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Analysis of the crystal structures of 1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazasilol-2-ylidene and 1,3-di-*tert*-butyl-2,2-dichloro-1,3-diaza-2-sila-4-cyclopentene

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The crystal structures of the title compounds, 1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazasilol-2-ylidene, $C_{10}H_{20}N_2Si$ (**1**) and 1,3-di-*tert*-butyl-2,2-dichloro-1,3-diaza-2-sila-4-cyclopentene, $C_{10}H_{20}N_2SiCl_2$ (**3**) were solved and are reported. Compound (**1**) crystallized in space group P mmn and each molecule has a mirror plane, which bisects the C-C backbone of the N-C-C-N framework. Compound (**1**) was also found to have a 2-fold twin component. In compound (**3**) the space group P 2_1/m results with the mirror plane passing through the N-C-C-N backbone. We compare these structures with the gas phase determination previously reported for (**1**) and the incomplete single crystal data for (**3**).

Introduction

Silylenes (R_2Si:), divalent, dicoordinate silicon compounds, are the silicon analogues to carbenes known in organic chemistry. These compounds, first reported over 40 years ago, have only in the last 10 years been structurally characterized by X-ray single crystal studies [1]. The first R_2-N-Si-N-R_2 complex characterized was done by Gehrhus, Lappert, Heinickle, Boese and Blaser [2] using the N,N'-dineopentyl-1,2-phenylenediamido ligand (**2**). The only other such complex was synthesized and crystallized by Schafer and co-workers [3] with the 1,2-di-*tert*-butylaminoethane ligand.

Experimental

The title compounds were synthesized according to literature methods [4]. Crystals suitable for X-ray diffraction were sublimed at room temperature at 10^{-4} Torr.

Data was collected using a Bruker SMART CCD (charge coupled device) based diffractometer equipped with an LT-3 low-temperature apparatus operating at 213 K. A suitable crystal was chosen and mounted on a glass fiber using grease. Data were measured using omega scans of 0.3 ° per frame for 30 seconds, such that a hemisphere was collected. A total of 1271 frames were collected with a maximum resolution of 0.75 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART [5] software and refined using SAINT [6] on all observed reflections. Data reduction was performed using the SAINT software, which corrects for Lp and decay. The structures are solved by the direct method using the SHELXS-97 [7] program and refined by least squares method on F^2, SHELXL-97 [8], incorporated in SHELXTL V5.10 [9].

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The structure of (**1**) was solved in the space group Pmmn (No. 59) by analysis of systematic absences. All non-hydrogen atoms are refined anisotropically. The twin law used was 0 1 0 1 0 0 0 0 -1 and BASF value refined to 0.10438. This improved the refinement considerably from R(1) of 0.2687 isotropically to R(1) of 0.1167 isotropically. All other aspects of the refinement of both compounds proceeded normally. Hydrogens were calculated by geometrical methods and refined as a riding model. The crystal used for the diffraction study showed no decomposition during data collection.

The structure of (**3**) was solved in the space group $P2_1/m$ (No. 11). All non-hydrogen atoms are refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. The crystal used for the diffraction study showed no decomposition during data collection.

Results and discussion

Compound (**1**) represents the third compound of this type to be studied crystallographically. Gerhus and co-workers [10] report the reactivity of the complex to oxidative addition reactions. These reactions to form dimeric disilanes suggested to us that we should study the structures of the silyene and the dichloro derivative as volatile precursors potentially suitable for deposition of SiO_2 thin films.

Compound (**1**) is shown in Figure 1 and crystallized with a mirror plane passing through the backbone of the ligand. The crystal was found to be twined with a 2-fold rotation of 180 degrees about the 1 1 0 reciprocal lattice direction. The bond lengths and angles are found to be similar to those reported for the phenylenediamido ligand. The N-Si-N of 88.2(3)° shows the strain and carbene nature of the molecule. This bond opens up in 1,3-di-*tert*-butyl-2,2-dichloro-1,3-diaza-2-sila-4-cyclpentene (**3**) to 95.90(12)° when the silicon increases oxidation state and coordination number to 4.

