New Dichlorosilanes, Cyclotrisilanes, and Silacyclopropanes as Precursors of Intramolecularly Coordinated Silylenes

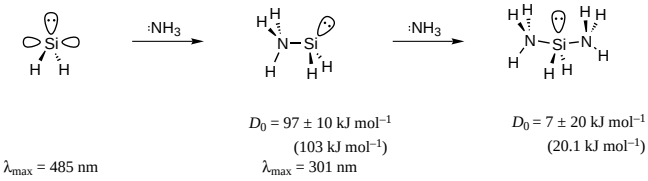
Johannes Belzner,* Uwe Dehnert, Heiko Ihmels, Matthias Hübner, Peter Müller, and Isabel Usón

Abstract: Three highly coordinated dichlorosilanes, **11a**, **12**, and **13**, were synthesized, and their structures were investigated in solution as well as in the solid state (**12** and **13**). The reductive dehalogenation of **11a** and **12** with magnesium yielded cyclotrisilanes **14** and **20**, which are in equilibrium with silylenes **15** and **24** as shown by trapping and silylene-exchange experiments. Treatment of **13** with magnesium metal afforded a mixture of benzosilacyclobutene **38** and disilane **40**, which also was obtained by the thermolysis of silacyclopropane **44**. Trapping experiments corroborated the involvement of silylene **43** in these reactions.

Keywords: cyclotrimerizations · intramolecular coordination · NMR spectroscopy · silicon · silylenes

Introduction

Silylenes are an important species of highly reactive organosilicon compounds. Their chemistry has been investigated for more than thirty years, and interesting similarities and differences to the chemistry of carbenes have been discovered.[1] One of the striking contrasts is the fact that carbenes may adopt, depending on their substituents, either a singlet or a triplet ground state, whereas up to now only silylenes with a singlet ground state have been observed. Consequently, silylenes are ideal candidates for a coordinative interaction with Lewis bases that can donate a lone pair of electrons into the empty p orbital of the divalent silicon compound. The first evidence for the formation of Lewis base $\cdots$ silylene adducts was obtained from the observation that dimethylsilylene inserts into the O–H bond of alcohols more selectively in polar solvents, such as Et_2O or THF, than in nonpolar hydrocarbons.[2] This was interpreted in terms of the formation of solvent $\cdots$ silylene complexes, which are supposed to be less reactive and hence more selective than the noncoordinated silylene. Some years later, the UV-spectroscopic identification of matrix-isolated complexes between photochemically generated silylenes and various Lewis bases, such as ethers, alcohols, or amines, was reported.[3] The major evidence for the formation of donor $\cdots$ silylene complexes was the hypsochromic shift of its UV absorption.[3] In a theoretical study of the reaction of NH_3 with $:SiH_2$, the bond-dissociation enthalpy D_0 of the dative Si $\cdots$ N bond in $H_3N \cdots SiH_2$ was calculated to be $97 \pm 10\,kJ\,mol^{-1}$ (Scheme 1).[4a] A more recent calculation of this complex, which utilizes all valence electron basis sets and relativistic-corrected effective core potential methods, gave a bond dissociation enthalpy of $103\,kJ\,mol^{-1}$.[4b] A blue shift of the UV absorption, which is ascribed to the $S_0 \rightarrow S_1$ transition, was computed at the CIS/6-31+G* level on going from the free to the coordinated silylene,[4a] and these results are in good agreement with the experimental data.[3] In addition, the formation of a ternary complex between $H_2Si:$ and two molecules of NH_3 was predicted by theory. However, in this case the dative bonds are expected to be significantly weaker than those in $H_3N \cdots SiH_2$, as is evident from the considerably smaller D_0 value of



Scheme 1. Coordination of NH_3 to SiH_2: Computational results[4a] (values in parentheses refer to ref. [4b]).

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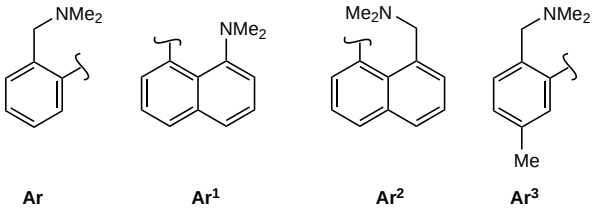
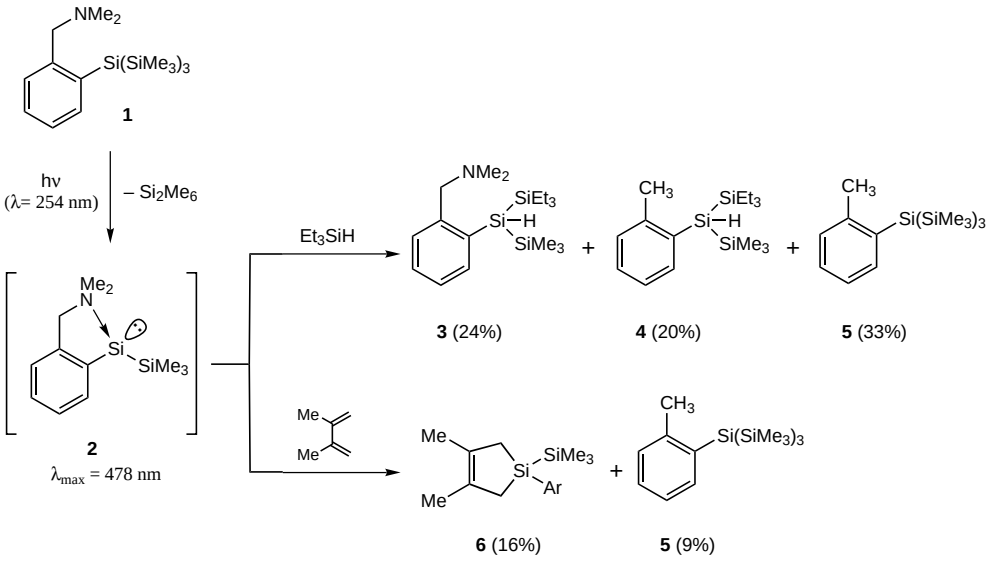
the new Si···N bond ($7 \pm 20\ kJ\,mol^{-1}$);[4a] a value of $20.1\ kJ\,mol^{-1}$ was estimated at a higher level of theory.[4b] Finally, the isolation of the first stable silylene–Lewis base complexes from the reaction of a sterically congested disilene with isonitriles was recently reported.[5]

The free enthalpy of the intermolecular coordination reaction between a silylene and one or two external molecules of a Lewis base suffers severely from the less favorable entropic term of this reaction. This restriction may be overcome by the use of chelating substituents at the silicon center. To this end various approaches to intramolecularly coordinated silylenes have been investigated over the last few years. Corriu, Auner, Conlin et al. utilized difluorosilanes, substituted by one or two bidentate aminoaryl groups **Ar**, **Ar¹** or **Ar²** as precursors of

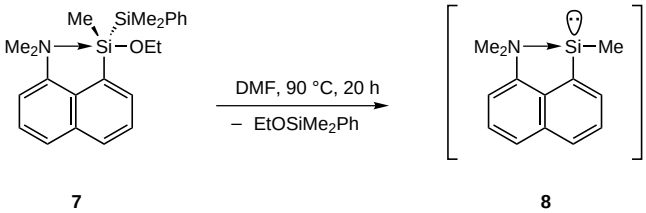


silylenes, which were supposed to be intramolecularly coordinated.[6] When treated with lithium metal or lithium naphthalenide in the presence of excess 2,3-dimethyl-1,3-butadiene, the corresponding silacyclopentenes were obtained, presumably via a coordinated silylene or silylenoid intermediate. Photolysis of tetrasilane **1** in the presence of 2,3-dimethyl-1,3-butadiene or Et_3SiH yielded, besides hexamethyldisilane, the trapping products **3** and **6** in moderate yield.[6] However, a major drawback of this method, with regard to its synthetic utility, is the formation of appreciable amounts of



Scheme 2. Generation of a highly coordinated silylene by photolysis of a trisilane; $Ar = 2\text{-}Me_2NCH_2C_6H_4$.

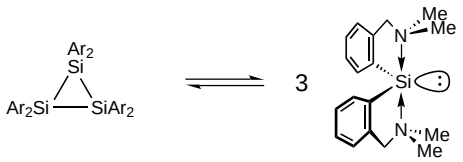
tolyl-substituted silanes **4** and **5**, which result from the photolytic cleavage of the benzylic C–N bond (Scheme 2). When the photolysis of **1** was performed in a hydrocarbon matrix at $-196\,^{\circ}C$, an intense absorption at $\lambda_{max} = 478$ nm was observed, which was attributed to the intramolecularly coordinated silylene **2**. In contrast, similar trisilanes which bear the substituent **Ar¹** are reported by Tamao et al.[7] to be stable towards UV radiation. However, their transition metal-catalyzed degradation, which yielded 1,2-disilacyclo-3-butenes in the presence of acetylenes, provides strong evidence for chelated silylenes or silylene–metal complexes as reactive intermediates. More recently, it was reported that pentacoordinated alkoxydisilane **7**, also substituted with **Ar¹**, undergoes a smooth reaction to give silylene **8** at $90\,^{\circ}C$ (Scheme 3). The



Scheme 3. Generation of a highly coordinated silylene by thermolysis of a disilanyl ether.

surprising ease of the reaction was attributed to the intramolecular coordination of the amino group to the silicon center in the starting material as well as in silylene **8**.[8] Finally, we have shown that the readily accessible cyclotrisilane **9**,[9a] which bears six **Ar** substituents, is in equilibrium with silylene **10** at room temperature (Scheme 4).[9b] The concentration of **10** is too low for it to be detected by NMR spectroscopy. However, it can be transferred to a variety of substrates under total disintegration of the three-membered ring. Thus, this cyclotrisilane is a valuable, waste-free synthetic equivalent of **10**. This unprecedented thermal equilibrium between a cyclotrisilane and the corresponding silylenes was explained by an

Abstract in German: *Die neuen Dichlorsilane **11a**, **12** und **13** besitzen sowohl in Lösung als auch im Festkörper (**12** und **13**) ein hochkoordiniertes Siliciumzentrum. **11a** und **12** wurden mittels Magnesium in die Cyclotrisilane **14** und **20** überführt, die im thermischen Gleichgewicht mit den entsprechenden Silandiylen **15** und **24** stehen. Die Reduktion von **13** hingegen lieferte nicht das entsprechende Cyclotrisilan, sondern verlief unter Bildung des Benzosilacyclobutens **38** und des Disilans **40**, die auch bei der Thermolyse des Silacyclopropans **44** entstehen. Abfangexperimente zeigten, daß bei beiden Reaktionen ein Silandiyl **43** als reaktive Zwischenstufe durchlaufen wird.*



9 **10**

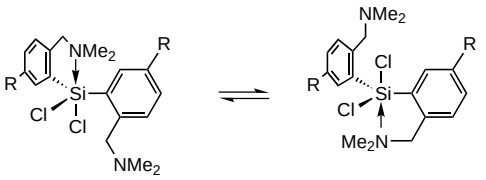
Scheme 4. Thermal equilibrium of cyclotrisilane **9** and highly coordinated silylene **10**; Ar = 2-$Me_2NCH_2C_6H_4$.

intramolecular coordination of one or two dimethylamino groups to the silicon center.[9b,c] In addition, the coordinative stabilization of silylene **10** may also account for the pronounced nucleophilic reactivity of **10**,[9c] which is in marked contrast to the electrophilic character of other silylenes.[10]

Inspired by these results, we investigated whether other cyclotrisilanes with potentially chelating substituents are synthetically accessible and whether such cyclotrisilanes show a silylene activity similar to **9**, that is whether they are in thermal equilibrium with intramolecularly coordinated silylenes. In particular, we were interested in the question as to whether *one* chelating substituent at the silicon center is sufficient to establish a cyclotrisilane – silylene equilibrium similar to that found for cyclotrisilane **9**. Herein we report our investigations on the synthesis of cyclotrisilanes consisting of three silylene subunits with either two **Ar**[3] substituents or with one **Ar** and one bulky Mes or Tip substituent (Mes = 2,4,6-trimethylphenyl; Tip = 2,4,6-tris(isopropyl)phenyl).

