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Reaction studies on hypervalent silicon hydride compounds

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Abstract

The versatile reaction chemistry of penta-coordinated silanes of type $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)(CH_3)SiH$ (**1a**) and $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)SiH_2$ (**1b**) with different substrates is described. The reaction behavior along with the structure and bonding of the compounds obtained is compared with tetravalent silicon molecules. Hypervalent **1a** and **1b** react, without added catalysts, with alcohols, water and benzoylic acid to produce alcoxysilanes, siloxanes and carboxysilanes, respectively. Compounds $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)(CH_3)Si(OCH_3)$ (**3**), $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)Si(OR)_2$ (**4a**: $R = CH_3$, **4b**: $R = C_2H_5$, **4c**: $R = {}^iC_3H_7$, **4d**: $R = CH_2C{\equiv}CH$), $\{[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)(CH_3)Si\}_2O$ (**5a**), $\{[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)SiO\}_n$ (**5b**) as well as $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)Si(H)[OC(O)C_6H_5]$ (**8**) are formed in quantitative yields. The carboxysilane **8** reacts with $C_6H_5CO_2H$ (**7**) further to give the polymeric siloxane **5b** and benzoylic anhydride. Moreover, H_2PtCl_6-catalyzed head–tail polymerization of **1b** yields the oligomeric carbosilane $\{[C_6H_4CH_2N(CH_3)_2\text{–}2](H)Si\text{–}CH_2CH_2\text{–}\}_n$ (**6**). Due to the intramolecular nitrogen–silicon interaction in hypervalent **1a** as well as **1b**, the hydrosilylation reaction with $C_6H_5N{=}C{=}X$ (**11a**: $X = S$, **11b**: $X = O$) takes place without a catalyst added, whereas hydrosilylation of isocyanates and isothiocyanates does not occur with tetravalent silanes. The obtained products $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)(R)Si(C_6H_5NCHX)$ (**12a**: $R = CH_3$, $X = S$; **12b**: $R = H$, $X = S$; **12c**: $R = H$, $X = O$) are suitable catalysts for the cyclooligomerization of isocyanates and isothiocyanates. While compounds **12a**–**12c** are stable in the solid state, **12c** starts to rearrange in solution to afford oligomeric **5b** along with 1,3,5-triphenylhexahydro-1,3,5-triazine (**13**). A possible mechanism for the formation of the latter compounds is discussed. An example for an insertion–elimination process of compound **1b** is given by the insertion of sulfur into the silicon–hydrogen bonds, yielding $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)Si(SH)_2$ (**15**) as an intermediate first; elimination of H_2S affords the intermolecular donor-stabilized silanethion $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)Si{=}S$ (**16**). The X-ray structure analysis of compound **12b** is reported. Crystals of **12b** are monoclinic, space group $P2_1/n$ with the cell constants $a = 9.356(3)$, $b = 10.890(4)$, $c = 17.236(6)$ Å, $\beta = 99.80(3)°$, $V = 1730(1)$ Å^3 and $Z = 4$. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Silicon; Silicon hydride; Hypervalent silicon

1. Introduction

Silicon compounds with a coordination number larger than 4 are the object of many studies with respect to their application as catalysts in organic as well as organometallic synthesis, and as starting materials for the preparation of a variety of different organosilicon compounds [1].

Moreover, their use as model compounds to study the mechanism of nucleophilic substitution reactions is of wide interest, as the silicon atom possesses the possibility of extending its coordination number effortlessly [1,2].

In this respect, we discuss the reaction chemistry of penta-coordinated silicon hydrides towards different substrates.

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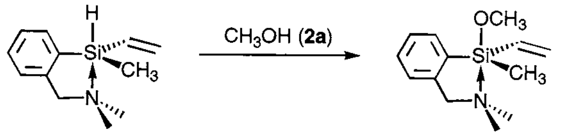
2. Results and discussion

The preparation of the penta-coordinated silanes $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)(CH_3)SiH$ (**1a**) and $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)SiH_2$ (**1b**) succeeded by treatment of $LiC_6H_4CH_2N(CH_3)_2\text{–}2$ with the corresponding chloro, dichloro or alcoxy silanes, followed by the reaction with $LiAlH_4$ in diethylether solutions [3].

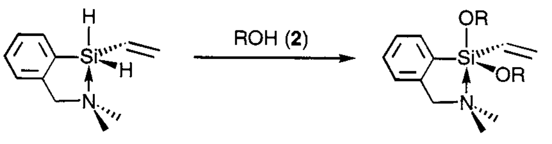
Due to the intramolecular coordination of the nitrogen atom of the dimethylaminomethylene group to the central silicon atom, an enhanced reactivity, as compared with tetravalent silicon compounds, is observed [3,4]. This increased reactivity accompanied by the intramolecular N–Si coordination can be explained by the coordinative expansion of the silicon atom [1,2]. We describe the manifold reaction chemistry of the hypervalent silanes **1a** and **1b**.

2.1. Nucleophilic substitution reactions

The highly reactive penta-coordinated silanes $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)(CH_3)SiH$ (**1a**) and $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)SiH_2$ (**1b**) react with alcohols ROH (**2a**: $R = CH_3$; **2b**: $R = C_2H_5$; **2c**: $R = {}^{i}C_3H_7$; **2d**: $R = CH_2C{\equiv}CH$) in strongly exothermic reactions to produce the mono- or all-substituted compounds **3** or **4a**–**4d**. The alcoxysilanes **3** and **4a**–**4d** are obtained as colorless oils in high yields and can best be purified by vacuum distillation.



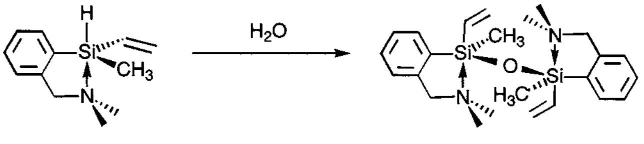
1a **3**



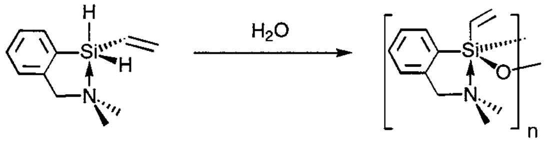
1b

4a: $R = CH_3$
4b: $R = C_2H_5$
4c: $R = {}^{i}C_3H_7$
4d: $R = CH_2C{\equiv}CH$

While hydrolysis of compound **1a** affords the siloxane $\{[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)(CH_3)Si\}_2O$ (**5a**), hydrolysis of **1b** yields oligomeric $\{[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)SiO\}_n$ (**5b**). However, the formation of hypervalent silanols of type $\{[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)(R)SiOH$ as intermediates could not be detected.



1a **5a**

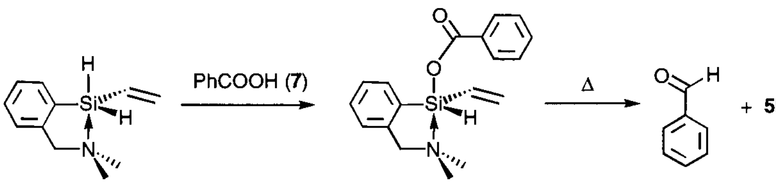


1b **5b**

After appropriate work-up, the disiloxane **5a** is obtained as a colorless powder, whereas oligomeric **5b** could be isolated as a very viscous colorless oil in quantitative yields. Both the disiloxane **5a** and the oligosiloxane **5b** are stable to air.

A further possibility to synthesize oligomeric pentavalent silicon compounds is given by heating **1b** in the presence of catalytic amounts of H_2PtCl_6. In a head-to-tail addition reaction, the oligomeric carbosilane $\{[C_6H_4CH_2N(CH_3)_2\text{–}2)(H)Si\text{–}CH_2CH_2\text{–}\}_n$ (**6**) is obtained as a pale-yellow liquid (for a detailed discussion of compound **6** see below).

