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FORMATION OF ORGANOSILICON COMPOUNDS

CIV *. INVESTIGATION INTO THE FORMATION AND DECOMPOSITION OF THE 1,1,3,3-TETRAMETHYL-2,4-BIS(TRIMETHYLSILYL)-1,3-DISILABICYCLO[1.1.0]BUTANE **, ***

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Summary

The reaction of $Me_3SiCCl_2SiMe_2Cl$ with LiBu in Et_2O proceeds through the carbenoid $Me_3SiCCl(Li)SiMe_2Cl$ (**6a**) to *cis*- and *trans*-2,4-dichloro-2,4-bis(trimethylsilyl)-1,1,3,3-tetramethyl-1,3-disilacyclobutane (**2** and **3**), these being the intermediates in the formation of 1,1,3,3-tetramethyl-2,4-bis(trimethylsilyl)-1,3-disilabicyclo[1.1.0]butane (**1**). They react with the carbenoid **6a** through metal-halogen exchange to produce the lithiated *cis*- and *trans*-carbenoids (**2a** and **3a**) with the regeneration of $Me_3SiCCl_2SiMe_2Cl$ to produce **1**. Compounds **2** and **3** react with LiBu in THF to produce silylated ethylenes, along with different *C*-substituted 1,3-disilacyclobutanes. These compounds were formed from the primary product, the 1,3-disilabicyclobutane **1**, which decomposes with an excess of LiBu to give these compounds. The reactions of $Me_3SiCCl_2SiMe_2X$ (X = F, Cl, Br, Tos (*p*-toluensulfonic acid), OR) are influenced by the substituent X: when X = F, the reaction with LiBu under analogous conditions gives $Me_3SiCCl_2SiMe_2Bu$.

$Me_3SiCCl_2SiMeCl_2$ (**17**) reacts with LiBu in THF, through the carbenoid $Me_3SiCCl(Li)SiMeCl_2$ (**17a**), to form the ethylene derivatives *cis*- and *trans*-$(Me_3Si)(Cl_2MeSi)C{=}C(SiMeCl_2)(SiMe_3)$, (**18** and **19**). Their formation was not through a carbene intermediate. Two molecules of $Me_3SiCCl(Li)SiMeCl_2$ react through the elimination of LiCl to form $(Cl_2MeSi)(Me_3Si)ClCC(Li)(SiMe_3)(SiMeCl)$, which on further elimination of LiCl gives the ethylene derivatives **18** and **19**.

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* For Part CIII see ref. 1.

** Editorial note. This name is retained here as it has been used before, but the correct systematic name is 2,2,4,4-tetramethyl-1,3-bis(trimethylsilyl)-2,4-disilabicyclo[1.1.0]butane.

*** Dedicated to Professor Makoto Kumada.

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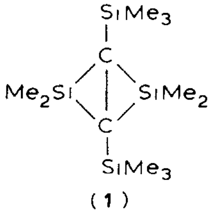
Introduction

In previous investigations it was shown that in the reaction of $Me_3SiCCl_2SiMe_2Cl$ with LiBu at temperatures of about −100 °C the lithiation of the CCl_2 group was achieved. Subsequent warming caused the elimination of LiCl, to form 1,1,3,3-tetramethyl-2,4-bis(trimethylsilyl)-1,3-disilabicyclo[1.1.0]butane (**1**) [2].



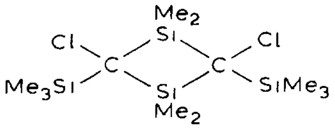
(1)

The aim of further investigations was to provide an explanation for the formation of **1**, its reactivity with metallation compounds, and for the influence of functional groups on the reaction pathway; for instance, to investigate the behaviour of $Me_3SiCCl_2SiMe_2X$ (where X = F, Cl, Br, OR, Tos) and of $Me_3SiCCl_2SiMeCl_2$ under the conditions of the reaction of $Me_3SiCCl_2SiMe_2Cl$ to form **1**. On this investigation the following is reported.

Results and discussion

1. The formation of 1

It is already known that the first stage in the formation of **1** from $Me_3SiCCl_2SiMe_2Cl$ and LiBu is the metallation to give $Me_3SiCCl(Li)SiMe_2Cl$ (solvent THF/Et_2O at −100 °C) [3]. From the reaction between $Me_3SiCCl_2SiMe_2Cl$ and LiBu at −100 °C in Et_2O, and subsequent warming to 20 °C, it was possible to separate, with the help of HPLC, the compounds **2**, **3**, **24** and **25**, of which **2** and **3** were the main products. The X-ray determination of the crystal structure of *cis*-2,4-dichloro-2,4-bis(trimethylsilyl)-1,1,3,3-tetramethyl-1,3-disilacyclobutane (**2**) has been published [1]. As a result, it was presumed that 1,3-disilacyclobutane was a suitable precursor in the synthesis of **1**.



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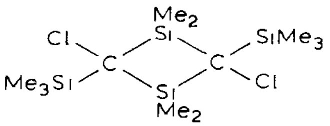

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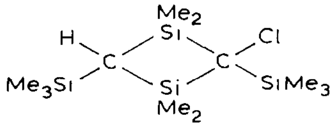

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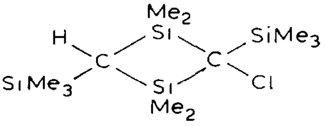

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The formation of **2** and **3** was also obtained by the reaction between $Me_3SiCCl_2SiMe_2Br$ and LiBu under conditions where halogen exchange did not occur. This lack of exchange occurred when $Me_3SiCCl_2SiMe_2H$ was reacted with Br_2 at −40 °C. On the other hand, when halogen exchange was permitted, **1** was produced. The reaction pathway was determined by the polarity of the solvent used and by the nature of substituent X in $Me_3SiCCl_2SiMe_2X$. The reaction of $Me_3SiCCl_2SiMe_2Cl$ with LiBu in Et_2O produced the compounds **2** and **3** (about 80%). Lithiation of $Me_3SiCCl_2SiMe_2Cl$ with LiBu gave $Me_3SiCCl(Li)SiMe_2Cl$ which by the addition of Me_3SiCl produced $(Me_3Si)_2CClSiMe_2Cl$ in Et_2O in a 12% yield. The same reaction in THF leads to $(Me_3Si)_2CClSiMe_2Cl$ in a 90% yield. This explains why the reaction of $Me_3SiCCl_2SiMe_2Cl$ with LiBu in THF produced the bicyclic **1**. The influence of the substituents is shown by the following examples: $Me_3SiCCl_2SiMe_2F$ reacts with LiBu forming $Me_3SiCCl_2SiMe_2Bu$, while $Me_3SiCCl_2SiMe_2Br$ and $Me_3SiCClSiMe_2Tos$ react with LiBu through CCl_2-lithiation, to produce the 1,3-disilacyclobutanes **2** and **3**.

1.1 Reactions of cis- and trans-1,3-disilacyclobutanes 2 and 3 with metallation reagents

The most favourable conditions for the formation of **1** is at low temperatures in THF and THF-contained solvents [2]. Therefore the reaction of compounds **2** and **3** with LiBu should proceed under analogous conditions (addition of LiBu to a mixture of **2** and **3** in THF at −105 °C). The investigation shows that the bicyclic **1** will form with a yield of only 10%, with a 30% recovery of the starting material, **2**

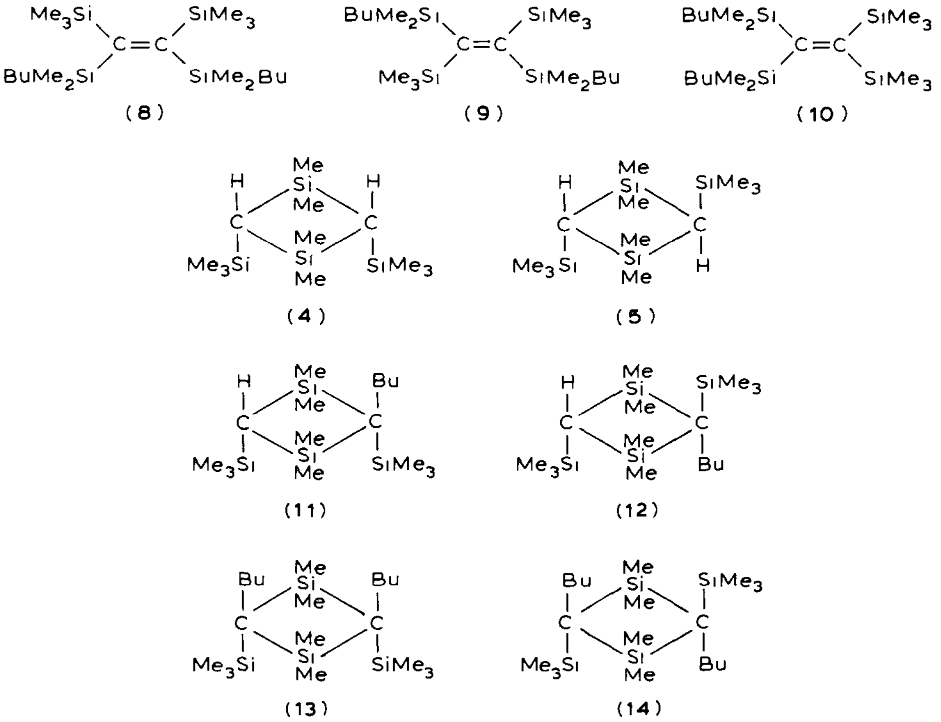


Fig. 1. Compounds from the reaction of the *cis*- and *trans*-1,3-disilacyclobutanes **2** and **3** with LiBu in THF.

