SOME NEW NUCLEOPHILE-INDUCED REACTIONS INVOLVING GeCl₂, SiCl₂ AND GeMe₂ TRANSFER

W. – W. du Mont*, E. Seppälä, T. Gust, J. Mahnke, and L. Müller

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig
Hagenring 30, D-38106 Braunschweig, Germany

Considering the stable compound Me₃GeSiCl₃ (**1**) as potential nucleophile-induced source of SiCl₂ moieties, and to evaluate properties of Me₂Ge(SiCl₃)₂ (**6a**) as potential nucleophile-induced source of SiCl₂ and of GeMe₂ moieties that could be generated by a kind of *domino-α-elimination*, alkylidenediphosphanes **10a-c** [(Me₃Si)₂C=P-PRR'; R, R' = *i*-propyl, *t*-butyl] were chosen as new multifunctional trapping reagents for six-electron species GeCl₂, SiCl₂ and GeMe₂. Reactions of **10a-c** with GeCl₂-dioxane lead to novel diphosphene intermediates of the type (Me₃Si)₂(Cl₃Ge)C=P=P-C(SiMe₃)₂GeCl₂PRR' (R, R' = *i*-Pr, **11a**; R = *t*-Bu, R' = *i*-Pr, **11b**; R, R' = *t*-Bu, **11c**) that decompose by liberation of chlorophosphanes RR'PCl providing bicyclic [PC(SiMe₃)₂GeCl₂]₂ (**12**). Reactions of **10b** with **1** or **6a** as SiCl₂ precursors, however, lead to formation of a stable *P*-phosphanylphosphasilirane **13b**. This observation indicates, that trichlorosilylgermanes will be of importance as sources for the generation of nucleophile-stabilized dichlorosilylene under very mild conditions.

INTRODUCTION

Different from well established coordination / insertion / α-elimination equilibria involving GeCl₂ and the P-Cl bonds of chlorophosphanes,^[1] the intended GeCl₂ insertion into the P-Cl bond of the *P*-chloroalkyldenediphosphane (Me₃Si)₂C=P-Cl led to an unexpected diphosphene R*-P=P-R* [R* = (Me₃Si)₂(Cl₃Ge)C-] with Ge-C bonds^[2]. The attempt to use Si₂Cl₆ in a similar fashion as SiCl₂ transfer reagent gave a related diphosphene R**=P=P-R** with R** = (Me₃Si)₂(Cl₃Si)C-^[2]. To gain insight into the way of formation of these unusual functionalised diphosphenes, we are studying reactions of alkylidenephosphane derivatives with reagents that can be expected to act as sources of GeCl₂, SiCl₂, and GeMe₂ moieties.

MATERIALS AND METHODS

All experiments were carried out with exclusion of air and moisture. Solvents were dried according to standard procedures. Solution NMR spectra were determined with BRUKER AC 200 instruments (200 MHz for ¹H, 39.8 MHz for ²⁹Si, 81.0 MHz for ³¹P); shifts are given relative to TMS (¹H, ²⁹Si) and 85% H₃PO₄ (³¹P); solvent [D₆]benzene. - MS. Finigan Mat 8430. - Elemental analyses: Carlo Erba analytical gas chromatograph.

Reaction of compound 10a with GeCl₂-dioxane.

a) To a suspension of 0.38 g (1.6 mmol) GeCl₂-dioxane in 30 ml toluene at –20 °C 0.31 g (0.9 mmol) **10a**^[6] were added. After letting the mixture warm to room temperature and 2 h stirring, the solution is separated from the solid residue. ³¹P NMR indicates the presence of **11a** (see table 1) and of (*i*-Pr₂P)₂GeCl₂ [δ (³¹P) = 19 ppm (s)]^[8] as main products. Removal of the solvent is accompanied by formation of decomposition products. the adduct of (*i*-Pr₂P)₂ with GeCl₂ [δ (³¹P) = 1.5 ppm (s, broad)], *i*-Pr₂PCl, *i*-Pr₂PGeCl₃, and **12** (see table 1).