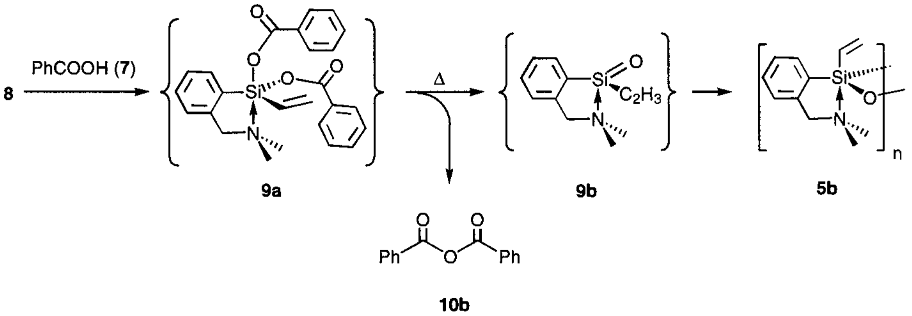
Changing from weaker Brönsted acids, e.g. alcohols and water, to stronger acidic carboxylic acids, the substitution of the hydrogen atoms in compound **1b** proceeds more rapidly and at lower temperatures, when compared with the above mentioned substrates for the synthesis of compounds **3**–**5**. The reaction of **1b** with benzoylic acid is described exemplary. Without added catalyst, **1b** reacts spontaneously with $C_6H_5CO_2H$ (**7**) in chloroform at 0°C with evolution of dihydrogen. The benzoyloxysilane $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)Si(H)[OC(O)C_6H_5]$ (**8**) is obtained as a colorless oil in 98% yield after appropriate work-up. By heating the latter compound to above 120°C, elimination of benzaldehyde (**10a**) is observed and the formation of oligomeric **5b** takes place. Similar observations were made by Corriu and coworkers; a possible reaction mechanism is discussed ([1]a,b, [5]).



1b **8**

Moreover, we found that on addition of further benzoic acid to compound **8**, the formation of benzanhydride (**10b**) along with oligomeric **5b** is observed. These products are formed in quantitative yields. **10b** could be separated from **5b** by column chromatography.

The formation of compounds **5b** and **10b** by reacting **7** with **8** can best be explained by the intermediate formation of $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)Si[OC(O)C_6H_5]_2$ (**9a**), from which benzanhydride (**10b**) is eliminated, thus forming the silanone **9b** as an intermediate. The latter molecule oligomerizes under the reaction conditions applied to produce **5b**. However, isostructural compounds to **9a** could be isolated for penta-coordinated $[C_6H_4CH_2N(CH_3)_2\text{–}2](C_{10}H_7\text{–}8)Si[OC(O)C_6H_5]_2$ ([4]a).

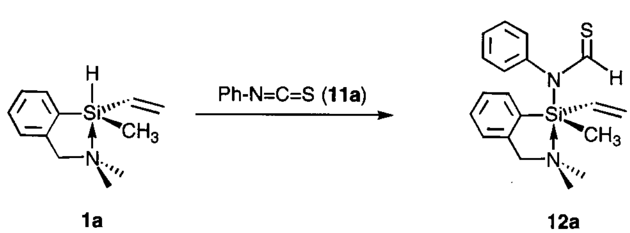


From the results obtained, it can be concluded that the hydrogen atoms in neutral pentavalent silicon compounds show an enhanced reactivity towards different Brönsted acids, as compared with tetravalent silanes. This points to a stronger hydridic character of the hydrogen atoms in hypervalent silicon compounds, when compared with their tetravalent analogs. The stronger hydridic character can be explained with a charge transfer from the dative-bonded nitrogen atom of the N,N-benzyldimethylamino ligand to the silicon center, and results in a higher electron density on the silicon atom.

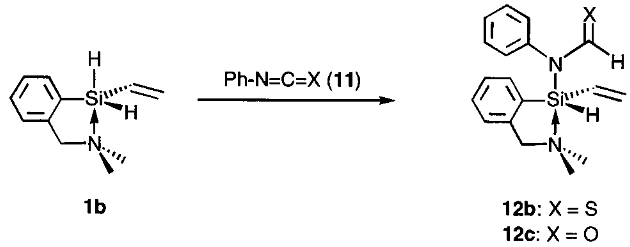
2.2. Hydrosilylation reactions

There are not many reactions known for the synthesis of N-acyl formamides and N-acyl thioformamides ([1]a,b, [6]). The high reactivity of penta-coordinated silanes should provide an easy access to these type of compounds. For this reason, the silanes **1a** and **1b** were reacted with $C_6H_5N{=}C{=}X$ (**11a**: X = S; **11b**: X = O).

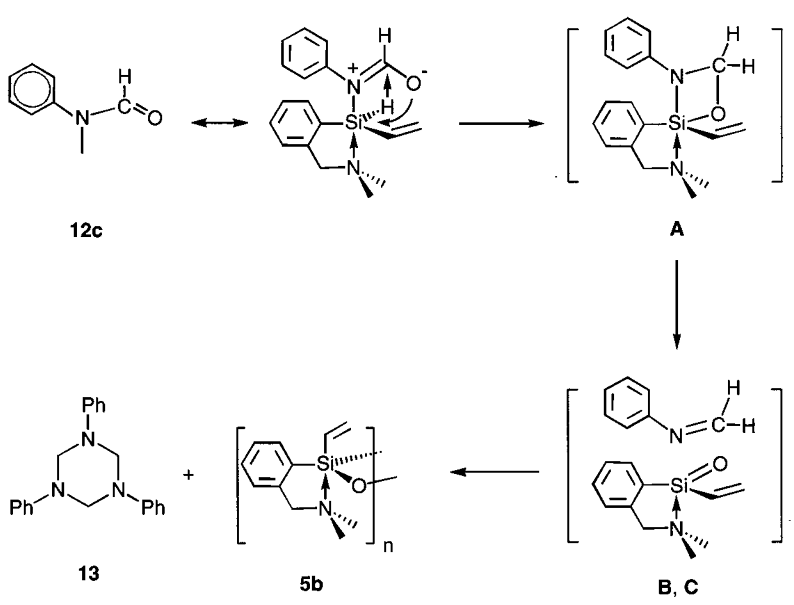
The reaction of $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)(CH_3)SiH$ (**1a**) with $C_6H_5N{=}C{=}S$ (**11a**) yields, by means of a hydrosilylation-type reaction, the hypervalent thioformamide compound $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)(CH_3)Si[C_6H_5NC(S)H]$ (**12a**). Compound **12a** is obtained as a pale-yellow solid by crystallization from saturated dichloromethane/*n*-pentane solutions at −30°C.



The penta-coordinated silane **1a** reacts, as compared with the corresponding tetravalent silane, much faster and without the requirement of any added catalyst. The same observations are made by the hydrosilylation reactions of the penta-coordinated vinyl-substituted dihydridosilane $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)SiH_2$ (**1b**) with stoichiometric amounts of the heterocumulenes $C_6H_5N{=}C{=}X$ (**11a**: X = S; **11b**: X = O) in chloroform solutions at 25°C. The mono-substituted silyl-thioformamide and -formamide compounds $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)Si(H)(C_6H_5NCHX)$ (**12b**: X = S; **12c**: X = O) are obtained in 94% (**12b**) or 83% (**12c**) yield.



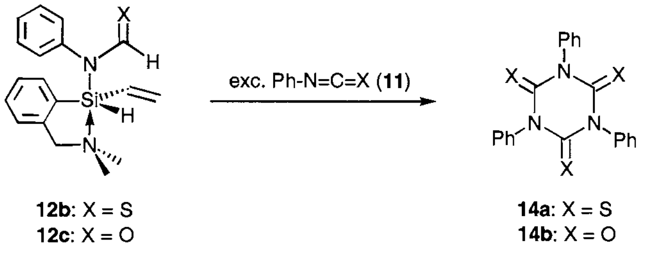
Compounds **12a**–**12c** are soluble in most common polar organic solvents, but insoluble in nonpolar ones, such as *n*-pentane or toluene. They can best be purified by distillation (**12c**) or crystallization (**12a**, **12b**) from saturated methylenechloride/*n*-pentane solutions at −30°C. While solutions, containing isothiocyanate building blocks, as given in molecules **12a** and **12b**, are stable even at 25°C for a long period of time, it is found that when the silyl isocyanate **12c** is kept in solution for a number of weeks, trimeric 1,3,5-triphenyl-1,3,5-hexahydrotriazine (**13**) along with oligomeric $\{[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)SiO\}_n$ (**5b**) is formed. One possible explanation for the formation of compounds **5b** and **13** by starting out from pentavalent silyl isocyanate **12c** is presented in Scheme 1.



Scheme 1. Possible mechanism for the formation of compounds **5b** and **13** from **12c**.

Presumably in the first step an intramolecular hydrosilylation process takes place to afford the 1-sila-2-aza-4-oxetane intermediate **A** (Scheme 1). In means of a [2 + 2] retrocycloaddition reaction of postulated cyclic **A**, the two intermediates phenylimine (Type **B** molecule) and the base-stabilized silanone of structural type **C** are built. Both species are not stable under the conditions used, and by trimerization of the phenylimine **B**, compound **13** is formed, while oligomerization of the silanone **C** affords the oligosiloxane **5b** (Scheme 1).