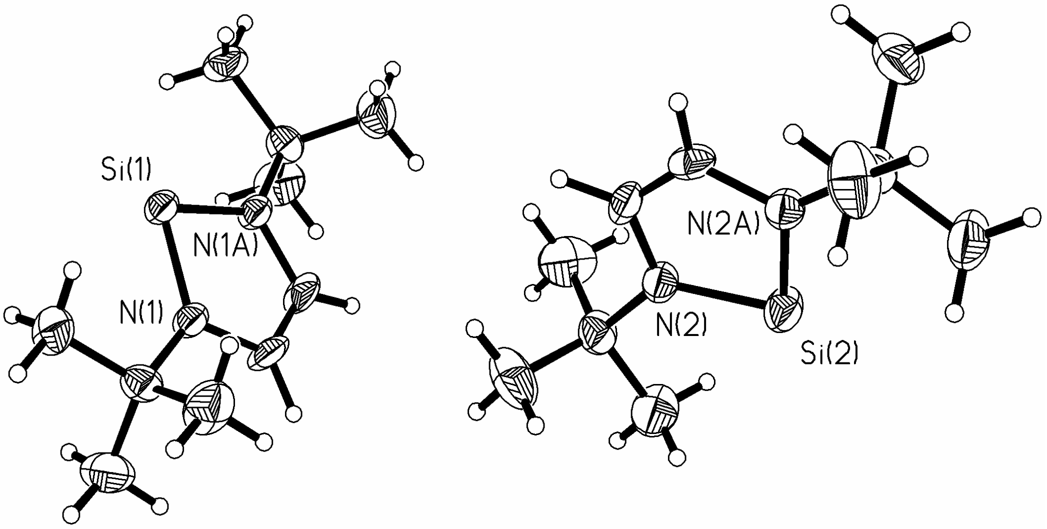


Fig. 1 A diagram of the molecular structure of 1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazasilol-2-ylidene (**1**) showing 50% probability ellipsoids.

Table 1 gives some significant parameters reported in this paper for 1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazasilol-2-ylidene (**1**) and compares those values with the previously reported gas phase structure values for (**1**) and the related silylene (**2**). The values are surprisingly very close to the solid state structure reported here. Only two values differ from the standard deviations and those are the N-Si-N and N-C-C bond angles, which are larger in the gas phase structure. This supports a more compact structure in the reported gas phase structure, as evident in the smaller cell values for the structure and the slightly longer Si---Si interaction in the solid-state structure.

Table 2 shows the bond distances and angles reported in the incomplete structure for 1,3-di-tert-butyl-2,2-dichloro-1,3-diaza-2-sila-4-cyclpentene (3) and those found in this study as well as those for (4) and (5). There does not appear to be any significant deviations from the previously reported numbers.

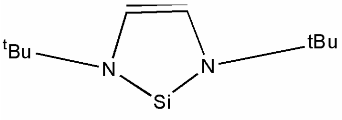
Table 1 Crystallographic and geometric parameters for the solid-state structure, 1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazasilol-2-ylidene (**1**) reported here and compared to those values with the previously reported gas phase structure values for (**1**) and the related silylene, Phenylenediamido (**2**).

Parameter	Gas phase Structure [2]	Solid State Structure	Phenylenediamido (2) [10]
a (Å)	13.643(2)	13.729(3)	21.219
b (Å)	13.821(8)	13.920(3)	5.932
c (Å)	6.345(6)	6.3981(11)	13.633, ß = 104.32°
Residual	R(F) = 0.165	$R(F^2)$ = 0.0907	R(F)= 0.0472
Si-N (Å)	1.753(5)	1.751(5)	1.746, 1.752
N-C1 (Å)	1.400(9)	1.383(8)	1.380, 1.384
C1-C1a (Å)	1.347(21)	1.341(13)	1.416
N-Si-N (°)	90.5(10)	88.2(3)	88.229
N-C1-C1a (°)	114.1(5)	109.5(4)	
Closest Si-Si contact (Å)	6.346	6.398	

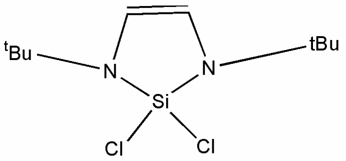
Table 2 Crystallographic and geometric parameters previously reported for 1,3-di-*tert*-butyl-2,2-dichloro-1,3-diaza-2-sila-4-cyclopentene (**3**) reported here and those previously reported for (**3**) and related compounds (**4**) and (**5**).