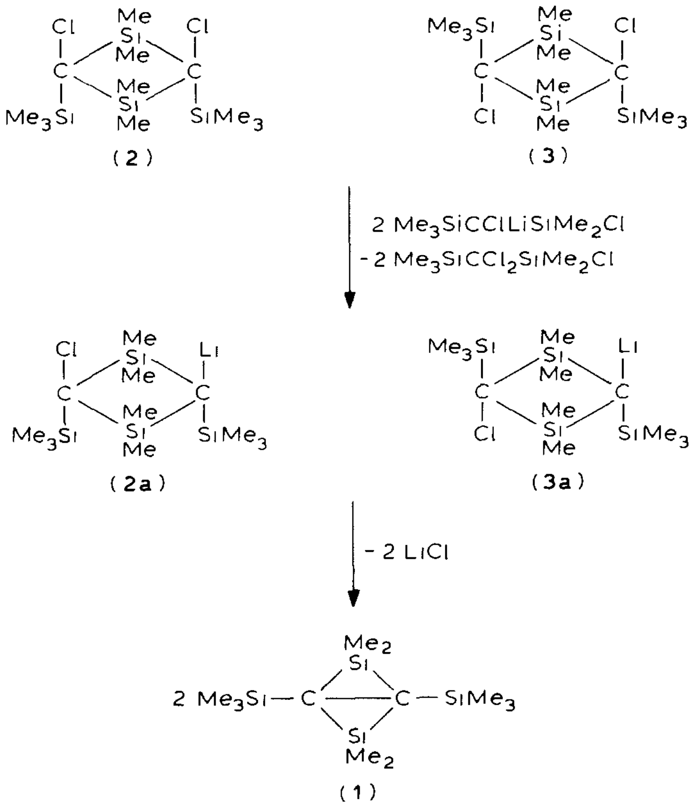
and **3**, even though an equimolar amount of LiBu was used. During the reaction the mol ratio of the *cis*- and *trans*-compounds changes (originally 3/2) in such a way that the *cis*-compound **2** becomes less in comparison. This means the *cis*-compounds **2** reacts preferentially (see structure of **2**, [1]). The majority of the reaction product is a yellow oily liquid which contains the compounds **8**, **9** and **10** (Fig. 1). The difference in reactivity of **2** and **3** towards LiBu can be shown if the reaction is carried out with one isomer at a time. The *cis*-compound, **2**, react best with LiBu in either THF or a solvent mixture of THF, Et_2O and pentane (4/1/1), while the *trans*-compound, **3**, was observed to react to a limited extent in only pure THF.

*1.2 Reactions of **2** and **3** with $Me_3SiCCl(Li)SiMe_2Cl$ (**6a**) in THF*

It was observed that compounds **2** and **3** reacted with LiBu to a limited extent to produce the bicyclic compound **1**. If one imagines that the 1,3-disilacyclobutanes **2** and **3** act as precursors for the formation of **1**, then in this case, and under these reaction conditions, only the carbenoid $Me_3SiCCl(Li)SiMe_2Cl$ (**6a**) can be used as the metallation reagent in the formation of the C–C bridge in **1**.

$Me_3SiCCl(Li)SiMe_2Cl$ (**6a**) is the first identified intermediate in the reaction of $Me_3SiCCl_2SiMe_2Cl$ with LiBu, the evidence for this being the reaction of **6a** with MeI to form $Me_3SiCClMeSiMeCl_2$ (90%). On the other hand, reacting $Me_3SiCCl_2SiMe_2Cl$ with LiBu in THF in the absence of MeI produced the bicyclic **1** in 30–35% yield, with 30–35% recovery of $Me_3SiCCl_2SiMe_2Cl$ from the reaction

SCHEME 1



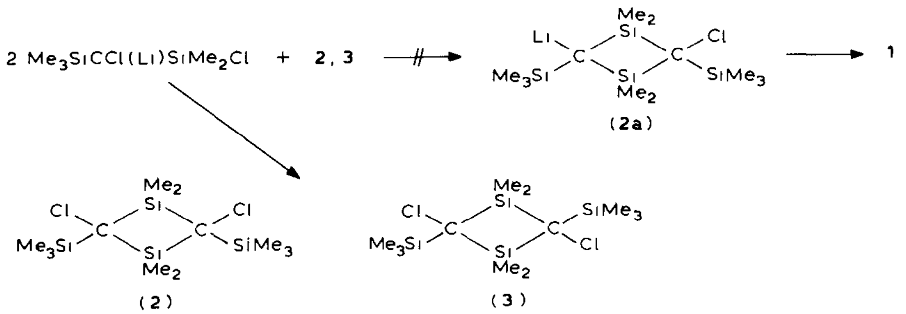
mixture. This came about by reaction of the intermediates **2** and **3** with **6a** through Li/Cl exchange. This was determined by separately reacting **2** and **3** with $Me_3SiCCl(Li)SiMe_2Cl$ in THF.

The carbenoid $Me_3SiCCl(Li)SiMe_2Cl$ was formed at −105 °C by dropping LiBu into $Me_3SiCCl_2SiMe_2Cl$ in THF, and at this temperature, a mixture of the *cis*- and *trans*-compounds **2** and **3** in equivalent mol ratios was added. After warming to 20 °C and working up of the reaction mixture only compound **1** and $Me_3SiCCl_2SiMe_2Sl$ were found. The primary step is the Li/Cl exchange between $Me_3SiCCl(Li)SiMe_2Cl$ and compounds **2** and **3**, in which $Me_3SiCCl_2SiMe_2Cl$ was reformed and the *C*-lithiated four-membered rings produced. Further, the intermediates **2a** and **3a** reacted by fast intramolecular elimination to produce the bicyclic **1**. Attempts to react the intermediates **2a** and **3a** with MeI and with Me_3SiCl proved unsuccessful. In both cases the reactions lead to the formation of **1** (Scheme 1).

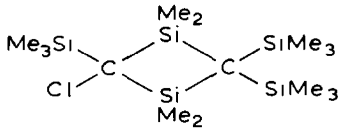
1.3 The reaction of 2 and 3 with $Me_3SiCCl(Li)SiMe_2Cl$ in Et_2O

The reaction of **2** and **3** with $Me_3SiCCl(Li)SiMe_2Cl$ should bring forward more information on whether the Li/Cl exchange between $Me_3SiCCl(Li)SiMe_2Cl$ and the disilacyclobutanes **2** and **3**, already observed in THF, is also possible in Et_2O. For this reaction the previously mentioned reaction were conditions maintained. On working up the reaction products it was shown that the total amount of the 1,3-disilacyclobutanes **2** and **3** isolated was much higher than the starting material, which shows that a reaction to form the products **2** and **3** takes place. The yield of the bicyclic compound **1** was very low, being only 3%. It follows on that, through dimerization of the primary carbenoid $Me_3SiCCl(Li)SiMe_2Cl$, the 1,3-disilabutanes **2** and **3** were produced preferentially, whereas the metallation reaction to produce **1** occurred to a slight degree only (Scheme 2).

SCHEME 2



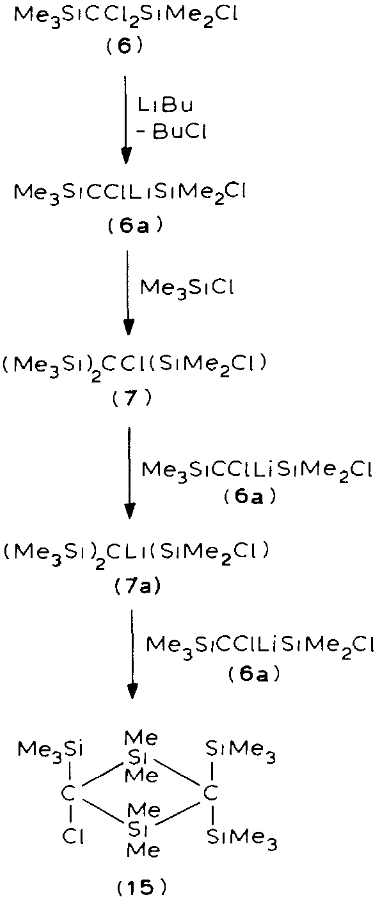
From these results it is clear just how compound **15** is produced from the reaction of $Me_3SiCCl_2SiMe_2Cl$ with LiBu and Me_3SiCl in Et_2O.



