Aminochlorodisilanes: precursors to multifunctionalized disilane derivatives

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Abstract

Multifunctionalized disilane derivatives containing silicon bonded to such elements as carbon, chlorine, hydrogen, nitrogen and iron were synthesized from bis(trimethylsilyl)aminopentachlorodisilane (1), 1,2-bis[bis(trimethylsilyl)amino]tetrachlorodisilane (2) or bis(phenyldimethylsilyl)aminopentachlorodisilane (3). 1, 2 and 3 were easily prepared from the reaction of Si_2Cl_6 with one or two equivalents of $LiN(SiMe_3)_2$ or $LiN(SiMe_2Ph)_2$, respectively. Partially hydrogenated chlorodisilanes were obtained from the corresponding aminodisilanes and dry HCl. © 1997 Elsevier Science S.A.

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1. Introduction

Amino groups can be easily attached to silicon by employing the reaction of halosilanes with amines or alkali metal amides using standard literature procedures [1]. In a recent study, we were able to demonstrate that $-NR_2-$ groups can even be introduced into rather reactive oligosilane molecules, such as $H_3SiSiXHSiXH-SiH_3$ or $XH_2SiSiH_2SiH_2SiH_2X$ (X = Cl, Br), if mild reaction conditions are applied [2]. In general, the Si–N bonds in silyl amines proved to be rather stable against nucleophilic attack subsequently allowing chemical reactions to be carried out at the Si-center without the $Si-NR_2$ moiety being affected. For instance, in amino substituted silyl triflates such as $(Et_2N)_2MeSi-OTf$ the triflate group can be substituted by MeO^-, $LiSiPh_3$ or LiR (R = alkyl) while the Si–N bond remains intact [3]. The stability of Si–N linkages is even enhanced if more than one Si-atom is attached to nitrogen or bulky substituents like *t*-butyl or aryl-groups are present. Consequently, silazanes or cyclosilazanes are moderately stable towards hydrolysis and can be easily metallated with alkyl- or aryl-alkali metal compounds [4]. In organic chemistry the bulky *t*-butyl-diphenylsilyl group is used for protecting primary amines to various alkylating and acylating agents, to basic and hydrolytic reaction condi-

tions or in order to allow chromatography [5]. Despite of the relative stability of Si–N bonds they are readily cleaved by acids and various electrophiles, both organic and inorganic. The hydrogen halides or their acids, for instance, readily convert triorganoaminosilanes to the appropriate halosilanes R_3SiX (X = F, Cl, Br) [6,7]. This provides an excellent route for the removal of amino substituents from silicon substrates with concurrent formation of Si–halogen bonds.

The ease with which Si–N bonds can be made and broken together with the remarkable chemical stability of aminosilanes towards various nucleophiles, provides an attractive basis for the synthesis of multifunctionalized polysilane derivatives. In this paper we report the synthesis of priorily unknown polychlorodisilanes bearing $(R_3Si)_2N-$ groups and their facile conversion to multifunctionalized disilanes by various selective substituent exchange reactions. Compounds of this type may be useful for the study of substituent/substituent interactions in polysilanes and as potential precursors to extended functionalized polysilane frameworks.
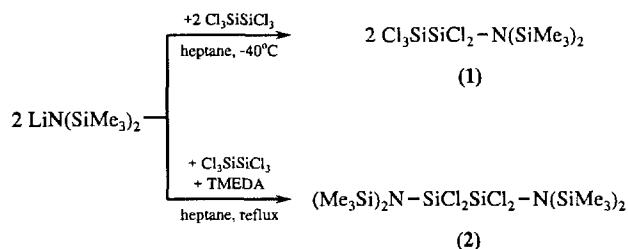
2. Results and discussion
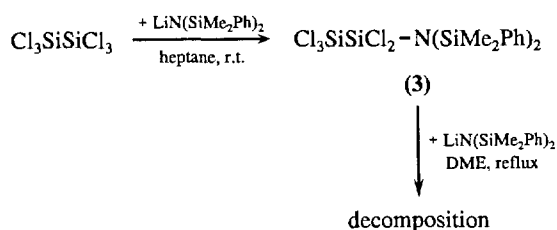
2.1. Synthesis of bissilylaminochlorodisilanes

When Si_2Cl_6 is reacted with one equivalent of $LiN(SiMe_3)_2$ under mild reaction conditions (−40°C,

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heptane solution), the monosubstituted product bis(trimethylsilyl)aminopentachlorodisilane (1) is obtained nearly exclusively. The introduction of a second $(Me_3Si)_2N$-group requires the presence of stoichiometric amounts of strong Lewis bases such as TMEDA in order to enhance the reactivity of the lithium amide reagent:

$$2\ LiN(SiMe_3)_2 \begin{cases} \xrightarrow[\text{heptane, -40°C}]{+2\ Cl_3SiSiCl_3} & 2\ Cl_3SiSiCl_2-N(SiMe_3)_2 \quad (1) \\ \\ \xrightarrow[\text{heptane, reflux}]{\substack{+\ Cl_3SiSiCl_3 \\ +\ TMEDA}} & (Me_3Si)_2N-SiCl_2SiCl_2-N(SiMe_3)_2 \quad (2) \end{cases}$$