From the oily residue, a single crystal of **11a** suitable for X-ray diffraction was isolated.

b) Carrying the above reaction out at room temperature and working up after 5 h stirring provides after removal of volatile products an orange oil that contains enriched **12**. Crystallisation from pentane gave **12** as a yellow solid (about 50 % yield) that melts at 125 °C. **12**: EI-MS (70 eV) *m/z* (%) 650 (<1) [M⁺ - CH₃], 522 (14) [M⁺ - GeCl₂], 378 (16) [M⁺ - 2 GeCl₂], 305 (6) [M⁺ - 2 GeCl₂ - SiMe₃], 189 (18) [(Me₃Si)₂CP⁺], 174 (10) [(Me₃Si)(Me₂Si)CP⁺], 73 (96) [(Me₃Si)⁺]. ¹H-NMR: δ = 0.3 ppm (s), 0.4 (s). ³¹P-NMR: δ = 126.3 ppm (s).

C₁₄H₃₆Cl₄Ge₂P₂Si₄ (M = 665.7 g/mol): Calc. C 25.26, H 5.45, found. C 24.92, H 5.40 %.

RESULTS AND DISCUSSION

Trialkyl(trichlorosilyl)germanes and –stannanes.

Our recent observation, that the syntheses of trichlorosilylgermanes and –stannanes R₃MSiCl₃ (M = Ge, Sn) from R₃MCl/HSiCl₃/NEt₃ are accompanied by their amine-catalysed disproportionation into Me₃MCl, SiCl₄ and neopentane-like branched products (R₃M)₂Si(SiCl₃)₂^[3,4], led us to consider the stable compound Me₃GeSiCl₃ as potential nucleophile-induced source of SiCl₂ moieties. Chlorotrimethylgermane reacts with

trichlorosilane and triethylamine to provide trichlorosilylgermanes Me₃GeSiCl₃ (**1**) in fair yield as distillable liquid. The formation of **1** is, however, followed by incomplete base-catalysed decomposition reactions leading to novel solid (Me₃Ge)₂Si(SiCl₃)₂ **2**.

Distilled **1** is thermally stable, but it decomposes, upon addition of small amounts of Et₃N or *i*-Pr₃P, incompletely into **2**, Me₃GeCl, and SiCl₄.

Chlorotrialkylstannanes R₃SnCl (R = CH₃, C₂H₅, *n*-C₄H₉) react with trichlorosilane and triethylamine providing only traces of silylstannanes R₃SnSiCl₃ **3a - c**, but substantial amounts of the branched silylstannanes (R₃Sn)₂Si(SiCl₃)₂ **4a - c**. Neopentane-like branched compounds **2** or **4** are also formed, when dialkyl(trialkylgermyl- and -stannyl)phosphanes R'R''PGeMe₃ or R'R''PSnR₃ are cleaved by hexachlorodisilane.^[1,2] Following the latter reactions by heteronuclear NMR reveals, that a sequence of several reaction steps involving transmetalation / transsilylation reactions can lead to **2** (or **4**):

i) Me₃Ge / Si₂Cl₅ exchange at phosphorus leading from R'R''PGeMe₃ / Si₂Cl₆ to R'R''PSi₂Cl₅ and Me₃GeCl.

ii) SiCl₂ (or SiCl₃⁻) transfer from R'R''PSi₂Cl₅ to germanium yielding Me₃GeSiCl₃ (**1**) and R'R''PSiCl₃.

iii) dismutation of Me₃GeSiCl₃ into (Me₃Ge)₂Si(SiCl₃)₂ (**2**), Me₃GeCl, and SiCl₄. The latter step iii) implies the nucleophile-induced transfer of one Me₃Ge group and two SiCl₃ groups to the Si atom of a Me₃GeSiCl₃ molecule. We assume, that nucleophilic attack at the silicon atom of Me₃GeSiCl₃ molecule can give the Me₃Ge moiety the character of an anionic leaving group that attacks another Me₃GeSiCl₃ molecule under nucleophilic substitution of a Cl atom, leading to a (Me₃Ge)₂SiCl₂ intermediate that does not allow the attack of another Me₃Ge group but is susceptible to subsequent trichlorosilylation by latent SiCl₃⁻ nucleophiles (Cl / SiCl₃ exchange at Si) or by nucleophile-coordinated dichlorosilylene (i.e. by SiCl₂ insertions into Si-Cl bonds of (Me₃Ge)₂SiCl₂) providing **2**.