(15)

It was worthwhile to consider the possibility that at first the Cl-contained rings **2** and **3** are present, and that after *C*-metallation, the lithiated intermediates formed react with Me_3SiCl to produce compound **15**. This possibility was discarded because the attempted synthesis of **2a** and **3a** in Et_2O from **2** and **3** with LiBu or with $Me_3SiCCl(Li)SiMe_2Cl$ was unsuccessful, not to mention that the metallated intermediates **2a** and **3a** prefer to undergo intramolecular LiCl exchange to form the bicyclic **1**. The formation of **15** is shown in Scheme 3.

SCHEME 3

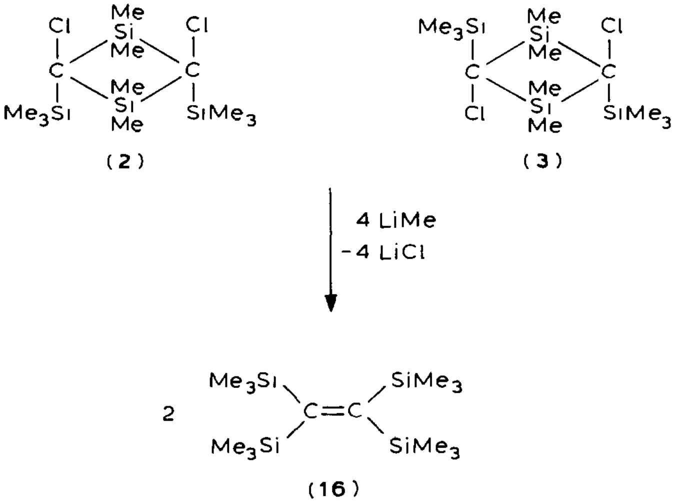


The carbenoid **6a**, first formed, reacts at relatively low temperatures by the addition of excess Me_3SiCl to produce **7**. As this reaction does not proceed to completion, a definite quantity of **6a** remains in solution. Through metal exchange from **6a** to **7** a more stable lithium compound **7a** is produced, which by the elimination of 2 equivalents of LiCl in reaction with **6a**, forms the cyclic compound **15**.

The reaction of $Me_3SiCCl(Li)SiMe_2Br$ proceeds similarly in the presence of compounds **2** and **3**. It follows that this carbenoid diplays, also in THF, not enough basic character to achieve metallation of **2** and **3**, which means that the reaction pathway ends at this stage.

1.4 The reaction of cis- and trans-1,3-disilacyclobutanes 2 and 3 with LiMe

The reaction of **2** and **3** with LiBu results essentially in the formation of silylated ethylene derivatives. The question arises as to whether the change from LiBu to the less basic LiMe would partially, or totally, hinder ring cleavage. The reaction of **2** and **3** with LiMe at −105 °C was done in THF; in this a stoichiometric amount of LiMe (dissolved in Et_2O) was added dropwise to a solution of **2** and **3** in THF. The working up of the reaction mixture resulted in the isolation of the unreacted starting reagents **2** and **3**, along with the isolation of the yellow crystalline compound **16**, which is already known in the literature [4,5].



Obviously, the decomposition of the four ring systems by the weaker base LiMe is still the dominating reaction. The analogous reaction of **2** and **3** with MeMgCl leads to $(Me_3Si)_2C{=}C(SiMe_3)_2$ (**16**) (45%) as well as formation of a small amount of the bicyclic **1** (3%).

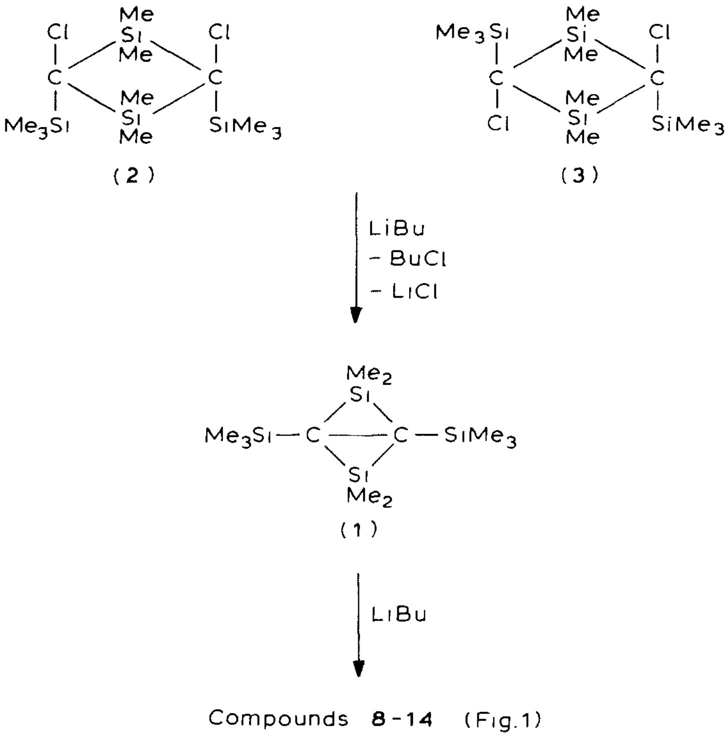
1.5 Reactions of the cis- and trans-1,3-disilacyclobutanes 2 and 3 with lithium

The reaction of the 1,3-disilacyclobutanes **2** and **3** in THF with lithium metal proceeds via ether cleavage, namely solvent interaction of the lithiated intermediate, to produce compounds **4** and **5**.

2. The relationship of the 1,3-disilabicyclo[1.1.0]butane towards organometallic compounds

It was intended to try to find an explanation for the formation of compounds **8–14** (Fig. 1) from the reaction of **2** and **3** with LiBu. For this was it important to establish to what degree the 1,3-disilabicyclobutane **1** acts as a precursor in the formation of these compounds. The investigation showed that the reaction of **1** with LiBu produces the compounds in Fig. 1. It was then proposed, that the reactions of **2** and **3** with LiBu initially produce the bicyclic **1**, which reacts further with other metallation reagents to form compounds **8–14**. In the reaction of the bicyclic **1** with LiBu at −105 °C in THF, the same reaction conditions as for the reaction of **2** and **3** with LiBu (Fig. 1) were employed. Compounds **8–14** comprised 60% of the product mixture. Approximately 5% of the mixture was separable but not identified;

SCHEME 4



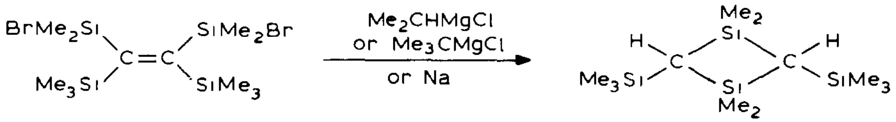
the rest consisted of polymeric compounds. This result is evidence for Scheme 4.

As the LiBu was added in an equimolar amount, it is recognized that the first step of the reaction mechanism is not quantitative. This is because further reaction of the lithiated compounds **2a** and **3a** is quicker than the metallation of **2** and **3**. Therefore it leaves a sufficient concentration of LiBu in the reaction mixture to form the compounds of Fig. 1 from the bicyclic **1**.