Attempts to attach more than two $(Me_3Si)_2N$- groups to the disilane moiety failed even under harsh conditions (excess $LiN(SiMe_3)_2$ and TMEDA, refluxing THF or DME, prolonged reaction times). ^{29}Si-NMR indicated that increasing amounts of unidentified decomposition products arising from Si–Si bond scission and redistribution reactions had been formed. Presumably the relatively low nucleophilic character of the $(R_3Si)_2N$- group combined with its steric bulk prevent the introduction of the third amino substituent, what is substantiated by the observation, that only the monosubstitution product 3 can be synthesized by the reaction of Si_2Cl_6 with the extremely bulky amide $LiN(SiMe_2Ph)_2$ even in the presence of TMEDA:

$$Cl_3SiSiCl_3 \xrightarrow[\text{heptane, r.t.}]{+\ LiN(SiMe_2Ph)_2} Cl_3SiSiCl_2-N(SiMe_2Ph)_2 \quad (3)$$

$$\downarrow \substack{+\ LiN(SiMe_2Ph)_2 \\ DME,\ reflux}$$
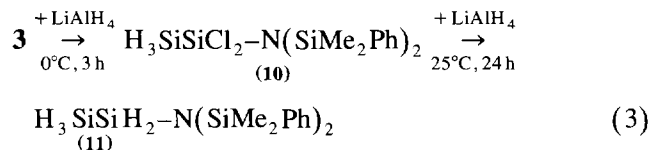
$$decomposition$$

2.2. Chemical properties of bissilylaminochlorodisilanes

The stability of Si–N bonds towards nucleophilic attack allows the introduction of additional functional groups into the bissilylaminochlorodisilanes 1, 2 and 3. This leads to the formation of multifunctionalized disilane derivatives (Scheme 1). Treatment of 1 with t-butyllithium or with the transition metal anion $[Fe(CO)_2Cp]^-$ cleanly affords the corresponding α,β-disubstituted tetrachlorodisilanes 4 and 5 without any
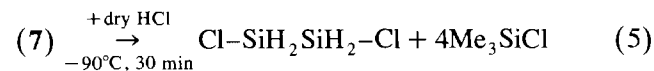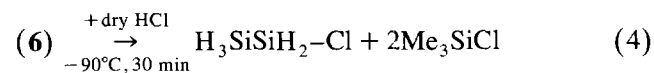
detectable scission of the Si–N linkages. Furthermore, hydrogenation of the remaining Si–Cl bonds in 1, 2, 4 and 5 using $LiAlH_4$ in diethylether at 0°C can be used to prepare the priorily unknown disilanyl hydrides 6, 7, 8 and 9, respectively, in excellent yields. Cleavage of the Si–Si, Si–Fe or the Si–N bond is not observed.

When the highly sterically hindered compound 3 is treated with $LiAlH_4$ the partially hydrogenated derivative 10 is primarily obtained. Only after prolonged reaction times can 10 be further hydrogenated to yield the perhydroaminodisilane 11:

$$3 \xrightarrow[\substack{0°C,\ 3\ h}]{+LiAlH_4} H_3SiSiCl_2-N(SiMe_2Ph)_2 \xrightarrow[\substack{25°C,\ 24\ h}]{+LiAlH_4}$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad (10)$$
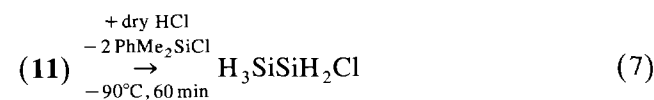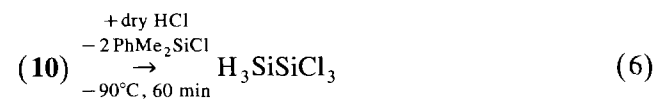$$H_3SiSiH_2-N(SiMe_2Ph)_2 \quad\quad\quad\quad (3)$$
$$\quad (11)$$

2.3. Chlorinating reactions

The general sensitivity of Si–N bonds under acidic conditions can be utilized to remove the amino groups in compounds 6, 7, 8, 10 and 11 from the disilane moiety and to restore the original Si–Cl functionalities. This provides an easy access to partially hydrogenated chlorodisilanes, which are otherwise rather troublesome to obtain. For instance, the attempted synthesis of 1,2-dihalodisilanes X-$(SiH_2)_2$-X (X = Cl or Br) from 1,2-diphenyldisilane and HX usually affords azeotropic mixtures of the corresponding dihalodisilane and benzene [8,9]. When 6 or 7 are stirred with an excess of liquid anhydrous HCl for 30 min at $-90°C$, the corresponding chlorodisilanes $ClSiH_2SiH_3$ or $ClSiH_2SiH_2Cl$ are obtained together with Me_3SiCl, which again cannot be separated by distillation.

