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1.4-Addition of 1.1.2.2-tetrachlorodimethyldisilane to 1.4-diaza-1.3-dienes, synthesis and molecular structure of 1.6-disila-2.5-diaza-1.1.6.6-tetrachloro-1.6-dimethyl-2.5-di-*p*-tolyl-3.4-diphenyl-hexa-3-ene

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Abstract

Reaction of 1.1.2.2-tetrachlorodimethyldisilane (**4**) with 1.4-diazadienes like benzildianil (**1**), benzildi-*p*-tolil (**2**) and benzildi-*p*-anisil (**3**) leads to a 1.4-addition product of the disilane under cleavage of the Si–Si bond (**1a**, **2a**, **3a**). The structure of **2a** was determined by X-ray crystallography (crystal data: monoclinic, $P2_1/n$, $a = 14.661(4)$, $b = 12.283(2)$, $c = 17.564(5)$ Å, $\beta = 103.13°$, $Z = 4$, $R = 0.0585$ for 5992 independent reflections). Surprisingly, **2a** was found to be in the *cis*-configuration with almost C_2 symmetry and a torsion angle of only 13°. Owing to statistical disorder, some bond lengths are not in the expected range.

Keywords: Silicon; Disilanes; 1.4-Diazadienes

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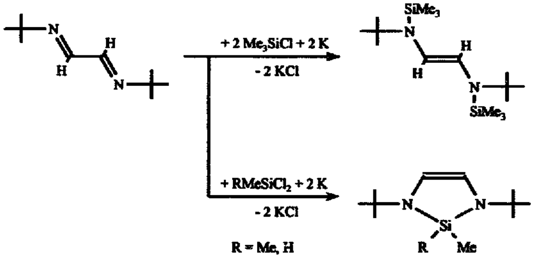
1. Introduction

1.6-disila-2.5-diazahexa-3-enes and 2-sila-1.3-diazacyclopent-4-enes were prepared earlier by tom Dieck et al. [1] starting from 1.4-diazadienes, R_3SiCl and potassium:



(1)

Weidenbruch et al. [2] obtained 1.4-diaza-2.3-disilacyclohexa-5-enes as products of a [4 + 2]-cycloaddition of

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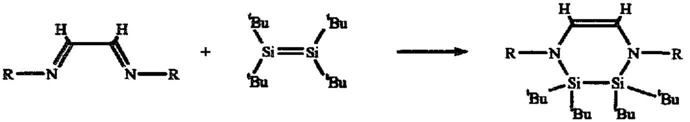
tetra-*t*-butyldisilene (generated photochemically from cyclo-$Si_3{}^tBu_6$) with 1.4-diisopropyl- as well as 1.4-dicyclohexyl-1.4-diazadiene:



R = i-Pr, cyclo-C_6H_{11}

(2)

Because of the bulky substituents, the X-ray structure analysis for R = cyclo-C_6H_{11} revealed a very long SiSi bond distance of 246.9 pm within this strained six-membered ring. 1.3-Diaza-2-silacyclopent-4-enes with two ${}^tBu$ substituents at the silicon atom were prepared from the same 1.4-diazadienes with Li and ${}^tBu_2SiCl_2$ according to Ref. [1]. The X-ray structure analysis for R = cyclo-C_6H_{11} showed a nearly planar five-membered ring with almost normal SiC, SiN as well as CN bond distances. With an angle sum of 360°, the nitrogen atoms are planar surrounded in the five- as well as in the six-membered ring.

We report a new, very surprising way to obtain 1.6-disila-2.5-diazahexa-3-enes starting from methylchlorodisilanes.