In the series of related trialkylstannyl compounds **3**, related formation and decomposition reactions were both faster than with germysilane **1**. When stannylphosphane / hexachlorodisilane or trialkylchlorostannane / trichlorosilane / triethylamine reactions were carried out using the *n*-Bu₃Sn substituent, formation of *n*-Bu₃SnSi(SiCl₃)₃ (**5c**) from intermediate *n*-Bu₃SnSiCl₃ (**3c**) was preferred to that of (*n*-Bu₃Sn)₂Si(SiCl₃)₂ (**4c**).^[2-4] This suggests, that steric reasons might limit the ability for R₃M groups to attack R₃MSiCl₃ (M = Ge, Sn) molecules in a way that they have to compete with the trichlorosilylation of R₃MSiCl₃ leading to R₃MSi₂Cl₅ intermediates that are rapidly further silylated. As further experimental probes for the SiCl₃⁻ or SiCl₂ transfer reactions, trapping experiments of R₃MSiCl₃ with benzyl chloride in presence of nucleophiles did lead to benzyltrichlorosilane.^[3-5]

Dialkylbis(trichlorosilyl)germanes. Dialkyldichlorodimethylgermanes R₂GeCl₂ (R = CH₃, C₂H₅, *n*-C₄H₉) react with trichlorosilane and triethylamine furnishing dialkylbis(trichlorosilyl)germanes R₂Ge(SiCl₃)₂ (**6a-c**). Different from **1**, compounds **6a-c** are fairly stable in presence of triethylamine. This resistance allows their isolation from the reaction mixtures in high yield. Studying the behaviour of **6a** (R = CH₃) towards a number of other nucleophiles, however, allowed to detect its decomposition under certain conditions, for instance in presence of *i*-Pr₃P. The decomposition pathway of **6a** is apparently quite different from that of **1**: As germanium-containing main product the 1,2-bis(trichlorosilyl)digermane Cl₃SiGeMe₂GeMe₂SiCl₃ (**7**) was detected.

For the formation of this chain-like compound **7**, a "domino- α -elimination"-like sequence of reactions of **6a** can be postulated:

- i) α -elimination at one silicon atom of **6a**, leading to SiCl_2 coordinated by the nucleophile $i\text{-Pr}_3\text{P}$ and to the intermediate $\text{Me}_2\text{Ge}(\text{Cl})\text{SiCl}_3$;
- ii) α -elimination at the germanium atom of $\text{Me}_2\text{Ge}(\text{Cl})\text{SiCl}_3$, leading to SiCl_4 and GeMe_2 , that may be coordinated with $i\text{-Pr}_3\text{P}$;
- iii) insertion of GeMe_2 into a Ge-Si bond of **6a**, leading to digermene **7**.

The fate of the proposed intermediate $i\text{-Pr}_3\text{P}\text{SiCl}_2$ is yet not quite clear: ^{31}P - and ^{29}Si -NMR spectra confirm, that the catalyst $i\text{-Pr}_3\text{P}$ remains unconsumed after the decomposition of **6a**, and that apart from **7** and SiCl_4 , other yet not identified soluble silicon species are present in solution before work-up of the reaction mixture.

Alkylidenediphosphanes $(\text{Me}_3\text{Si})_2\text{C}=\text{P}-\text{PRR}'$ ($\text{R}, \text{R}' = i\text{-propyl}, t\text{-butyl}$).

In course of the reactions of the *P*-chloroalkylidenediphosphane $(\text{Me}_3\text{Si})_2\text{C}=\text{PCl}$ with GeCl_2 to unexpected diphosphene $\text{R}^*\text{-P}=\text{P}-\text{R}^*$ [**8a**, $\text{R}^* = (\text{Me}_3\text{Si})_2(\text{Cl}_3\text{Ge})\text{C}-$] with Ge-C bonds, and with Si_2Cl_6 to $\text{R}^{**}\text{-P}=\text{P}-\text{R}^{**}$ [**8b**, $\text{R}^{**} = (\text{Me}_3\text{Si})_2(\text{Cl}_3\text{Si})\text{C}-$]^[2], doublet-doublet ^{31}P NMR patterns of reactive intermediates could be detected. In course of the Si_2Cl_6 reaction, the ^{31}P NMR shifts as well as $^1J(^{31}\text{P}, ^{31}\text{P})$ are consistent with the structure $(\text{Me}_3\text{Si})_2\text{C}=\text{P}-\text{P}(\text{SiCl}_3)[\text{C}(\text{SiMe}_3)_2(\text{SiCl}_3)]$ (**9a**). In the related intermediate **9b** from the GeCl_2 reaction, however, the less shielded ^{31}P nucleus appears too far upfield and the more shielded ^{31}P nucleus appears too far downfield, compared with expectations for a structure of the kind $(\text{Me}_3\text{Si})_2\text{C}=\text{P}-\text{P}(\text{GeCl}_3)[\text{C}(\text{SiMe}_3)_2(\text{SiCl}_3)]$.^[2] This inconsistency stimulated our interest to evaluate properties of yet unknown Ge-functionalized alkylidenediphosphanes and their silicon relatives.