$$(6) \xrightarrow[\substack{-90°C,\ 30\ min}]{+\ dry\ HCl} H_3SiSiH_2-Cl + 2Me_3SiCl \quad (4)$$

$$(7) \xrightarrow[\substack{-90°C,\ 30\ min}]{+\ dry\ HCl} Cl-SiH_2SiH_2-Cl + 4Me_3SiCl \quad (5)$$

However, pure Cl_3SiSiH_3 or $ClSiH_2SiH_3$ are easily synthesized from 10 or 11 and HCl under similar conditions because, in this case, the second reaction product $PhMe_2SiCl$ exhibits a much higher boiling point than the desired halodisilanes:

$$(10) \xrightarrow[\substack{-90°C,\ 60\ min}]{\substack{+dry\ HCl \\ -2PhMe_2SiCl}} H_3SiSiCl_3 \quad (6)$$

$$(11) \xrightarrow[\substack{-90°C,\ 60\ min}]{\substack{+dry\ HCl \\ -2PhMe_2SiCl}} H_3SiSiH_2Cl \quad (7)$$

8 can easily be converted to 1-t-butyl-2-chlorodisilane (12) by treatment with dry HCl gas in pentane for 30

$$H_3SiSiH_2-N(TMS)_2 \quad (6)$$

$$(TMS = Me_3Si\text{-})$$
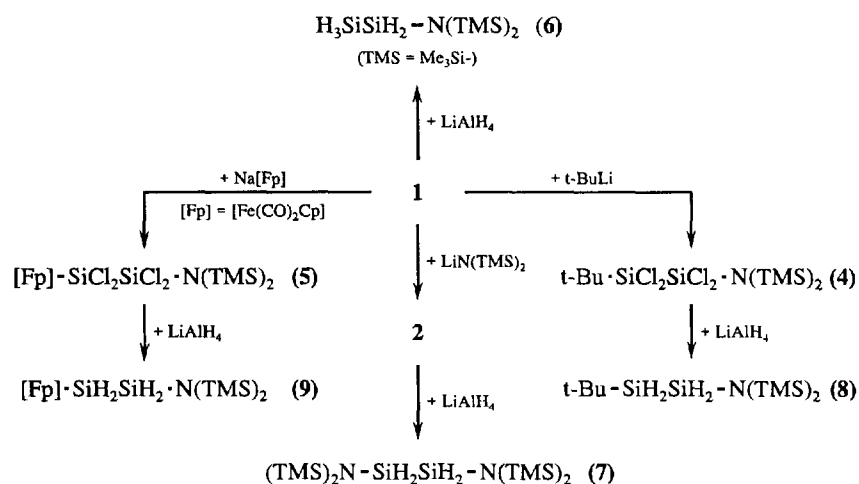
Scheme 1.

min at 0°C. After filtration and distillation pure **12** is obtained in 80% yield:

$$(8) \xrightarrow[\text{pentane,0°C}]{+\text{dry HCl}} (CH_3)_3C-SiH_2SiH_2-Cl \,(12) \qquad (8)$$
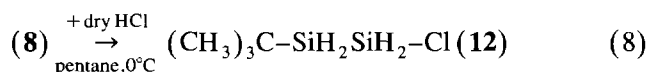
2.4. NMR spectroscopy

All substances were characterized by standard spectroscopic techniques such as MS, IR, ^{1}H- and ^{29}Si-NMR

Table 1
^{29}Si chemical shifts δ[ppm] of multifunctionalized disilane derivatives **1–12** (C_6D_6 solution vs. ext. TMS)