On performing the reaction of **1** with LiBu in Et_2O and pentane, only compounds **8**, **9**, **4** and **5** are isolated. Hence, the solvents have a large effect on what and how much of each compound can be isolated from the reaction mixture. The following compounds were formed (with % yields) in THF: **8** + **9** (28), **10** (12), **4** (6), **5** (5), **11** + **12** (6), **13** (1), **14** (2); in Et_2O: **8** + **9** (42), **4** (8), **5** (1); in pentane: **8** + **9** (38), **6** (4), **5** (3). Because the separation of the isomeric compounds was not possible, yields were calculated by integration of the ^1H NMR spectra. Different mechanisms can be discussed for the formation of these compounds. However because the intermediates could not be isolated, suitable reaction mechanisms could not be described. Sakurai et al. [5] showed that an exchange of silyl substituents on such double bonds systems was possible, as described by:

$$(BrMe_2Si)(Me_3Si)C{=}C(SiMe_3)(SiMe_2Br) \xrightarrow[-2\ LiBr]{2\ LiBu\text{-}t} (Me_3Si)_2C{=}C(SiMe_2\text{-}t\text{-}Bu)_2$$

It should also be mentioned, that silyl-substituted ethylene-derivatives react with sodium to build a four ring system [5]:

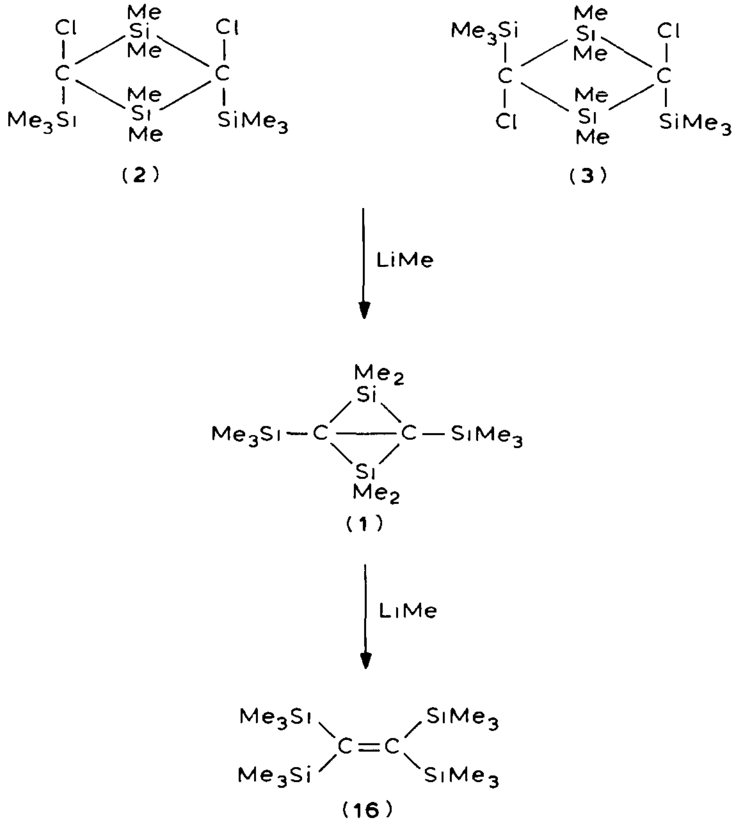


Our attempts to produce 1,3-disilacyclobutanes by reaction of **8**, **9**, and **10** with LiBu proved unsuccessful.

2.1 The reaction of the 1,3-disilabicyclo[1.1.0]butane with LiMe

The reaction of **1** with LiMe in THF will only proceed to (Me$_3$Si)$_2$C=C(SiMe$_3$)$_2$, **16**. Compound **16** is also formed by the reaction of the four-membered ring system **2** and **3** with LiMe. The explanation for this lies in the primary formation of the bicyclic **1** from the reaction of **2** and **3** with LiMe. This is described in Scheme 5.

SCHEME 5



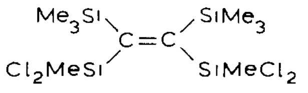
The formation of the double bond is derived from the cleavage of two Si–C bonds situated opposite to each other in the bicyclic system **1** by a further LiMe. Details of this cleavage mechanism are still not clear.

2.2 The reaction of the 1,3-disilabicyclo[1.1.0]butane 1 with lithium

The investigations that to date have not been successful are those referring to cleavage of the C–C bridge bond (178 pm). This came about because the polar reagents used preferred to cleave the more polar Si–C bond [2]. The reaction of **1** with a suspension of Li in THF at −20 °C, with subsequent warming to room temperature (it was originally a brown colour which changed to yellow), leads to compounds **4** and **5** (26%) in a ratio of 3/2. The cleavage of the C–C bridge in the bicyclic **1** is assumed for the formation of the compounds **4** and **5**. For the first time it is possible to obtain cleavage of the C–C bridge without decomposition of the four-membered ring system.

3. Investigation into metallation of $Me_3SiCCl_2SiMeCl_2$ 17 and subsequent reactions of its lithiated derivatives

The previous investigation leaned towards the reaction of $Me_3SiCCl_2SiMeCl_2$ (**17**) with lithium in a mol ratio of 1/2. It should be noted however, that on beginning the reaction (adding dropwise a solution of **17** in THF to a suspension of Li in THF) the solution must be cooled to −50 °C and a further amount of **17** quickly added. Thereupon the colour of the solution changed to a deep green as the lithium reacted. After warming to 20 °C the colour of the solution is yellow. From the reaction mixture unreacted starting material was obtained, and by sublimation (10^{-2} Torr, 60 °C), compounds were isolated which were crystalline at room temperature. They were reduced with $LiAlH_4$ to yield the compounds **20** and **21**.



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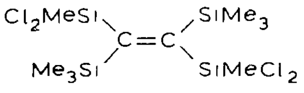

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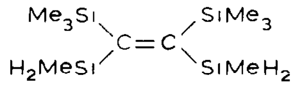

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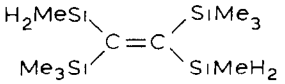


(21)

In an analogous reaction, $Me_3SiCCl_2SiMeCl_2$ was reacted with LiBu in THF to form the *cis*- and *trans*-isomers **18** and **19** in 74% yield. The behaviour of the carbenoids $Me_3SiCCl(Li)SiMe_2Cl$ (**6a**) and $Me_3SiCCl(Li)SiMeCl_2$ (**17a**) are evidently very different. While from **6a**, the 1,3-disilacyclobutanes **2** and **3** are produced, the silylated ethylenes **18** and **19** are produced from **17a**.

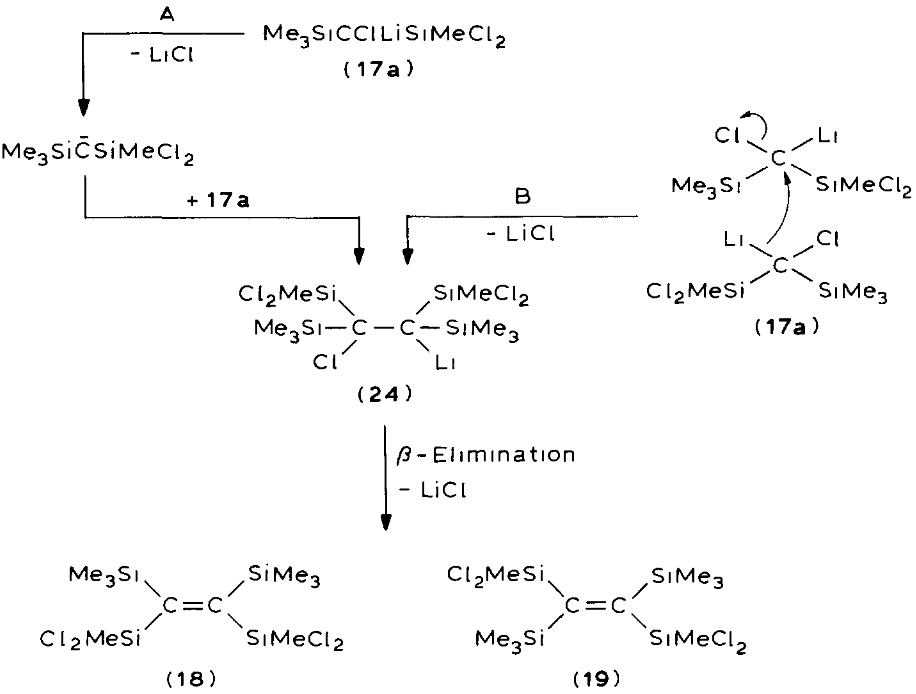
4. Investigations into the formation of the silylated ethylenes 18 and 19

The first identified intermediate in the formation of **18** and **19** is $Me_3SiCCl(Li)SiMeCl_2$ (**17a**) which is determined by its reaction with MeI. Starting from **17a** there are two possibilities of interest in forming the C–C double bond.

(a) An intramolecular LiCl elimination (pathway A in Scheme 6) to give the carbene $Me_3SiCSiMeCl_2$, which, in reaction with a further molecule of **17a**, is inserted into the C–Li bond (the dimerization between two carbenes need not be taken into account [6,7]). The resulting intermediate **24** reacts quickly by β-elimination [8] of LiCl, to form the ethylene derivatives **18** and **19**.

(b) In pathway B, two molecules of **17a** react by intermolecular LiCl elimination to form **24**, in which one carbenoid molecule acts as a nucleophile, the other maintaining electrophilic character.

