 9).



Scheme 9. Possible interactions of of *P*-phosphanylalkylidenephosphanes with $SiCl_2$.

4. Reactions of $SiCl_2$ and $GeCl_2$ sources with bis(trimethylsilyl)alkylidenephosphanes

P-Di-*i*-propylphosphanylbis(trimethylsilyl)alkylidenephosphane reacts with **1** furnishing two main products, a di-*i*-propylphosphanyl-substituted diphosphene and a di-*i*-propylphosphanyl-sustituted 2,3-disilaphosphetane (Scheme 10) [27]. The ratio of these products is determined by the amount of **1** added to the trapping reagent: the 1:1 ratio favours the diphosphene, excess **1** favours the heterocylic product.

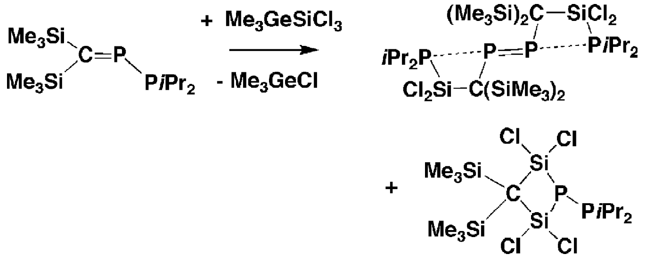
The diphosphene formation appears analogous to that of the $(Me_3Si)_2C{=}PCl/Si_2Cl_6$ reaction (Scheme 6) [18]; in the latter case a transient ^{31}P-NMR signal at +371 ppm suggests the formation of $(Me_3Si)_2C{=}PSiCl_3$ [28] that is apparently the precursor of the transient "unsymmetric" dimer from Scheme 6; in the former case neither hypothetic $(Me_3Si)_2C{=}PSiCl_2$-P-*i*-Pr_2 nor an unsymmetric dimer was observed when the reaction was monitored by ^{31}P-NMR.

With **1** as a source of $SiCl_2$ added to $(Me_3Si)_2C{=}PCl$, ^{31}P-NMR monitoring allowed to trace the transient +371 ppm ^{31}P-NMR signal as well as large amounts of the unsymmetric dimer, the symmetric diphosphene, and another species that gives a ^{31}P-NMR pattern that is closely related to that of the phosphanyl-substituted 2-phospha-1,3-disiletane from Scheme 10 [28]. The surprising double $SiCl_2$ attack on the P=C bond is achieved only by silylgermane **1,** but not by Si_2Cl_6.

When the $GeCl_2$dioxane complex reacts with *P*-dialkylphosphanylbis(trimethylsilyl)-alkylidenephosphanes, only *unsymmetric* diphosphenes, accompanied by dichlorogermanes $(R_2P)_2GeCl_2$, were observed by solution NMR (Scheme 11) [23].

A solid diphosphene (R = *i*-Pr) was characterised by a crystal structure determination at low temperature, but all compounds decompose at room temperature with liberation of R_2PCl and a bicyclic diphosphane [23]. When $SnCl_2$ is added to the above unsymmetric diphosphenes, the PR_2 group is transferred from Ge(IV) to Sn(II), and Cl exchange from Sn(II) to Ge(IV) furnishes the symmetric diphosphene $[Cl_3Ge(Me_3Si)_2C]_2P_2$. Similarly, the diphosphene from Scheme 10 is cleaved by SnX_2 (X = F, Cl) to give symmetric diphosphenes $[XCl_2Si(Me_3Si)_2C]_2P_2$ by PR_2/X exchange reaction [29].

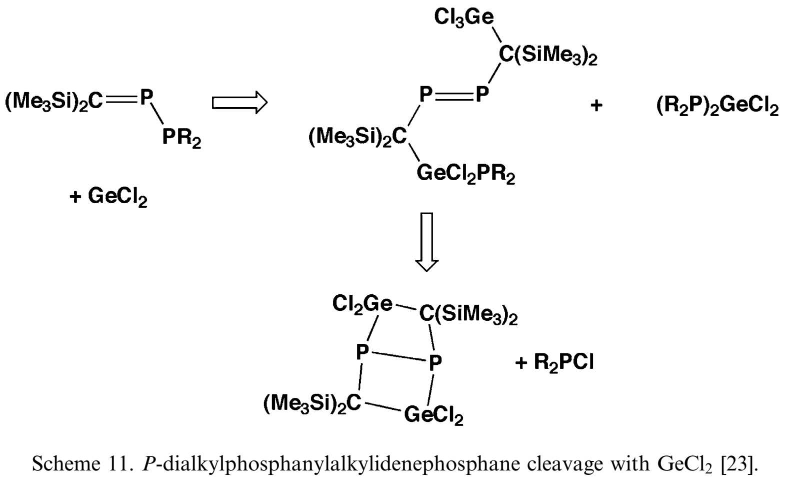
Extensions of this study to further phosphaalkenes, iminophosphanes and related substrates as well as to silylgermanes with different substitution patterns are under way.



Scheme 10. $SiCl_2$ transfer to di-*i*-propylphosphanylbis(trimethylsilyl)alkylidenephosphane [27].

5. Summary

Compound **1** is a new source for $SiCl_2$ transfer reactions under mild, aprotic conditions. It shows analogies to Si_2Cl_6, but also enhanced reactivity towards *P*-phosphanylalkylidene phosphanes giving P=C double bond cleavage that has not been observed in related reactions with $GeCl_2$ or other carbene analogs. The mechanistic aspects of this reaction require further studies.



Scheme 11. *P*-dialkylphosphanylalkylidenephosphane cleavage with $GeCl_2$ [23].

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