		δSi(1)	δSi(2)	δSi(3)
$\overset{2\ 1}{Cl_3SiSiCl_2}\overset{3}{N(SiMe_3)_2}$	**1**	−19.41	−0.11	+9.50
$\overset{3}{(Me_3Si)_2}N\overset{1}{SiCl_2}SiCl_2 N(SiMe_3)_2$	**2**	−14.55	−	+7.04
$\overset{2\ 1}{Cl_3SiSiCl_2}\overset{3}{N(SiMe_2Ph)_2}$	**3**	−17.26	+0.02	+2.65
$\overset{2}{(CH_3)_3C}\overset{1}{SiCl_2}SiCl_2\overset{3}{N(SiMe_3)_2}$	**4**	−13.79	+17.68	+8.86
$\overset{2}{[Fe(CO)_2Cp]}\overset{1}{SiCl_2}SiCl_2\overset{3}{N(SiMe_3)_2}$	**5**	−12.89	+85.04	+8.21
$\overset{2\ 1}{H_3SiSiH_2}\overset{3}{N(SiMe_3)_2}$	**6**	−49.52	−96.55	+6.27
$\overset{3}{(Me_3Si)_2}N\overset{1}{SiH_2}SiH_2 N(SiMe_335y)_2$	**7**	−45.61	−	+5.56
$\overset{2}{(CH_3)_3C}\overset{1}{SiH_2}SiH_2\overset{3}{N(SiMe_3)_2}$	**8**	−49.98	−38.16	+6.59
$\overset{2}{[Fe(CO)_2Cp]}\overset{1}{SiH_2}SiH_2\overset{3}{N(SiMe_3)_2}$	**9**	−41.89	−44.39	+5.48
$\overset{2\ 1}{H_3SiSiCl_2}\overset{3}{N(SiMe_2Ph)_2}$	**10**	−1.09	−80.73	+2.20
$\overset{2\ 1}{H_3SiSiH_2}\overset{3}{N(SiMe_2Ph)_2}$	**11**	−49.23	−99.32	−2.43
$\overset{2}{(CH_3)_3C}\overset{1}{SiH_2}SiH_2Cl$	**12**	−24.35	−44.49	−

as well as by elemental analysis. As can be expected, ^{29}Si-NMR spectroscopy was found to be particularly useful to prove the proposed structures of the previously unknown disilanes **1–12**. The ^{29}Si-chemical shift values and the ^{29}Si–^{1}H coupling constants depicted in Tables 1 and 2 are as expected.

The coupled ^{29}Si-NMR spectra of the disilanyl hydrides **6–12** exhibit rather complex splitting patterns due to extensive ^{29}Si–^{1}H-coupling. The signals for Si(1) and Si(2) are split into triplets (except for compounds **6**, **10** and **11**, where the SiH$_3$-groups give rise to quartets) by coupling directly to the attached hydrogens. The resulting resonance lines show additional hyperfine structures (except for compound **10** which exhibits an unperturbed quartet for Si(2) due to the absence of β-hydrogens) caused by long range ^{29}Si–^{1}H couplings to the hydrogen atoms at the adjacent silicon atoms and occasionally to the protons of the Me$_3$C-groups. This allows an unequivocal structure assignment in each case.

As in the case of asymmetrical 1,2-disubstituted ethanes, the SiH$_2$ hydrogen atoms in compounds **8**, **9** and **12** are not magnetically equivalent giving rise to AA′XX′ four spin systems [10]. Complex non-first order splitting patterns would therefore be expected in the ^{1}H-NMR spectra. The experimental proton NMR spectra of **8**, **9** and **12**, however, turned out to be surprisingly simple. Each of the spectra of **8** and **9** exhibited two doublets in the Si–H region between 3.5 and 5 ppm. These were occasionally broadened due to long range couplings to the protons of the Me$_3$C- or [Fe(CO)$_2$Cp]-groups, respectively. The spectrum of **12** shows a 1:2:1 triplet at 4.74 ppm and a poorly resolved multiplet at 3.63 ppm (SiH$_2$ triplet further split by the adjacent Me$_3$C- group). This finding, nevertheless, is still consistent with the presence of AA′XX′ spin systems which, under certain conditions, can give spectra with the appearance of a true first order A$_2$X$_2$ (two

Table 2
Selected ^{29}Si–^{1}H coupling constants J[Hz] of multifunctionalized disilanyl hydrides (t = triplet; q = quartet; m = multiplet)

		Si(1)		Si(2)	
		^1J(Si–H)	^2J(Si–H)	^1J(Si–H)	^2J(Si–H)
$\overset{2}{H_3Si}\overset{1}{SiH_2}N(SiMe_3)_2$	6	201.6 (t)	6.4 (q)	188.7 (q)	14.8 (t)
$(Me_3Si)_2NSiH_2\overset{1}{SiH_2}N(SiMe_3)_2$	7	192.5 (t)	14.6 (t)	–	–
$(CH_3)_3C\overset{2}{SiH_2}\overset{1}{SiH_2}N(SiMe_3)_2$	8	194.4 (t)	7.2 (t)	179.5 (t)	m
$[Fe(CO)_2Cp]\overset{2}{SiH_2}\overset{1}{SiH_2}N(SiMe_3)_2$	9	190.3 (t)	7.2 (t)	172.5 (t)	15.7 (t)
$\overset{2}{H_3Si}\overset{1}{SiCl_2}N(SiMe_2Ph)_2$	10	–	9.1 (q)	206.5 (q)	–
$\overset{2}{H_3Si}\overset{1}{SiH_2}N(SiMe_2Ph)_2$	11	202.3 (t)	m	192.9 (q)	m
$(CH_3)_3C\overset{2}{SiH_2}\overset{1}{SiH_2}Cl$	12	205.7 (t)	8.7 (t)	183.1 (t)	m

1:2:1 triplets, compound 12) or of two independent AX spin systems (two 1:1 doublets, compounds 8 and 9) [11]. The shape of the observed spectra only depends upon the relative magnitudes and signs of the coupling constants J_{AX}, $J_{A'X}$, $J_{AA'}$, $J_{XX'}$ and upon the chemical shift difference $\Delta\delta_{AX}$.

