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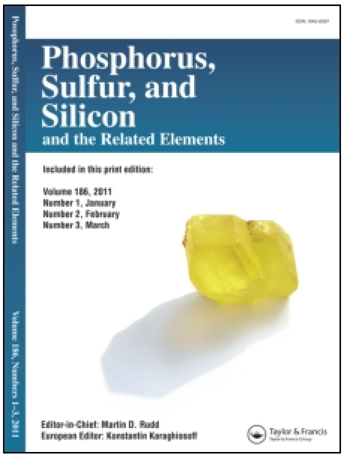

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REACTIVITY OF A BASE-STABILIZED GERMANIMINE AND GERMANETHIONE

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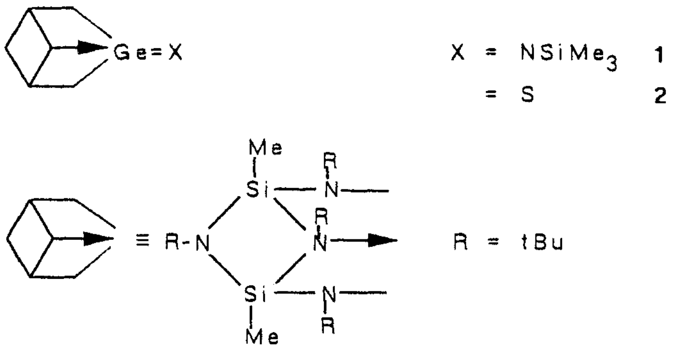
Abstract

After studying the reactivity of the base-stabilized germanimine $(MeSi)_2(NtBu)_4Ge{=}NSiMe_3$ **1** and germanethione $(MeSi)_2(NtBu)_4Ge{=}S$ **2** towards simple polar molecules, we were interested in their cycloaddition chemistry. **1** gives no reaction with ketones (e. g. benzophenone) and dienes (e. g. 2,3-dimethylbutadiene). The reaction of **1** with an excess of CS_2 gives **2** and trimethylsilylisothiocyanate **4**. **2** reacts with the dichlorocarbene to give the bis(amino)dichlorogermane **5**.

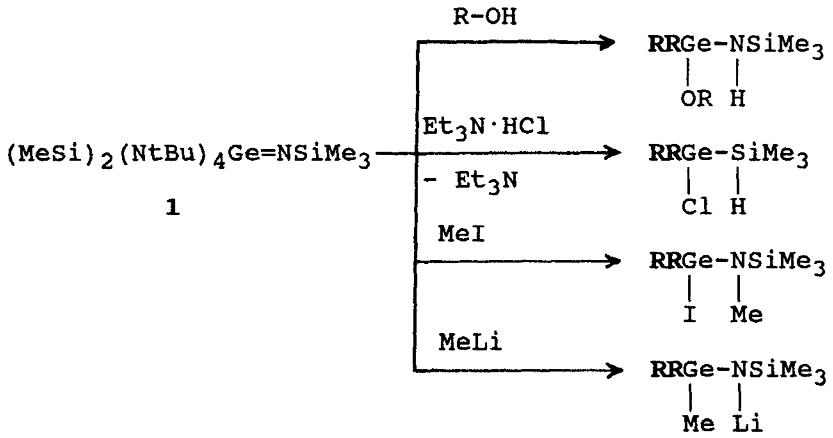
Key words: Base stabilized germanimine, germanethione, cycloaddition reactions of

INTRODUCTION

Recently, we were successful in synthesizing a polycyclic system with a stable germanium-nonmetal-double bond. The reaction of a base-stabilized germylene with trimethylsilylazide or sulfur leads, at room temperature, to the germanimine 1 and germanethione 2[1,2].



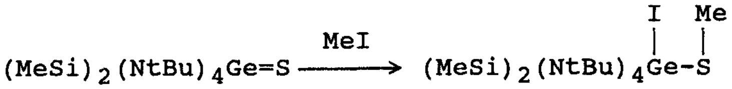
We have studied the reactions of these compounds with some simple polar molecules[3]. The results for 1 are collected in equation (1).



RR = $(MeSi)_2(NtBu)_4$ (1)

The Ge=S double bond of **2** is less reactive than the Ge=N double bond of **1**. This is probably explained by the larger contribution to the overall molecular structure of the mesomeric form ($Ge^{+}-X^{-}$).