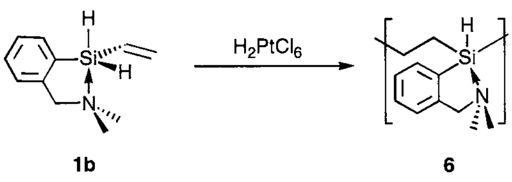
Attempts to induce a desirable second insertion of a formamide or thioformamide entity into the remaining silicon–hydrogen bond in compounds **12b** and **12c** failed. However, it was found that upon treatment of the silylthioformamide **12b**, as well as the silylformamide **12c** with a 10-fold excess of $C_6H_5N{=}C{=}X$ (**11a**: X = S; **11b**: X = O) produces the trimers of phenyl isothiocyanate (compound **14a**) and phenyl isocyanate (compound **14b**) in chloroform solutions at 25°C.



Additionally, the latter compounds can be obtained in much better yields by the direct reaction of the dihydridosilane **1b** with an 10-fold excess of **11a** or **11b** in chloroform solutions at 25°C.

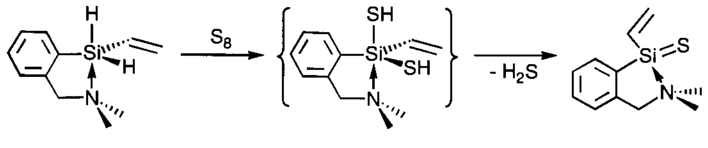
The trimerization of the isocyanates and isothiocyanates relies upon a repeated insertion of **11a** or **11b** into the silicon–nitrogen bond of the $Si{-}N(C_6H_5)(CHX)$ moiety in **12b** or **12c** ([6]b). After two insertions of $PhN{=}C{=}X$ molecules, the elimination of trimeric **14a** (X = S) or **14b** (X = O) occurs with reformation of the hypervalent dihydrosilane **1b**.

A further hydrosilylation-type reaction, which finally leads to an oligomeric hypervalent carbosilane, is given in the head-to-tail oligomerization of compound **1b** in the presence of catalytic amounts of Speier's catalyst. This hydrosilylation reaction is performed by slowly heating neat **1b** to 200°C and keeping the reaction mixture at this temperature for 2 h. Oligomeric $\{[C_6H_4CH_2N(CH_3)_2{-}2](H)Si{-}CH_2CH_2{-}\}_n$ (**6**) is obtained as a pale-yellow oil, which hydrolysis slowly on exposure to air and which is soluble in most common organic solvents. Cryoscopic molecular weight determination in benzene [7] denotes that compound **6** is oligomeric with $n = 3.6$.



2.3. Insertion–elimination reaction

Pentavalent dihydridosilanes can also be used successfully for the preparation of donor-stabilized low-coordinated silicon compounds ([1]a, [8,9]). We describe an access to 1-thia-2-sila-1,3-dienes by treatment of **1b** with sulfur in chloroform as solvent at 25°C. The heterobutadiene $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)Si{=}S$ (**16**) is obtained in 93% yield as a colorless solid with a putrid smell. It appears that compound **16** is extremely sensitive to moisture and by elimination of H_2S oligomeric **5b** is formed.



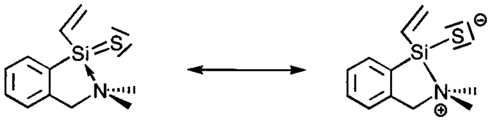
1b **15** **16**

The formation of compound **16** can best be explained by the insertion reaction of sulfur into the silicon–hydrogen bonds in **1b**, yielding $[C_6H_4CH_2N(CH_3)_2\text{–}2]$-$(H_2C{=}CH)Si(SH)_2$ (**15**) first. From this intermediate, the elimination of H_2S occurs. A similar reaction sequence has been postulated for the synthesis of oligomeric **5b**, but it could not be infallibly found out, whether the condensation step proceeds inter- or intramoleculary. However, the intermediate formation of isostructural oxygen containing compounds could not be perceived.

For the silanethione structure of **16** a ylidic character is reasonable, which possibly can be expressed by a mesomeric structure shown in Scheme 2. ([1]a).

2.4. Structure and bonding

All synthesized compounds could be unequivocally characterized by elemental analysis and spectroscopic methods (IR, ^1H-, $^{13}C\{^1H\}$-, $^{29}Si\{^1H\}$-NMR, MS). It appeared that the IR technique is the most suitable one for the surveillance of the reactions performed, as well as for a rapid characterization of the products obtained. In general, it is observed that the two Si–H stretching frequencies at 2131 and 2088 cm^{-1} in $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)(CH_3)SiH$ (**1a**), due to different conformations in which the hydrogen atom is located in an apical or equatorial position in the trigonal-bipyramidal coordination sphere of the silicon atom, disappear by alcoholysis, hydrolysis or hydrosilylation of the latter compound. New characteristic IR absorptions are found for the appropriate groups OR or PhNCHS introduced. Similar observations are made when the dihydridosilane $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)SiH_2$ (**1b**) is reacted with water or alcohols. While in the monohydrogen-substituted silane **1a**, two Si–H stretching frequencies are found, in compounds $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)(H)Si[OC(O)Ph]$ (**8**) and $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)(H)Si(C_6H_5NCHX)$ (**12b**: R = H, X = S; **12c**: R = H, X = O) only one $\nu_{Si\text{–}H}$ absorption band in the region of 2125–2140 cm^{-1} is recognized, which is typical for tetravalent silanes [10]. This indicates that the hydrogen atoms in these compounds are located exclusively in equatorial positions of the penta-coordinated silicon center, whereas the apical position of the coordination polyeder is occupied by the hydrogen atom in **1a** as well. However, the introduced groups OC(O)Ph and PhNCHX (X = O, S) in the products formed are orientated in the apical position, which can be explained by the increased ease of stretching the oxygen–silicon bond or the nitrogen–silicon bond, and the increased ability in delocalizing electron density as compared with the silicon–carbon bonds of the vinyl or the methyl group and the silicon–hydrogen bond.



Scheme 2. Mesomeric formula of the silanethione **16**.

In the ^1H-NMR spectra of compounds **12a**, **12b** and **16** intramolecular nitrogen coordination to the silicon atom can be observed by the appearance of diastereotopic methylene protons of the $C_6H_4CH_2N(CH_3)_2$ unit with coupling constants of $^2J_{HH} = 12.4$ Hz for **12a**, 14.3 Hz for **12b** or 8.0 Hz for **16**. Additionally, the ^1H-NMR spectrum of the intramolecular base-stabilized low-valent silanethion **16** also represents diastereotopic methyl groups at 2.26 and 2.44 ppm, respectively.

The molecule ion peaks M^+ of the new synthesized compounds, with the exception of silanes **5a** and **12**, are found in EI-MS experiments. As typical fragments M^+ $-CH_3$, M^+-C_2H_3, $CH_2N(CH_3)_2{}^+$ as well as $N(CH_3)_3{}^+$ are observed. Similar fragmentation is found for compounds **5a** and **12** under FAB conditions.

The result of the X-ray structure analysis, which was carried out exemplary for $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)(H)Si(C_6H_5NCHS)$ (**12b**) is in agreement with the spectroscopic findings (Fig. 1). Crystallographic parameters are given in Table 1, selected interatomic distances and angles are presented in Table 2 and atomic coordinates are listed in Table 3.

Compound **12b** crystallizes in the monoclinic space group $P2_1/n$ and is characterized by a trigonal-bipyramidal coordinated silicon atom. The vinyl group (C17, C18), the aryl entity of the built-in ligand $C_6H_4CH_2N(CH_3)_2\text{–}2$ (C1–C6), as well as the silicon-

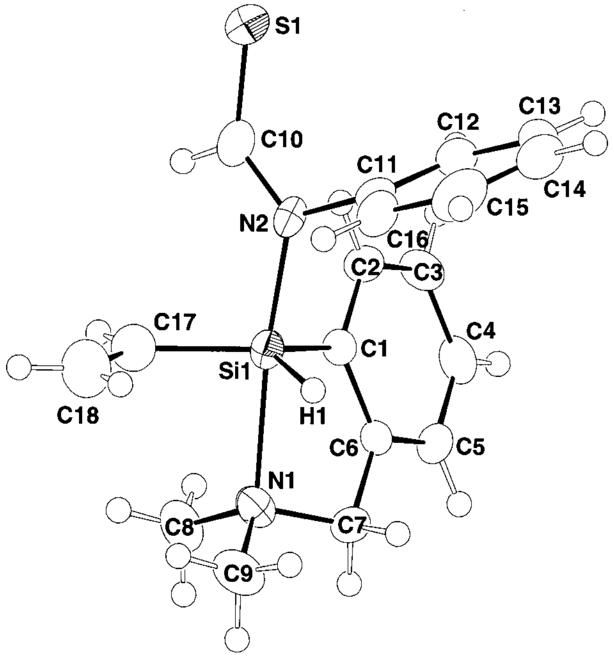


Fig. 1. ZOPTEP drawing (drawn at 50% probability level) of compound **12b** with the atom numbering scheme (hydrogen labels, except H(1), omitted for better clarity).