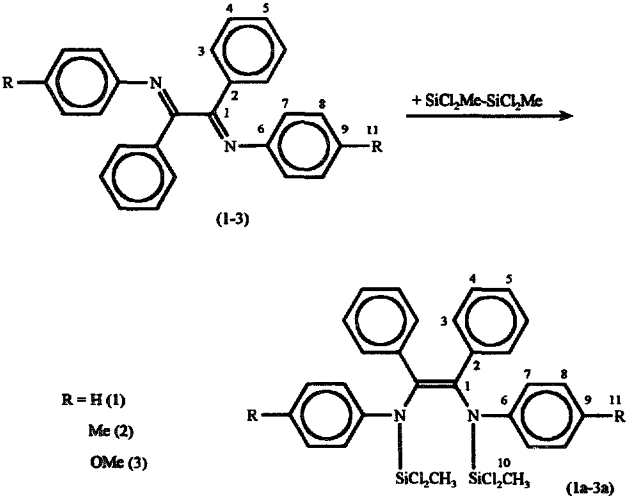
During our investigations concerning the partial hydrogenation of methylchlorodisilanes with tributylstannane in the presence of a Lewis base catalyst [3–5], we also investigated 1.4-diazadienes like **1** as catalyst:

$$R_2MeSi{-}SiMeRCl + Bu_3SnH \xrightarrow{cat.} R_2MeSi{-}SiMeRH + Bu_3SnCl \quad R = Cl, Me \qquad (3)$$

Whereas $SiClMe_2{-}SiClMe_2$ (**5**) could be hydrogenated to $SiHMe_2{-}SiClMe_2$ and $SiHMe_2{-}SiHMe_2$ in the presence of **1**, surprisingly no hydrogenation took place with $SiCl_2Me{-}SiCl_2Me$ (**4**). Using a higher content of **1** (solvent:toluene), small amounts of $SiHClMe{-}SiCl_2Me$ and $SiH_2Me{-}SiCl_2Me$ could be detected, but after standing overnight colourless crystals of a compound having the elemental composition $Si_2Cl_4Me_2 \cdot$ **1** were formed.

2. Results and discussion

Reaction of **4** with the 1.4-diazadienes **1**, **2** and **3** respectively in a 1:1 molar ratio in toluene at ambient temperature yields the 1.4-addition products **1a**, **2a** and **3a**:



(1-3)

(1a-3a)

(4)

Table 1
Melting points and results of the elemental analysis of **1a**, **2a** and **3a**

Compound	M.p. (°C)	H. (mass%)		Elemental analysis			
		Calc.	Found	C (mass%)		N (mass%)	
				Calc.	Found	Calc.	Found
1a	184–185 [a]	4.45	4.54	57.15	57.22	4.76	4.74
2a	161–163 [a]	4.91	5.02	58.44	58.70	4.54	4.49
3a	decomp. > 165	4.66	4.83	55.56	55.79	4.32	4.30

[a] Melts under decomposition (turns yellow).

Table 2
NMR chemical shifts of **1a**, **2a** and **3a** (ppm)

Compound		**1a**	**2a**	**3a**
^{1}H	SiMe	0.07	0.06	0.09
	R(CH$_3$)	—	2.29	3.77
	Ar–H	7.05–7.80	7.05–7.50	6.80–7.50
^{13}C	1 and 2	140.1	139.8 (163.7)	139.9
		140.6	140.7 (137.6)	140.7
	3 and 4	128.3	128.0 (128.2)	128.0
		128.3	128.2 (128.6)	128.2
	5	130.9	130.9 (130.9)	131.0
	6	147.9	144.8 (146.8)	140.0
	7	121.0	121.2 (120.4)	123.1
	8	129.6	129.9 (129.0)	114.1
	9	123.5	132.8 (134.5)	156.0
	10	7.1	7.1	6.9
	11	—	20.7 (20.9)	55.5
^{29}Si		−2.9	−3.2	−3.2

Values in brackets are those for **2**.

On the contrary, no addition products could be detected using **5** instead of **4**.

Table 1 shows the melting points as well as the results of the elemental analysis, and Table 2 the ^{1}H, ^{13}C and ^{29}Si NMR chemical shifts of compounds **1a**, **2a** and **3a**.