Following the above experimental results, we consider the stable compound $\text{Me}_3\text{GeSiCl}_3$ (**1**) as potential nucleophile-induced source of SiCl_2 moieties, and the stable compound $\text{Me}_2\text{Ge}(\text{SiCl}_3)_2$ (**6a**) as potential nucleophile-induced source of SiCl_2 and GeMe_2 moieties that could be generated by a kind of *domino- α -elimination*. As new multifunctional trapping reagents for six-electron species, we chose alkylidenediphosphanes $(\text{Me}_3\text{Si})_2\text{C}=\text{P}-\text{PRR}'$ (**10a**: $\text{R}, \text{R}' = i\text{-propyl}$, **10b**: $\text{R} = t\text{-butyl}$, $\text{R}' = i\text{-propyl}$, **10c**: $\text{R}, \text{R}' = t\text{-butyl}$)^[6].

Experiments with GeCl_2 led - to our surprise - not to simple insertion products, nor to $\text{P}^{\text{III}} \rightarrow \text{Ge}^{\text{II}}$ coordination (as observed in reaction of tetraalkyldiphosphanes with GeCl_2)^[17], but novel intermediates of the type $\text{R}^*\text{-P}=\text{P}-\text{C}(\text{SiMe}_3)_2\text{GeCl}_2\text{PRR}'$ (**11a-c**) could be identified by their characteristic ^{31}P NMR AMX patterns (table 1)^[18]. The structure of compound **11a** could be determined by X-ray diffraction at low temperature^[8]. **11a** contains a $\text{P}=\text{P}$ bond just like that in $\text{R}^*\text{-P}=\text{P}-\text{R}^*$ [$\text{R}^* = (\text{Me}_3\text{Si})_2(\text{Cl}_3\text{Ge})\text{C}-$]^[2] and a remote $\text{C}-\text{GeCl}_2-\text{P}i\text{Pr}_2$ moiety.^[18]

Table 1: ³¹P-NMR data of compounds 10, 11, 12, 13

	δ ³¹ P [ppm]		P_X	$\pm J(^{31}\text{P}, ^{31}\text{P})$ [Hz]		
	P_A	P_M				
10a [6]	453.7	1.6		220.8		
10b [6]	452.1	13.0		227.2		
10c [6]	453.7	21.9		240.1		
11a	581.9	547.3	25.2	649.9(AM)	26.4(AX)	13.1(MX)
11b	580.6	548.0	44.3	651.5(AM)	11.4(AX)	6.5(MX)
11c	574.6	545.7	62.2	654.7(AM)	10.6(AX)	2.5(MX)
12	126.3					
13b	45.6	-112.3		195.6		

The Ge-P bonds of compounds 11 can be cleaved by reaction with SnCl₂ suspended in toluene furnishing R*-P=P-R*. At room temperature all compounds 11 decompose in the same surprising manner: liberation of chlorophosphanes RR'PCl from R*-P=P-C(SiMe₃)₂GeCl₂PRR' (11a-c) provides the bicyclic molecule [PC(SiMe₃)₂GeCl₂]₂ (12) that can be recognized by its ¹H and ³¹P NMR resonances (table 1).

The reactions of the SiCl₂ precursors 1 and 6a with 10b gave not compounds related to 11, but furnished a new compound 13b that exhibits a ³¹P-NMR doublet, doublet pattern involving one P nucleus with a large upfield shift (see table 1) whereas the ³¹P NMR resonance of the *i*-Pr(*t*-Bu)P group (P_A) appears at „normal“ 45.6 ppm. The upfield shift of P_M (-112.3 ppm) indicates the presence of a phosphasilirane ring system, that was apparently formed by 1+2 cycloaddition of SiCl₂ with the P=C double bond of 10b. This experiment supports the suggested role of trichlorosilylgermanes as SiCl₂ precursors.

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