bonded hydrogen atom H1 are located in equatorial positions; whereas the nitrogen atoms of the dimethylamino group N1 and the N-acyl thioformamide unit N2 occupy the axial positions of the coordination polyeder [angle N1–Si1–N2 174.5(1)°]. The internal comparison of the Si1–N1 [2.225(3) Å] and the Si1–N2 [1.898(3) Å] bond lengths confirm that a covalent silicon–nitrogen bonding (Si1–N2) is present next to a coordinative-bonded nitrogen atom (N1). One discernable feature of compound **12b** is the trigonal planar environment around the nitrogen atom N2 (sum of angles: 359.68°). In accord with this is the interatomic bond distance N2–C10 at 1.322(5) Å, which is typical for C=N bond lengths in imines [11]. Moreover, the S1–C10 bond length at 1.646(4) Å is specific for carbon–sulfur single bond lengths in thiols and mercaptals [11]. These findings indicate that the N-acyl thioformamide unit in compound **12b** can best be described as a zwitterionic moiety with a 1-imminum-2-thiolate component (Scheme 3).

3. Conclusion

In general, it could be shown that the penta-coordinated silicon hydrides $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)(CH_3)SiH$ (**1a**) and $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)SiH_2$ (**1b**), as compared with their tetravalent analogs, show an enhanced reactivity towards different substrates. This is well-documented in the alcoholysis or hydrolysis of compounds **1a** and **1b** without added catalyst. In a similar manner, the synthesis of penta-coordinated silyl carboxylates, such as $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)(H)Si[OC(O)C_6H_5]$ (**8**) and $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)Si[OC(O)(C_6H_5)]_2$ (**9a**) can be achieved. On heating these compounds they show different types of reactions: while **8** is suitable for the preparation of benzaldehyde, **9a** yields benzanhydride by means of a dehydration-type reaction. The high reactivity of the penta-coordinated dihydrosilane **1b** can also be used for the preparation of oligomeric carbosilanes, as well as for the synthesis of N-functionalized formamide and thioformamide compounds. While in a one-to-one reaction of **1b** with PhN=C=X (X = O, S) the hydrosilylation product $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)(H)Si(C_6H_5NCHX)$ (**12b**: X = S; **12c**: X = O) is formed, the latter compounds are suitable as catalysts for the cyclotrimerization of the heterocumulenes PhN=C=X, respectively. In addition, the formamide **12c** affords the synthesis of the oligomeric siloxane **5b** and the 1,3,5-triphenyl-1,3,5-hexahydrotriazine **13** by means of a redox reaction. The synthesis of the novel intramolecular donor-stabilized 1-thia-2-sila-1,3-diene $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)Si{=}S$ (**16**) by an insertion–elimination mechanism is discussed.

Table 1
Crystallograhic parameters for compound **12b**

Empirical formula	$C_{18}H_{22}N_2SSi$
Formula weight	326.53
Temperature (K)	205
Radiation (λ, Å)	Mo–K_α, $\lambda = 0.71069$
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	9.356(3)
b (Å)	10.890(4)
c (Å)	17.236(6)
β (°)	99.80(3)
V (Å^3)	1730(1)
Z	4
$D_{calc.}$ (g cm^{-3})	1.253
Absorption coefficient, μ (mm^{-1})	0.255
Crystal size (mm)	0.20 × 0.30 × 0.10
Diffractometer model	Siemens (Nicolet) R3m/V
2θ range (°)	4.4–42.1
Index ranges	$-9 \leq h \leq 9$, $-1 \leq k \leq 10$, $-17 \leq l \leq 17$
Scan mode	ω-scan
Scan range (°)	0.75
Scan speed (° min^{-1})	5.8–29.3
Unique reflections	2012
Observed reflections [$I \leq 2\sigma(I)$]	1871
Refined parameters	212
Min/max residual electron density (eÅ^{-3})	0.432/−0.180
R_1/wR_2^a [$I > 2\sigma(I)$]	0.0421/0.0957
R_1/wR_2^a (all)	0.0600/0.1049
S (goodness-of-fit)^b on F^2	1.067

[a] $R_1 = \sum\left[(\|F_o|-|F_c\|)/\sum|F_o|\right]$, $wR_2 = \sum\left[(w(F_o{}^2-F_c{}^2)^2)/\sum(wF_o{}^4)\right]^{1/2}$.

[b] $S = \left[\sum w(F_o{}^2-F_c{}^2)^2\right]/(n-p)^{1/2}$, n, number of reflections, p, parameters used. Definition of w [where $P = (F_o{}^2+2F_c{}^2)/3$]: **12b**, $w = 1/[\sigma^2(F_o{}^2)+(0.0482)^2+1.23P]$.

Table 2
Selected bond lengths (Å) and angles (°) of compound **12b**[a]

Bond lengths (Å)			
Si1–N1	2.225(3)	N2–C11	1.442(5)
Si1–N2	1.898(3)	N1–C7	1.463(5)
Si1–C1	1.872(4)	N1–C8	1.480(5)
Si1–C17	1.853(4)	N1–C9	1.474(5)
Si1–H1	1.390(3)	C10–S1	1.646(4)
N2–C10	1.322(5)	C17–C18	1.320(6)
Angles (°)			
N1–Si1–N2	174.5(1)	C7–N1–C8	108.7(3)
C1–Si1–H1	115.4(1)	C7–N1–C9	110.7(3)
C1–Si1–C17	124.7(1)	C7–N1–Si1	101.6(2)
C17–Si1–H1	115.6(1)	C8–N1–C9	108.9(3)
N1–Si1–H1	81.9(1)	C8–N1–Si1	113.9(2)
N1–Si1–C1	80.3(1)	C9–N1–Si1	112.8(2)
N1–Si1–C17	87.0(1)	Si1–N2–C10	122.8(2)
N2–Si1–H1	95.0(1)	Si1–N2–C11	118.8(2)
N2–Si1–C1	97.0(1)	C10–N2–C11	118.1(3)
N2–Si1–C17	98.5(2)	C10–N2–C11	130.4(3)

[a] Numbers in parentheses are estimated S.D. in the least significant digits.

4. Experimental

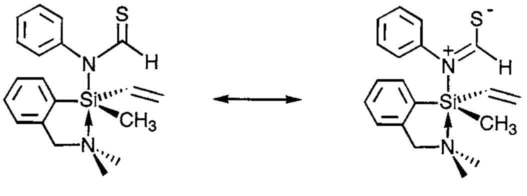
4.1. General comments

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Diethylether and tetrahydrofuran were purified by distillation from sodium/benzophenone ketyl; *n*-pentane and *n*-hexane were purified by distillation from calcium hydride. Dichloromethane and chloroform were distilled from P_2O_5. IR spectra were obtained with a Perkin-Elmer 983G spectrometer (KBr pellets or as film between NaCl plates). ^{1}H-NMR spectra were recorded on a Bruker AC 200 spectrometer operating at 200.132 MHz in the Fourier transform mode; ^{13}C{^{1}H}-NMR spectra were recorded at 50.323 MHz and ^{29}Si{^{1}H}-NMR spectra were recorded at 39.763 MHz. Chemical shifts are reported in δ units (ppm) downfield from tetramethylsilane ($\delta = 0$) with the solvent as the reference signal; ^{1}H-NMR: $CDCl_3$ $\delta = 7.27$, ^{13}C-NMR: $CDCl_3$ $\delta = 77.0$. EI- or FAB-MS were recorded on a Finnigan 8400 mass spectrometer, operating in the positive ion mode. Melting points were determined using analytically pure samples, sealed off in nitrogen-purged capillaries on a Gallenkamp MFB 595 010 M melting point apparatus. Microanalyses were performed by the Organisch-Chemisches Institut der Universität Heidelberg. The molecular weights of oligomeric compounds were determined by cryoscopic methods in benzene as solvent [7].