Parameter	Reported Structure[a]	Structure reported here	10[b]	11[b]
a (Å)	NA	7.2284(8)	31.860	19.502
b (Å)	NA	10.0449(11)	8.890	9.312
c (Å)	NA	10.3103(11)	19.552	16.160
ß (°)	NA	104.845(2)	127.59	113.42
Residual	NA	$R(F^2)$ = 0.0463	$R(F^2)$= 0.03.3	$R(F^2)$ = 0.0348
Si-N (Å)	1.695(3), 1.700(3)	1.686(3), 1.699(2)	1.697, 1.704	1.703, 1.701
N-C1 (Å)	1.416(5), 1.414(4)	1.422(4), 1.414(4)	1.441, 1.436	1.415, 1.416
C-C (Å)	1.322(4)	1.324(4)	1.3348	1.328
N-Si-N (°)	95.4(1)	95.90(12)	97.184	94.319
N-C-C (°)	115.3(3), 114.4(3)	109.0(2), 109.6(3)		

[a] [11] Reported some values for this structure, the complete data is not reported.; [b] [13]



1



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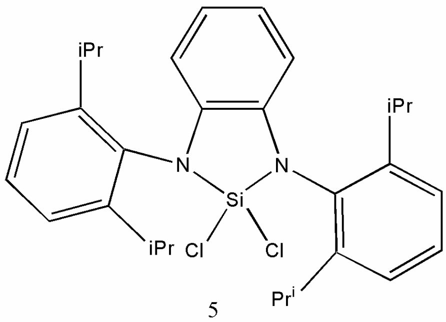

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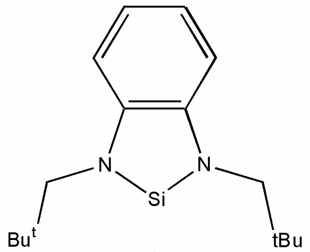

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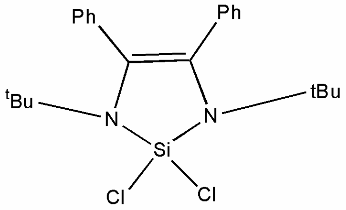

4

The structure of 1,3-di-*tert*-butyl-2,2-dichloro-1,3-diaza-2-sila-4-cyclpentene (**3**) was reported to have been done [11], but we could only find specific bond distances and angles reported in the original paper. The lack of additional crystallographic information and the failure to find the compound reported in the Cambridge Crystallographic Database [12] caused us to investigate the crystal structure.

The compound is shown in Figure 2 and crystallized with a mirror plane passing through the N-C-C-N backbone of the ligand. The bond distance and angles are similar to those found for similar compounds [13] (**4**) and (**5**).

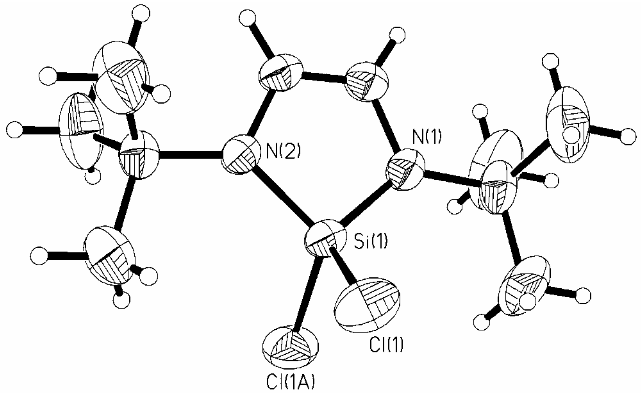

Fig. 2 A diagram of the molecular structure of 1,3-di-*tert*-butyl-2,2-dichloro-1,3-diaza-2-sila-4-cyclpentene (**3**) showing 50% probability ellipsoids.

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