2.1. Molecular structure of 2a

2a crystallizes monoclinically, in space group $P2_1/n$ (No. 14). The unit cell has dimensions: $a = 14.661(4)$, $b = 12.283(2)$, $c = 17.564(5)$ Å and $\beta = 103.13(2)°$, $Z = 4$. Fig. 1 shows an ORTEP drawing [6] of the molecular

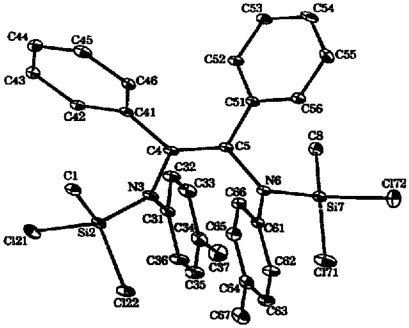
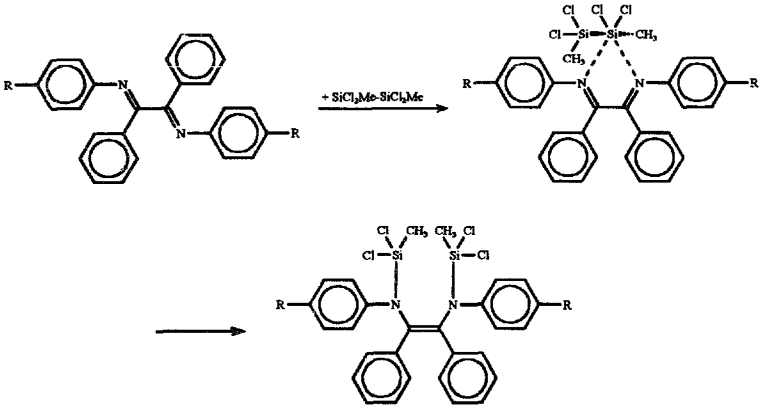


Fig. 1. ORTEP drawing of **2a** (30% probability).

structure of **2a**. The quality of the X-ray structure analysis does not allow a discussion of the geometric details of the molecule. The shape of the thermal ellipsoids proposes that during cooling the crystal down to 200 K several disorders of the molecule are frozen, which could not be resolved by X-ray.

Nevertheless, the structure found shows clearly that **2a** occurs in the *cis*-configuration with a twist of only 12.8(4)° between both halves of the molecule. This can be explained following the reaction path



(5)

In the case of 2.2′ bipyridyl, the first formed complex is stable up to ambient temperature [7]. Further heating or addition of a donor solvent led to a cleavage of the Si–Si bond. The most characteristic features of **4** · bipy are the stretched Si–Si bond and the unequal and comparatively long Si–Cl bonds at the six-fold coordinated silicon atom [8].

3. Experimental

3.1. Preparation of 1a, 2a and 3a

3 g (13 mmol) **4** and 10 mmol **1**, **2** and **3** respectively were dissolved in 30 ml of dried toluene. After standing for two days the solvent and excess **4** were removed in vacuum and the residue was recrystallized from dried n-hexane. **1a** and **2a** are colourless, **3a** is pale yellow. Single crystals of **2a** were prepared by slow crystallization from a hot saturated solution in n-hexane. **1a** crystallizes in thin plates not suitable for X-ray study.

Table 3
Crystallographic data for **2a**

wavelength	0.71073 Å
crystal size	0.6 × 0.4 × 0.3 mm^3
θ range	2.19–26.00°
index ranges	$-17 \leq j \leq 18$, $-14 \leq k \leq 15$, $-21 \leq l \leq 21$
reflections collected	20297
independent reflections	5992
absorption correction	none
refinement method	full-matrix least-squares on F^2
goodness-of-fit on F^2	0.992
R_1 [$I > 2\sigma(I)$]	0.0585
wR_2 ($I > 2\sigma(I)$]	0.1465
final difference map peaks	-0.634 to 0.560 e Å^{-3}

3.2. Characterization

Elemental analyses were carried out using a Voss-Heraeus CHN–O Rapid. NMR measurements were performed using a Bruker MSL 300 at resonance frequencies of ^{1}H: 300.13 MHz and ^{13}C: 75.470 MHz with broad band decoupling and ^{29}Si: 59.627 MHz with inverse gated decoupling. All chemical shift data have been determined in $CDCl_3$ with TMS as internal standard.

3.3. X-ray crystallographic analysis of **2a**

The measurements were carried out on a Stoe IPDS diffractometer [9] at 200 K under nitrogen. For structure solution and refinement a SHELX program system [10] was used. See Table 3.

Further details of the structure determination may be obtained from the Fachinformationszentrum Karlsruhe (depository number CSD-405737).

Acknowledgements

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