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$ Å^2) for compound **12b**[a]

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
Si1	840(1)	6413(1)	8685(1)	27(1)
N2	−146(3)	7940(3)	8532(2)	27(1)
S1	−193(1)	10333(1)	8127(1)	45(1)
N1	1886(3)	4595(3)	8963(2)	32(1)
C1	1839(4)	6729(3)	9702(2)	24(1)
C2	2154(4)	7884(3)	10036(2)	29(1)
C3	2828(4)	8011(4)	10806(2)	35(1)
C4	3197(4)	6985(4)	11266(2)	34(1)
C5	2901(4)	5834(4)	10953(2)	31(1)
C6	2229(4)	5702(3)	10178(2)	25(1)
C7	1837(4)	4483(3)	9804(2)	31(1)
C8	3419(4)	4544(4)	8852(2)	45(1)
C9	1083(5)	3581(4)	8519(3)	47(1)
C10	422(4)	8918(4)	8248(2)	33(1)
C11	−1506(4)	8080(3)	8811(2)	29(1)
C12	−1574(4)	8649(3)	9520(2)	37(1)
C13	−2877(5)	8747(4)	9783(3)	46(1)
C14	−4118(5)	8281(4)	9349(3)	53(1)
C15	−4059(5)	7694(4)	8644(3)	51(1)
C16	−2757(4)	7600(4)	8376(2)	37(1)
C17	1676(5)	6413(4)	7785(2)	43(1)
C18	992(6)	5956(4)	7114(3)	61(1)

[a] Estimated S.D. in units of the last significant digit in parentheses; U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.



Scheme 3. Mesomeric formula of compound **12b.**

4.2. Synthesis of [$C_6H_4CH_2N(CH_3)_2$–2](H_2C=CH)(CH_3)SiH (*1a*) and [$C_6H_4CH_2N(CH_3)_2$–2](H_2C=CH)SiH_2 (*1b*) [3]

A solution of 30.0 g (124.0 mmol) [$C_6H_4CH_2$-$N(CH_3)_2$–2](H_2C=CH)(CH_3)SiCl [3] in 500 ml of diethylether or 16.0 g (62.0 mmol) [$C_6H_4CH_2N(CH_3)_2$–2](H_2C=CH)$SiCl_2$ [3,12] in 300 ml of diethylether is added dropwise to a suspension of 2.6 g (68.4 mmol) $LiAlH_4$ in 500 ml diethylether under vigorous stirring at 0°C. The reaction mixture is allowed to warm slowly to 25°C and then refluxed for 1 h. All volatile materials are removed at 0°C and the grey residue is extracted with 500 ml of *n*-pentane. Following filtration through a pad of Celite and distillation of the eluate obtained in vacuum, produces 14.3 g (70 mmol, 54%) of [$C_6H_4CH_2N(CH_3)_2$–2](H_2C=CH)(CH_3)SiH (**1a**) or 6.7 g (35.3 mmol, 57%) of [$C_6H_4CH_2N(CH_3)_2$–2](H_2C=CH)SiH_2 (**1b**) as colorless oils.

4.2.1. Data for compound **1a**

Boiling point 63°C/10^{-1} mbar. Anal. Calc. for $C_{12}H_{19}NSi$ (205.37): C, 70.16; H, 9.32. Found: C, 70.23; H, 9.24. ^{1}H-NMR (CDCl$_3$): δ 0.55 (d, $^{3}J_{\mathrm{HH}} = 3.6$ Hz, 3H, SiCH_3), 2.29 (s, 6H, NCH_3), 3.59 (s, 1H, CH_2), 3.61 (s, 1H, CH_2), 4.75 (dq, $^{3}J_{\mathrm{HH}} = 2.6$ Hz, $^{3J}{}_{\mathrm{HH}} = 3.6$ Hz, 1H, SiH), 5.96 (dd, $^{2}J_{\mathrm{HH}} = 4.2$ Hz, $^{3}J_{\mathrm{HH}} = 19.9$ Hz, 1H, C$_2H_3$), 6.19 (dd, $^{2}J_{\mathrm{HH}} = 4.2$ Hz, $^{3}J_{\mathrm{HH}} = 14.4$ Hz, 1H, C$_2H_3$), 6.49 (ddd, $^{3}J_{\mathrm{HH}} = 2.6$ Hz, $^{3}J_{\mathrm{HH}} = 14.4$ Hz, $^{3}J_{\mathrm{HH}} = 19.9$ Hz, 1H, C$_2H_3$), 7.3–7.4 (m, 3H, C$_6H_4$), 7.7–7.8 (m, 1H, C$_6H_4$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 4.4 (SiCH$_3$), 44.5 (NCH$_3$), 64.6 (CH$_2$), 126.5 (C_6H$_4$), 128.3 (C_6H$_4$), 129.1 (C_6H$_4$), 132.4 (C_6H$_4$), 136.0 (C_6H$_4$), 136.2 (C_2H$_3$), 137.8 (C_6H$_4$), 145.8 (C_2H$_3$). ^{29}Si{^{1}H}-NMR (CDCl$_3$): δ -31.9. EI-MS [m/z (rel. intensity)] M^{+} 205 (13), M^{+}-CH$_3$ 190 (53), M^{+}-C$_2$H$_3$ 178 (14), M^{+}-CH$_3$–C$_2$H$_4$ 162 (100), M^{+}-3CH$_3$ 160 (61), (C$_6$H$_4$CH$_2$)Si(C$_2$H$_3$)$^{+}$ 145 (77). IR (NaCl): $\nu_{\mathrm{CH}} = 3043$ (s), 2997 (s), 2965 (s), 2937 (s), 2851 (s), 2817 (vs), 2773 (vs); $\nu_{\mathrm{SiH}} = 2133$ (vs), 2094 (m); $\nu_{\mathrm{C=C}} = 1586$ (m) cm^{-1}.

4.2.2. Data for compound **1b**

Boiling point 64–68°C/10^{-1} mbar. Anal. Calc. for $C_{11}H_{17}NSi$ (191.34): C, 69.05; H, 8.95. Found: C, 68.28; H, 9.04. ^{1}H-NMR (CDCl$_3$): δ 2.35 (s, 6H, CH_3), 3.67 (s, 2H, CH_2), 4.73 (d, $^{3}J_{\mathrm{HH}} = 3.2$ Hz, 2H, SiH), 6.13 (dd, $^{2}J_{\mathrm{HH}} = 4.4$ Hz, $^{3}J_{\mathrm{HH}} = 19.5$ Hz, 1H, C$_2H_3$), 6.28 (dd, $^{2}J_{\mathrm{HH}} = 4.4$ Hz, $^{3}J_{\mathrm{HH}} = 14.1$ Hz, 1H, C$_2H_3$), 6.5–6.7 (m, 1H, C$_2H_3$), 7.3–7.4 (m, 1H, C$_6H_4$), 7.4–7.5 (m, 2H, C$_6H_4$), 7.8–7.9 (m, 1H, C$_6H_4$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 46.1 (CH$_3$), 61.9 (CH$_2$), 126.6 (C_6H$_4$), 126.9 (C_6H$_4$), 129.4 (C_6H$_4$), 133.2 (C_6H$_4$), 133.5 (C_2H$_3$), 136.9 (C_6H$_4$), 139.5 (C_6H$_4$), 145.7 (C_2H$_3$). ^{29}Si{^{1}H}-NMR (CDCl$_3$): δ -46.2. EI-MS [m/z (rel. intensity)] M^{+} 191 (36), M^{+}-H 190 (55), M^{+}-CH$_3$ 176 (57), M^{+}-C$_2$H$_3$ 164 (64), M^{+}-CH$_3$–C$_2$H$_4$ 148 (98), (C$_6$H$_4$CH$_2$)Si(C$_2$H$_3$)$^{+}$ 145 (100). IR (NaCl): $\nu_{\mathrm{CH}} = 3045$ (s), 2969 (s), 2937 (s), 2852 (s), 2817 (s), 2781 (s); $\nu_{\mathrm{SiH}} = 2135$ (vs), 2081 (s); $\nu_{\mathrm{C=C}} = 1586$ (s) cm^{-1}.