Results and Discussion

Preparation and properties of dichlorosilanes: Dichlorosilane **11a** was prepared by the reaction of two equivalents of the corresponding aryllithium compound[11] with tetrachlorosilane. The ^{1}H NMR spectrum of **11a** in $CDCl_3$ at room temperature showed broad, unresolved signals for the aromatic protons as well as for the protons of the (dimethylamino)methyl substituent. This is assumed to reflect an intramolecular dynamic coordination of the dimethylamino groups to silicon, as has been reported for **11b** (Scheme 5).[12] The ^{29}Si

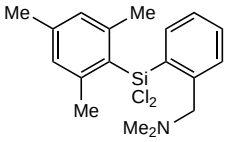


11a R = Me (≡ $(Ar^3)_2SiCl_2$)
11b R = H (≡ Ar_2SiCl_2)

Scheme 5. Dynamic coordination process in **11a** (R = Me) and **11b** (R = H).

NMR signal of **11a** at $\delta = -32.6$ is shifted appreciably upfield of the value for the tetracoordinate Ph_2SiCl_2 ($\delta = +6.30$).[13a] Thus, the observed value for **11a** is in agreement with the formation of a pentacoordinate silicon center.[13b]

The dichlorosilanes **12** and **13** with mixed substituents were obtained by treatment of mesityl- or 2,4,6-tris(isopropyl)phenyltrichlorosilane, respectively, with one equivalent of *ortho*-lithiated dimethylbenzylamine in Et_2O. From the respective



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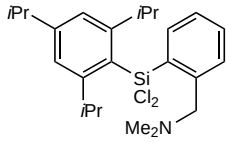

13

^{29}Si NMR shifts at high field ($\delta = -23.5$ and -24.0) it is evident that the silicon centers of both compounds interact coordinatively with the dimethylamino group of the **Ar** substituent. Further insight into the solution structure of these dichlorosilanes was obtained from the temperature-dependent NMR spectra. The ^{29}Si NMR signal of **12** undergoes a significant highfield shift upon cooling and is eventually observed at $\delta = -54.1$ at 159 K. This temperature dependence indicates an equilibrium between tetra- and pentacoordinate modifications of the dichlorosilane, which is rapid at room temperature and is shifted towards the pentacoordinate, magnetically more shielded species as the temperature decreases.[14] The existence of such an equilibrium is supported by the temperature-dependent ^{1}H NMR spectra of **12**. At room temperature the NMe groups, as well as the benzylic protons of the **Ar** substituent, are chemically equivalent proving that the coordination – dissociation – recoordination process of the dimethylamino group is fast on the NMR time scale. Rotation of the mesityl substituent is not hindered at room temperature, as is evident from the chemical equivalence of the *ortho*-methyl groups. Upon cooling, a broad AB coupling pattern develops for the benzylic protons along with two singlets for the NMe groups. This is expected for the rigid, pentacoordinate modification of **12**. Moreover, the *ortho*-methyl groups of the mesityl substituent, which are chemically equivalent at room temperature, are observed as two singlets at low temperature. This diastereotopicity is assumed to arise because of the hindered rotation of the mesityl substituent in the pentacoordinate form of **12**. The free enthalpy of activation for the dissociation of the dative N···Si bond is estimated from the coalescence of NMe groups to be 39.5 ± 0.8 kJ mol^{-1} at 215 K. This value is in agreement with $\Delta G^{\neq} = 40.7$ kJ mol^{-1} for $Ph(Ar)SiCl_2$.[12b] We attribute the observed diastereotopicity of the NMe and the *ortho*-methyl protons at low temperatures to the freezing of the process occurring, which is assumed to be, in line with the observed highfield shift of the ^{29}Si NMR signal of **12** on lowering the temperature, the coordination of the dimethylamino group to the silicon center. As a consequence of the freezing of this dissociation – recoordination process, the rotation of the mesityl substituent stops. This hypothesis is supported by the fact that the free enthalpy of activation, when estimated from the coalescence of the *ortho*-methyl signals ($\Delta G^{\neq} = 40.6 \pm 0.6$ kJ mol^{-1}), is in good agreement with the value obtained from the coalescence temperature of the NMe signals. In the solid-state structure of **12**, the silicon is at the

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center of a trigonal bipyramid in which the equatorial plane is defined by the *ipso*-carbon atoms of the aryl substituents and one chlorine atom, and the nitrogen center of the dimethylamino group and the second chlorine atom Cl(2) occupy the axial positions (Figure 1). The distance between the N atom

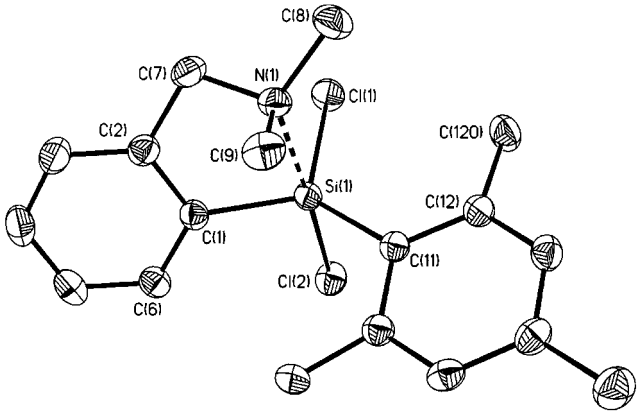


Figure 1. Crystal structure of **12**. Hydrogen atoms are omitted for clarity, displacement ellipsoids are at the 50% probability level. Selected bond lengths [pm] and angles [°]: Si(1)···N(1) 223.6(2), Si(1)–Cl(2) 221.5(1), Si(1)–Cl(1) 209.0(1), Si(1)–C(1) 188.6(2), Si(1)–C(11) 189.9(2); C(1)-Si(1)-C(11) 128.1(1), C(1)-Si(1)-Cl(1) 108.4(1), C(11)-Si(1)-Cl(1) 122.0(1), C(1)-Si(1)-Cl(2) 96.9(1), C(11)-Si(1)-Cl(2) 92.7(1), Cl(1)-Si(1)-Cl(2) 92.7(0), C(1)-Si(1)···N(1) 80.5(1), C(11)-Si(1)···N(1) 89.3(1), Cl(1)-Si(1)···N(1) 87.6(1), Cl(2)-Si(1)···N(1) 177.3(0).

and the nearly planar silicon center (sum of the bond angles: 358.5°) is 223.6 pm, which is slightly shorter than the 229.1 pm found for **11b**.[12a] The axial Si(1)–Cl(2) bond is longer than the equatorial Si(1)–Cl(1) bond, as is expected for a trigonal bipyramidal coordination geometry around a pentacoordinate silicon center. The steric demand of the mesityl substituent gives rise to an enlarged C(11)-Si(1)-C(1) angle of 128.1°, and a significantly reduced C(1)-Si(1)-Cl(1) angle of 108.4°.

According to the NMR spectra, more heavily substituted **13** equilibrates, in a similar manner to **12**, in solution at room temperature between two modifications with a tetracoordinate and a pentacoordinate silicon center. The activation parameters of the dissociation process ($\Delta G^{\ddagger} = 40.2 \pm 1.7\ \mathrm{kJ\,mol^{-1}}$; $\Delta H^{\ddagger} = 53.23 \pm 0.21\ \mathrm{kJ\,mol^{-1}}$; $\Delta S^{\ddagger} = 60.88 \pm 0.97\ \mathrm{J\,K^{-1}}$) were obtained by an analysis of the line shapes of the NMe signals between −25 and −78 °C with the programs DNMR5[15] and ACTPAR.[16] Figure 2 shows a comparison of the experimental and calculated line shapes. The solid-state structure of **13** (Figure 3) resembles that of **12**. However, the dative Si···N interaction appears to be slightly weaker in solid dichlorosilane **13,** as indicated by the longer Si···N distance of 226.8 pm as well as a shorter apical Si–Cl bond of 218.8 pm. Accordingly, the sum of the equatorial bond angles around silicon (357.46°) is smaller than in **12**. The enhanced bulkiness of the Tip substituent compared with the Mes substituent is reflected by a more pronounced distortion of the bond angles in the plane of the trigonal bipyramid: The C(11)-Si(1)-C(1) angle is widened to 131.6°, whereas the C(1)-Si(1)-Cl(1) angle is compressed to 105°.

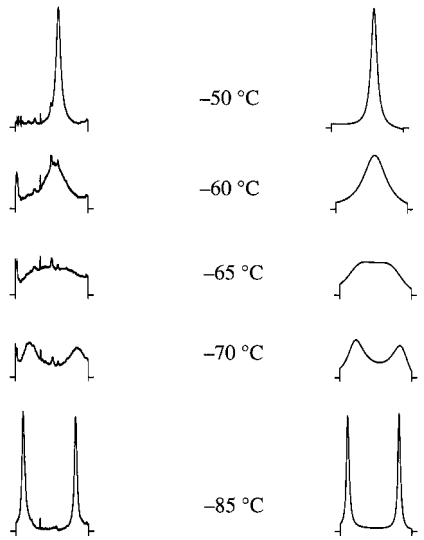


Figure 2. Comparison of the experimentally observed and the calculated line shapes of the NMe signals of **13**.

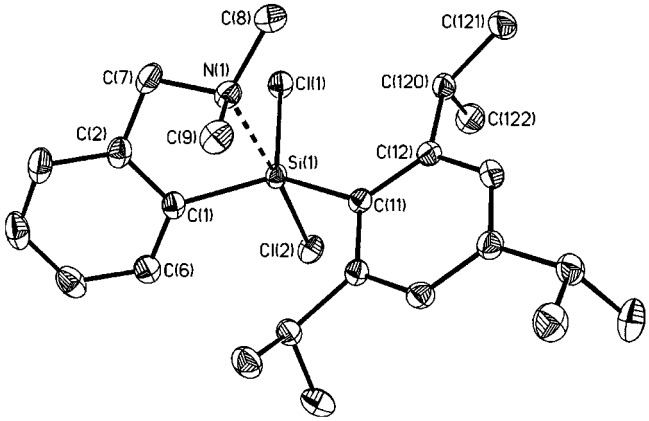
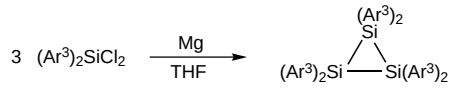


Figure 3. Crystal structure of **13**. Hydrogen atoms are omitted for clarity, displacement ellipsoids are at the 50% probability level. Selected bond lengths [pm] and angles [°]: Si(1)···N(1) 226.8(1), Si(1)–Cl(2) 218.8(1), Si(1)–Cl(1) 209.6(1), Si(1)–C(1) 189.8(2), Si(1)–C(11) 191.4(2); C(1)-Si(1)-C(11) 131.6(1), C(1)-Si(1)-Cl(1) 105.0(1), C(11)-Si(1)-Cl(1) 120.9(1), C(1)-Si(1)-Cl(2) 96.4(1), C(11)-Si(1)-Cl(2) 94.9(1), Cl(1)-Si(1)-Cl(2) 94.2(0), C(1)-Si(1)···N(1) 79.7(1), C(11)-Si(1)···N(1) 87.8(1), Cl(1)-Si(1)···N(1) 87.7(0), Cl(2)-Si(1)···N(1) 176.1(0).

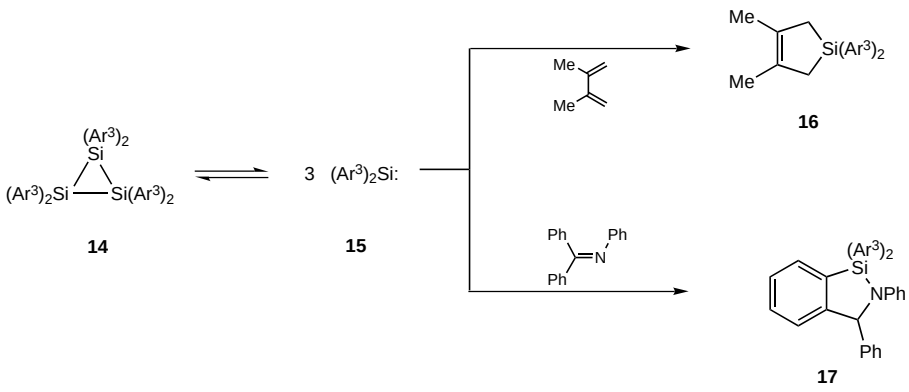
Synthesis and properties of cyclotrisilane 14: Treatment of dichlorosilane **11a** with magnesium turnings in THF produced an exothermic reaction, and cyclotrisilane **14** was obtained in 98% yield as a yellow viscous oil, which solidified on prolonged standing (Scheme 6). According to the ^{1}H NMR spectrum, the oil contained traces of an unknown impurity. Attempts to purify **14** by crystallization were not successful. The ^{29}Si NMR shift of **14** ($\delta = -66.0$ in C_6D_6), which lies in the



11a **14**

Scheme 6. Synthesis of cyclotrisilane **14**; $Ar^3 = 2\text{-}Me_2NCH_2\text{-}4\text{-}Me\text{-}C_6H_3$.