3. Experimental

All experiments were performed under a nitrogen atmosphere using standard Schlenk techniques. All solvents were dried with sodium–potassium alloy and distilled under nitrogen prior to use. HCl 4.5, purchased from Messer Grießheim, and hexachlorodisilane, generously donated by Wacker Chemie, Burghausen, Germany, were used without further purification. $(Me_3Si)_2NLi$ and $(PhMe_2Si)_2NLi$ were synthesized as previously reported [12,13].

^{1}H (300.13 MHz), ^{29}Si (59.62 MHz) and ^{13}C (75.4 MHz) NMR spectra were recorded on a Bruker 300-MSL spectrometer in C_6D_6 solution versus ext. TMS. Mass spectra were run either on a HP 5971/A/5890-II GC/MS coupling (HP 1 capillary column, length 25 m, diameter 0,2 mm, 0.33 μm polydimethylsiloxane) or on a Kratos Profile mass spectrometer equipped with a solids probe inlet. Infrared spectra were obtained in Nujol mull on a PERKIN ELMER 883 spectrometer.

3.1. Bis(trimethylsilyl)aminopentachlorodisilane (1)

Twenty-four grams (0.144 mol) of lithium bis(trimethylsilyl)amide dissolved in 200 ml pentane was added dropwise to a solution of 50 g (0.186 mol) of hexachlorodisilane in 100 ml of pentane at $-30°$C. The reaction mixture was allowed to warm to room temperature over a period of 30 min and stirred for additional 3 h. After filtration and removal of the solvent distillation of the liquid residue gave 48.6 g (86%) of 1.

B.p.: 75°C (0.05 mbar). Anal. Found: C, 18.46; H, 4.70%. $C_6H_{18}Cl_5NSi_4$ (393.81) calcd.: C, 18.30%; H, 4.61%. ^{29}Si-NMR: Table 1. ^{1}H-NMR (ext. TMS, ppm) δ: 0.27 (s, –SiMe$_3$). MS (70 eV) m/e (rel. Int.): 393 (0.2 M$^+$), 378 (21 M$^+$–CH$_3$), 280 (100 M$^+$–SiCl$_2$CH$_3$); 258 (16 M$^+$–SiCl$_3$). IR (cm^{-1}, rel. Int.): 1258 vvs, 971 vs, 815 vs, 769 vw, 722 vw, 602 m, 577 s, 556 m, 522 m, 438 s.

3.2. 1,2-Bis[bis(trimethylsilyl)amino]tetrachlorodisilane (2)

A solution of 22.3 g (0.134 mol) of lithium bis(trimethylsilyl)amide and 15.5 g (0.134 mol) of N,N,N',N'-tetramethylethylenediamine in 200 ml heptane was added dropwise to 16 g (0.06 mol) of hexachlorodisilane in 100 ml heptane at $-30°$C. The reaction mixture was allowed to warm to room temperature and then refluxed for 3 h. After filtration and removal of the solvent the monosubstitution product 1 was distilled off at 0.05 mbar. Subsequent crystallization of the oily residue by addition of 100 ml of n-pentane and cooling to $-80°$C gave 22 g (71%) of pure crystalline 2.

M.p.: 72–73°C. Anal. Found: C, 27.52; H, 7.13%. $C_{12}H_{36}Cl_4N_2Si_6$ (518.74) calcd.: C, 27.78; H, 6.99%. ^{29}Si-NMR: Table 1. ^{1}H-NMR (ext. TMS, ppm) δ: 0.22 (s, CH$_3$). MS (70 eV) m/e (rel. Int.): 503 (5 M$^+$–CH$_3$), 395 (3 M$^+$–Me$_3$SiCl), 315 (3 (Me$_3$Si)$_2$NSiCl$_2$SiNMe), 259 (100 M$^+$/2). IR (cm^{-1}, rel. Int.): 948 vs, 864 vs, 759 w, 679 w, 582 w, 539 m, 511 m, 422 m, 401 vw.