SCHEME 6



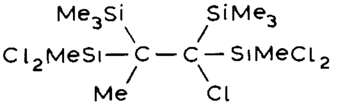
As carbenes are electrophilic they react well with electron-rich olefins [9,10]. The carbene $Me_3SiCSiMeCl_2$, mentioned in pathway A, should react with cyclohexene to form a cyclopropane. This possibility was investigated in a low temperature metallation of $Me_3SiCCl_2SiMeCl_2$ (**17**) with LiBu in the presence of an excess of cyclohexene. From the reaction products, however, no compound was found which would indicate, in this way, the interaction of a carbene and olefin. The isolated compounds, **18** and **19**, were produced in the yields obtained without cyclohexene, which therefore excludes a carbene as a reactive intermediate.

Investigations have shown that $Me_3SiCCl_2SiMeCl_2$ with LiBu in THF forms the carbenoid **17a**, which is proved in the side-reaction with MeI at −105 °C.

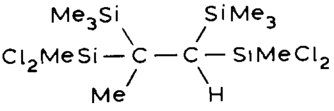
$$\underset{(\mathbf{17})}{\mathrm{Me_3SiCCl_2SiMeCl_2}} + \mathrm{LiBu} \xrightarrow[-\mathrm{BuCl}]{} \underset{(\mathbf{17a})}{\mathrm{Me_3SiCClLiSiMeCl_2}}$$

$$\underset{(\mathbf{17a})}{\mathrm{Me_3SiCClLiSiMeCl_2}} + \mathrm{MeI} \xrightarrow[-\mathrm{LiI}]{} \underset{(\mathbf{17b})}{\mathrm{Me_3SiCClMeSiMeCl_2}}$$

If, after the metallation reaction (−105 °C) had been carried out, the reaction mixture is warmed (−105 to −55 °C) before the MeI is added, it is shown that the following compounds, **22** and **23**, are obtained.



(22)



(23)

(Continued on p. 121)

TABLE 1

NMR DATA [a]

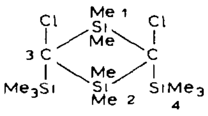
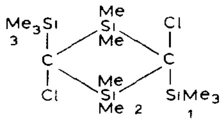
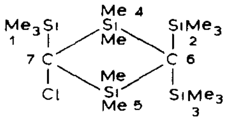
Structure	Spectrum	Assignment	δ(ppm) *J*(Hz)
 (2)	^{1}H	SiMe$_3$	0.11
		SiMe(1)	0.54
		SiMe(2)	0.45
	^{29}Si	SiMe$_3$	0.7 (10)
		J(SiCH)	6.3
		SiMe$_2$	13.9 (7)
		J(SiCH)	6.5
	^{13}C	C(4)	−0.4
		C(1)	2.7
		C(2)	−2.1
		C(3)	40.5
 (3)	^{1}H	SiMe$_3$	0.17
		SiMe$_2$	0.47
	^{29}Si	SiMe$_3$	2.1 (10)
		J(SiCH)	6.4
		SiMe$_2$	15.6 (7)
		J(SiCH)	6.7
	^{13}C	C(1)	−0.1 (4)
		J(CH)	119
		C(2)	0.4 (4)
		J(CH)	122
		C(3)	38.6
$(\overset{1}{\mathrm{Me_3Si}})_2\overset{3}{\mathrm{C}}\mathrm{Cl}(\overset{2}{\mathrm{SiMe_2Cl}})$	^{1}H	SiMe$_3$	0.25
		SiMe$_2$Cl	0.58
	^{13}C	C(1)	0.6
		C(2)	3.9
		C(3)	37.5
	^{29}Si	SiMe$_3$	5.9 (10)
		J(SiCH)	6.5
		SiMe$_2$Cl	23.3 (7)
		J(SiCH)	6.9
 (15)	^{1}H	SiMe$_3$(1)	0.261
		SiMe$_3$(2,3)	0.142
			0.178
		SiMe(4,5)	0.474
			0.484
	^{13}C	C(1)	6.8
		C(2,3)	6.5
			−0.2
		C(4,5)	3.2
			5.4
		C(6)	7.9
		C(7)	37.1
	^{29}Si	SiMe$_3$(1)	−1.3 (10)
		J(SiCH)	6.4
		SiMe$_3$(2)	−1.1 (10)
		J(SiCH)	6.4
		SiMe$_3$(3)	1.3
		J(SiCH)	6.4
		SiMe$_2$	10.2 (7)
		J(SiCH)	6.7

TABLE 1 (continued)

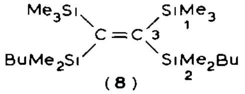
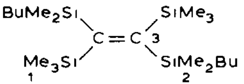
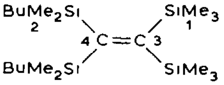
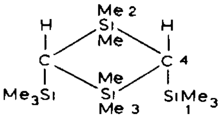
Structure	Spectrum	Assignment	δ(ppm) J(Hz)
$Me_3SiCCl_2SiMe_2F$	^1H	$SiMe_3$	0.27
		$SiMe_2F$	0.47 (2)
		J(FSiCH)	7
	^{19}F	$SiMe_2F$	6.3 (7)
		J(HCSiF)	7
$Me_3SiCCl_2SiMe_2OMe$	^1H	$SiMe_3$	0.28
		$SiMe_2$	0.35
		OMe	3.63
 (8)  (9)	^1H	*Isomer* **a**	
		$SiMe_3$	0.225
		$SiMe_2$	0.208
		Bu	0.9 (M)
		Isomer **b**	
		$SiMe_3$	0.229
		$SiMe_2$	0.210
		Bu	0.9 (M)
	^{13}C	*Isomer* **a**	
		C(1)	4.8
a and **b** cannot be assigned		C(2)	2.4
		C(3)	196.4
			196.8
		C(4)	14.3
			19.3
			27.3
	^{29}Si	*Isomers* **a** *and* **b**	
		$SiMe_3$	−8.1 (10)
			−8.4 (10)
		$SiMe_2Bu$	−6.4 (M)
			−6.7 (M)
 (10)	^1H	$SiMe_3$	0.206
		$SiMe_2$	0.23
		Bu	0.9 (M)
	^{13}C	C(1)	4.8
		C(2)	2.4
		C(3,4)	196.1
			197.5
	^{29}Si	$SiMe_3$	−8.3 (10)
		$SiMe_2Bu$	−6.3 (M)
 (4)	^1H	$SiMe_3$	−0.03
		SiMe(2)	0.23
		SiMe(3)	0.31
		C–H	−0.33
	^{13}C	C(1)	2.0 (4)
		J(CH)	118.4
		C(2)	1.9 (4)
		C(3)	5.5 (4)
		J(CH)	120.6
		C(4)	10.5 (2)
		J(CH)	104.2

TABLE 1 (continued)

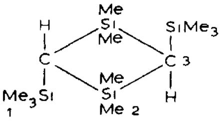
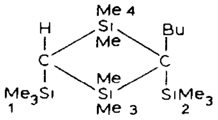
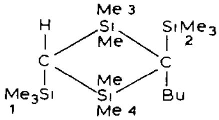
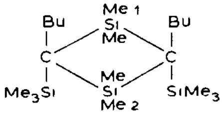
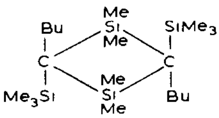
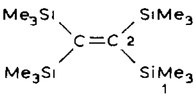
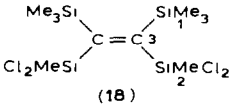
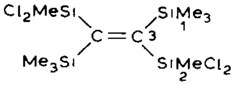
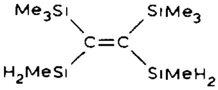
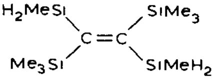
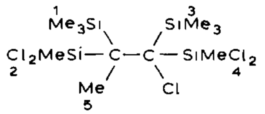
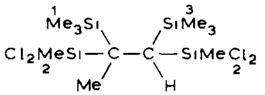
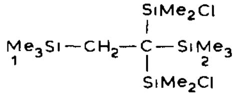
Structure	Spectrum	Assignment	δ(ppm) J(Hz)
	^{29}Si	SiMe$_3$	−2.9 (10)
		J(SiCH)	5.9
		SiMe$_2$	3.9
		J(SiCH)	7.9
 (5)	^{1}H	SiMe$_3$	−0.01
		SiMe$_2$	0.27
		C–H	−0.30
	^{13}C	C(1)	2.0 (4)
		J(CH)	118 4
		C(2)	3.7
		C(3)	9.9 (2)
		J(CH)	107.4
	^{29}Si	SiMe$_3$	−2.5 (10)
		J(SiCH)	5.9
		SiMe$_2$	3.0 (7)
		J(SiCH)	6.8
 (11)	^{1}H	*Isomer* **a**	
		SiMe$_3$(1)	−0.020
		SiMe$_3$(2)	0.05
		SiMe(3,4)	0.20
			0.33
		C–H	−0.05
		C–Bu	0 91 (M)
 (12)		*Isomer* **b**	
		SiMe$_3$(1)	−0.029
		SiMe$_3$(2)	0.11
		SiMe(3,4)	0.25
			0.29
		C–H	−0.43
		C–Bu	0.91 (M)
a and **b** cannot be assigned			
 (13)	^{1}H	SiMe$_3$	0.08
		SiMe(1)	0.39
		SiMe(2)	0.27
		C–Bu	0.89 (M)
	^{29}Si	SiMe$_3$	0.07
		SiMe$_2$	11.46
 (14)	^{1}H	SiMe$_3$	0.10
		SiMe$_2$	0.28
	^{29}Si	SiMe$_3$	0.16
		SiMe$_2$	11.40
 (16)	^{1}H		0.24
	^{29}Si		8.7 (10)
		J(SiCH)	6.3
	^{13}C	C(1)	4.3
		C(2)	195.3
 (18)	^{1}H	*Isomer* **a**	
		SiMe$_3$	0.41
		SiMeCl$_2$	1.18
	^{13}C	C(1)	4.1
		C(2)	11.5

