

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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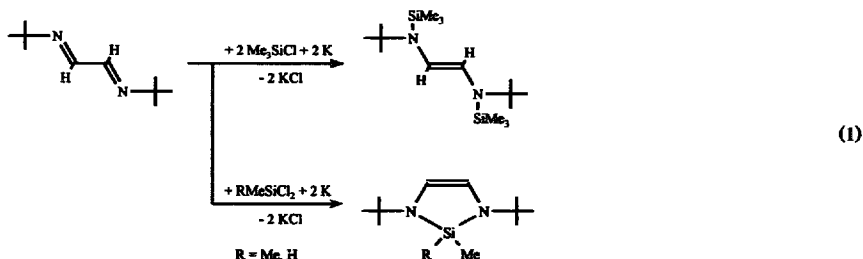
Abstract

Reaction of 1.1.2.2-tetrachlorodimethyldisilane (4) with 1.4-diazadienes like benzidiane (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, $\beta = 103.13^\circ$, $Z = 4$, $R = 0.0585$ 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

1. Introduction

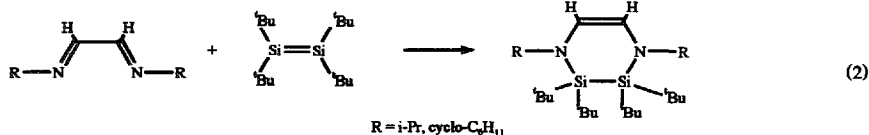
1.6-disila-2.5-diazahexa-3-enes and 2-sila-1.3-diazacyclopent-4-enes were prepared earlier by tom Dieck et al. [1] starting from 1.4-diazadienes, R_3SiCl and potassium:



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-Si₃'Bu₆) with 1,4-diisopropyl- as well as 1,4-dicyclohexyl-1,4-diazadiene:



Because of the bulky substituents, the X-ray structure analysis for R = cyclo-C₆H₁₁, revealed a very long SiSi bond distance of 246.9 pm within this strained six-membered ring. 1,3-Diaza-2-silacyclohex-4-enes with two ^tBu substituents at the silicon atom were prepared from the same 1,4-diazadienes with Li and ^tBu₂SiCl₂ according to Ref. [1]. The X-ray structure analysis for R = cyclo-C₆H₁₁, 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 methylchlorosilanes.

During our investigations concerning the partial hydrogenation of methylchlorosilanes with tributylstannane in the presence of a Lewis base catalyst [3–5], we also investigated 1,4-diazadienes like **1** as catalyst:



Whereas SiClMe₂-SiClMe₂ (**5**) could be hydrogenated to SiHMe₂-SiClMe₂ and SiHMe₂-SiHMe₂ in the presence of **1**, surprisingly no hydrogenation took place with SiCl₂Me-SiCl₂Me (**4**). Using a higher content of **1** (solvent:toluene), small amounts of SiHClMe-SiCl₂Me and SiH₂Me-SiCl₂Me could be detected, but after standing overnight colourless crystals of a compound having the elemental composition Si₂Cl₄Me₂ · **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**:

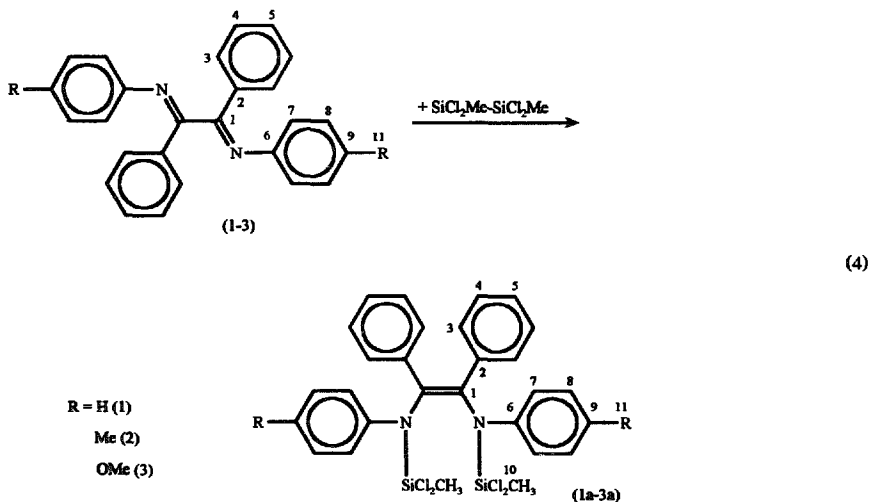


Table 1
Melting points and results of the elemental analysis of **1a**, **2a** and **3a**