MeI adds only at a high temperature and must be used in large excess (equ. (2)).



$$(MeSi)_2(NtBu)_4Ge{=}S \xrightarrow{MeI} (MeSi)_2(NtBu)_4\overset{I}{\overset{|}{Ge}}-\overset{Me}{\overset{|}{S}} \quad (2)$$

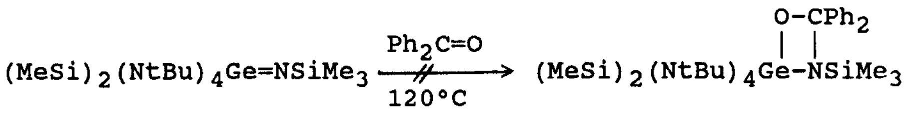
2

Further, we were interested to know, if our system could participate in cycloaddition reactions.

RESULTS AND DISCUSSION

Unstable germanimines can be chemically identified through their dimerization or [2+2]-cycloaddition reactions with ketones[4], e. g. dimethylgermanimine $Me_2Ge{=}N-SiMe_3$ reacts with benzophenone to form an unstable intermediate, which decomposes to $Ph_2C{=}NSiMe_3$ and other products.

Therefore, the reaction of **1** with benzophenone was expected to yield the appropriate 4-membered ring through a [2+2]-cycloaddition (equ. (3)).

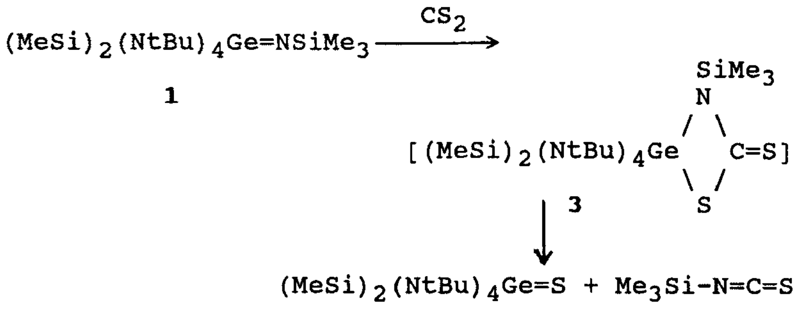


$$\mathrm{(MeSi)_2(NtBu)_4Ge{=}NSiMe_3} \overset{\mathrm{Ph_2C{=}O}}{\underset{120\,°\mathrm{C}}{\not\longrightarrow}} \mathrm{(MeSi)_2(NtBu)_4}\begin{array}{c}\mathrm{O{-}CPh_2}\\ |\quad|\\ \mathrm{Ge{-}NSiMe_3}\end{array}$$

1 (3)

However, no reaction occurs even after refluxing for two days in toluene. We believe that one of two possibilities is responsible for this: Either the steric bulk of the phenyl groups is sufficiently large to prevent the reaction or the polarity of the carbonyl group is too small.

In order to test these possibilities, we chose to react the germanimine **1** with CS_2. It has been shown that N-methyldiphenylgermanimine adds to CS_2 with the formation of the unstable 2-germa-4-thioxo-1,3-thiaazetidine[5]. The reaction of **1** with CS_2 follows an identical route (equ. (4)).



$$\mathrm{(MeSi)_2(NtBu)_4Ge{=}NSiMe_3} \xrightarrow{\mathrm{CS_2}} \left[\mathrm{(MeSi)_2(NtBu)_4Ge}\begin{array}{c}\mathrm{SiMe_3}\\ \mathrm{N}\\ /\ \ \backslash\\ \quad\ \ \mathrm{C{=}S}\\ \backslash\ \ /\\ \mathrm{S}\end{array}\right] \xrightarrow{\mathbf{3}} \mathrm{(MeSi)_2(NtBu)_4Ge{=}S} + \mathrm{Me_3Si{-}N{=}C{=}S}$$

1

2 **4**

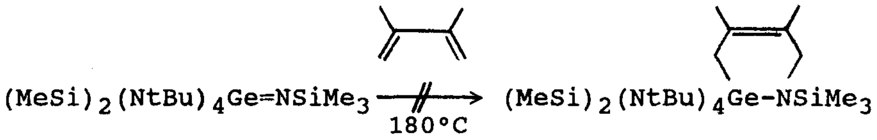
(4)

After 20 h of refluxing in benzene with 100% excess of CS_2, the ^1H-NMR spectrum shows the signals expected for the well known germanethione **2**. The intermediate **3** can not be isolated.