4.3. Synthesis of [$C_6H_4CH_2N(CH_3)_2$–2](H_2C=CH)(CH_3)Si(OCH_3) (**3**) and [$C_6H_4CH_2N(CH_3)_2$–2](H_2C=CH)Si($OR)_2$ (**4a**: $R = CH_3$, **4b**: $R = C_2H_5$, **4c**: $R = {}^{i}C_3H_7$, **4d**: $R = CH_2C{\equiv}CH$)

Under vigorous stirring, 50 mmol of [C$_6$H$_4$CH$_2$N(CH$_3$)$_2$–2](H$_2$C=CH)(R)SiH (**1a**: R = CH$_3$ 10.0 g, **1b**: R = H 9.5 g) are added to 50 ml ROH (**2a**: R = CH$_3$, **2b**: R = C$_2$H$_5$, **2c**: R = ^{i}C$_3$H$_7$, **2d**: R = CH$_2$C≡CH). When **1a** and **1b** are reacted with the alcohols **2a**, **2b** or **2d**, an exothermic reaction takes place. However, for the synthesis of [C$_6$H$_4$CH$_2$N(CH$_3$)$_2$–2](H$_2$C=CH)Si(O^{i}C$_3$H$_7$)$_2$ (**4c**), the reaction mixture has to be refluxed for 12 h. After purification by distillation in vacuum, compounds **3** (48 mmol, 95%), **4a** (48 mmol, 95%), **4b** (45 mmol, 90%) and **4c** (35 mmol, 70%) are obtained as colorless oils. Analytical pure **4d** (50 mmol, 100%) is obtained by distilling off all volatile components from the reaction mixture at 25°C.

4.3.1. Data for compound **3**

Boiling point 107°C/10^{-1} mbar. Anal. Calc. for $C_{13}H_{21}NOSi$ (235.40): C, 66.33; H, 8.99. Found: C, 66.13; H, 8.78. ^{1}H-NMR (CDCl$_3$): δ 0.59 (s, 3H, SiCH_3), 2.10 (s, 6H, NCH_3), 3.36 (d, $^{2}J_{\mathrm{HH}} = 13.1$ Hz, 1H, CH_2), 3.46 (s, 3H, OCH_3), 3.53 (d, $^{2}J_{\mathrm{HH}} = 13.1$ Hz, 1H, CH_2), 5.79 (dd, $^{2}J_{\mathrm{HH}} = 4.3$ Hz, $^{3}J_{\mathrm{HH}} = 19.7$ Hz, C$_2H_3$), 5.98 (dd, $^{2}J_{\mathrm{HH}} = 4.3$ Hz, $^{3}J_{\mathrm{HH}} = 15.4$ Hz, C$_2H_3$), 6.27 (dd, $^{3}J_{\mathrm{HH}} = 15.4$ Hz, $^{3}J_{\mathrm{HH}} = 19.7$ Hz, 1H, C$_2H_3$), 7.2–7.3 (m, 3H, C$_6H_4$), 7.7–7.8 (m, 1H, C$_6$H$_4$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ -0.8 (SiCH$_3$), 44.8 (NCH$_3$), 50.4 (OCH$_3$), 64.1 (CH$_2$), 126.3 (C_6H$_4$), 128.2 (C_6H$_4$), 129.3 (C_6H$_4$), 139.4 (C_6H$_4$), 132.5 (C_6H$_4$), 135.7 (C_2H$_3$), 136.3 (C_6H$_4$), 145.7 (C_2H$_3$). ^{29}Si{^{1}H}-NMR (CDCl$_3$): δ -12.4. EI-MS [m/z (rel. intensity)] M^{+} 235 (6), M^{+}-CH$_3$ 220 (17), M^{+}-CH$_3$–C$_2$H$_4$ 192 (43), M^{+}-2CH$_3$–C$_2$H$_3$ 178 (100). IR (NaCl): $\nu_{\mathrm{CH}} = 3044$ (s), 2965 (vs), 2938 (vs), 2897 (s), 2851 (vs), 2811 (vs), 2771 (s); $\nu_{\mathrm{C=C}} = 1587$ (m); $\nu_{\mathrm{SiO}} = 1076$ (vs) cm^{-1}.

4.3.2. Data for compound **4a**

Boiling point 118°C/10^{-1} mbar. Anal. Calc. for $C_{13}H_{21}NO_2Si$ (251.40): C, 62.11; H, 8.42. Found: C, 62.48; H, 8.89. ^{1}H-NMR (CDCl$_3$): δ 2.16 (s, 6H, NCH_3), 3.51 (s, 2H, CH_2), 3.59 (s, 6H, OCH_3), 5.8–5.9 (m, 1H, C$_2H_3$), 6.0–6.2 (m, 2H, C$_2H_3$), 7.3–7.4 (m, 3H, C$_6H_4$), 7.8–7.9 (m, 1H, C$_6H_4$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 44.7 (NCH$_3$), 50.1 (OCH$_3$), 63.8 (CH$_2$), 126.1 (C_6H$_4$), 128.0 (C_6H$_4$), 129.9 (C_6H$_4$), 131.7 (C_6H$_4$), 133.4 (C_6H$_4$), 133.7 (C_2H$_3$), 136.5 (C_6H$_4$), 146.5 (C_2H$_3$). ^{29}Si{^{1}H}-NMR (CDCl$_3$): δ -32.7. EI-MS [m/z (rel. intensity)] M^{+} 251 (24), M^{+}-CH$_3$ 236 (50), M^{+}-C$_2$H$_3$–CH$_4$ 208 (100). IR (NaCl): $\nu_{\mathrm{CH}} = 3047$ (s), 2967 (s), 2933 (vs), 2948 (m), 2827 (s), 2811 (s), 2771 (s); $\nu_{\mathrm{C=C}} = 1588$ (m); $\nu_{\mathrm{SiO}} = 1084$ (vs) cm^{-1}.

4.3.3. Data for compound **4b**

Boiling point 110°C/1.5 × 10^{-2} mbar. Anal. Calc. for $C_{15}H_{25}NO_2Si$ (279.46): C, 64.47; H, 9.02. Found: C, 63.99; H, 9.60. ^{1}H-NMR (CDCl$_3$): δ 1.20 (t, $^{3}J_{\mathrm{HH}} = 7.0$ Hz, 6H, OCH$_2$CH_3), 2.16 (s, 6H, NCH_3), 3.48 (s, 2H, NCH_2), 3.77 (q, $^{3}J_{\mathrm{HH}} = 7.0$ Hz, 4H, OCH_2CH$_3$), 5.6–5.9 (m, 1H, C$_2H_3$), 6.0–6.1 (m, 2H, C$_2H_3$), 7.2 (m, 1H, C$_6H_4$), 7.3 (m, 2H, C$_6H_4$), 7.6–7.8 (m, 1H, C$_6H_4$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 18.2 (OCH$_2$$CH_3$), 45.0 (N$CH_3$), 58.3 (O$CH_2CH_3$), 63.8 ($CH_2$), 126.0 ($C_6H_4$), 128.2 ($C_6H_4$), 129.9 ($C_6H_4$), 132.6 ($C_6H_4$), 133.9 ($C_2H_3$), 134.2 ($C_6H_4$), 136.4 ($C_6H_4$), 146.4 ($C_2H_3$). ^{29}Si{^{1}H}-

NMR ($CDCl_3$): δ −40.0. EI-MS [*m*/*z* (rel. intensity)] M^+ 279 (20), M^+-CH_3 264 (52), M^+-CH_3–C_2H_4 236 (100), M^+-OCH_2CH_3 234 (37). IR (NaCl): $\nu_{CH} = 3048$ (s), 2966 (s), 2937 (vs), 2873 (m), 2810 (s), 2768 (s); $\nu_{C=C} = 1588$ (m); $\nu_{SiO} = 1079$ (vs) cm^{-1}.

4.3.4. Data for compound **4c**

Boiling point 153°C/10^{-2} mbar. Anal. Calc. for $C_{17}H_{29}NO_2Si$ (307.51): C, 66.40; H, 9.50. Found: C, 64.61; H, 9.16. ^1H-NMR ($CDCl_3$): δ 1.27 [m*, 12H, $OCH(CH_3)_2$], 2.25 (s, 6H, NCH_3), 3.66 (s, 2H, NCH_2), 4.28 [m*, 2H, $OCH(CH_3)_2$], 6.0–6.2 (m, 3H, C_2H_3), 7.3–7.6 (m, 3H, C_6H_4), 7.9 (m, 1H, C_6H_4). * At 25°C a free rotation of the isopropoxy groups is sterically hindered. This leads to the observation of a multiplet structure for the methyl protons of these entities. $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 25.0 [$OCH(CH_3)_2$], 25.6 [$OCH(CH_3)_2$]**, 45.2 (NCH_3), 63.5 (NCH_2), 65.2 [$OCH(CH_3)_2$], 125.8 (C_6H_4), 128.1 (C_6H_4), 129.9 (C_6H_4), 133.2 (C_6H_4), 134.5 (C_6H_4), 134.9 (C_2H_3), 136.2 (C_6H_4), 146.0 (C_2H_3). ** Due to the hindered rotation of the isopropoxy groups at 25°C, two resonance signals for the methyl carbon atoms are observed. $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ −42.3. EI-MS [*m*/*z* (rel. intensity)] M^+ 307 (33), M^+-CH_3 292 (64), M^+-$CH(CH_3)_2$ 264 (100), M^+-$OCH(CH_3)_2$ 248 (58). IR (NaCl): $\nu_{CH} = 3049$ (m), 2965 (vs), 2936 (vs), 2882 (m), 2810 (s), 2767 (s); $\nu_{C=C} = 1588$ (m); $\nu_{SiO} = 1029$ (vs) cm^{-1}.