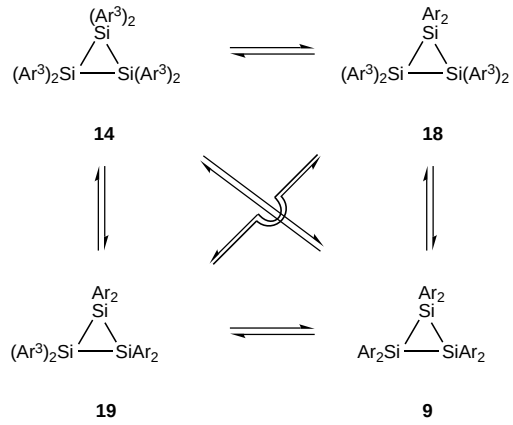
range expected for aryl-substituted cyclotrisilanes,[17] argues against a coordinative interaction between nitrogen and the silicon center in solution. Cyclotrisilane **14** exhibits a reactivity similar to that of **9**: if treated with three equivalents of 2,3-dimethyl-1,3-butadiene or benzophenone anil, the cyclotrisilane transfers all of its silylene units **15** to the substrate to yield silacyclopentene **16** or silazindane **17** (Scheme 7). From these results it seems reasonable that **14** is, in an analogous manner to **9**, in equilibrium with silylene **15**, which is then trapped by the diene or the anil. This shifts the cyclotrisilane–silylene equilibrium towards the silylene. However, the silylene-transfer rate of **14** is significantly lower than that of **9**: when a 1:1 mixture of cyclotrisilanes **9** and **14** was treated with three equivalents of 2,3-dimethyl-1,3-butadiene, only the trapping product of silylene **10** was formed. Further evidence for a cyclotrisilane–silylene equilibrium of **14** was obtained from an exchange experiment: while individual solutions of **9** and **14** in benzene are stable for days at 60 °C, a slow reaction occurred when a 1:1 mixture of these cyclotrisilanes was subjected to the same conditions. The product mixture which formed over a period of 48 h exhibited a complex ^{1}H NMR spectrum. The spectrum did not undergo further changes after longer reaction times. However, important information concerning the composition of the product mixture was obtained



Scheme 7. Reactions of cyclotrisilane **14**; $Ar^3 = 2\text{-}Me_2NCH_2\text{-}4\text{-}Me\text{-}C_6H_3$.

from the ^{29}Si NMR spectrum: it exhibits only six signals located between $\delta = -64.7$ and -66.0; this is the range that is typical for aryl-substituted cyclotrisilanes.[17] The signals at $\delta = -64.7$ and -66.0 are easily assigned to the starting compounds **9** and **14**. The four remaining signals may be explained by the formation of two new cyclotrisilanes **18** and **19**, both of which possess two chemically inequivalent ^{29}Si nuclei. Hence, we assume that thermal treatment of a mixture of cyclotrisilanes **9** and **14** produced a mixture of four cyclotrisilanes **9**, **14**, **18**, and **19** through a mutual interchange of silylene units (Scheme 8). Further evidence for a silylene exchange between cyclotrisilanes will be given below.

Synthesis and properties of cyclotrisilane 20: Dichlorosilane **12** underwent slow reaction with excess magnesium in THF. After five days all the starting material had been consumed and analytically pure cyclotrisilane **20** was isolated in 65% yield. Careful examination of the ^{1}H NMR spectrum of the



Scheme 8. Silylene exchange reaction by cothermolysis of cyclotrisilanes **9** and **14**; $Ar = 2\text{-}Me_2NCH_2C_6H_4$; $Ar^3 = 2\text{-}Me_2NCH_2\text{-}4\text{-}Me\text{-}C_6H_3$.

crude product revealed that only the *cis*,*trans* isomer of **20** was formed; the all-*cis* isomer was not detected.[18] The ^{1}H NMR and ^{13}C NMR spectra of **20** display two sets of signals for each type of substituent (ratio 1:2) and indicate an averaged C_s symmetry in solution. Unexpectedly, if a polarization transfer delay (which was optimized for a silicon–hydrogen coupling constant of 12 Hz) was used, then only one sharp signal at $\delta = -64.5$ was observed in the ^{29}Si NMR spectrum.[19] However, direct acquisition at room temperature revealed another signal as a shoulder at $\delta = -64.3$. The spectrum is only slightly temperature-dependent and therefore excludes any significant coordinative interaction between the amino groups and the silicon centers of **20** in solution: upon heating to 65 °C, the shoulder develops into a separate, broad signal at $\delta = -62.5$ with a relative intensity of 2. The signal at $\delta = -64.5$ is shifted to lower field by 1.1 ppm; the concomitant sharpening of this signal enables the detection of ^{29}Si satellite signals (Figure 4). The

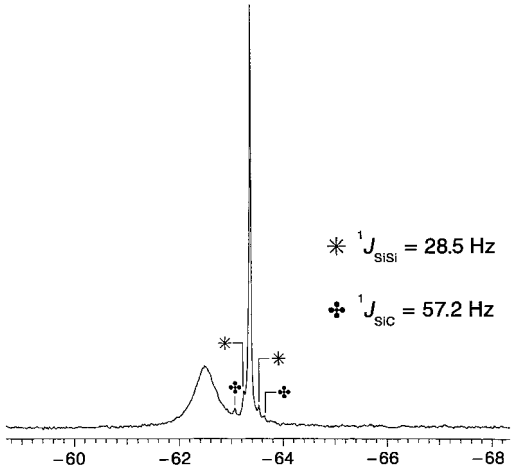


Figure 4. ^{29}Si NMR spectrum of **20** (99.3 MHz, 65 °C)

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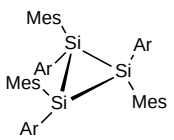
value of 28.5 Hz determined for the direct $^{29}Si-^{29}Si$ coupling constant is in agreement with the unusually small value of 24.1 Hz found for cyclotrisilane **21**.[20] A further satellite signal with a spacing of 57.2 Hz was attributed, based on the relative intensity of the satellite signal in comparison to the signal of the main isotopomer, to the coupling of the ^{29}Si nucleus to the *ipso* ^{13}C nuclei of both aromatic substituents.

The selective reaction of **12** with magnesium is in contrast to the formation of two diastereomeric cyclotrisilanes **22a** and **22b** upon reductive dehalogenation of the corresponding dichlorosilane,[21] but is parallel to the selective formation of another *cis,trans*-cyclotrisilane, **23** (Cy = cyclohexyl) from the corresponding diiodosilane.[22] Apparently, the difference in



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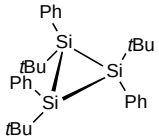

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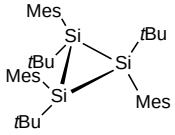
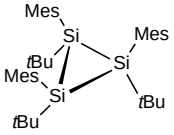
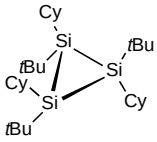


22a



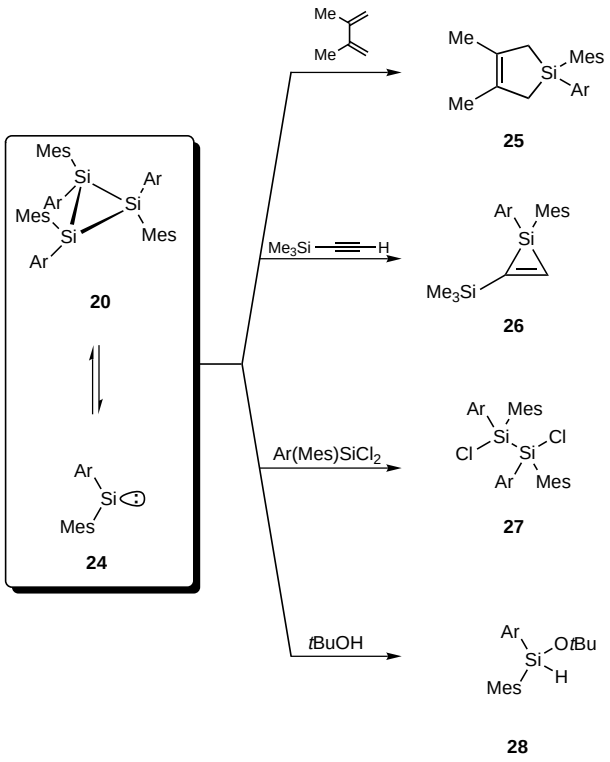
22b



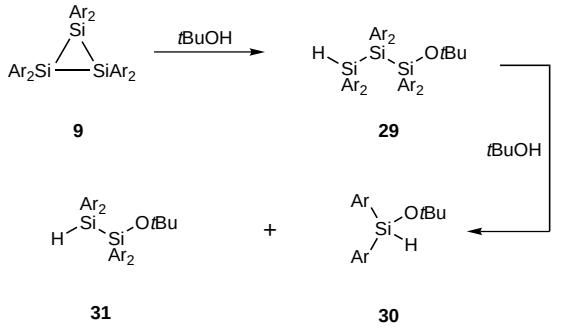
23

steric demand between the 2-(dimethylaminomethyl)phenyl and the mesityl substituent is more pronounced than that between the *tert*-butyl and the mesityl substituent. Thus, the all-*cis* isomer of **20** is thermodynamically considerably less favored than the *cis,trans* isomer.

As observed for cyclotrisilanes **9** and **14**, cyclotrisilane **20** also appears to be in equilibrium with silylene **24** and can be used (most conveniently at temperatures around 90 °C) as a versatile synthetic equivalent for this silylene (Scheme 9): treatment of **20** with excess 2,3-dimethyl-1,3-butadiene gave the silylene trapping product **25** exclusively. Moreover, in analogy to the chemical behavior of **9** towards alkynes,[9d] **20** was quantitatively converted with excess trimethylsilylacetylene to silacyclopropene **26**. In addition to the ^{29}Si NMR signal at $\delta = -116.4$, the signal of the vinylic proton at $\delta = 9.86$ is most indicative for the silacyclopropene structure of **26**. This signal displays a characteristic satellite pattern due to coupling with one ^{13}C and two different ^{29}Si nuclei. The reaction of **20** with chlorosilane **12** afforded a diastereomeric mixture of dichlorodisilane **27** in 34 % yield, thus paralleling the reactivity of **9** towards chlorosilanes.[23a] However, the reactivity of cyclotrisilanes **20** and **9** towards excess *tert*-butyl alcohol differs appreciably: after 30 min at room temperature **9** was transformed into a 1:1 mixture of **30** and **31** (Scheme 10), whereas the reaction of **20** with *tert*-butyl alcohol was complete only after 20 h at 60 °C and yielded exclusively **28**, the insertion product of silylene **24** into the O–H bond of the alcohol. It is assumed that this difference in reactivity is the result of the difference in steric shielding between **20** and **9**. Cyclotrisilane **9** appears to undergo



Scheme 9. Reactions of cyclotrisilane **20**; Ar = 2-$Me_2NCH_2C_6H_4$.

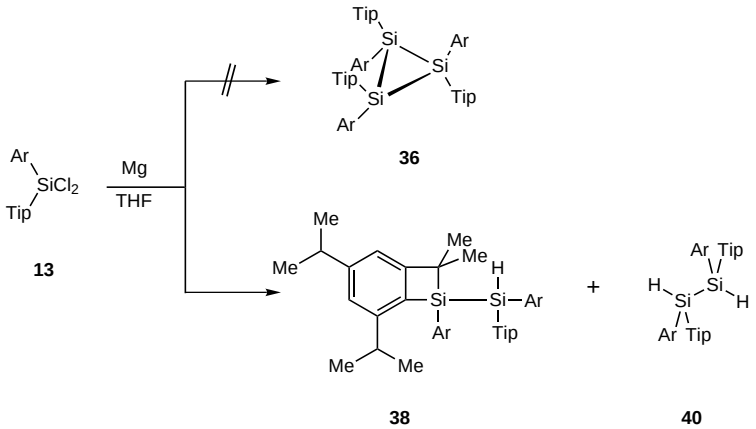


Scheme 10. Reaction of cyclotrisilane **9** with *tert*-butyl alcohol; Ar = 2-$Me_2NCH_2C_6H_4$.

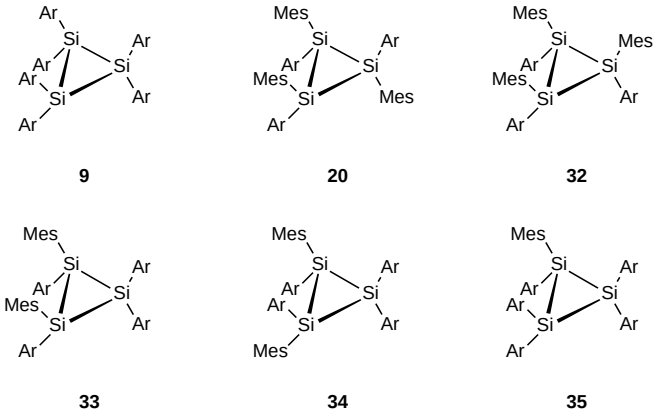
nucleophilic ring cleavage with *tert*-butyl alcohol under formation of trisilane **29**. Further attack of the alcohol on the less shielded Si–H terminus of **29** eventually yields monosilane **30** and disilane **31** in a 1:1 ratio (Scheme 10). In contrast, the bulky Mes substituents of **20** prevent direct nucleophilic attack of *tert*-butyl alcohol on the silicon centers. Instead the three-membered ring is cleaved indirectly by the alcohol via trapping of silylene **24** out of the equilibrium mixture of cyclotrisilane and silylene.

Although **20** is thermally stable when heated in C_6D_6 to 90 °C for 20 h, a slow reaction, which could be monitored conveniently by ^1H NMR spectroscopy, occurred in the presence of two equivalents of cyclotrisilane **9**. After 14 h at 90 °C the reaction ceased. However, the complex ^1H NMR spectrum of the product mixture allowed only the unambiguous identification of **9**. The ^{29}Si NMR spectrum of the

product mixture at room temperature showed, in addition to the signals of the starting compounds **9** and **20**, six signals at $\delta = -58.5$, -62.6, -63.3, -69.1, -70.4, and -71.9, some of which were very broad. Taking into account that all new signals fall into the range of shifts typical of perarylated cyclotrisilanes, this reaction was interpreted as an intermutal exchange of silylene units **10** and **24**, which eventually results in an equilibrium mixture of differently substituted cyclotrisilanes. If silylenes **10** and **24** are used as building blocks, six different cyclotrisilanes can be constructed. Bearing in mind that the sterically most congested three-membered ring **32** is not formed if **20** is synthesized from dichlorosilane **12** nor if **20** is heated to 90 °C, this



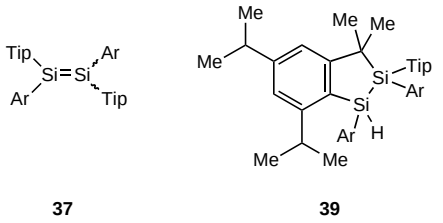
Scheme 11. Reductive dehalogenation of dichlorosilane **13**; Ar = 2-$Me_2NCH_2C_6H_4$.



cyclotrisilane can be excluded as a likely product of the exchange reaction between **9** and **20**. Therefore, only three new cyclotrisilanes **33**–**35** may be formed in this reaction. They would give rise to six new ^{29}Si NMR signals, which is in agreement with the experimental results. When the equilibration experiment was repeated starting with the reciprocal stoichiometry of cyclotrisilanes (**20**:**9** = 2:1), the product mixture exhibited, as expected, a similar ^{29}Si NMR spectrum with changed relative intensities of the signals. However, an unambiguous assignment of the new signals to cyclotrisilanes **33**–**35** was not possible due to partial overlap of the signals as well as the low signal-to-noise ratio. However, it is noteworthy that the ^{29}Si NMR spectra of the newly formed cyclotrisilanes **33**–**35** are more temperature-dependent than those of **9** and **20**: at 65 °C only three signals at $\delta = -61.6$, -66.0, and -68.5 are observed for these cyclotrisilanes besides the slightly shifted signals of **9** and **20**. In addition, the sharp signals at $\delta = -61.6$ and -68.5 show a $^1J_{Si,Si}$ coupling of 28.2 and 30.1 Hz, respectively, at this temperature, which is the typical order of magnitude known for cyclotrisilanes.[20]

All new cyclotrisilanes are thermal precursors of silylenes **10** and **24**: if the product mixture formed from the thermal treatment of a 2:1 mixture of **9** and **20** was treated with excess 2,3-dimethyl-1,3-butadiene, a 2:1 mixture of the corresponding silacyclopentenes was obtained.

Metal-mediated reactions of dichlorosilane 13: As previously discussed, the reductive dehalogenation of highly coordinated dichlorosilanes **11a**, **11b**, and **12** with magnesium proceeded under exclusive formation of the corresponding cyclotrisilanes **9**, **14**, and **20**. In contrast, when dichlorosilane **13** was treated with magnesium in THF, no cyclotrisilane **36** was obtained. Instead a product mixture formed, which was partially separated by column chromatography into two fractions A and B with heavy loss of material (Scheme 11). The DCI mass spectrum of fraction A exhibited a parent peak, which would be in agreement with disilene **37**. However,



the formation of diastereomeric disilenes **37** is excluded by the ^{29}Si NMR signals at $\delta = -46.7$, -49.9, -23.7, and -23.2, as well as by the multiplicity of the two highfield signals that are split into doublets by a Si–H coupling of 183 Hz. In addition, the occurrence of Si–H units in the product mixture was clearly shown by two ^{1}H NMR signals at $\delta = 5.96$ and 6.08. This analytical data is in agreement with a benzosilacyclobutene structure **38**. This interpretation is further supported by two signals (one for each diastereomer of **38**) of the benzylic quaternary carbon atoms at $\delta = 26.8$ and 27.0. However, a benzodisilacyclopentene structure **39** cannot be excluded with certainty. Fraction B was identified as disilane **40** by mass spectrometry and NMR spectroscopy. Only one diastereomer of **40** was detected. Attempts to elucidate the relative configuration of the adjacent silicon centers by determination of the vicinal ^{1}H–^{1}H coupling constant of the unsymmetrical ^{28}Si–^{29}Si isotopomer were unsuccessful: the broadened SiH signal did not allow the detection of the corresponding satellite signals.

The mechanism by which **38** and **40** are formed remains unclear. However, based on results reported by other groups, one might speculate that both compounds were formed via an intermediate disilene **37**, which might be the reductive coupling product of dichlorosilane **13**.[24] Tetramesityldisilene (**41**), for example, is known to rearrange to benzosilacyclo-

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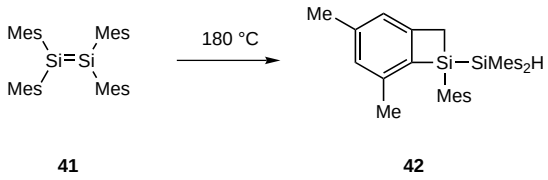
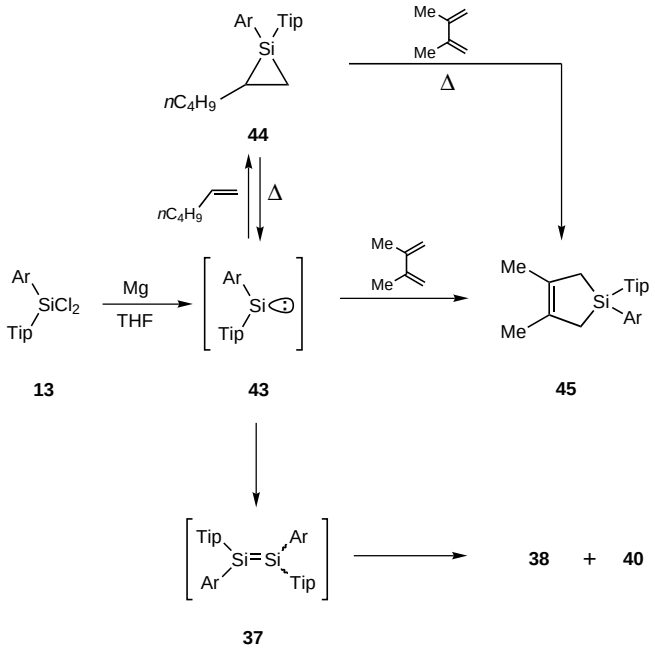
butene **42** above 180 °C (Scheme 12),[25] and a similar process, albeit at an appreciably lower temperature, might transform



41 **42**

Scheme 12. Thermolysis of disilene **41**.

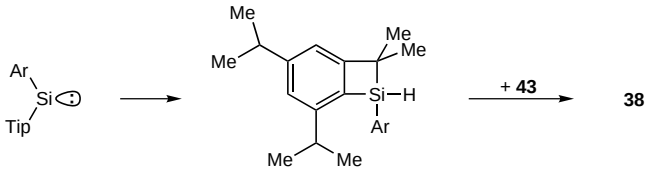
37 into **38**. In addition, the formation of disilanes, presumably via the corresponding disilenes, upon treatment of 1,2-dichlorodisilanes with metals has also been reported.[26] Further experiments confirmed that a silylene **43**, or a corresponding silylenoid, was involved in the reaction of magnesium with **13**: when the dichlorosilane was dehalogenated by magnesium in the presence of substrates such as 1-hexene or 2,3-dimethyl-1,3-butadiene, silacyclopropane **44** or silacyclopentene **45**, the trapping products of silylene **43**, were obtained (Scheme 13). Silacyclopropane **44** is a thermal



Scheme 13. Synthesis and trapping reactions of silylene **43**; Ar = 2-$Me_2NCH_2C_6H_4$.

precursor of **43** (Scheme 13): when heated in the presence of excess 2,3-dimethyl-1,3-butadiene to 100 °C for 21 h, silylene-trapping product **45** was obtained exclusively. Thermolysis of **44** at 110 °C for 6 h in vacuo without a silylene trapping agent afforded a 1:1 mixture of **38** and **40** along with volatile 1-hexene. At this point, it has to be stressed that the release of silylene **43** from silacyclopropane **44** requires significantly higher temperatures than for that of **10** from the corresponding silacyclopropanes.[9b] This observation might reflect the less effective thermodynamic stabilization of **43** compared to **10** due to the formation of only *one* dative N···Si bond.

To sum up, we assume that the formation of **38** and **40** by the dehalogenation of **13** as well as by the thermolysis of **44** proceeds via disilene **37** as a dimerization product of the initially formed silylene **43**.[27] An alternative pathway to **38**, which proceeds via rearrangement of **43** to benzosilacyclobutene **46**[28] and subsequent insertion of a second silylene in the Si–H bond of **46** (Scheme 14), appears less likely in view of the reluctance of the donor-stabilized silylene **6** to insert into Si–H[23b] bonds and because of the considerable shielding imposed on the Si–H bond of **46** by its bulky substituents.



43 **46**

Scheme 14. Alternative mechanism for the formation of benzosilacyclobutene **38**; Ar = 2-$Me_2NCH_2C_6H_4$.

Conclusion

We have shown that pentacoordinate dichlorosilanes such as **11a** and **12** are smoothly transformed by treatment with magnesium to cyclotrisilanes **14** and **20**, respectively. These are, in a manner similar to cyclotrisilane **9**, in equilibrium with their ring-constituting silylenes **15** and **24**. Therefore, these cyclotrisilanes may serve as a synthetic equivalent of the corresponding silylene. The silylene activity of **20** shows, in particular, that intramolecular coordination of only one dimethylamino group to the silicon center of a silylene provides a thermodynamic stabilization which is high enough to make **24** energetically accessible from the corresponding cyclotrisilane **20**. However, the relatively high temperatures required for the release of **24** from **20** may be a consequence of the fact that the silicon center of **24** is, in contrast to **10**, coordinated by only *one* dimethylamino group. A similar silylene, **43**, which is presumably a tricoordinate species as well, can be generated by the reduction of dichlorosilane **13** or, alternatively, by thermolysis of silacyclopropane **44**. Unlike **15** and **24**, this silylene does not trimerize to yield cyclotrisilane **36** in the absence of trapping agents, but forms, possibly via its dimer **37**, benzosilacylobutene **38** and disilane **40**.

Experimental Section

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM250 (^{1}H NMR, 250 MHz; ^{13}C NMR, 62.9 MHz) as well as on a Bruker AMX300 (^{1}H NMR, 300 MHz; ^{13}C NMR, 75.5 MHz). C_q, CH, CH_2 and CH_3 were determined by using the DEPT or APT pulse sequence. ^{29}Si NMR spectra were recorded on a Bruker AMX300 (59.6 MHz) as well as on a Varian XL500 (99.3 MHz) by means of a refocused INEPT pulse sequence or by direct excitation and acquisition. Chemical shifts are referenced to $\delta_{TMS} = 0.0$. If no temperature is stated, the NMR spectra were recorded at 297 K.

Mass spectra were recorded on a Varian MAT 731; high-resolution mass spectra (HRMS) were determined with a Varian MAT 311 A, with preselected ion peak matching at $R \approx 10000$ to be within ± 2 ppm of the exact mass. FAB spectra were obtained with a *o*-nitrophenyl-*n*-octyl ether matrix. Merck silica gel (230–400 mesh) was used for column chromatography and thin-layer chromatography was carried out on aluminum sheets precoated with silica gel (Macherey & Nagel, Alugram SIL G/UV$_{254}$). Melting points are uncorrected. Elemental analyses were performed at the Mikroanalytisches Labor der Georg-August-Universität Göttingen.

All manipulations were carried out under an inert argon atmosphere in carefully dried glassware. Solvents used were dried by refluxing over sodium and distilled immediately prior to use.

Mesityltrichlorosilane[29] and 2,4,6-tris(isopropyl)phenyltrichlorosilane[30] were prepared according to previously reported procedures. 2,4,6-Tris(isopropyl)phenyltrichlorosilane was isolated and used in further reactions as a mixture of 2,4,6-tris(isopropyl)phenyltrichlorosilane (63 %) and 1-bromo-2,4,6-tris(isopropyl)benzene (37 %).

Bis[2-(dimethylaminomethyl)-5-methylphenyl]dichlorosilane (**11a**): To a solution of *n*BuLi (167.5 mmol) in hexane (70 mL) and Et_2O (100 mL) was added 1-dimethylaminomethyl-4-methylbenzene (25.00 g, 167.5 mmol) at 0 °C. The mixture was stirred for 2 days at room temperature. The resulting suspension was transferred by a Teflon cannula under a positive Ar pressure into a solution of $SiCl_4$ (9.6 mL, 84 mmol) in Et_2O (100 mL) maintained at 0 °C. The slurry was stirred for 12 h at room temperature, precipitated LiCl was removed by filtration, and the filtrate was reduced to about half of its volume in vacuo. After the mixture had been left to stand overnight at 4 °C, colorless crystals of **11a** (15.2 g, 44 %; m.p. 101–103 °C) were isolated. An additional batch of slightly contaminated **11a** (7.3 g, 21 %; m.p. 99–102 °C) was obtained from the concentrated mother liquor. ^{1}H NMR ($CDCl_3$): $\delta = 1.95$ (br s, 6H; NMe_2), 2.42 (s, 3H; CH_3), 3.53 (br s, 2H; CH_2N), 7.21 (br s, 4H; arom H), 8.01 (br s, 2H; arom H); ^{13}C NMR ($CDCl_3$): $\delta = 21.6$ (CH_3), 45.5 (NMe_2), 63.5 (CH_2N), 127.8 (arom CH), 131.4 (arom CH), 135.0 (arom C_q), 136.1 (arom CH), 136.5 (arom C_q), 140.6 (arom C_q); ^{29}Si NMR ($CDCl_3$, Cr(acac)$_2$, 30 °C): $\delta = -32.6$; MS (EI, 70 eV): *m/z* (%): 394 (< 1) [M^+], 359 (1) [$M^+ - Cl$], 246 (46) [$M^+ - Ar^3$], 206 (100) [$C_{14}H_{10}Si$ (HRMS)], 148 (12) [$(Ar^3)^+$], 58 (31) [$CH_2NMe_2^+$]; $C_{20}H_{28}Cl_2N_2Si$ (395.5): calcd C 60.75, H 7.14, N 7.08; found C 60.61, H 7.26, N 7.04.

Hexakis[2-(dimethylaminomethyl)-5-methylphenyl]cyclotrisilane (**14**): A suspension of **11a** (6.94 g, 17.6 mmol) and Mg turnings (1.28 g, 52.7 mmol) in THF (34 mL) was stirred at room temperature in a flask equipped with a reflux condenser. After an induction period of 30 min (repeating the experiment under analogous conditions needed an induction period of 10 h) the slurry started to boil. After 60 min the solvent was removed in vacuo from the slurry, hexane (40 mL) was added to the brownish residue, and the resulting slurry was filtered. After removal of the hexane from the filtrate in vacuo, **14** (5.59 g, 98 %) was obtained as a yellow viscous oil, which solidified on standing for two months. UV (hexane/THF): λ_{max} (lg ε) = 370 nm (2.9); ^{1}H NMR (C_6D_6): $\delta = 1.83$ (s, 18H; CH_3), 2.10 (s, 36H; NMe_2), 3.65, 3.91 (br AB system, ^2J not resolved, 12H; CH_2N), 6.92–7.20 (m, 12H; arom H), 7.62 (d, $^3J = 8$ Hz, 6H; arom H); ^{13}C NMR (C_6D_6): $\delta =$ 20.7 (Me), 45.7 (NMe_2), 65.1 (CH_2N), 129.3 (arom CH), 130.1 (arom CH), 135.2 (arom C_q), 135.3 (arom C_q), 138.5 (arom CH), 144.8 (arom C_q); ^{29}Si NMR (C_6D_6): $\delta = -66.0$.

1,1-Bis[2-(dimethylaminomethyl)-5-methylphenyl]-3,4-dimethyl-1-silacyclopent-3-ene (**16**): A solution of **14** (98 mg, 0.10 mmol) and 2,3-dimethylbuta-1,3-diene (0.2 mL) in toluene (10 mL) was stirred at 40 °C for three days. Solvent and excess diene were removed in vacuo and **16** (47 mg, 40 %) was obtained by kugelrohr distillation at 180 °C/0.13 Pa as a sticky white foam, which solidified on standing. ^{1}H NMR ($CDCl_3$): $\delta = 1.72$ (s, 6H; CH_3), 1.82 (s, 16H; NMe_2, 2,5-CH_2), 2.32 (s, 6H; arom CH_3), 3.10 (s, 4H; CH_2N), 7.06–7.17 (m, 4H; arom H), 7.47 (s, 2H; arom H); ^{13}C NMR ($CDCl_3$): $\delta = 19.2$ (CH_3), 21.2 (arom CH_3), 25.6 (CH_2), 45.0 (NMe_2), 64.2 (CH_2N), 127.3 (arom CH), 128.4 (arom CH), 130.4 (C_q), 135.0 (C_q), 136.3 (C_q), 136.5 (arom CH), 142.3 (arom C_q); ^{29}Si NMR (C_6D_6): $\delta = -2.3$; MS (EI, 70 eV): *m/z* (%): 406 (25) [M^+], 325 (5) [$(Ar^3)_2Si^+ + H$], 309 (100) [$(Ar^3)_2Si^+ - Me$], 258 (46) [$M^+ - Ar^3$]; $C_{24}H_{34}N_2Si$ (378.6): calcd C 76.79, H 9.42, N 6.89; found C 76.54, H 9.32, N 6.98.

Competition reaction of 9 and 14 with 2,3-dimethylbuta-1,3-diene: A solution of **9** (59 mg, 0.07 mmol), **14** (68 mg, 0.07 mmol), and 2,3-dimethylbuta-1,3-diene (0.02 mL, 0.20 mmol) in C_6D_6 (0.4 mL) was heated to 75 °C for 105 min. According to the ^{1}H NMR spectrum, the diene was totally consumed after this period; the solution contained, besides unchanged **14**, only 1,1-bis[2-(dimethylaminomethyl)phenyl]-3,4-dimethyl-1-silacyclopent-3-ene.

4,5-Benzo-1,1-bis[2-(dimethylaminomethyl)-5-methylphenyl]-2,3-diphenyl-2-aza-1-silacyclopent-4-ene (**17**): A solution of **14** (35 mg, 0.04 mmol) and benzophenone anil (30 mg, 0.12 mmol) in C_6D_6 (0.4 mL) was heated to 60 °C for two days. The solvent was removed in vacuo; recrystallization of the residue from hexane yielded **17** (20 mg, 31 %) as a colorless solid. ^{1}H NMR (C_6D_6): $\delta = 1.68$ (s, 6H; NMe_2), 2.00 (s, 3H; arom CH_3), 2.05 (s, 3H; arom CH_3), 2.14 (s, 6H; NMe_2), 2.80, 3.46 (AB system, $^2J = 13$ Hz, 2H; CH_2N), 3.50, 4.01 (AB system, $^2J = 14$ Hz, 2H; CH_2N), 6.11 (s, 1H; 3-H), 6.57 (dd, $^3J = 7$ Hz, $^3J = 7$ Hz, 1H; arom H), 6.94 (m, 11H; arom H), 7.31 (d, $^3J = 8$ Hz, 2H; arom H), 7.53 (s, 2H; arom H), 7.86 (s, 2H; arom H), 7.98–8.00 (m, 1H; arom H), 8.30 (br s, 1H; arom H); MS (EI, 70 eV): *m/z* (%): 581 (27) [M^+], 537 (16) [$M^+ - CH_2NMe_2$], 521 (65) [$M^+ - CH_2NMe_2 - 2H$], 478 (100) [$M^+ - CH_2NMe_2 - NMe_2 - 2H$], 433 (90) [$M^+ - Ar^3$].

Reaction of 9 with 14: A solution of **9** (100 mg, 0.11 mmol) and **14** (100 mg, 0.10 mmol) in C_6D_6 (0.4 mL) was heated in an NMR tube to 60 °C for 84 h. ^{1}H NMR: (C_6D_6, the relative intensity as well as coupling constants could not been determined due to strong overlapping of the signals): $\delta = 1.76$ (s; arom H), 1.80 (s; arom CH_3), 1.82 (s; arom CH_3), 2.10 (s; NMe_2), 2.13 (s; NMe_2), 3.10, 4.10 (2 × br AB system; CH_2N), 6.72 (dd; arom H), 6.93-7.30 (m; arom H), 7.38-7.53 (m; arom H), 7.62 (dd; arom H), 7.79 (d or 2s; arom H); ^{29}Si NMR (C_6D_6): $\delta = -64.7$ (**9**), -64.8, -65.1, -65.7, -65.8, -66.0 (**14**).

[2-(Dimethylaminomethyl)phenyl]-[2,4,6-trimethylphenyl]dichlorsilane (**12**): To a solution of mesityltrichlorosilane (1.00 g, 3.9 mmol) in Et_2O (20 mL) was added a suspension of 2-(dimethylaminomethyl)phenyllithium (0.56 g, 3.9 mmol) in Et_2O (20 mL) at 0 °C by a Teflon cannula under a positive pressure of Ar. The slurry was stirred for 16 h at room temperature, and precipitated LiCl was removed by filtration. The filtrate was concentrated in vacuo ($\approx$ 15 mL) and left to stand overnight at -15 °C to give colorless crystals of **12** (0.953 g, 69 %). Crystals suitable for X-ray analysis were obtained by cooling a saturated solution of **12** in Et_2O to 3 °C. M.p. 123–124 °C; ^{1}H NMR (C_6D_6): $\delta = 1.54$ (s, 6H; NMe_2), 2.05 (s, 3H; CH_3), 2.50 (s, 6H; CH_3), 3.09 (s, 2H; CH_2N), 6.60 (s, 2H; arom H), 6.79 (d, $^3J = 7$ Hz, 1H; arom H), 7.11 (ddd, $^3J = {}^3J = 7$ Hz, $^4J = 1$ Hz, 1H; arom H), 7.10–7.25 (m, 1H; arom H), 8.60–8.75 (m, 1H; arom H); ^{13}C NMR (C_6D_6): $\delta = 20.9$ (CH_3), 24.9 (CH_3), 44.8 (NMe_2), 63.2 (CH_2N), 126.7 (arom CH), 128.1 (arom CH), 129.9 (arom CH), 130.9 (arom CH), 132.7 (arom C_q), 136.3 (arom C_q), 138.0 (arom CH), 138.6 (arom C_q), 141.1 (arom C_q), 144.3 (arom C_q); ^{29}Si NMR (C_6D_6): $\delta = -23.5$; MS (EI, 70 eV): *m/z* (%): 353/351 (2/4) [M^+], 318/316 (9/23) [$M^+ - Cl$], 308/306 (12/18) [$M^+ - NMe_2 - H$], 293/291 (4/6) [$M^+ - CH_2NMe_2 - 2H$], 234/232 (4/10) [$M^+ - Mes$], 218/216 (68/100) [$M^+ - Ar - H$], 58 (31) [$(CH_2NMe_2)^+$]; $C_{18}H_{23}Cl_2NSi$ (352.4): calcd C 61.35, H 6.58; found C 61.45, H 6.66.

[2-(Dimethylaminomethyl)phenyl]-[2,4,6-tris(isopropyl)phenyl]dichlorosilane (**13**): A solution of 2,4,6-tris(isopropyl)phenyltrichlorosilane (8.72 g, 25.8 mmol) in Et_2O (15 mL) was added to a suspension of 2-(dimethylaminomethyl)phenyllithium (3.64 g, 25.8 mmol) in Et_2O (85 mL) maintained at 0 °C. The slurry was stirred for 15 h at room temperature, precipitated LiCl was removed by filtration, and the solvent was evaporated in vacuo. The oily residue was purified by distillation to yield **13** (6.68 g, 77 %) as a colorless oil (b.p. 150–160 °C/0.07 Pa), which solidified slowly (colorless crystals, m.p. 85 °C). Crystals suitable for X-ray analysis were obtained by cooling a saturated solution of **13** in hexane to -15 °C. ^{1}H NMR (C_6D_6): $\delta = 1.19$ (d, $^3J = 7$ Hz, 6H; CH_3), 1.28 (d, $^3J =$ 7 Hz, 12H; CH_3), 1.60 (s, 6H; NMe_2), 2.75 (sept, $^3J = 7$ Hz, 1H; CH), 3.10 (s, 2H; CH_2N), 4.01 (sept, $^3J = 7$ Hz, 2H; CH), 6.81 (d, $^3J = 7$ Hz, 1H; arom H), 7.07–7.22 (m, 4H; arom H), 8.66 (d, $^3J = 7$ Hz, 1H; arom H); ^{13}C NMR (C_6D_6): $\delta = 24.0$ (CH_3), 24.9 (CH_3), 32.7 (CH), 34.5 (CH), 45.4 (NMe_2), 63.7 (CH_2N), 121.6 (arom CH), 126.9 (arom CH), 128.1 (arom CH), 130.7 (arom CH), 131.0 (arom C_q), 136.8 (arom C_q), 137.2 (arom CH), 143.7 (arom C_q), 150.4 (arom C_q), 153.4 (arom C_q); ^{29}Si NMR (C_6D_6): $\delta = -24.0$; MS (EI, 70 eV): *m/z* (%): 437/435 (6/7) [M^+], 402/400 (3/8) [$M^+ - Cl$], 394/392 (14/22) [$M^+ - Me_2CH$], 349/347 (14/10) [$M^+ - NMe_2 - Me_2CH - H$], 234/232 (13/21) [$M^+ - Tip$], 217/215 (69/100) [$M^+ - Ar - Me_2CH$], 58 (28) [$(CH_2NMe_2)^+$], 43 (14) [Me_2CH^+]; $C_{24}H_{35}Cl_2NSi$ (436.5): calcd C 66.03, H 8.08; found C 65.91, H 8.08.

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***cis,trans*-1,2,3-Tris[2-(dimethylaminomethyl)phenyl]-1,2,3-tris(2,4,6-trimethylphenyl)cyclotrisilane** (**20**): A suspension of **12** (3.87 g, 11.0 mmol) and Mg turnings (700 mg, 28.8 mmol) in THF (30 mL) was stirred at room temperature for 7 d. The solvent was removed in vacuo, hexane (20 mL) was added to the residue .and the resulting suspension filtered. The remaining solid material was extracted with toluene (30 mL). Removal of toluene from the filtrate in vacuo yielded **20** (1.90 g, 61 %) as a yellow solid. An additional batch of **20** (124 mg, 4 %) was obtained by cooling the hexane filtrate to 3 °C. M.p. 76–78 °C; ^{1}H NMR (C_6D_6): $\delta = 2.04$ (s, 15 H; CH_3), 2.08 (s, 6 H; CH_3), 2.11 (s, 6 H; CH_3), 2.2–2.5 (m, 18 H; CH_3), 3.46 (s, 2 H; CH_2N), 3.50, 3.70 (AB system, $^2J = 14$ Hz, 4 H; CH_2N), 6.6–6.8 (m, 9 H; arom H), 7.0–7.1 (m, 1 H; arom H), 7.13 (ddd, $^3J = {}^3J = 7$ Hz, $^4J = 1$ Hz, 2 H; arom H), 7.25 (d, $^3J = 7$ Hz, 2 H; arom H), 7.45 (dd, $^3J = 7$ Hz, $^4J = 1$ Hz, 1 H; arom H), 7.69 (d, $^3J = 8$ Hz, 1 H; arom H), 7.74 (d, $^3J = 7$ Hz, 2 H; arom H); ^{13}C NMR (C_6D_6): $\delta = 21.0$ (CH_3), 21.1 (CH_3), 26.4 (CH_3), 45.4 (NMe_2), 45.7 (NMe_2), 64.6 (CH_2N), 64.7 (CH_2N), 125.6 (arom CH), 126.3 (arom CH), 126.7 (arom CH), 128.5 (arom CH), 128.6 (arom CH), 129.0 (arom CH), 129.1 (arom CH), 129.3 (arom CH), 132.0 (arom C_q), 132.3 (arom C_q), 135.7 (arom CH), 137.2 (arom C_q), 137.4 (arom CH), 137.9 (arom C_q), 138.7 (arom C_q), 145.3 (arom C_q), 145.5 (arom C_q), 147.1 (arom C_q), 147.2 (arom C_q); ^{29}Si NMR (C_6D_6, 99.3 MHz, 338 K): $\delta = -62.5$ (br s, 2 ArMesSi), −63.4 (s (d, $^1J_{Si,C} = 57.2$ Hz, d, $^1J_{Si,Si} = 28.5$ Hz); MS (EI, 70 eV): *m/z* (%): 562 (2) [M^+ − ArMesSi], 574 (2) [M^+ − ArMesSi − Me], 504 (2) [M^+ − ArMesSi − CH_2NMe_2], 356 (71) [M^+ − ArMesSi − CH_2NMe_2 − Me+H], 282 (71) [M^+ − 2 ArMesSi+H], 92 (59) [$C_7H_8^+$], 91 (100) [$C_7H_7^+$]; (FAB) *m/z* (%): 562 (100) [M^+ − ArMesSi]; $C_{52}H_{69}N_3Si_3$ (844.4): calcd C 76.81, H 8.24; found C 76.78, H 8.33.

2-(Dimethylaminomethyl)phenyl-2,4,6-trimethylphenyl-*tert*-butyloxysilane (**28**): A solution of **20** (53 mg, 0.06 mmol) and *tert*-butyl alcohol (30 mg, 0.40 mmol) in C_6D_6 (0.4 mL) was heated to 60 °C for 20 h. The volatile components were removed in vacuo and the pure residue (^{1}H NMR spectroscopy) was further purified by kugelrohr distillation. At 200 °C/0.67 Pa analytically pure **28** (36 mg, 54 %) was obtained as a colorless solid. M.p. 92 °C; ^{1}H NMR (C_6D_6): $\delta = 1.33$ (s, 9 H; $C(CH_3)_3$), 1.78 (s; 6 H; NMe_2), 2.12 (s, 3 H; CH_3), 2.46 (s, 6 H; Me), 2.86, 3.30 (AB system, $^2J = 13$ Hz, 2 H; CH_2N), 6.01 (s (d, $^1J_{Si,H} = 222$ Hz); 1 H; SiH), 6.73 (s, 2 H; arom H), 7.10 (d, $^3J = 7$ Hz, 1 H; arom H), 7.20 (ddd, $^3J = {}^3J = 7$ Hz, $^4J = 1$ Hz, 1 H; arom H), 7.23 (dd, $^3J = {}^3J = 7$ Hz, 1 H; arom H), 8.40 (d, $^3J = 7$ Hz, 1 H; arom H); ^{13}C NMR (C_6D_6): $\delta = 19.7$ (CH_3), 22.0 (CH_3), 30.0 ($C(CH_3)_3$), 43.2 (NMe_2), 63.4 (CH_2N), 70.9 ($C(CH_3)_3$), 125.6 (arom CH), 126.4 (arom CH), 127.3 (arom CH), 127.9 (arom CH), 131.0 (arom C_q), 135.6 (arom C_q), 135.9 (arom CH), 136.9 (arom C_q), 142.3 (arom C_q), 144.0 (arom C_q); ^{29}Si NMR (C_6D_6): $\delta = -34.9$ (d, $^1J_{Si,H} = 223$ Hz); MS (EI, 70 eV): *m/z* (%): 355 (2) [M^+], 310 (7) [M^+ − NMe_2 − H], 298 (11) [M^+ − CMe_3], 282 (26) [M^+ − $OCMe_3$], 254 (31) [M^+ − $OCMe_3$ − NMe_2], 253 (30) [M^+ − $OCMe_3$ − NMe_2 − H], 239 (58) [M^+ − $OCMe_3$ − CH_2NMe_2 − H], 220 (97) [M^+ − Ar − H], 164 (100) [M^+ − Ar − $OCMe_3$], 58 (16) [$(CH_2NMe_2)^+$]; $C_{22}H_{33}NSiO$ (355.6): calcd C 74.31, H 9.35; found C 74.45, H 9.50.

1-[2-(Dimethylaminomethyl)phenyl]-1-(2,4,6-trimethylphenyl)-3,4-dimethyl-1-silacyclopent-3-ene (**25**): A solution of **20** (91 mg, 0.11 mmol) and 2,3-dimethyl-1,3-butadiene (182 μL, 1.61 mmol) in C_6D_6 (0.4 mL) was heated to 90 °C for 16.5 h. The volatile components were removed in vacuo, and **25** (64 mg, 54 %) was obtained by kugelrohr distillation at 145 °C/1.33×10^{-3} Pa as a colorless oil. ^{1}H NMR (C_6D_6): $\delta = 1.79$ (s, 6 H; NMe_2), 1.90 (s, 6 H; 3,4-CH_3), 2.00, 2.08 (AB system, $^2J = 19$ Hz, 4 H; 2,5-H), 2.15 (s, 3 H; arom CH_3), 2.33 (s, 6 H; arom CH_3), 3.17 (s, 2 H; CH_2N), 6.76 (s, 2 H; arom H), 7.11 (ddd, $^3J = {}^3J = 7$ Hz, $^4J = 1$ Hz, 1 H; arom H), 7.19 (ddd, $^3J = {}^3J = 7$ Hz, $^4J = 2$ Hz, 1 H; arom H), 7.39 (d, $^3J = 7$ Hz, 1 H; arom H), 7.69 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 1 H; arom H); ^{13}C NMR ($CDCl_3$): $\delta = 19.0$ (CH_3), 21.0 (CH_3), 24.5 (CH_3), 28.7 (CH_2Si), 45.2 (NMe_2), 63.9 (CH_2N), 126.4 (arom CH), 128.5 (arom CH), 128.6 (arom CH), 129.0 (arom CH), 130.9 (C3,4), 132.1 (arom C_q), 135.3 (arom CH), 137.6 (arom C_q), 138.6 (arom C_q), 144.4 (arom C_q), 145.3 (arom C_q); ^{29}Si NMR (C_6D_6): $\delta = -1.8$; MS (EI, 70 eV): *m/z* (%): 363 (9) [M^+], 348 (6) [M^+ − Me], 281 (98) [ArMesSi$^+$], 266 (100) [M^+ − C_6H_{10} − Me], 243 (75) [M^+ − Mes − H], 236 (54) [M^+ − C_6H_{10} − NMe_2 − H], Ar], 228 (62) [M^+ − Ar − H]; $C_{24}H_{33}NSi$ (363.6): calcd C 79.28, H 9.15; found C 79.27, H 9.30.

1-[2-(Dimethylaminomethyl)phenyl]-1-(2,4,6-trimethylphenyl)-2-trimethylsilyl-1-silacyclopropene (**26**): A solution of **20** (70 mg, 0.06 mmol) and trimethylsilylacetylene (74 μL, 0.53 mmol) in C_6D_6 (0.4 mL) was heated in an NMR tube to 90 °C for 13 h. The mixture was transferred into a Schlenk flask and the volatile components were removed in vacuo. A highly air- and moisture-sensitive, yellowish viscous oil remained, which consisted of pure **26** (by ^{1}H NMR spectroscopy) (64 mg, 95 %). ^{1}H NMR (C_6D_6): $\delta = 0.27$ (s, 9 H; $SiMe_3$), 1.88 (s, 6 H; NMe_2), 2.11 (s, 3 H; CH_3), 2.36 (s, 6 H; CH_3), 2.92, 3.05 (AB system, $^2J = 13$ Hz, 2 H; CH_2N), 6.70 (s, 2 H; arom H), 6.89 (dd, $^3J = 6$ Hz, $^4J = 1$ Hz, 1 H; arom H), 7.15–7.25 (m, 2 H; arom H), 7.72–7.82 (m, 1 H; arom H), 9.86 (s ($^1J_{CH} = 178$ Hz, $J_{SiH} = 8$ Hz, $J_{SiH} = 10$ Hz); 1 H; H3); ^{13}C NMR (C_6D_6): $\delta = -1.4$ ($SiMe_3$), 20.6 (CH_3), 23.9 (CH_3), 44.3 (NMe_2), 63.6 (CH_2N), 126.6 (arom CH), 126.9 (arom CH), 127.7 (arom CH), 128.7 (arom CH), 131.4 (arom C_q), 135.4 (arom CH), 137.4 (arom C_q), 138.0 (arom C_q), 143.3 (arom C_q), 144.4 (arom C_q), 169.8 (C3), 177.0 (C2); ^{29}Si NMR (C_6D_6): $\delta = -12.7$ ($SiMe_3$), −116.4 (Si1); MS (FAB): *m/z* (%): 380 (100) [M^++H].

1,2-Dichloro-1,2-bis[2-(dimethylaminomethyl)phenyl]-1,2-bis(2,4,6-trimethylphenyl)disilane (**27**): A solution of **20** (400 mg, 0.47 mmol) and **12** (500 mg, 1.42 mmol) in toluene (9 mL) was heated to 85 °C for 13 h. The solvent was removed in vacuo, the residue suspended in pentane (37 mL) and then filtered. The colorless filtercake consisted of a diastereomeric mixture (*dr* = 3:1) of pure **27** (by ^{1}H NMR spectroscopy) (338 mg, 38 %). **27**: M.p. (for *dr* = 1.4:1) 149–201 °C). **27** (main diastereomer): ^{1}H NMR (C_6D_6): $\delta = 1.90$ (s, 12 H; NMe_2), 2.03 (s, 6 H; CH_3), 2.42 (s, 12 H; CH_3), 3.43, 3.74 (AB system, $^2J = 14$ Hz, 4 H; CH_2N), 6.63 (s, 4 H; arom H), 6.94 (dd, $^3J = {}^3J = 7$ Hz, 2 H; arom H), 7.14–7.26 (m, 2 H; arom H), 7.74 (d, $^3J = 6$ Hz, 2 H; arom H), 8.04 (br s, 2 H; arom H); ^{13}C NMR (C_6D_6): $\delta = 20.9$ (CH_3), 25.9 (CH_3), 45.1 (NMe_2), 64.1 (CH_2N), 126.6 (arom CH), 129.2 (arom CH), 129.8 (arom C_q), 130.1 (arom CH), 130.7 (arom CH), 137.6 (arom CH), 140.2 (arom C_q), 145.4 (arom C_q), 145.9 (arom C_q), 146.7 (arom C_q); ^{29}Si NMR (C_6D_6): $\delta = -2.5$. **27** (minor diastereomer): ^{1}H NMR (C_6D_6): $\delta = 1.95$ (s, 12 H; NMe_2), 2.06 (s, 6 H; CH_3), 2.36 (s, 12 H; CH_3), 3.35, 3.60 (AB system, $^2J = 14$ Hz, 4 H; CH_2N), 6.66 (s, 4 H; arom H), 6.94 (dd, $^3J = {}^3J = 7$ Hz, 2 H; arom H), 7.14–7.26 (m, 2 H; arom H), 7.60 (d, $^3J = 7$ Hz, 2 H; arom H), 8.14 (d, $^3J = 7$ Hz, 2 H; arom H); ^{13}C NMR (C_6D_6): $\delta = 21.0$ (Me), 25.8 (Me), 45.4 (NMe_2), 64.2 (CH_2N), 126.9 (arom CH), 135.0 (arom C_q), 135.7 (arom C_q); ^{29}Si NMR (C_6D_6): $\delta = -2.6$; MS (FAB): *m/z* (%): 631 (100) [M^+ − 1]; (EI, 70 eV): *m/z* (%): 614 (<1) [M^++H_2O − Cl − H], 596 (<1) [M^+ − Cl − H], 479 (<1) [M^++H − Cl − Mes], 462 (<1) [M^+ − Cl − Ar − H], 316 (4) [M^+/2], 282 (9) [ArMesSiH$^+$], 43 (100) [$(NMe_2)^+$ − H].

Bis[2-(dimethylaminomethyl)phenyl]-*tert*-butyloxysilane (**30**) and **1-*tert*-butoxy-1,1,2,2-tetrakis[2-(dimethylaminomethyl)phenyl]disilane** (**31**): A solution of *tert*-butyl alcohol (50 mg, 0.67 mmol) in toluene (3 mL) was slowly added to a solution of **9** (300 mg, 0.34 mmol) in toluene (5 mL) at −78 °C. After warming up to room temperature the slurry was stirred for additional 30 min. The volatile components were removed in vacuo and **30** (110 mg, 88 %) was obtained by kugelrohr distillation at 215 °C/0.13 Pa as a colorless oil. The remaining yellowish viscous oil consisted of analytically pure **31** (226 mg, 100 %). **30**: ^{1}H NMR (C_6D_6): $\delta = 1.34–1.35$ (m, 9 H; $C(CH_3)_3$), 1.87 (s, 12 H; NMe_2), 3.37, 3.42 (AB system, $^2J = 14$ Hz, 4 H; CH_2N), 5.73 (s (d, $^1J_{Si,H} = 226$ Hz); 1 H; SiH), 7.17–7.30 (m, 4 H; arom H), 7.26–7.39 (m, 2 H; arom H), 7.99–8.13 (m, 2 H; arom H); ^{13}C NMR (C_6D_6): $\delta = 31.6$ ($C(CH_3)_3$), 44.9 (NMe_2), 64.3 (CH_2N), 72.5 ($C(CH_3)_3$), 126.4 (arom CH), 128.0 (arom CH), 129.2 (arom CH), 136.8 (arom CH), 137.8 (arom C_q), 145.3 (arom C_q); ^{29}Si NMR (C_6D_6): $\delta = -33.8$ (d, $^1J_{SiH} = 225$ Hz); MS (EI, 70 eV): *m/z* (%): 370 (1) [M^+], 369 (1) [M^+ − H], 310 (13) [M^+ − NMe_2 − Me − H], 297 (22) [M^+ − $OCMe_3$], 254 (49) [M^+ − CH_2NMe_2 − $OCMe_3$ − H), 236 (100) [M^+ − Ar]; HRMS: calcd for $C_{22}H_{34}N_2SiO$ 370.2440; found 370.2440. **31**: ^{1}H NMR (C_6D_6): $\delta = 1.18$ (s, 9 H; $C(CH_3)_3$), 1.91 (s, 12 H; NMe_2), 2.03 (s, 12 H; NMe_2), 3.17, 3.36 (AB system, $^2J = 15$ Hz, 4 H; CH_2N), 3.52 (s, 4 H; CH_2N), 5.95 (s (d, $^1J_{Si,H} = 190$ Hz); 1 H; SiH), 7.00 (dd, $^3J = {}^3J = 7$ Hz, 2 H; arom H), 7.12 (dd, $^3J = {}^3J = 7$ Hz, 2 H; arom H), 7.25 (dd, $^3J = {}^3J = 8$ Hz, 2 H; arom H), 7.32 (dd, $^3J = {}^3J = 8$ Hz, 2 H; arom H), 7.42 (d, $^3J = 8$ Hz, 2 H; arom H), 7.82 (d, $^3J = 7$ Hz, 2 H; arom H), 7.94 (d, $^3J = 7$ Hz, 2 H; arom H), 8.43 (d, $^3J = 7$ Hz, 2 H; arom H); ^{13}C NMR (C_6D_6): $\delta = 32.0$ ($C(CH_3)_3$), 45.2 (NMe_2), 45.4 (NMe_2), 63.4 (CH_2N), 64.7 (CH_2N), 74.6 ($C(CH_3)_3$), 126.1 (arom CH), 126.2 (arom CH), 128.2 (arom CH), 129.2 (2 arom CH), 130.0 (arom CH), 135.7 (arom C_q), 136.5 (arom CH), 138.2 (arom C_q), 138.7 (arom CH), 145.9 (arom C_q), 146.6 (arom C_q); ^{29}Si NMR (C_6D_6): $\delta = -13.0$ ($Ar_2SiOCMe_3$), −46.9 (d, $^1J_{Si,H} = 190$ Hz, Ar_2SiH); MS (EI, 70 eV): *m/z* (%): 666 (<1) [M^+], 621 (<1) [M^+ − NMe_2 − H], 608 (11) [M^+ − CH_2NMe_2], 369 (24) [M^+ − Ar_2SiH), 297 (86) [Ar_2SiH^+], 73 (100) [$(OCMe_3)^+$]; $C_{40}H_{58}N_4Si_2O$ (667.1): calcd C 72.02, H 8.76, N 8.40; found C 71.89, H 8.77, N 8.34.

Reaction of 9 with 20 and subsequent reaction with 2,3-dimethyl-1,3-butadiene:

Experiment A: A solution of **20** (67 mg, 0.08 mmol) and **9** (133 mg, 0.15 mmol) in C_6D_6 (0.4 mL) was heated in an NMR tube to 90 °C for 14 h. ^{1}H NMR (C_6D_6): $\delta = 1.7-2.8$ (m, 39H; CH_3), 3.0–4.4 (m, 10H; CH_2N), 6.6–6.9 (m, 6H; arom H), 7.0–7.3 (m, 7H; arom H), 7.3–7.6 (m, 5H; arom H), 7.6–8.1 (m, 4H; arom H); ^{29}Si NMR (C_6D_6, 99.3 MHz, 297 K): $\delta = -58.5$ (brs), -62.6 , -63.3 (brs), -64.3 (brs, **20**), -64.5 (**20**), -64.7 (**9**), -69.1, -70.4 (brs), -71.9 (brs); ^{29}Si NMR (C_6D_6, 99.3 MHz, 338 K): $\delta = -61.6$ (s, $^1J_{Si,Si} = 28.2$ Hz), -62.5 (brs, **20**), -63.4 (s (d, $^1J_{Si,Si} = 28.5$ Hz)), -64.1 (**9**) -66.0, -68.5 (s, $^1J_{Si,Si} = 30.1$ Hz)). To this mixture 2,3-dimethyl-1,3-butadiene (0.30 mL, 2.7 mmol) was added. After heating the NMR sample to 90 °C for 15 h quantitative formation of a 2:1 ratio of 1,1-bis[2-(dimethylaminomethyl)phenyl]-3,4-dimethyl-1-silacyclopent-3-ene and **25** was observed by ^{1}H NMR spectroscopy.

Experiment B: A solution of **20** (135 mg, 0.16 mmol) und **9** (67 mg, 0.08 mmol) in C_6D_6 (0.4 mL) was heated in an NMR tube to 90 °C for 14 h. The number and the shift values of the ^{29}Si signals of the resulting product mixture were identical with those found for Method A, although different relative signal intensities were observed.

1,2-Bis[2-(dimethylaminomethyl)phenyl]-1,2-bis[2,4,6-tris(isopropyl)phenyl]disilane (**40**) and **1-[2-(dimethylaminomethyl)phenyl-2,4,6-tris(isopropyl)phenyl]silyl-2,3-[4,6-bis(isopropyl)benzo]-4-dimethyl-1-silacyclobutene** (**38**): A suspension of **13** (1.53 g, 3.5 mmol) and Mg turnings (1.34 g, 56.0 mmol) in THF (20 mL) was stirred at room temperature for five days. The volatile compounds were removed by vacuum distillation and the residue was suspended in hexane (10 mL). The slurry was filtered and the filtrate evaporated in vacuo. Column chromatography of the crude product (1.08 g) on silica gel (hexane/NEt_3 97.5:2.5) gave two fractions with $R_f =$ 0.35 (**38**, 247 mg, 19%) and $R_f = 0.36$ (**40**, 67 mg, 5%), respectively. Compound **38** was obtained as a diastereomeric mixture (the diastereomeric ratio varied from 2:1 to 3:1) and was contaminated with traces of **40**. Kugelrohr distillation of this fraction at 250 °C/1.33×10^{-3} Pa did not result in any change of the relative composition. An unambiguous assignment of the ^{1}H and ^{13}C NMR signals of **38** was not possible due to severely overlapping signals and the high complexity of the spectra. **38**: ^{1}H NMR (C_6D_6): $\delta = 5.96$ (s, 1H; SiH, main isomer) 6.08 (s, 1H; SiH); ^{13}C NMR (C_6D_6, APT): $\delta = 26.8$ (C_q), 27.0 (C_q); ^{29}Si NMR (C_6D_6): $\delta = -23.2$ (Si2), -49.9 (d, $^1J_{Si,H} = 183$ Hz, SiH); -23.7 (Si2, main isomer), -46.7 (d, $^1J_{Si,H} =$ 183 Hz, SiH, main isomer); MS (DCI, NH_3): *m/z* (%): 747 (100) [M^++NH_3]. **40**: ^{1}H NMR (C_6D_6): $\delta = 0.59$ (dd, $^3J = 7$ Hz, 12H; CH_3), 1.1–1.3 (m, 12H; CH_3), 1.43 (d, $^3J = 7$ Hz, 12H; CH_3), 2.03 (s, 12H; NMe_2), 2.71 (sept, $^3J = 7$ Hz, 2H; C*H*Me_2), 3.3–3.5 (m, 2H; C*H*Me_2), 3.34, 3.72 (AB System, $^2J = 14$ Hz, 4H; CH_2N), 3.57 (sept, $^3J = 7$ Hz, 2H; C*H*Me_2), 6.15 (s, 2H; SiH), 6.91 (dd, $^3J = {}^3J = 7$ Hz, 2H; arom H), 7.02 (s, 4H; arom H), 7.21 (dd, $^3J = 8$ Hz, $^3J = 7$ Hz, 2H; arom H), 7.80 (d, $^3J = 8$ Hz, 2H; arom H), 7.97 (d, $^3J = 7$ Hz, 2H; arom H); ^{13}C NMR ($CDCl_3$): $\delta = 23.6$ (CH_3), 23.9 (CH_3), 24.0 (CH_3), 24.5 (CH_3), 31.1 (*C*HMe_2), 34.3 (*C*HMe_2), 34.8 (*C*HMe_2), 45.5 (NMe_2), 63.4 (CH_2N), 121.5 (arom CH), 126.0 (arom CH), 126.2 (arom CH), 127.3 (arom CH), 129.5 (arom C_q), 134.8 (arom C_q), 138.6 (arom CH), 146.0 (arom C_q), 150.4 (arom C_q), 155.5 (arom C_q); ^{29}Si NMR (C_6D_6): $\delta = -51.5$ (d, $^1J_{SiH} = 185$ Hz); MS (EI, 70 eV): *m/z* (%): 731 (<1) [$M^+ - H$], 687 (1) [$M^+ - NMe_2$], 644 (<1) [$M^+ - 2NMe_2$], 598 (<1) [$M^+ -$ Ar], 366 (100) [$M^+/2$], 43 (30) [Me_2CH^+]; MS (DCI, NH_3): *m/z* (%): 733 (70) [M^++H], 368 (100) [$M^+/2$+2H].

1-[2-(Dimethylaminomethyl)phenyl]-1-[2,4,6-tris(isopropyl)phenyl]-2-*n*-butyl-1-silacyclopropane (**44**): A suspension of **13** (1.00 g, 2.29 mmol), 1-hexene (8.6 mL, 68 mmol), and Mg turnings (223 mg, 9.2 mmol) in THF (10 mL) was stirred at room temperature for seven days. The volatile compounds were removed by vacuum distillation and the residue was suspended in hexane (15 mL). The slurry was filtered and the filtrate was evaporated in vacuo. The oily residue consisted of nearly pure **44** (^{1}H NMR spectroscopy) (873 mg, 85%). ^{1}H NMR (C_6D_6): $\delta = 0.75$ (dd, $^3J_{trans} = 7$ Hz, $^2J = 7$ Hz, 1H; 3-H_{cis}), 0.90 (t, $^3J = 7$ Hz, 3H; butyl-CH_3), 1.17 (d, $^3J = 7$ Hz, 3H; CH_3), 1.18 (d, $^3J = 7$ Hz, 3H; CH_3), 1.41 (d, $^3J = 7$ Hz, 6H; CH_3), 0.81–2.05 (m, 14H; 2-H, 3-H_{trans}, butyl-CH_2, CH_3), 2.07 (s, 6H; NMe_2), 2.76 (sept, $^3J = 7$ Hz, 1H; C*H*Me_2), 3.48, 3.62 (AB system, $^2J = 14$ Hz, 2H; CH_2N), 4.05–4.26 (m, 2H; C*H*Me_2), 7.01 (dd, $^3J = {}^3J = 7$ Hz, 1H; arom H), 7.16 (s, 2H; arom H), 7.20 (ddd, $^3J = 8$ Hz, $^3J = 7$ Hz, $^4J = 1$ Hz, 1H; arom H), 7.62 (d, $^3J = 8$ Hz, 1H; arom H), 7.77 (dd, $^3J = 7$ Hz, $^4J = 1$ Hz, 1H; arom H); ^{13}C NMR (C_6D_6): $\delta = 9.5$ (C3), 14.2, 14.5 (C2, butyl-CH_3), 22.9 (butyl-CH_2), 24.0, 24.1, 24.7, 26.1 (CH_3), 32.3, 33.3 (butyl-CH_2), 34.8, 35.9, (*C*HMe_2), 45.3 (NMe_2), 63.6 (CH_2N), 121.6 (arom CH), 126.2 (arom C_q), 126.6 (arom CH), 129.1 (arom CH), 130.0 (arom CH), 134.0 (arom C_q), 146.8 (arom C_q), 151.7 (arom C_q), 157.1 (arom C_q); ^{29}Si NMR (C_6D_6): $\delta = -81.6$; MS (FAB): *m/z* (%): 450 (100) [M^++H].

Thermolysis of 44: A flask containing **44** (112 mg, 0.25 mmol) was connected to a cold trap (77 K) and then heated in a dynamic vacuum (1.33×10^{-2} Pa) to 110 °C for 6 h. 1-Hexene was collected in the cold trap and identified by ^{1}H NMR spectroscopy. The residue (80 mg) was identified as a 1:1 mixture of **38** and **40** by ^{1}H NMR spectroscopy.

1-[2-(Dimethylaminomethyl)phenyl]-1-[2,4,6-tris(isopropyl)phenyl]-3,4-dimethyl-1-silacyclopent-3-ene (**45**): A suspension of **13** (445 mg, 1.02 mmol), 2,3-dimethyl-1,3-butadiene (573 μL, 5.12 mmol), and Mg turnings (98 mg, 4.03 mmol) in THF (3 mL) was stirred for 66 h at room temperature. The volatile compounds were removed in vacuo and the residue was suspended in hexane (15 mL). The slurry was filtered and the filtrate then evaporated in vacuo. Kugelrohr distillation of the residue gave **45** (78 mg, 17%) at 140 °C/1.33×10^{-3} Pa as a colorless oil. ^{1}H NMR ($CDCl_3$): $\delta = 1.13$ (d, $^3J = 7$ Hz, 12H; CH_3), 1.27 (d, $^3J = 7$ Hz, 6H; CH_3), 1.75 (s, 6 H 3,4-CH_3), 1.85, 2.05 (AB system, $^2J = 14$ Hz, 4H; 2,5-H), 2.14 (s, 6H; NMe_2), 2.90 (sept, $^3J = 7$ Hz, 1H; CH), 3.00 (sept, $^3J = 7$ Hz, 2H; CH), 3.38 (s, 2H; CH_2N), 7.03 (s, 2H; arom H), 7.10 (dd, $^3J = {}^3J = 8$ Hz, 1H; arom H), 7.27-7.40 (m, 2H; arom H), 7.56 (d, $^3J = 8$ Hz, 1H; arom H); ^{13}C NMR ($CDCl_3$): $\delta = 18.9$ (CH_3), 23.9 (CH_3), 25.1 (CH_3), 29.3 (CH_2Si), 34.2 (*C*HMe_2), 34.4 (*C*HMe_2), 45.5 (NMe_2), 63.4 (CH_2N), 121.4 (arom CH), 125.8 (arom CH), 128.2 (arom CH), 129.2 (arom CH), 131.1 (arom C_q), 131.2 (C3,4), 136.5 (arom CH), 137.6 (arom C_q), 145.3 (arom C_q), 150.1 (arom C_q), 155.6 (arom C_q); ^{29}Si NMR ($CDCl_3$): $\delta = -1.1$; MS (EI, 70 eV): *m/z* (%): 447 (10) [M^+], 402 (3) [$M^+ - NMe_2 - H$], 365 (17) [$M^+ - C_6H_{10}$], 350 (39) [$M^+ - C_6H_{10} -$ Me], 243 (17) [$M^+ -$ Tip $- H$], 204 (48) [Is$^+$Tip+H], 189 (100) [$M^+ -$ Me+H]; $C_{30}H_{45}NSi$ (447.8): calcd C 80.47, H 10.13; found C 80.38, H 10.03.

Thermolysis of **44** *in presence of 2,3-dimethyl-1,3-butadiene*: A solution of **44** (63 mg, 0.14 mmol) and 2,3-dimethyl-1,3-butadiene (157 μL) in C_6D_6 (0.4 mL) was heated in an NMR tube to 100 °C for 21 h. ^{1}H NMR spectroscopic analysis with poly(dimethylsiloxane) as an internal integration standard showed the presence of **45** in high yield (92%). Pure **45** (35 mg, 56%) was obtained by kugelrohr distillation at 200 °C/1.33 Pa.

Crystal structure analysis: Crystals were mounted on a glass fiber in a shock-cooled perfluoropolyether.[31] Diffraction data were collected on a Stoe–Siemens–Huber four-circle diffractometer coupled to a Siemens CCD area-detector at 133(2) K (**12**) and on a Stoe-Siemens-AED four-circle diffractometer at 153(2) K (**13**), both with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), and φ and ω scans, respectively. The structures were solved by direct methods using SHELXS-96[32] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[33] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined with a riding model.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100702. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +(44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal structure analysis of **12**: $C_{18}H_{23}NSiCl_2$, $M_r = 352.36$, crystal dimensions $0.80 \times 0.40 \times 0.40$ mm^3; monoclinic, $P2_1/c$, $a = 8.023(5)$, $b = 13.555(8)$, $c = 16.463(9)$ Å, $\beta = 96.09(2)°$; $V = 1780(2)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.315$ g cm^{-3}, $\mu = 0.428$ mm^{-1}; total number of reflections measured 25971, unique 3366 ($R_{int} = 0.029$). Data/restraints/parameters: 3366/0/204. Final R indices: $R1 = 0.0289$, $wR2 = 0.0767$ on data with $I > 2\sigma(I)$ and $R1 = 0.0338$, $wR2 =$ 0.0796 on all data, goodness-of-fit $S = 1.039$; ($R1 = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $S = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(n-p)]^{1/2}$); weighting scheme: $w^{-1} = \sigma^2(F_o)^2 + (0.0414P)^2 + 0.9117P$; $P = [F_o^2 + 2F_c^2]/3$; largest difference peak and hole: 0.323 and -0.283 e A^{-3}.

Crystal structure analysis of **13:** $C_{24}H_{35}NSiCl_2$, $M_r = 436.52$, crystal dimensions: $0.90 \times 0.80 \times 0.50$ mm^3; monoclinic, $P2_1/c$, $a = 9.089(1)$, $b =$ 16.769(2), $c = 15.700(2)$ Å, $\beta = 99.31(1)°$; $V = 2361.5(5)$ Å^3; $Z = 4$; $\rho_{calcd} =$ 1.228 g cm^{-3}, $\mu = 0.336$ mm^{-1}; total number of reflections measured 6346, unique 4176 ($R_{int} = 0.0191$). Data/restraints/parameters: 4176/0/261. Final R

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indices: $R1 = 0.0296$, $wR2 = 0.0749$ on data with $I > 2\sigma(I)$ and $R1 = 0.0333$, $wR2 = 0.0776$ on all data, goodness-of-fit: $S = 1.067$; weighting scheme: $w^{-1} = \sigma^2(F_o)^2 + (0.0353\,P)^2 + 1.2326\,P$; largest difference peak and hole: 0.315 and -0.228 e A^{-3}.

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