TABLE 1 (continued)

Structure	Spectrum	Assignment	δ(ppm) J(Hz)
 (19)		C(3)	189.5
	^{29}Si	SiMe$_3$	−2.6 (10)
		J(SiCH)	6.5
		SiMeCl$_2$	13.7 (4)
		J(SiCH)	7
a and **b** cannot be assigned			
		Isomer **b**	
	^{1}H	SiMe$_3$	0.44
		SiMeCl$_2$	1.08
	^{13}C	C(1)	4.6
		C(2)	10.7
		C(3)	190.2
	^{29}Si	SiMe$_3$	−2.2 (10)
		J(SiCH)	6.5
		SiMeCl$_2$	11.4 (4)
		J(SiCH)	7.3
		Isomer **a**	
 (20)	^{1}H	SiMe$_3$	0.24
		SiMe	0.33 (3)
		J(HSiCH)	3.9
		SiH$_2$	4.19 (M)
 (21)		*Isomer* **b**	
	^{1}H	SiMe$_3$	0.246
		SiMe	0.28 (3)
		J(HSiCH)	4.1
a and **b** cannot be assigned		SiH$_2$	4.19 (M)
	^{1}H	SiMe$_3$(1)	0.323
 (22)		SiMe$_3$(3)	0.355
		SiMeCl$_2$(2)	0.85
		SiMeCl$_2$(4)	1.089
		C–Me	1.73
 (23)	^{1}H	SiMe$_3$(1)	0.326
		SiMe$_3$(3)	0.382
		SiMeCl$_2$(2)	0.80
		SiMeCl$_2$(4)	1.078
		C–Me	1.70
		C–H	0.07
	^{1}H	SiMe$_3$(1)	0.17
		SiMe$_3$(2)	0.25
		SiMe$_2$Cl	0.6
		CH$_2$	1.13

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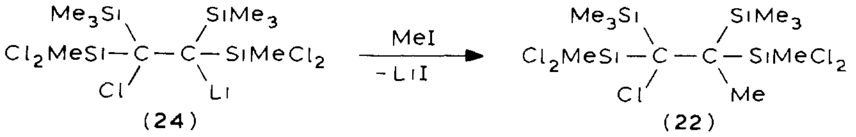
[a] Chemical shifts stated in this paper, in ppm, refer to the δ-scale. Coupling constants are given in Hz. The numbers in brackets refer to the multiplicity of the particular signals received, unresolved signals being indicated in brackets by M. CDCl$_3$ was always used as solvent and internal standard.

The reaction to form these compounds **22** and **23** is strongest at −35 °C and proceeds to a much larger extent than that to produce $Me_3SiCClMeSiMeCl_2$ on increasing the temperature. The formation of **22** is evidence for the occurrence of the lithiated compound **24**, as shown. The formation of compound **23** is achieved by metal exchange between **22** and **17a**, followed by ether cleavage.



5. NMR investigations

The ^1H, ^{13}C, and ^{29}Si NMR chemical shifts are shown in Table 1. Because separation of the isomers **8**–**10** was not possible, difficulties were experienced in assigning the NMR peaks. The ^1H and ^{29}Si NMR spectra of these compounds were similar, and the only observed differences were in the ^{13}C NMR spectra. Because there is a symmetrical arrangement of silyl substituents around each ethylene carbon atom in **8** and **9**, only one NMR peak was observed. On the other hand in **10**, because of substituent exchange, two peaks were observed. For the ^{13}C spectra of the C–C double bond one sees a total of four peaks. Distinctive are the extremely high field shifts in the region of δ 180–200 ppm and characteristic of silyl-substituted ethylene derivatives [4]. By a comparison of the spectra for isomers **8**, **9** and **10** and those containing only the *cis*- and *trans*-isomers **8** and **9**, the peaks pertaining to **10** could be assigned. However it was impossible by spectroscopic means to differentiate between **8** and **9**. Because of different substitutions on the ring carbon atoms of compounds **11** and **12**, the $SiMe_3$ group on the rings were not equivalent. In the proton spectra of the *cis*-, *trans*-mixture, two singlets per isomer were observed. Different substituents on the carbon atoms of the ring were responsible for the methyl protons on the ring silicon atoms experiencing differing neighboring effects. Moreover, two peaks were observed for the methyl groups on the ring silicon atom for each isomer. It is to be recognized, that both four-membered rings show the same number of NMR peaks, which could therefore not be assigned. The distinct characterization of compounds **13** and **14** by ^{13}C NMR and ^{29}Si NMR can be achieved only when these compounds are produced in other ways in better yields.

Results of mass spectral investigations are listed in Table 2.

Experimental details

As the compounds were sensitive to oxidation and hydrolysis, all reactions were carried out in a closed system under nitrogen.

6.1 Reactions of $Me_3SiCCl_2SiMe_2X$ with LiBu

Since the low temperature metallation reactions were all carried out in a similar fashion, methods presented will be confined to a description of individual reactions and amounts of substances isolated. Low temperature metallations were carried out using a three-necked round-bottomed flask with dropping funnel, low temperature thermometer and pressure outlet to the mercury valve. The 1,3-disilapropane is firstly dissolved in the appropriate solvent, and the reaction mixture is then cooled