This reaction provides a new possibility for the synthesis of trimethylsilylisothiocyanate[6,7] **4**, which can be indentified by its ^1H-NMR-data (ppm -0.18; s; $SiMe_3$) as the other reaction product.

The ^1H-NMR spectrum of an equimolar mixture of **2** and CS_2 shows peaks corresponding only to the germanethione. However, without either the isolation, or spectral evidence for an intermediate formed by cycloaddition, we cannot say whether **2** and CS_2 actually react.

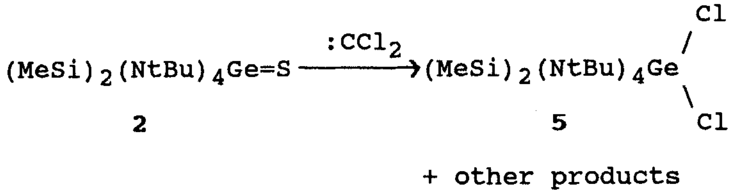
Dimethylbutadiene can be used as "trapping" reagent for e. g. digermenes[8]. Attempts to add it to **1** at 180°C in a sealed tube failed; after three days **1** could be recovered quantitatively (equ. (5)).



$$(MeSi)_2(NtBu)_4Ge{=}NSiMe_3 \xrightarrow[180°C]{\not} (MeSi)_2(NtBu)_4Ge{-}NSiMe_3$$

1 (5)

A [2+1] cycloaddition was expected from the reaction of **2** (which is stable in $CHCl_3$) with dichlorocarbene. However, to our surprise, we obtained together with unreacted **2** the dichlorogermane $(MeSi)_2(NtBu)_4Ge(Cl)_2$ **5**. At present, the mechanism for this process is not fully understood (equ. (6)).



$$\underset{\mathbf{2}}{(MeSi)_2(NtBu)_4Ge{=}S} \xrightarrow{:CCl_2} \underset{\mathbf{5}}{(MeSi)_2(NtBu)_4GeCl_2} + \text{other products} \qquad (6)$$

CONCLUSION

Our work has shown that 1 and 2 behave as polar double bonds with respect to their reactivity towards polar molecules. However, their cycloaddition chemistry is somewhat limited, possibly due to their bulky substituents. Our study into the chemistry of these interesting compounds continues.

EXPERIMENTAL

The compounds described are air- and moisture-sensitive. Therefore, all reactions were carried out under an atmosphere of dry nitrogen in a modified Stock vacuum line.

-^{1}H-NMR were recorded using a Bruker WP 80, 80 MHz in C_6H_6/C_6D_6, and referenced to the benzene signal;

elemental analyses were performed by Beller, Göttingen.

Reaction of **1** with CS_2: Preparation of **2**

A solution of **1** [100 mg; 0.188 mmol] in benzene (5 ml) was mixed with CS_2 (1 ml, 100% excess). After 20 hrs. of reflux, the ^{1}H-NMR spectrum shows the signals of **2** and **4** in a molar ratio of 1:1. The solvent was removed *in vacuo* and the residue was sublimed under vacuum (80°C; 10^{-2} Torr) to give 73% yield of **2**[2] [65 mg; 0.137 mmol]. The compound **4** was indentified by its ^{1}H-NMR spectrum (δ = -0.18 ppm), which was identical to a product obtained by a literature method[6].

-^{1}H-NMR of **2**: δ = 0.48 (s, 6H, $SiCH_3$), 1.32 (s, 18H, CCH_3), 1.52 (s, 18H, CCH_3).

$C_{18}H_{42}GeN_4Si_2S$ (475.6)	Calc.	C 45.8	H 8.9
	Found	C 45.4	H 8.9

Reaction of **2** with Dichlorocarbene: Preparation of **5**

A solution of **2** [250 mg; 0.525 mmol] in ether (10 ml) was added dropwise to a stirred equimolar ether (10 ml) solution of dichlorocarbene (from $CHCl_3$ and KOtBu[9]), cooled to 0°C. The resulting solution was then stirred for 2 days at R. T. The solvent was removed and the residue recrystallized from benzene to give 61% of **5** [165 mg; 0.326 mmol].

-^{1}H-NMR: δ = 0.61 (s, 3H, $SiCH_3$), 1.31 (s, 18H, CCH_3), 1.53 (s, 18H, CCH_3).

$C_{18}H_{42}Cl_2GeN_4Si_2$ (513.9)

Calc.	C 42.07	H 8.24	N 10.90
Found	C 41.92	H 8.23	N 10.88

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