3.3. Bis(phenyldimethylsilyl)aminopentachlorodisilane (3)

A solution of 20.4 g (0.07 mol) lithium bis(phenyldimethylsilyl)amide dissolved in 200 ml heptane was added dropwise to a solution of 20 g (0.074 mol) of hexachlorodisilane in 100 ml of heptane at −30°C. Subsequently the reaction mixture was stirred at room temperature for 12 h and finally refluxed for 30 min. After filtration and removal of the solvent 50 ml of n-pentane was added to the oily residue. Cooling the solution to −80°C gave 24.3 g (60%) of colorless crystalline 3.

M.p.: 62–64°C. Anal. Found: C, 37.09; H, 4.33%. $C_{16}H_{22}Cl_5NSi_4$ (517.97) calcd.: C, 37.11%; H, 4.28%. ^{29}Si-NMR: Table 1. ^{1}H-NMR (ext. TMS, ppm) δ: 0.24 (s, 6H, −CH₃); 7.2–7.4 (m, 5H, −C₆H₅). MS (70 eV) m/e (rel. Int.): 517 (12 M⁺), 502 (93 M⁺−CH₃), 482 (14 M⁺−Cl), 466 (14 M⁺−CH₄Cl), 440 (6 M⁺−C₆H₅), 402 (100 M⁺−MeSiCl₂), 382 (82 M⁺−SiCl₃), 366 (96 M⁺−PhMe₂SiN). IR (cm⁻¹, rel. Int.): 1262 s, 1114 s, 1043 w, 998 w, 957 vs, 850 vs, 802 m, 729 s, 703 s, 653 w, 598 w sh, 577 s, 537 w, 475 m, 457 m, 422 w, 388 w, 374 vw, 350 vw, 310 vw.

3.4. 1-t-butyl-1,1,2,2-tetrachloro-2-(bistrimethylsilyl)aminodisilane (4)

A 10.5 ml, 1.7 M solution of tert-butyllithium in hexane were slowly added to 12.7 g (0.032 mol) of 1 dissolved in 70 ml of heptane at −70°C. Subsequently the reaction mixture was stirred at room temperature for 12 h. After filtration of the salts and removal of the solvents distillation of the liquid residue under reduced pressure afforded 5.6 g (76%) of liquid colorless 4.

B.p.: 94–96 °C (0.1 mbar). Anal. Found: C, 29.11; H, 6.45; Cl, 34.13%. $C_{10}H_{27}Cl_4NSi_4$ (415.47) calcd.: C, 28.91; H, 6.55; Cl, 34.13%. ^{29}Si-NMR: Table 1. ^{1}H-NMR (ext. TMS, ppm) δ: 0.35 (s, 18 H, Si−CH₃); 1.13 (s, 9H, C−CH₃). MS (70 eV) m/e (rel. Int.): 415 (0.7 M⁺); 400 (100 M⁺−CH₃), 364 (2 M⁺−CH₃Cl), 326 (0.8 M⁺−Me₄Si), 302 (3.7 M⁺−CH₃SiCl₂). IR (cm⁻¹, rel. Int.): 1270 m, sh, 1256 s, 1007 w, 961 s, 855 s, 816 w, sh, 770 w, 722 w, 679 w, 655 w, 623 w, 585 w, 559 s, 539 m, 514 m, 465 m, 404 m.

3.5. 1-[(Dicarbonyl)cyclopentadienyliron]-1,1,2,2-tetrachloro-2-(bistrimethylsilyl)aminodisilane (5)

A solution of Na[Fe(CO)₂Cp], prepared by the cleavage of 1.4 g of [Fe(CO)₂Cp]₂ with Na/Hg in 150 ml of THF [14], was added dropwise to 3.1 g of 1 in 100 ml heptane at −70°C. After the reaction mixture has been stirred at room temperature for 3 h the solvents were stripped off, 150 ml of pentane was added and the salts were removed by filtration over celite. Recrystallization

of the resulting red oily residue from n-pentane at −80°C gave 3.2 g (76%) of yellow crystalline 5.

M.p.:128–130°C. Anal. Found (M⁺): 532.8914. $C_{12}H_{13}NO_2Si_4{}^{35}Cl_4$ calcd.: 532.8909. ^{29}Si-NMR: Table 1. ^{1}H-NMR (ext. TMS, ppm) δ: 0.47 (s, 18H, −SiMe₃); 4.21 (s, 5H, C₅H₅⁻). ^{13}C-NMR (ext. TMS, ppm) δ: 211.94 (CO); 85.45 (C₅H₅⁻); 6.40 (−CH₃). MS (70 eV) m/e (rel. Int.): 535 (3 M⁺), 520 (20 M⁺−CH₃), 507 (7 M⁺−CO), 479 (5 M⁺−2CO), 186 (19 Cp₂Fe), 93 (100 CpSi). IR (cm⁻¹, rel. Int.): 2031 vs, 1985 vs, 984 vs, 955 vs, 632 s, 590 s, 553, m, 524 m, 502 m, 485 m, 402 w, 280 w.