TABLE 2

RESULTS OF MASS SPECTRAL INVESTIGATIONS

Compound	Exact mass	Ion	Found	Diff. (10^{-3}u)
Isomers	$Si_4C_{12}H_{30}{}^{35}Cl_2$	M^+	356.0796	−0.5
2, **3**	$Si_4C_{12}H_{30}{}^{35}Cl^{37}Cl$		358.0793	2.1
	$Si_4C_{11}H_{27}{}^{35}Cl_2$	$M^+ - Me$	341.0562	−0.5
	$Si_4C_{12}H_{30}$	$M^+ - Cl_2$	286.1399	−2.5
$(Me_3Si)_2CCl$-	$Si_3C_9H_{24}{}^{35}Cl_2$	M^+	288.0530	−0.4
$(SiMe_2Cl)$	$Si_3C_9H_{24}{}^{35}Cl^{37}Cl$		286.0561	−0.2
	$Si_3H_8H_{21}{}^{35}Cl_2$	$M^+ - Me$	271.0314	−1.4
15	$Si_5C_{15}H_{39}{}^{35}Cl$	M^+	394.1584	−0.3
	$Si_5C_{14}H_{36}{}^{35}Cl$	$M^+ - Me$	379.1344	−0.8
	$Si_4C_{12}H_{30}{}^{35}Cl$	$M^+ - SiMe_3$	321.1090	−2.3
Isomers	$Si_4C_{12}H_{31}{}^{35}Cl$	M^+	322.1154	−3.7
24, **25**	$Si_4C_{11}H_{28}{}^{35}Cl$	$M^+ - Me$	307.0954	−0.1
	$Si_3C_9H_{22}{}^{35}Cl$	$M^+ - SiMe_3$	249.0738	0.6
Isomers	$Si_4C_{20}H_{48}$	M^+	400.2820	−1.4
8, **9**, **10**	$Si_4C_{19}H_{45}$	$M^+ - Me$	385.2629	3.1
	$Si_3C_{17}H_{39}$	$M^+ - SiMe_3$	327.2341	−1.8
	$Si_3C_{14}H_{33}$	$M^+ - SiMe_2Bu$	285.1845	−4.5
Isomers	$Si_4C_{12}H_{32}$	M^+	288.1567	−1.4
4, **5**	$Si_4C_{12}H_{31}$	$M^+ - H$	287.1567	0.8
	$Si_4C_{11}H_{29}$	$M^+ - Me$	273.1339	−0.7
Isomers	$Si_4C_{16}H_{40}$	M^+	344.2232	2.5
11, **12**	$Si_4C_{15}H_{37}$	$M^+ - Me$	329.1969	−0.3
	$Si_4C_{11}H_{31}$	$M^+ - Bu$	287.1482	−2.1
	$Si_3C_{13}H_{31}$	$M^+ - SiMe_3$	271.1741	0.7
Isomers	$Si_4C_{20}H_{48}$	M^+	400.2838	0.5
13, **14**	$Si_4C_{19}H_{45}$	$M^+ - Me$	385.2589	−1.0
	$Si_4C_{17}H_{39}$	$M^+ - SiMe_3$	327.2345	−1.5
16	$Si_4C_{14}H_{36}$	M^+	316.1893	−0.2
	$Si_4C_{13}H_{33}$	$M^+ - Me$	301.1674	1.5
	$Si_3C_{11}H_{27}$	$M^+ - SiMe_3$	243.1436	1.3
Isomers	$Si_4C_{10}H_{24}{}^{35}Cl_2{}^{37}Cl_2$	M^+	399.9603	−4.7
18, **19**	$Si_4C_{10}H_{24}{}^{35}Cl_3{}^{37}Cl$		397.9641	−3.9
	$Si_4H_9H_{21}{}^{35}Cl_4$	$M^+ - Me$	380.9467	−0.8
	$Si_4C_9H_{21}{}^{35}Cl_3{}^{37}Cl$		382.9427	−1.8
	$Si_4C_{10}H_{24}{}^{35}Cl_3$	$M^+ - Cl$	361.0052	3.1
Isomers	$Si_4C_{10}H_{28}$	M^+	260.1235	−3.3
20, **21**	$Si_4C_9H_{25}$	$M^+ - Me$	245.1030	−0.3
	$Si_3C_7H_{19}$	$M^+ - SiMe_3$	187.0799	−0.5
22	$Si_4C_{10}H_{24}{}^{35}Cl_4{}^{37}Cl$	$M^+ - Me$	432.9408	3.9
	$Si_4C_{10}H_{24}{}^{35}Cl_3{}^{37}Cl_2$		434.9396	5.7
	$Si_4C_{11}H_{27}{}^{35}Cl_3{}^{37}Cl$	$M^+ - Cl$	412.9930	1.6
23	$Si_4C_{10}H_{25}{}^{35}Cl_4$	$M^+ - Me$	396.9760	−2.8
	$Si_4C_{10}H_{25}{}^{35}Cl_3{}^{37}Cl$		398.9775	1.7
	$Si_3C_8H_{18}{}^{35}Cl_4$	$M^+ - SiMe_3H$	337.9492	2.2

to −105 °C (THF), or −110 °C (trap-mixture). A solution of LiBu in hexane is added dropwise and after this the solution is stirred for a further 30 min at −100 °C, after which the temperature bath is removed and/or an intercept reagent added. The work-up procedure was as follows: distillation of the polar solvent, dissolution of the reaction mixture in pentane, filtration of precipitated substances, and distillation of any remaining solvent and the pentane which was added to the reaction mixture. Fractional distillation, condensation, column chromatography over silica gel, and reversed-phase HPLC were used as far as possible in the isolation of products.

Reaction of $Me_3SiCCl_2SiMe_2Br$ with LiBu. Amounts: 9 g $Me_3SiCCl_2SiMe_2Br$ (0.031 mol), 18 ml (0.031 mol) LiBu solution (1.72 *M*), 200 ml trap-mixture. Isolated amounts: 1.6 g $Me_3SiCCl_2SiMe_2Br$, 4.1 g **2** and **3** (0.012 mol) (74% in relation to compound converted).

*Reaction of $Me_3SiCCl_2SiMe_2Cl$ (**6**) with LiBu in Et_2O.* Amounts: 39 g **6** (0.156 mol), 91 ml (0.156 mol) LiBu solution (1.72 *M*), 800 ml Et_2O. Isolated amounts: 2 g **6**, 22.5 g **2** and **3** (0.063 mol) (81% of compound **6** converted). The chromatographic separation on silica gel allowed further identification of the compounds *cis*- and *trans*-$Si_4C_{12}H_{31}Cl$ (**24** and **25**), as well as $Me_3CH_2C(SiMe_2Cl)_2SiMe_3$, always found in trace amounts (3%) in the reaction mixture.

*Reaction of **6** with LiBu and Me_3SiCl in Et_2O.* Amounts: 6.4 g **6** (0.026 mol), 15 ml (0.026 mol) LiBu solution (1.72 *M*), 150 ml Et_2O, 7 ml Me_3SiCl (0.054 mol). Isolated amounts: 0.4 g **6**, 0.9 g $(Me_3Si)_2CCl(SiMe_2Cl)$ (12%), 2 g $Si_5C_{15}H_{39}$ **15** (0.05 mol) (38% of compound **6** converted).

*Reaction of **6** with LiBu in THF.* Amounts: 60 g **6** (0.241 mol), 143 ml (0.241 mol), LiBu solution (1.69 *M*), 800 ml THF. Isolated amounts: 21 g **6**, 12.1 g $Si_4C_{12}H_{30}$, **1**, (0.042 mol) (35% of compound **6** converted).

Reaction of $Me_3SiCCl_2SiMe_2Tos$ with LiBu. Amounts: 3 g $Me_3SiCCl_2SiMe_2Tos$ (7.7 mmol), 4.6 ml (7.7 mmol) LiBu solution (1.69 *M*), 200 ml THF. 0.6 g **2** and **3** (40% yield) was obtained from chromatographic separation on silica gel.

Reaction of $Me_3SiCCl_2SiMe_2OMe$ with LiBu. Amounts: 4.2 g $Me_3SiCCl_2SiMe_2OMe$ (0.017 mol), 10.1 ml (0.017 mol) LiBu solution (1.69 *M*), 200 ml trap-mixture. Isolated amounts: 0.6 g $Me_3SiCCl_2SiMe_2OMe$, 1.1 g $Me_3SiCClHSiMe_2OMe$ (30%), 0.9 g $Me_3SiCH_2SiMe_2OMe$ (30%).

Reaction of $Me_3SiCCl_2SiMe_2F$ with LiBu. Amounts: 7.3 g $Me_3SiCCl_2SiMe_2F$ (0.034 mol), 20 ml (0.034 mol), 20 ml (0.034 mol) LiBu solution (1.69 *M*). Isolated amount: 8.3 g $Me_3SiCCl_2SiMe_2Bu$ (90%).

*6.2 Reaction of **2** and **3** with metallation reagents*

Reactions with LiBu: 7 g (0.02 mol) of a mixture of **2** and **3** (mol ratio 3/2) was dissolved in 300 ml THF and to the reaction mixture, previously cooled to −105 °C, was added a 1.69 *M* solution of LiBu (intensive yellow colour). (Refer to section 6.1.) The relatively volatile 1,3-disilacyclobutanes **4** and **5** (yield 7%) as well as the bicyclic **1** (yield 10%) were isolated from the reaction mixture by low pressure fractional distillation. Qualitative separation of the distillation residue on silica gel, followed by quantitative separation by reversed-phase HPLC delivered compounds **8**–**10** and **11**–**14**, while 2.1 g of the isomer mixture of **2** and **3** was retrieved. The mol ratio of compounds **1**/**2** was 2/3.

*Reaction of **2** and **3** with $Me_3SiCCl(Li)SiMe_2X$.* The carbenoid $Me_3SiCCl(Li)SiMe_2X$ was produced by adding dropwise a solution of LiBu at −105 °C (THF) or −110 °C (Et_2O) to a solution of the 1,3-disilapropane $Me_3SiCCl_2SiMe_2X$, and a solution of **2** and **3** in pentane was poured into the reaction mixture immediately after the dropwise addition of LiBu was complete. The reaction mixture was maintained for a further 30 min at −100 °C, when the cooling-bath was removed. (Refer section 6.1 for further details.)

*Reaction of **2** and **3** with $Me_3SiCCl(Li)SiMe_2Cl$ in THF.* Amounts: 2.5 g **6** (0.01 mol), 6 ml (0.01 mol) LiBu solution (1.67 *M*), 3.6 g **2** and **3** (0.01 mol), 200 ml THF. The bicyclic **1** and compound **6** were obtained in quantitative yield.

*Reaction of **2** and **3** with $Me_3SiCCl(Li)SiMe_2Cl$ in Et_2O.* Amounts: 2.5 g **6** (0.01 mol), 6 ml (0.01 mol) LiBu solution (1.67 *M*), 3.6 g **2** and **3** (0.01 mol), 200 ml Et_2O. Isolated amounts: 4.9 g *cis*- and *trans*-**2** and **3** (73%), 0.04 g **1** (3%).