Compound	M.p. (°C)	H. (mass%)		Elemental analysis			
		Calc.	Found	C (mass%)		N (mass%)	
				Calc.	Found	Calc.	Found
1a	184–185 *	4.45	4.54	57.15	57.22	4.76	4.74
2a	161–163 *	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

* 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 ¹H, ¹³C and ²⁹Si 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 $\beta = 103.13(2)^\circ$, $Z = 4$. Fig. 1 shows an ORTEP drawing [6] of the molecular

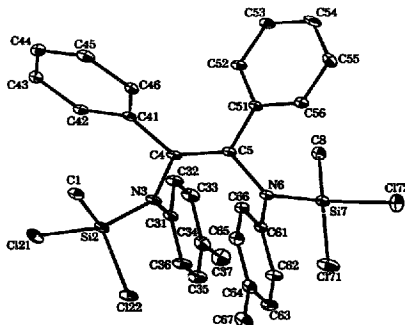
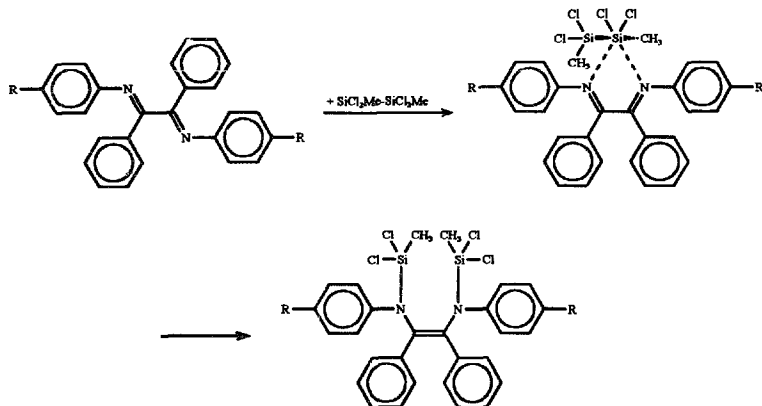


Fig. 1. ORTEP drawing of **2a** (30% probability).

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



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**

3g (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 ≤ j ≤ 18, –14 ≤ k ≤ 15, –21 ≤ l ≤ 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 > 2σ(I)]	0.0585
wR ₂ [I > 2σ(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 ^1H : 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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References

- [1] H. tom Dieck, B. Bruder and K.-D. Franz, *Chem. Ber.*, 116 (1983) 136.
- [2] M. Weidenbruch, A. Lesch and K. Peters, *J. Organomet. Chem.*, 407 (1991) 31.
- [3] U. Herzog, G. Roewer and U. Pätzold, *J. Organomet. Chem.*, 494 (1995) 143.
- [4] U. Herzog, G. Roewer and K. Herzog, in N. Auner and J. Weis (eds.), *Organosilicon Chemistry II*, VCH, Weinheim, 1996, pp. 31–36.
- [5] U. Pätzold, G. Roewer and U. Herzog, *J. Organomet. Chem.*, 508 (1996) 147.
- [6] C.K. Johnson, *FORTAN Thermal Ellipsoid Plot, Program for Crystal Structure Illustrations*, ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
- [7] D. Kummer, A. Balkir and H. Köster, *J. Organomet. Chem.*, 178 (1979) 29.
- [8] G. Sawitzki and H.G. von Schnering, *Chem. Ber.*, 109 (1976) 3728.
- [9] Stoe computer software IPDS diffractometer, 1996.
- [10] G.M. Sheldrick, *Acta Crystallogr.*, A46 (1993) 467.