4.3.5. Data for compound **4d**

Boiling point 25°C/10^{-3} mbar. Anal. Calc. for $C_{17}H_{21}NO_2Si$ (299.45): C, 68.19; H, 7.07. Found: C, 68.29; H, 7.14. ^1H-NMR ($CDCl_3$): δ 2.14 (s, 6H, CH_3), 2.43 (t, $^4J_{HH} = 2.5$ Hz, 2H, $\equiv CH$), 3.53 (s, 2H, NCH_2), 4.46 (d, $^4J_{HH} = 2.5$ Hz, 4H, OCH_2), 5.89–5.92 (m, 1H, C_2H_3), 6.0–6.1 (m, 2H, C_2H_3), 7.2–7.4 (m, 3H, C_6H_4), 7.9–8.0 (m, 1H, C_6H_4). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ −35.4. EI-MS [*m*/*z* (rel. intensity)] M^+ 299 (13), M^+-CH_3 284 (37), M^+-C_2H_3 272 (20), M^+-CH_3–C_2H_3 257 (42), M^+-OCH_2CCH 244 (63), M^+–$N(CH_3)_2$–C_2H_3 228 (47), $CH_2N(CH_3)_2{}^+$ 58 (100). IR (NaCl): $\nu_{CH} =$ 3047 (m), 3001 (s), 2972 (vs), 2940 (vs), 2855 (vs), 2815 (vs), 2775 (vs); $\nu_{C\equiv C} = 2119$ (m); $\nu_{C=C} = 1588$ (s); $\nu_{SiO} =$ 1083 (vs) cm^{-1}.

4.4. Synthesis of $\{[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)(CH_3)Si\}_2O$ (**5a**) and $\{[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)SiO\}_n$ (**5b**)

$[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)(R)SiH$ (**1a**: R = CH_3, 4.1 g; **1b**: R = H, 3.8 g) (20 mmol) in 100 ml of tetrahydrofuran is reacted with 1.0 ml (55.0 mmol) of water at 25°C. The reaction mixture is refluxed for 3 h and all volatile materials are removed in vacuum. The resulting oil is extracted with 100 ml of dichloromethane and the colorless solution is dried over $MgSO_4$. After evaporation of dichloromethane, the product is dried for 3 h at 25°C/10^{-3} mbar. While **5a** is a colorless solid, **5b** is obtained as a colorless oil.

4.4.1. Data for compound **5a**

Yield: 4.24 g (10.0 mmol, 100%). Anal. Calc. for $C_{24}H_{36}N_2OSi_2$ (424.73): C, 65.11; H, 8.65. Found: C, 65.65; H, 7.99. ^1H-NMR ($CDCl_3$): δ 0.53 (s, 6H, $SiCH_3$), 2.26 (s, 12H, NCH_3), 3.33 (d, $^2J_{HH} = 12.2$ Hz, 2H, NCH_2), 3.83 (d, $^2J_{HH} = 12.2$ Hz, 2H, NCH_2), 5.8–6.5 (m, 6H, C_2H_3), 7.2–7.6 (m, 6H, C_6H_4), 7.8–7.9 (m, 2H, C_6H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ −1.5 ($SiCH_3$), 45.0 (NCH_3), 64.2 (NCH_2), 126.0–145.0 (m, C_2H_3 and C_6H_5). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ −20.3. FAB-MS [*m*/*z* (rel. intensity)] M^+ 425 (9), M^+-CH_3 410 (19), M^+-C_2H_3 398 (10), M^+-$N(CH_3)_2$–C_2H_3–CH_4 338 (79), $[C_6H_4CH_2N(CH_3)_2\text{–}2](C_2H_3)(CH_3)Si\}^+$-H 204 (60). IR (NaCl): $\nu_{C\text{–}H} = 2944$ (vs), 2817 (vs), 2777 (vs); $\nu_{C=C} =$ 1588 (w); $\nu_{SiO} = 1044$ (vs) cm^{-1}.

4.4.2. Data for compound **5b**

Yield: 4.1 g (20.0 mmol, 100%). Anal. Calc. for $[C_{11}H_{15}ONSi]_n$: C, 64.35; H, 7.36. Found: C, 64.98; H, 7.01. ^1H-NMR ($CDCl_3$): 2.0–2.3 (m, 6H, NCH_3), 3.4–3.7 (br, 2H, NCH_2), 5.6–6.4 (m, 3H, C_2H_3), 7.0–8.0 (m, 4H, C_6H_4). IR (NaCl): $\nu_{C=C} = 1594$ (w); $\nu_{SiO} = 1080$ (vs) cm^{-1}. M: 600 g mol^{-1} (*n*: 2.9).

4.5. Synthesis of $\{[C_6H_4CH_2N(CH_3)_2\text{–}2](H)Si\text{–}CH_2CH_2\text{–}\}_n$ (**6**)

$[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)SiH_2$ (**1b**) (600 mg, 3.13 mmol) and 0.1 ml of H_2PtCl_6 (5% solution in isopropanol), are heated for 8 h to 200°C. The oily product is extracted in three stages each with 30 ml of *n*-pentane and filtered through a pad of Celite. After removal of the solvent in vacuum, 540 mg (2.8 mmol, 90%) of compound **6** are obtained as a pale-yellow oil.

Anal Calc. for $[C_{11}H_{17}NSi]_n$: C, 69.05; H, 8.95. Found: C, 70.13; H, 8.31. ^1H-NMR ($CDCl_3$) 0.8–1.3 (m, 4H, $SiCH_2$), 1.7–2.5 (m, 6H, CH_3), 3.3–3.7 (m, 2H, NCH_2), 4.0–4.5 (m, 1H, SiH), 6.9–7.8 (m, 4H, C_6H_4). IR (NaCl): $\nu_{SiH} = 2136$ (vs, br) cm^{-1}. M: 680 g mol^{-1} (*n*: 3.6).

4.6. Synthesis of $[C_6H_4CH_2N(CH_3)_2\text{–}2](H_2C{=}CH)(H)Si[OC(O)C_6H_5]$ (**8**)

At 25°C, 780 mg (4.08 mmol) $[C_6H_4CH_2N(CH_3)_2\text{–}2]$-$(H_2C{=}CH)SiH_2$ (**1b**) are dissolved in 30 ml of chloroform and 500 mg (4.08 mmol) of benzoic acid are added in one portion. Evolution of H_2 is observed. After removal of all volatile materials in vacuum, 1.25 g (4.01 mmol, 98%) of analytically pure **8** are obtained as a colorless oil.

Anal. Calc. for $C_{18}H_{21}NO_2Si$ (311.46): C, 69.41; H, 6.80. Found: C, 69.70; H, 7.01. ^{1}H-NMR ($CDCl_3$): δ 2.30 (s, 6H, CH_3), 3.66 (s, 2H, CH_2), 5.15 (br, 1H, Si*H*), 5.82 (dd, $^2J_{HH} = 4.8$ Hz, $^3J_{HH} = 20.1$ Hz, 1H, C_2H_3), 6.03 (dd, $^2J_{HH} = 4.8$ Hz, $^3J_{HH} = 14.8$ Hz, 1H, C_2H_3), 6.47 (ddd, $^3J_{HH_{Si}} = 2.2$ Hz, $^3J_{HH} = 14.8$ Hz, $^3J_{HH} = 20.1$ Hz, 1H, C_2H_3), 7.2–7.3 (m, 2H, C_6H_4 and C_6H_5), 7.4–7.7 (m, 5H, C_6H_4 and C_6H_5), 8.1–8.3 (m, 2H, C_6H_4 and C_6H_5). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 44.8 (CH_3), 62.7 (CH_2), 125.2, 127.1, 127.9, 129.7, 129.8, 131.1, 131.9, 132.8, 133.8, 134.5, 136.9, 144.4 (C_2H_3, C_6H_4 and C_6H_5), 167.9 ($C{=}O$). $^{29}Si\{^1H\}$-NMR ($CDCl_3$) δ −61.9. EI-MS [*m*/*z* (rel. intensity)] M^+ 311 (5), M^+-CH_3 296 (31), M^+-$C_6H_5CO_2$ 190 (46) M^+-$C_6H_5CO_2$–CH_3 165 (35), M^+-$C_6H_5CO_2$–C_2H_3 163 (15), $C_6H_5CO^+$ 105 (100), $C_6H_5{}^+$ 77 (58). IR (NaCl): ν_{SiH} = 2127 (vs); $\nu_{C=O}$ = 1655 (vs); $\nu_{C=C}$ = 1595 (m) cm^{-1}.