*Reaction of **2** and **3** with $Me_3SiCCl(Li)SiMe_2Br$.* Amounts: 2.2 g $Me_3SiCCl_2SiMe_2Br$ (7.4 mmol), 4.4 ml (7.4 mmol) LiBu solution (1.69 *M*), 2.6 g **2** and **3** (7.4 mmol), 200 ml THF. Isolated amounts: 0.4 g $Me_3SiCCl_2SiMe_2Br$, 3.3 g **2** and **3** (53% of $Me_3SiCCl_2SiMe_2Br$ converted).

*Reaction of **2** and **3** with LiMe.* A mixture of **2** and **3**, 1.9 g (5 mmol) was dissolved in 150 ml THF and cooled to −105 °C. To this solution was added, dropwise, 3.1 ml of 1.75 *M* LiMe solution in Et_2O (an intensely yellow reaction mixture resulted). Completion of the reaction resulted after a further 30 min stirring of the solution at 20 °C and the compounds **2**, **3** and **16** were identified, **16** being separated by column-chromatography. Isolated amounts: 0.7 g **16** (66% compounds **2** and **3** reacted), 0.7 g **2** and **3**, m.p. of **16** 101°C (Lit. 102 °C [4]).

*Reaction of **2** and **3** with MeMgCl.* 1.1 g (3 mmol) of the isomer mixture **2** and **3** was dissolved in 150 ml THF, cooled to −20 °C, followed by dropwise addition of 5 ml of a 0.6 *M* MeMgCl solution in Et_2O. Isolated amounts: 0.2 g **16** (45% compound **2** and **3** reacted), 0.6 g **2** and **3**.

*Reaction of **2** and **3** with Li.* To a suspension of 0.05 g lithium (7.2 mmol) in 50 ml THF at 0 °C was added dropwise 1.2 g (3.4 mmol) of a mixture **2** and **3** in THF. Since no reaction occurred at 0 °C, the solution was warmed to 40 °C, whereupon the solution assumed a dark red colour. After 8 h no lithium remained in the then orange coloured solution. The solvent was distilled off, the residue was dissolved in pentane and the precipitated lithium chloride filtered off, and the filtrate was fractionally distilled. The *cis*- and *trans*-compounds **4** and **5** (0.3 g, 31%) were isolated and what remained was a viscous, sticky yellow mass.

*Synthesis of the 1,3-disilacyclobutanes **13** and **14**.* Amounts: 24 g $Me_3SiCClBuSiMe_2Br$, 3 g $Me_3SiCBrBuSiMeCl$ (0.086 mol), 50 ml (0.086 mol) LiBu solution (1.72 *M*), 500 ml trap-mixture. The low temperature metallation of $Me_3SiCClBuSiMe_2Br$ was done correspondingly with LiBu in a trap-mixture. The separation was achieved by column chromatography over silica gel of compounds **13** and **14** from the reaction mixture; the *trans*-compound **14** crystallized out and it was recrystallized in pentane to a purer form, m.p. 112°C; yields: 1.9 g **13** (14%), 2.9 g **14** (21%).

*6.3 Reaction of **1** with lithium*

Amounts: 2.2 g **1** (7.7 mmol), 0.11 g lithium (15.9 mmol), 50 ml THF. A solution of **1** in THF was added to the suspension of lithium in THF at 0 °C, resulting in a red-brown colour on further reaction. The metallation was complete after 1 h, in which time lithium had completely disappeared. Isolated amounts: 0.3 g **1**, 0.5 g *cis*-**4** and *trans*-**5** (26% in relation to reacted compound **1**).

*Reaction of **1** with LiBu.* Amounts: 2.9 g **1** (0.01 mol), 6 ml (0.01 mol) LiBu solution (1.69 *M*), 100 ml solvents (THF, Et_2O, pentane). The compounds formed and the influence of solvents thereon have been described in section 2.

*Reaction of **1** with LiMe.* Amounts: 1.6 g **1** (5.6 mmol), 3.2 ml (5.6 mmol) LiMe solution (1.75 *M*), 100 ml THF. After distillation of unreacted starting material **1**, the residue, **16**, was sublimed onto a water-cooled cold-finger. Isolated amounts: 0.6 g **1**, 0.7 g **16** (70% in relation to reacted compound **1**).

6.4 Reaction of $Me_3SiCCl_2SiMeCl_2$ (17) with lithium

Amounts: 27 g $Me_3SiCCl_2SiMeCl_2$ (0.1 mol), 1.4 g lithium (0.2 mol), 150 ml THF. To a suspension of Li in THF was added a few drops of a solution of **17** in THF. After the reaction began, the solution was cooled to −50 °C and the rest of the solution was quickly added. With progressive reaction of lithium the solution assumed a deep green colour. After slowly warming to 20 °C the solution turned yellow. After 12 h, the solvent was evaporated and the residue added to pentane, and the unsoluble, slimy compounds filtered through a glass filter tunnel. The volatile compound **17** and $(Me_3Si)_2CCl(SiMeCl_2)$ were immediately separated by vacuum distillation, and the compounds **18** and **19** were sublimed from the residue at 60 °C/10^{-2} Torr. Yields: 2.2 g $(Me_2Si)_2CCl(SiMeCl_2)$ (14%); 2 g **18** and **19** (10% in relation to starting compound **17**).

*6.4.1 Reaction of **17** with LiBu.* Amounts: 9.1 g **17** (0.034 mol), 19.6 ml (0.034 mol) LiBu solution (1.72 *M*), 200 ml THF. Low temperature metallation and separation analogous to section 6.4. Isolated amounts: 5 g **18** and **19** (74% in relation of starting material **17**), 0.9 g $(Me_3Si)_2CCl(SiMeCl_2)$ (17%).

*6.4.2 Reaction of **18** and **19** with $LiAlH_4$.* 2 g (5 mmol) of the isomer mixture **18** and **19** were dissolved in 50 ml of Et_2O. The hydrogenolysis was achieved by the dropwise addition of 3.2 ml of a 1.9 *M* $LiAlH_4$ solution in Et_2O at 0 °C, to produce quantitatively compounds **20** and **21**. After the Et_2O had been evaporated and the formed $LiAlCl_4$, as well as the excess of added $LiAlH_4$, filtered off, the mixture of **20** and **21** was purified by silica gel column chromatography.

Reaction of $Me_3SiCCl_2SiMeCl_2$ with LiBu and cyclohexene. Amounts: 13.6 g **17** (0.05 mol), 30.2 ml (0.05 mol) LiBu solution (1.67 *M*), 10.1 ml cyclohexene (0.1 mol), 350 ml THF. Cyclohexene was added in 100% excess to the carbenoid $Me_3SiCClLi$-$SiMe_2Cl$, which is produced by low temperature metallation at −100 °C. The nature, and amounts produced, of the reaction products are as discussed in section 6.4.1. The cyclohexene was retrieved quantitatively.

*Reaction of **17** with LiBu; interception of the lithiated intermediate product with MeI.* To form the lithiated compound **17a**, the following reaction and conditions were always executed; 2.7 g of $Me_3SiCCl_2SiMeCl_2$, **17**, (0.01 mol) in THF was cooled to −105 °C and an equimolar solution of LiBu was added dropwise. At a number of temperatures, varying between −105 and 35 °C, 1.3 ml of MeI (0.02 mol) at the desired temperature was poured into the reaction mixture. (The intercept reaction, through coupling of MeI, was done at intervals of 10 °C.) After the addition of MeI the reaction mixture was maintained at the corresponding temperature for 30 min after which the cooling-bath was removed. The procedure after that is analogous to that in section 6.1. From these reactions, the desired compounds were separated from the product mixture by fractional condensation. The reactions, in which the reaction of MeI was a step, occurred in the temperature region, −105 °C to −65 °C, producing $Me_3SiCClMeSiMeCl_2$ in 80–85% yield. In the addition of MeI between −55 °C and −45 °C, as well as formation of the coupling product $Me_3SiCClMeSiMeCl_2$ (yield 45%), the formation of **22** and **23** was observed. Both compounds can be condensed in high vacuum at 110 °C on a liquid nitrogen-cooled cold-finger. When the addition of MeI was carried out at −35 °C or higher temperatures, the compounds **22** and **23** were achieved in all cases in a mol ratio of 5/3.

*Hydrogenolysis of **22** and **23** with $LiAlH_4$.* The reaction and consequent separation was carried out in a manner analogous to that described in section 6.4.2. If a deficiency of $LiAlH_4$ was used the mass spectrum showed partly hydrogenated and chlorinated products. A separation of the mixture was not possible because of the differences in boiling points were too small.

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