3.6. Bis(trimethylsilyl)aminodisilane (6)

Eight milliliters of a 2 M solution of lithiumaluminumhydride in diethylether were slowly added to 12.7 g (0.032 mol) of 1 dissolved in 100 ml of pentane at 0°C. Subsequently the reaction mixture was stirred at room temperature for 2 h. Aqueous workup with 2 M H₂SO₄ and distillation of the resulting colorless liquid at reduced pressure afforded 6.7 g (93.8%) of pure 6.

B.p.: 32°C (0.1 mbar). Anal. Found: C, 32.27; H, 10.50%. $C_6H_{23}NSi_4$ (221.60) calcd.: C, 32.52; H, 10.46%. ^{29}Si-NMR (ext. TMS, ppm): Tables 1 and 2. ^{1}H NMR (ext. TMS, ppm) δ: 0.17 (s, 18H, −SiMe₃); 3.27 (m, 3H, −SiH₃); 4.84 (m, 2H, =SiH₂). MS (70 eV) m/e (rel. Int.): 221 (22 M⁺); 206 (86 M⁺−CH₃), 190 (100 M⁺−SiH₃) 174 (47 M⁺−CH₃SiH₄) IR (cm⁻¹, rel. Int.): 2142 s, 1252 vs, 931 vs, 896 w, 870 w, 842 s, 802 vs, 721 vw, 681 vw.

3.7. 1,2-bis[bis(trimethylsilyl)amino]disilane (7)

Following the procedure above 10 g (0.019 mol) of 2 were reacted with 19.3 ml of a 2 M solution of lithiumaluminumhydride in diethylether. After addition of 15 ml of n-pentane to the resulting yellow oil and cooling to −80°C 6.5 g (90%) of white crystalline 7 could be isolated.

M.p.: 65–67°C. Anal. Found: C, 37.86; H, 10.40%. $C_{12}H_{40}N_2Si_6$ (380.97) calcd.: C, 38.23; H, 10.58%; ^{29}Si-NMR (ext. TMS, ppm): Tables 1 and 2. ^{1}H-NMR: (ext. TMS, ppm) δ: 4.69 (s, 4H, = SiH₂); 0.22 (s, 36H, SiMe₃). MS (70 eV) m/e (rel. Int.): 380 (2 M⁺), 365 (5 M⁺−CH₃), 190 (45 M⁺/2), 174 (100 M⁺/2−CH₄). IR (cm⁻¹, rel. Int.): 2123 s, 1251 vs, 950 vs, 918 s, 842 s, 776 s, 741 w, 679 w, 618 vw.

3.8. 1-t-butyl-2-(bistrimethylsilyl)aminodisilane (8)

Sixteen milliliters of a 2 M solution of lithiumaluminumhydride in diethylether were slowly added to 6.9 g (0.017 mol) of 4 dissolved in 50 ml of ether at 0°C. Subsequently the reaction mixture was stirred at room temperature for 48 h. Aqueous workup with 2 M H₂SO₄

and distillation of the resulting colorless liquid at reduced pressure afforded 3.3 g (70%) of pure **8**.

B.p.: 45–47°C (0.1 mbar). Anal. Found: C, 43.12; H, 11.10%. $C_{10}H_{31}NSi_4$ (277.71) calcd.: C, 43.25; H, 11.25%. ^{29}Si-NMR (ext. TMS, ppm): Tables 1 and 2. ^{1}H NMR (ext. TMS, ppm) δ: 0.22 (s, 18H, –SiMe$_3$); 1.07 (s, 9H, –CMe$_3$); 3.71 (d, 2H, –SiH$_2$C); 4.95 (d, 2H, –SiH$_2$N). MS (70 eV) m/e (rel. Int.): 277 (5 M$^+$), 262 (11 M$^+$–CH$_3$), 220 (13 M$^+$–CMe$_3$), 190 (34 M$^+$–Me$_3$CSiH$_2$), 174 (100 M$^+$–CH$_3$–Me$_3$CSiH$_2$). IR (cm^{-1}, rel. Int.): 2122 s, 1264 w, sh, 1252 s, 1013 w, 933 vs, 882 w, 840 s, 825 w, sh, 778 w, sh, 758 s, 736 s, 680 w, 649 vw, 619 vw, 358 vw.

3.9. 1-[(Dicarbonyl)cyclopentadienyliron]-2-(bistrimethylsilyl)aminodisilane (9)

Sixteen milliliters of a 2 M solution of lithiumaluminumhydride in diethylether were slowly added to 4.1 g (0.017 mol) of **5** dissolved in 100 ml of *n*-heptane/diethylether (1:1) at 0°C. Subsequently the reaction mixture was stirred at room temperature for 30 min, cooled to 0°C again and 1 ml of Cl$_2$SiMe$_2$ was added to react with the remaining LiAlH$_4$. After another 30 min at room temperature the ether was removed under reduced pressure and the salts were filtered off. For purification the product was recrystallized twice from *n*-heptane at −80°C to give 1.82 g (62%) of slightly yellow crystalline **9**.

M.p.: 101–104 °C (0.1 mbar). Anal. Found (M$^+$): 382.0234. $C_{12}H_{24}O_2NFeSi_4$ calcd.: 382.0233. ^{29}Si-NMR (ext. TMS, ppm): Tables 1 and 2. ^{1}H NMR (ext. TMS, ppm) δ: 0.15 (s, 18H, –SiMe$_3$); 3.59 (d, 2H, –SiH$_2$); 4.19 (s, 5H, C$_5$H$_5^-$); 4.77 (d, 2H, –SiH$_2$). ^{13}C-NMR (ext. TMS, ppm) δ: 214.35 (CO); 83.44 (C$_5$H$_5^-$); 2.70 (–CH$_3$). MS (70 eV) m/e (rel. Int.): 382 (7, M$^+$–CH$_3$), 369 (91, M$^+$–CO), 309 (53, M$^+$–SiMe$_4$), 190 (10, SiH$_2$N(SiMe$_3$)$_2$), 178 (65, CpFeSi$_2$), 150 (16, CpFeSi), 121 (34, CpFe), 93 (100, CpSi). IR (cm^{-1}, rel. Int.): 2078 m, 2006 vs, 1958 vs, 938 vs, 921 s, 880 w, 845 m, 711 m, 679 w, 639 w, 590 s, 515 vw.

3.10. 1-Bis(phenyldimethylsilyl)amino-1,1-dichlorodisilane (10)

A 9.5 ml 2 M solution of lithiumaluminumhydride in diethylether were slowly added to 10 g (0.019 mol) of **3** dissolved in 100 ml of ether at −20°C. Subsequently the reaction mixture was stirred for 1 h at −20°C. In order to remove excess LiAlH$_4$ the ether was replaced by 50 ml of pentane, the salts were filtered off and 0.5 ml of 2 M H$_2$SO$_4$ were added at 0°C. Phase separation and removal of the solvent from the organic layer finally afforded 6.3 g (82%) of viscous liquid **10**, which finally can be purified by distillation at reduced pressure.

B.p.: 125–126°C (0.01 mbar). Anal. Found: C, 46.47;

H, 6.28%. $C_{16}H_{25}Cl_2NSi_4$ (414.63) calcd.: C, 46.35; H, 6.08%. ^{29}Si-NMR (ext. TMS, ppm): Tables 1 and 2. ^{1}H NMR (ext. TMS, ppm) δ: 0.45 (s, 6H, –CH$_3$); 3.03 (t, 3H, –SiH$_3$); 7.1–7.6 (m, 5H, –C$_6$H$_5$). MS (70 eV) m/e (rel. Int.): 412 (0.6 M$^+$–H), 398 (21 M$^+$–CH$_3$), 382 (23 M$^+$–SiH$_3$), 332 (8 M$^+$–CH$_3$SiH$_3$Cl), 304 (14 M$^+$–Me$_3$SiCl), 290 (25 M$^+$–CH$_3$–Me$_3$SiCl), 135 (100 PhMe$_2$Si). IR (cm^{-1}, rel. Int.): 2168 s, 2147 s, 1259 s, 1190 w, 1157 w, 1114 s, 998 w, 954 vs, 918 m, 863 vs, 839 s, 802 m, 748 w, 720 s, 702 s, 651 m, 619 w, 562 m, 511 s, 469 m, 421 m, 404 m, 384 w, 357 w.

3.11. Bis(phenyldimethylsilyl)aminodisilane (11)

Eight milliliters of a 2 M solution of lithiumaluminumhydride in diethylether were slowly added to 5 g (0.01 mol) of **3** dissolved in 100 ml of ether at 0°C. Subsequently the reaction mixture was refluxed overnight. Aqueous workup with 2 M H$_2$SO$_4$ and distillation of the resulting colorless liquid at reduced pressure afforded 1.9 g (70%) of pure **11**.

B.p.: 118–120°C (0.1 mbar). Anal. Found: C, 55.52; H, 8.02%. $C_{16}H_{27}NSi_4$ (345.74) calcd.: C, 55.58; H, 7.87%. ^{29}Si-NMR (ext. TMS, ppm): Tables 1 and 2. ^{1}H NMR (ext. TMS, ppm) δ: 0.36 (s, 6H, –CH$_3$); 3.19 (t, 3H, –SiH$_3$); 4.88 (q, 2H, –SiH$_2$N); 7.2–7.6 (m, 5H, –C$_6$H$_5$). MS (70 eV) m/e (rel. