Synthesis, Structure and Dehalogenation of the Disilene RClSi=SiClR [R = (tBu$_3$Si)$_2$MeSi][‡]

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Dedicated to Professor Hans Bürger on the occasion of his 65th birthday

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The reaction of $R^*_2MeSi–SiX_2X'$ (X/X′ = Cl/Br, Br/Cl) with NaR* (R* = supersilyl SitBu$_3$) leads, probably via the silylenes $R^*_2MeSi–SiX$, to the *trans*-configurated disilene (R^*_2MeSi)ClSi=SiCl(SiMeR^*_2), which could be isolated as orange-red crystals. According to an X-ray structure analysis, the central SiClSi=SiClSi framework of the disilene – the formation mechanisms of which are discussed – is planar. The Si=Si double bond is as short as 2.163(4) Å and shows a band in the Raman spectrum at 589 cm^{-1}. Due to its insolubility in organic solvents, no NMR spectra of the disilene in solution were obtained. The spatially overcrowded disilene is stable towards H_2O, MeOH, HF, and NaR*. It melts at 228 °C with decomposition. Reduction of the disilene occurs with $LiC_{10}H_8$ in THF with formation of a reaction mixture containing a chlorine-free product that gives a low field ^{29}Si NMR signal at δ = 91.5 (the region for unsaturated Si atoms). It transforms in solution with traces of oxygen into a substance which, according to mass spectrometry (chemical ionization), shows a mass for the disilyne R^*_2MeSi–Si≡Si–SiMeR^*_2 plus two oxygen atoms.

Introduction

Searching for a way to synthesize a disilyne RSi≡SiR, we recently tried to transform 1,2-bis[(disupersilyl)silyl]disilane $R^*_2HSi-SiH_2-SiH_2-SiHR^*_2$ into its tetrabromo derivative $R^*_2HSi-SiBr_2-SiBr_2-SiHR^*_2$ (R* = supersilyl SitBu$_3$),[1] as the latter might be a good starting point for the synthesis of the disilyne $R^*_2HSi-Si{\equiv}Si-SiHR^*_2$ (for a discussion of the disilyne problem see ref.[2]). Unfortunately, the spatially overcrowded 1,2-bis[(disupersilyl)silyl]disilane could only be dibrominated, probably for steric reasons (Scheme 1). The debromination of 1,2-dibromo-1,2-bis[(disupersilyl)silyl]disilane (**1**) with supersilylsodium, NaR*, leads to the disilene **2** as the main product, which was isolated as yellow, oxygen- and water-sensitive crystals [cf. Scheme 1; $\delta(^{29}Si)$ = 144.3 for the unsaturated silicon atoms].[3] Compound **2** slowly decomposes even at −20 °C with formation of the colorless product **3**.

Besides the above-mentioned yellow crystals, red crystals of the cyclotetrasilene **4** were also obtained (Scheme 1).[3] This compound may be formed by the elimination of two molecules of hydrogen bromide in the presence of NaR*, possibly via the desired disilyne $R^*_2HSi-Si{\equiv}Si-SiHR^*_2$ as a short-lived intermediate, although, of course, other pathways for the formation of **4** are also possible.

Obviously, the steric overcrowdedness of the (disupersilyl)silyl groups $SiHR^*_2$ used as substituents is not sufficient to stabilize a disilyne against further reactions. Therefore, we turned to the sterically more overcrowded methyldi(supersilyl)silyl group $SiMeR^*_2$ and first tried to prepare a disilene (R^*_2MeSi)HalSi=SiHal(SiMeR^*_2), the dehalogenation of which might lead to an isolable disilyne $R^*_2MeSi-Si{\equiv}SiMeR^*_2$. Here we report on the synthesis, structure and dehalogenation of the disilene (R^*_2MeSi)ClSi=SiCl(SiMeR^*_2).

(NB: We also make use of the sterically overloaded trimesitylsilyl group $SiMes_3$ and prepared a disilane $Mes_3Si-SiH_2-SiH_2-SiMes_3$.[4] Unfortunately, the extreme insolubility of this compound has prevented further experiments for the present.)

Results and Discussion

Synthesis of (R^*_2MeSi)ClSi=SiCl(SiMeR^*_2)

Whereas $R^*_2HSi-SiH_2-SiH_2-SiHR^*_2$ is easily prepared by dehalogenation of $R^*_2HSi-SiH_2Cl$ with so-

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[‡] On the Way to a Disilyne RSi≡SiR, II. − Part I: Ref.[3] Compounds of Silicon and Homologues, 153. − Part 152: N. Wiberg, T. Blank, H. Nöth, M. Suter, M. Warchhold, *Eur. J. Inorg. Chem.* **2002**, 929−934.
Unsaturated Silicon Compounds, 60. − Part 59: Ref.[3]

[‡‡] Mass spectra.

[‡‡‡] X-ray structure analysis.

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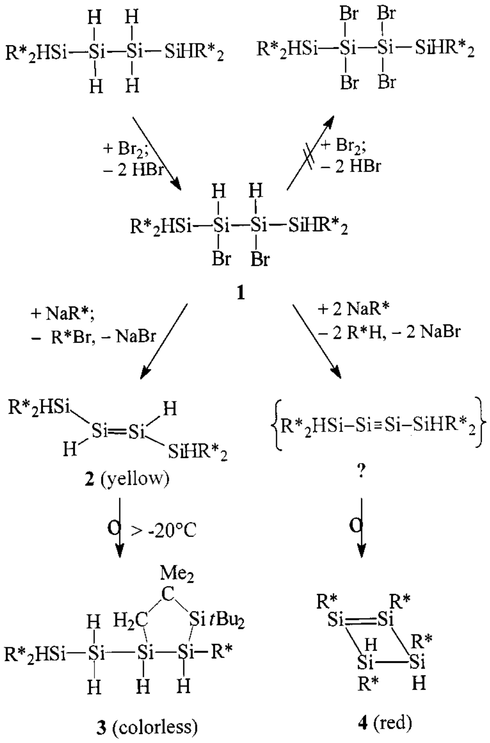
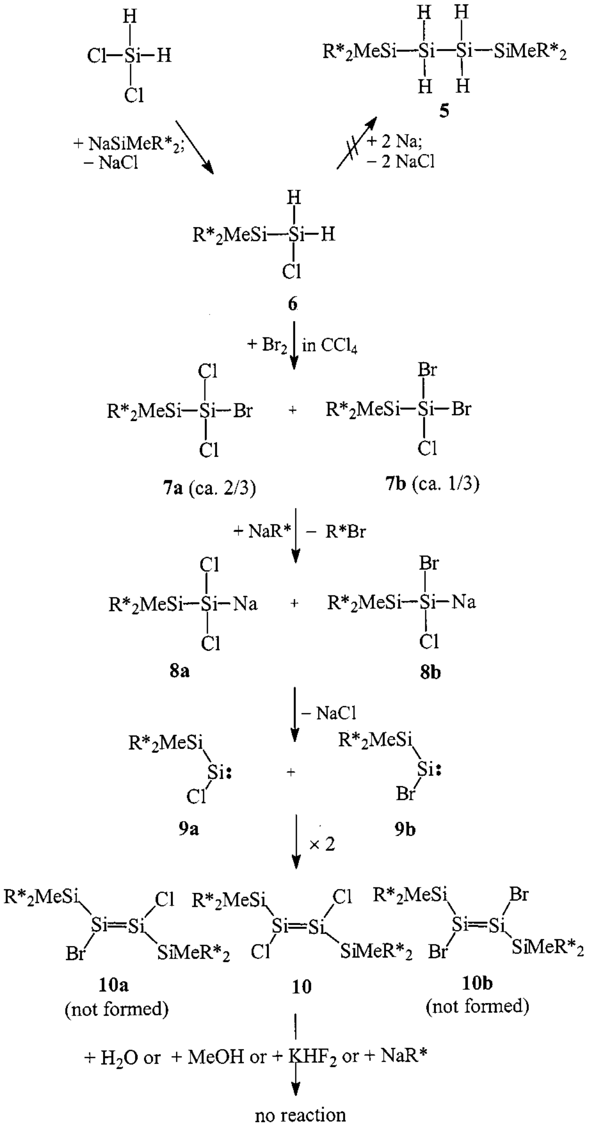


Scheme 1. Synthesis of the bis(silyl)disilane **1** and its reaction with supersilylsodium NaR* with formation of the disilene **2** (thermolysis under isomerization into product **3**) and the cyclotetrasilene **4** (R* = Si*t*Bu$_3$)

dium,[1] the same reaction is unsuitable for synthesizing $R^*_2MeSi-SiH_2-SiH_2-SiMeR^*_2$ (**5**) from $R^*_2MeSi-SiH_2Cl$ (**6**) and sodium (Scheme 2), probably for steric reasons. As a consequence, the reactions that lead to a disilene and, possibly, to a disilyne with $SiHR^*_2$ substituents (Scheme 1) are not practicable to obtain the corresponding compounds with $SiMeR^*_2$ substituents. However, we recently found that disilenes $R^*XSi=SiXR^*$ (X = Cl, Br, I) are intermediates in the reactions of silanes R^*SiX_3 with supersilylsodium NaR*.[5,6] We therefore tried to synthesize $R^*_2MeSi-SiX_3$ compounds and then to transform these into disilenes $(R^*_2MeSi)XSi=SiX(SiMeR^*_2)$. Indeed, the bromination of compound **6**, which was prepared by reaction of $NaSiMeR^*_2$ and SiH_2Cl_2,[6] with bromine in CCl_4 at 0 °C leads to a mixture of $R^*_2MeSi-SiCl_2Br$ (**7a**) and $R^*_2MeSi-SiClBr_2$ (**7b**) in a molar ratio of ca. 2:1 (Scheme 2), which we were not previously able to separate into its components by fractional crystallization.[1] Obviously, CCl_4 also acts as a halogenating agent for **6**. Heating a mixture of NaR* and **7** (mole ratio ca. 1.1:1) in tetrahydrofuran (THF) from −78 °C to room temperature causes the initial dark-red solution to become orange, and an orange residue precipitates slowly (in hours) leaving a nearly colorless solution. According to the mass spectrum, the amorphous residue is the disilene $(R^*_2MeSi)ClSi=SiCl(SiMeR^*_2)$ (**10**). This disilene forms crystals suitable for X-ray structure analysis (see below) after warming the residue for several weeks in benzene at 50 °C.



Scheme 2. Synthesis of the silylsilanes **7** and their reactions with NaR* with formation of the bis(silyl)disilene **10** (R = Si*t*Bu$_3$)

We have not studied in the mechanism of formation of **10** in detail. although we believe that the first step of the action of NaR* on **7** must involve an exchange of bromine for sodium with formation of the deep-red silanides **8**, which then eliminate NaCl with formation of the silylenes **9**. This proposal is supported by the extensively studied reaction of R^*SiCl_2Br (the same is valid for R^*SiBr_3, R^*SiI_3) with NaR* in THF which leads, at −78 °C, to the deep-colored silanide $NaSiCl_2R^*$ (no exchange of chloride for sodium has been observed).[5,6] $NaSiCl_2R^*$ then eliminates NaCl at about −50 °C to give the silylene R*SiCl, which inserts into the Na−Si bond of its precursor with formation of the disilanide $Na-R^*SiCl-SiCl_2R^*$.[6] The latter finally eliminates NaCl above −20 °C to give $R^*ClSi=SiClR^*$ as a short-lived intermediate.[7] An insertion of the silylenes **9** into the Na−Si bond of their precursors **8**, with formation of disilanides possessing four-coordinate central Si atoms, is unlikely for steric reasons (see below), therefore it makes sense that the disilene **10** is the product of a silylene dimerization (Scheme 2).

Of the three disilenes **10**, **10a**, **10b** conceivable as products of the dehalogenation of **7** with NaR* (cf. Scheme 2), only one disilene (**10**) is obtained. Furthermore, compound **10** precipitates from the THF solution only after several hours, but then is basically insoluble. These facts point to the existence of relatively long-lived silylenes **9** in solution at room temperature, whereby **9a**, which is obviously stable in the presence of NaR* (see below), slowly dimerizes to give **10**. The reaction of **9b** with **9a** or another molecule of **9b** is excluded for steric reasons, although excess NaR* may debrominate **9b** (see below). These proposals are confirmed by recently published results,[8] which show that the silylene $[(Me_3Si)_3C]BrSi{\cdot}D$ [D = THF or, more probably, Br^-; prepared from $(Me_3Si)_3C{-}SiBr_3$ and $LiC_{10}H_8$; trapped by alcohols or dienes] is metastable in THF at room temperature.

Characterization of $(R^*{}_2MeSi)ClSi{=}SiCl(SiMeR^*{}_2)$

The disilene **10** is the first silicon compound with halogen atoms bound to unsaturated silicon atoms to be isolated as a pure substance. Its characterization (see below) improves our knowledge of disilenes, whose syntheses, reactivity and geometric and electronic structures have been thoroughly studied in the last 20 years. In fact, up to date ca. 40 disilenes have been isolated and many disilenes are proved as intermediates (cf. in this connection the reviews, summarized in refs.[9−14]).

The disilene **10** forms orange-red crystals that are practically insoluble in organic solvents such as alkanes, benzene and THF. As a consequence, we have not yet been able to obtain NMR spectra for **10** even at slightly raised temperatures (see below). The orange solution that is first obtained after warming a mixture of **7** and NaR* to room temperature shows three ^{29}Si NMR signals in regions expected for unsaturated silicon atoms: δ = 153.9 (less intense), 140.9 (more intense) and 91.5 (less intense). The signals at δ = 153.9 and 140.9 are probably not due to the disilene **10** or a mixture of disilenes **10**, **10a**, **10b** as one would expect only one low-field ^{29}Si signal for **10**, and four signals for **10**, **10a** and **10b** (the normal regions for $>Si{=}Si<$ with four aryl substituents, two aryl and two silyl substituents or four silyl substituents are δ = 60−90, 90−130 and 140−160, respectively[14,15]). If, on the other hand, the reaction mixture contained the silylenes **9a** and **9b**, one would expect two low-field ^{29}Si signals (the normal regions for $>Si\mathbf{:}$ with aminyl substituents or alkyl substituents are δ = 70−100 and >500, respectively[16]). For a discussion of the signal at δ = 91.5 see below.

In the Raman spectrum the Si=Si double bond vibration occurs at 589 cm^{-1} (for comparison:[14,15,17] $Mes_2Si{=}SiMes_2$: 539 cm^{-1}; Mes(*t*Bu)Si=Si(*t*Bu)Mes: 522 cm^{-1}; R*PhSi=SiPhR*: 592 cm^{-1}. See also ref.[18]).

The disilene **10** is unreactive towards water, methanol, or hydrogen fluoride and decolorizes very slowly (over several days) when exposed to air. A change of the disilene **10** with three-coordinate central Si atoms to disilanes with four-coordinate central Si atoms is not favorable for steric reasons. In addition, **10** does not react with NaR*. Moreover, it is much more thermally stable than the previously mentioned bis[(disupersilyl)silyl]disilene **2** and only melts at 228 °C with decomposition. Obviously, the methyl(disupersilyl)silyl groups $SiMeR^*{}_2$ are much better substituents for stabilizing the disilenes RXSi=SiXR than the (disupersilyl)silyl groups $SiHR^*{}_2$, and probably the same must be valid for disilynes. Although, there is only a small difference between $SiHR^*{}_2$ and $SiMeR^*{}_2$ its effect is much larger.

Dehalogenation of $(R^*{}_2MeSi)ClSi{=}SiCl(SiMeR^*{}_2)$

To dehalogenate the disilene **10** we combined a suspension of **10** in THF at −78 °C with lithium naphthalenide ($LiC_{10}H_8$) in THF. After heating the reaction mixture to room temperature, all volatile products were evaporated under an oil pump vacuum and the residue was treated with benzene to obtain an orange-red solution with insoluble components (among others LiCl and unchanged **10**). The question then arises: does this oxygen-sensitive solution contain the disilyne $R^*{}_2MeSi{-}Si{\equiv}Si{-}SiMeR^*{}_2$? We have so far been unable to grow crystals from the solution suitable for an X-ray structure analysis. However, the ^{29}Si NMR spectrum of the solution has a signal at δ = 91.5, along with various other signals. This signal appears in a region that might be reasonable for disilyne Si atoms. It is worth mentioning here that the orange solution that is first obtained after warming the mixture of **7** and NaR* to room temperature also shows a less-intense ^{29}Si NMR signal at δ = 91.5 (see above). This could indicate that the dehalogenation of **7** with NaR* might in part not stop at silylenes or disilenes.

The mass spectrum of the solution obtained in chemical ionization mode indicates the presence of chlorine-free molecules with the mass of the desired disilyne $R^*{}_2MeSi{-}Si{\equiv}Si{-}SiMeR_2$ plus two oxygen atoms. The dehalogenation of **10** in THF might, in fact, give a disilyne in solution, which, due to its extreme sensitivity towards air, might react with molecular oxygen when transferring it into the mass spectrometer. This result corresponds to the observation that the mass spectrum of a solution of tetrasupersilyl-*tetrahedro*-tetrasilane[19] shows a mass peak for the tetrahedrane dioxide $R^*{}_4Si_4O_2$, as well as for the expected tetrahedrane $R^*{}_4Si_4$.[7]

Structure of $(R^*{}_2MeSi)ClSi{=}SiCl(SiMeR^*{}_2)$

Figure 1 shows the structure of the disilene **10** (local symmetry C_i) in the crystal (orange-red prisms, triclinic, $P\bar{1}$) together with selected bond lengths and angles.

The central SiClSi=SiClSi framework of **10** is practically planar (torsion angles at $>Si{=}Si<$ ca. 0°, angles sum at $>Si{=}$ ca. 360°) with both the chlorine atoms and the $SiMeR^*{}_2$ groups in *trans*-positions. Only a few disilenes (*trans*-RR′Si=SiR′R with R/R′ = Mes/*t*Bu, 2,4,6-$iPr_3C_6H_2$/*t*Bu or 2,4,6-$iPr_3C_6H_2/SiMe_3$) have similar struc-

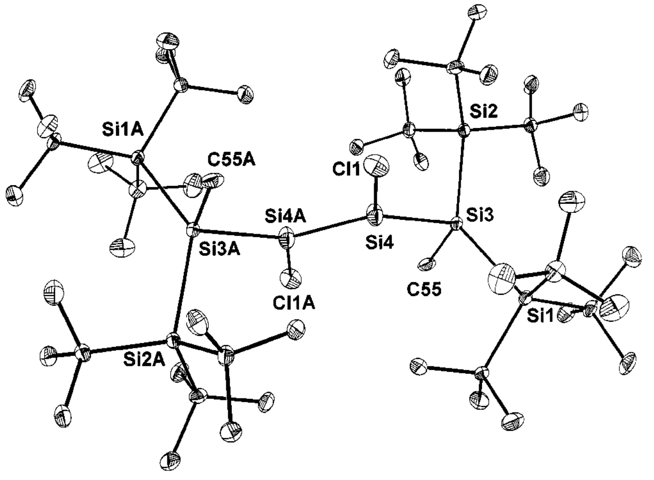


Figure 1. View of the molecule **10** (local symmetry C_i) in the crystal (ORTEP; H atoms excluded for clarity); selected bond lengths [Å] and angles [°]: Si1−Si2 2.553(3), Si2−Si3 2.531(3), Si3−Si4 2.401(3), Si4−Si4A 2.163(4) Si4−Cl1 2.091(3), Si3−C55 1.900(7), Si−C (mean value) 1.96; Si1−Si3−Si2 136.3(1), Si1−Si3−Si4 105.9(1), Si2−Si3−Si4 102.9(1), Si3−Si4−Si4A 132.0(2), Cl1−Si4−Si3 120.8(1), Cl1−Si4−Si4A 106.8(2), C55−Si3−Si1 101.3(2), C55−Si3−Si2 104.1(2), C55−Si3−Si4 102.0(3), C−Si−C (mean value) 109.7, C−Si−Si (mean value) 109.2; Si3−Si4−Si4A−Si3 180.0, Cl1−Si4−Si4A−Cl1A 180.0, Cl1−Si4−Si4A−Si3A 7.5, Cl1−Si4−Si3−C55 179.2, C55−Si3−Si3A−C55A 180.0, Cl1−Si4−Si3−Si1 73.6, Cl1−Si4−Si3−Si2 73.1, Si4A−Si4A−Si3−C55 9.2

tures, the other structurally studied disilenes show *trans*-bent angles between the >Si planes and the Si=Si vectors of up to 35° and/or twist angles of the >Si planes around the Si=Si bond of up to ca. 25°.[14,15] Obviously, the planar conformation of the central structural element of **10** is a consequence of a special three dimensional expansion of the SiMeR*$_2$ substituents at the Si=Si double bond. As mentioned previously, we believe that **10** is formed by dimerization of the silylene (R*$_2$MeSi)ClSi**:** (**9a**) which, as is normal for silylenes, should be in the singlet state (cf. Scheme 2 and ref.[6]). The approach of two such species must occur on the reaction coordinate with a *trans*-bent orientation of the silylene planes;[15] this requires a slowing down of the rate of dimerization.

The Si atom of one R* group of each SiMeR*$_2$ substituent is found above the Si atom of the other R* group below the central SiClSi=SiClSi plane, whereas the C atom of the Me group of each SiMeR*$_2$ substituent is located in the SiClSi=SiClSi plane. These Me groups are *trans* to each other (Me and Cl in *cis*-position). The same is true for the Si−Si−Si planes of both the SiMeR*$_2$ substituents, where the angle between the SiClSi=SiClSi and Si−Si−Si planes is 86.7°.

The Si=Si double bond in **10** is short (2.16 Å), despite the steric overcrowdedness of the SiMeR*$_2$ substituents. The Si=Si distances of acyclic tetraorganyl- or diorganyldisilyldisilenes lie typically in the range 2.14−2.16 Å, whereas the Si=Si distances in acyclic tetrasilyldisilenes can be as long as 2.25 Å.[9,14,15] Obviously, **10** possesses a comparatively strong double bond (see also the section describing the Raman spectrum above).

As a consequence of steric hindrance the R*$_2$MeSi−Si distances (2.40 Å) and especially the R*−Si (2.54 Å) and Si−Cl distances (2.09 Å) exceed the normal Si−Si and Si−Cl single bond lengths of 2.34 Å and 2.03 Å,[20] respectively. In addition, the Si−Si=Si and the Si−Si−Si angles (132.0° and 136.3°) are large. The central saturated Si atom of the $=\mathrm{Si}\boldsymbol{Si}\mathrm{MeR}^*_2$ moiety forms a flat pyramid (angles sum 345°) with its three Si neighbors, whereby the Me group at the top of the $\boldsymbol{Si}\mathrm{Si}_3$ pyramid is nearly symmetrically placed with regard to the three other Si atoms (C−Si−Si angles 101−104°).

Experimental Section

All experiments were carried out in flame-dried glassware using standard Schlenk techniques under dry argon or nitrogen. Air and moisture were strictly excluded. The solvents (pentane, benzene, THF) were distilled from sodium/lead or sodium/benzophenone. Br_2, MeOH, KHF_2, C_6D_6 are available commercially and were used without further purification. The following compounds were synthesized according to literature procedures: **6**,[1] NaR*·2THF,[21] $LiC_{10}H_8$/THF.[22]

NMR Spectra: Jeol GX-270 ($^1H/^{13}C/^{29}Si$: 270.17/67.94/53.67 MHz) and a Jeol EX-400 ($^1H/^{13}C/^{29}Si$: 399.78/100.54/79.43 MHz). The NMR spectra were recorded conventionally or with the INEPT and DEPT pulse sequences using empirically optimized parameters for the mentioned groups. Mass Spectra: Jeol MStation JMS 700. The mass spectra were recorded by electron ionization (EI) or chemical ionization (CI; NH_3 and $Me_2C=CH_2$ as ionization agents). Raman Spectra: Perkin−Elmer, 2000 NIR FT-Raman with Na-YAG Laser (1064 nm).

Synthesis of 7a/7b: These compounds were synthesized as described elsewhere[1] by adding Br_2 (3.37 mmol) dropwise to a solution of **6** (1.69 mmol) in CCl_4 (15 mL) at 0 °C. After 5 min all volatile components were removed with an oil-pump vacuum. The remaining residue consisted of **7a**, **7b** and R*$_2$MeSiBr in the mol ratio ca. 6:3:2 (R*$_2$MeSiBr is possibly formed by Si−Si bond cleavage of **6**; identification of the products was by comparison with authentic samples[1]). The mixture could not be separated by recrystallization.

Synthesis and Characterization of the Disilene 10: A solution of NaR*·2THF (22 mmol) in THF (40 mL) was dropped slowly into a solution of **7a/7b** (ca. 20 mmol, 12.4 g; ca. 13.7 mmol **7a** and 5.9 mmol **7b** according to the NMR spectrum) in pentane (7 mL) at −78 °C (as stated above, the mixture of **7a/7b** also contains some R*$_2$MeSiBr) to give a dark-red reaction mixture (possibly due to the formation of silanides **8** and of NaSiMeR*$_2$). In the course of warming this mixture to room temperature, the color changed to orange-red (formation of silylenes **9**?). An insoluble precipitate was slowly formed from the solution over several hours and the color lightened. After removing all the volatile components under an oil-pump vacuum, the residue was extracted for 4 h with 10 mL of boiling benzene. The disilene *trans*-1,2-dichloro-1,2-bis[methyl(disupersilyl)silyl]disilene (**10**) (1.20 g, 1.19 mmol; ca. 12%) precipitated from this benzene extract upon cooling, and was isolated at room temperature by filtration (m.p. 228 °C with decomposition). The disilene **10**: (i) is practically insoluble in benzene, alkanes or THF, (ii) does not react with either water or methanol, (iii) reacts very slowly with oxygen (decolorization in air only after eight days), and (iv) is also unreactive towards HF (used as KHF_2) and NaR* (no reaction after 3 weeks at 60 °C in THF). Disilene **10** crystallizes after warming to 50 °C in benzene for several weeks. As a consequence of the insolubility of **10**, no NMR spectra of the disilene could be obtained. MS (EI): m/z (%) = 1012/1010/1008 (24) [M^+], 955/953/951 (33) [$M^+ - t\mathrm{Bu}$], 869/867/865 (15) [$M^+ - t\mathrm{Bu} - 2C_3H_7$], 813/811/809 (56) [$M^+ - R^*$], 775/773 (32) [$M^+ - R^*H - Cl$], 755/753/751 (15) [$M^+ - R^*H - t\mathrm{Bu}$], 613/611/609 (28) [$M^+ - R^*H - R^*$], 575/573 (100) [$M^+ - R^*Cl - R^*$]; all isotopic patterns agree well with the calculated spectrum. Raman (Nujol mull): $\tilde{\nu}$ = 123 cm^{-1} s, 277 w, 295 w, 559 m, 589 s (Si=Si), 647 w, 816 m, 1180 s, 1451 w, 1469 w, 2852 w. No analytic data were obtained. For the X-ray structure analysis see Figure 1.

Remarks: As mentioned previously, **10** precipitates only slowly from the reaction mixture of **7** and NaR* in pentane/THF at room temperature. The freshly prepared solution shows three ^{29}Si NMR signals in the low-field region (as well as other signals at higher field) at δ = 153.9, 140.9, 91.5 as discussed above.

Reaction of the Disilene 10 with $LiC_{10}H_8$: A solution of $LiC_{10}H_8$ (0.154 mmol) in THF (1.4 mL) was added dropwise to a suspension of **10** (0.079 g, 0.078 mmol) in THF (3 mL) at −78 °C to give a dark-red reaction mixture. The color of this mixture changed to light orange whilst warming to room temperature. After removal of all the volatile components under an oil-pump vacuum (including naphthalene), the remaining residue was combined with 1 mL of C_6D_6. After 4 weeks at 6 °C the obtained suspension contained no crystals suitable for X-ray structure analysis. The solution showed one ^{29}Si NMR signal in the low-field region (besides other signals at higher field): δ = 91.5 (see above). The MS of the solution after filtration indicated the presence of one type of chlorine-free molecule with the mass M = (**10** $- Cl_2 + O_2$) = 970.7: MS (CI with $Me_2C{=}CH_2$): m/z (%) = 971 (100) [M^+], 914 (38) [$M^+ - t\mathrm{Bu}$], 772 (26) [$M^+ - R^*$], 740 (40) [$M^+ - R^* - C_3H_6$], 442 (25) [$R^*{}_2MeSi^+$]. MS (CI with NH_3): m/z (%) = 972 (20) [$M^+ + H$], 914 (2) [$M^+ - t\mathrm{Bu}$], 459 (43) [$R^*{}_2MeSi^+ + NH_3$], 442 (92) [$R^*{}_2MeSi^+$], 217 (100) [$R^{*+} + NH_3$]. The MS of the components that are insoluble in benzene indicated the presence of **10** as well as **10** $- Cl_2 + O_2$.

X-ray Structure Determination of 10: Orange-red prisms, 0.1 × 0.1 × 0.1 mm, $C_{50}H_{114}Cl_2Si_4$, M_r = 1011.04, triclinic, space group $P\bar{1}$, a = 9.020(1), b = 12.150(1), c = 14.767(1) Å, α = 80.580(2)°, β = 89.118(2)°, γ = 71.221(2)°, V = 1510.4(3) Å^3, Z = 2, $\rho_{calcd.}$ = 1.112 Mg m^{-3}, μ = 0.297 mm^{-1}, $F(000)$ = 560. Data collection: 2θ = 3.60−43.44°, $-9 \le h \le 9$, $-12 \le k \le 12$, $-15 \le l \le 15$, 5854 reflections of which 2997 were independent (R_{int} = 0.0496) and 2116 [$F > 4\sigma(F)$] refined. All non-hydrogen atoms were refined anisotropically and the H atoms were included in calculated positions. R_1 = 0.0681, wR_2 = 0.1648 [$F > 4\sigma(F)$], GOOF (F^2) = 1.031; max./min. residual electron density 1.377/−0.474 Å^3.

The intensities were measured with a Siemens SMART Area-detector (Mo-K_α, λ = 0.71073 Å). The crystals were mounted in perfluoropolyether oil at 193(2) K. The structure was solved by direct methods and refined against F^2 for all observed reflections. Structure solution with SHELXS-97 (Sheldrick, 1990), and refinement with SHELXL-97 (Sheldrick, 1997).

CCDC-171748 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

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