4.7. Synthesis of $[C_6H_4CH_2N(CH_3)_2$–$2](H_2C{=}CH)(CH_3)Si(C_6H_5NCHS)$ (**12a**) and $[C_6H_4CH_2N(CH_3)_2$–$2](H_2C{=}CH)(H)Si(C_6H_5NCHX)$ (**12b**: X = S, **12c**: X = O)

$[C_6H_4CH_2N(CH_3)_2$–$2](H_2C{=}CH)(R)SiH$ (2.73 mmol) (**1a**: R = CH_3, 560 mg; **1b** R = H 520 mg) are dissolved in 30 ml of chloroform and 2.73 mmol of PhN=C=X (**11a**: X = S 370 mg; **11b**: X = O, 330 mg) are added dropwise at 25°C. The reaction mixture is stirred for 3 h at 25°C and then all volatile materials are removed in vacuum. Purification of the products is carried out by crystallization of the residues from 20 ml methylenechloride/*n*-pentane (3:1) (**12a**, **12b**) or by extraction with diethylether/*n*-pentane (1:1) followed by vacuum distillation (**12c**). **12a** and **12b** are obtained as pale-yellow solids, while **12c** is obtained as a colorless oil.

4.7.1. Data for compound **12a**

Yield: 390 mg (1.13 mmol, 42%). M.p. 116°C. Anal. Calc. for $C_{19}H_{24}N_2SSi$ (340.56): C, 67.01; H, 7.10. Product rapidly decomposes in air. ^{1}H-NMR ($CDCl_3$,): δ 0.49 (s, 3H, $SiCH_3$), 2.24 (s, 6H, NCH_3), 3.32 (d, $^2J_{HH} = 12.4$ Hz, 1H, CH_2), 3.80 (d, $^2J_{HH} = 12.4$ Hz, 1H, CH_2), 6.30 (dd, $^2J_{HH} = 4.5$ Hz, $^3J_{HH} = 19.7$ Hz, 1H, C_2H_3), 6.05 (dd, $^2J_{HH} = 4.5$ Hz, $^3J_{HH} = 14.7$ Hz, 1H, C_2H_3), 6.30 (dd, $^3J_{HH} = 14.7$ Hz, $^3J_{HH} = 19.7$ Hz, 1H, C_2H_3), 7.1–7.4 (m, 8H, C_6H_4 and C_6H_5), 7.5–7.6 (m, 1H, C_6H_4), 9.81 (s, 1 H, *H*CS). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ −1.2 ($SiCH_3$), 45.0 (NCH_3), 61.8 (CH_2), 125.6, 126.0, 126.5, 127.2, 128.1, 128.7, 132.9, 133.1, 133.4, 139.2, 144.4, 145.4 (C_2H_3, C_6H_4 and C_6H_5), 198.0 (H*C*S). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ −10.5. FAB-MS [*m*/*z* (rel. intensity)] M^+-C_6H_5NCHS 204 (100).

4.7.2. Data for compound **12b**

Yield: 740 mg (2.26 mmol, 83%). M.p. 96–99°C. Anal. Calc. for $C_{18}H_{22}N_2SSi$ (326.53): C, 66.21; H, 6.79. Found: C, 64.95; H, 6.98. ^{1}H-NMR ($CDCl_3$): δ 2.22 (s, 6H, NCH_3), 3.57 (d, $^2J_{HH} = 14.3$ Hz, 1H, CH_2), 3.77 (d, $^2J_{HH} = 14.3$ Hz, 1H, CH_2), 4.70 (d, $^3J_{HH} = 1.8$ Hz, 1H, Si*H*), 5.6–5.7 (m, 1H, C_2H_3), 6.0–6.4 (m, 2H, C_2H_3), 7.1–7.4 (m, 8H, C_6H_4 and C_6H_5), 7.8–7.9 (m, 1H, C_6H_4), 9.85 (s, 1H, *H*CS). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 44.6 (CH_3), 62.2 (CH_2), 125.6, 125.9, 126.6, 127.6, 128.5, 128.7, 130.6, 132.0, 132.6, 137.5, 144.6, 145.1 (C_2H_3, C_6H_4 and C_6H_5), 196.6 (H*C*S). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ 55.3. FAB-MS [*m*/*z* (rel. intensity)] M^+ 326 (8), M^+-C_2H_3 299 (6), M^+-C_6H_5NCHS 190 (100). IR (KBr): ν_{SiH} = 2136 (s); $\nu_{C=C}$ = 1561 (m) cm^{-1}.

4.7.3. X-ray structure determination of compound **12b** [13]

The molecular structure of compound **12b** (Fig. 1) was determined from single crystal X-ray diffraction data, which were collected using a Siemens R3m/V (Nicolet Syntex) diffractometer. Crystallographic data for compound **12b** are given in Table 1, interatomic distances in Table 2 and atomic coordinates in Table 3.

The structure of **12b** was solved by direct methods (SHELXTL PLUS; Sheldrick, University of Göttingen, 1988) and refined by the least-squares method based on F^2 with all reflections (SHELXL 93; Sheldrick, University of Göttingen, 1993). All non-hydrogen atoms, as well as the silicon-bonded hydrogen atom H(1) were refined anisotropically; the hydrogen atoms were placed in calculated positions. An empirical absorption correction was applied. The structure plots have been made using ZORTEP (Zsolnai and Huttner, University of Heidelberg, Germany, 1994).

4.7.4. Data for compound **12c**

Yield: 800 mg (2.57 mmol, 94%). Anal. Calc. for $C_{18}H_{22}N_2OSi$ (310.46): C, 69.64; H, 7.14. Found: C, 69.23; H, 7.33. ^{1}H-NMR ($CDCl_3$): δ 2.27 (s, 6H, CH_3), 3.65 (s, 2H, CH_2), 4.76 (br, 1H, Si*H*), 5.82 (dd, $^2J_{HH}$ = 3.7 Hz, $^3J_{HH} = 20.0$ Hz, 1H, C_2H_3), 6.03 (dd, $^2J_{HH} = 3.7$ Hz, $^3J_{HH} = 14.7$ Hz, 1H, C_2H_3), 6.33 (dd, $^3J_{HH} = 14.7$ Hz, $^3J_{HH} = 20.0$ Hz, 1H, C_2H_3), 7.0–7.4 (m, 8H, C_6H_4 and C_6H_5), 8.0–8.1 (m, 1H, C_6H_4), 8.15 (br, 1H, *H*CO). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 45.0 (CH_3), 63.1 (CH_2), 123.0, 123.4, 124.2, 125.2, 127.4, 129.1, 130.2, 132.1, 132.7, 134.2, 138.0, 144.7 (C_2H_3, C_6H_4 and C_6H_5), 167.4 (H*C*O). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ −26.9. IR (KBr): ν_{SiH}: 2132 (br) cm^{-1}.

4.8. Synthesis of $[C_6H_4CH_2N(CH_3)_2$–$2](H_2C{=}CH)Si{=}S$ (**16**)

$[C_6H_4CH_2N(CH_3)_2$–$2](H_2C{=}CH)SiH_2$ **1b** (200 mg, 1.0 mmol) and 64.0 mg (2.0 mmol) of $1/_8$ S_8 are suspended in 30 ml of chloroform and reacted in an ultrasonic bath. The sulfur completely dissolves during 30 min. Under evolution of H_2S, 205 mg (0.93 mmol, 93%) of **16** precipitate as a colorless solid, which is extremely sensitive to oxygen and moisture.

Anal. Calc. for $C_{11}H_{15}NSSi$ (221.40): C, 59.67; H, 6.83: Found: C, 57.34; H, 7.02. Product rapidly decomposes in air. ^{1}H-NMR ($CDCl_3$): δ 2.26 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.50 (d, $^2J_{HH} = 8.0$ Hz, 1H, CH_2), 3.72 (d, $^2J_{HH} = 8.0$ Hz, 1H, CH_2), 5.8–6.1 (m, 2H, C_2H_3), 6.2–6.4 (m, 1H, C_2H_3), 7.1–7.4 (m, 3H, C_6H_4), 7.7–7.9 (m, 1H, C_6H_4). EI-MS [*m*/*z* (rel. intensity)]: M^+ 221 (21), M^+-CH_3 206 (62), M^+-CH_3–C_2H_3 179 (19), $N(CH_3)_3{}^+$ 59 (100).

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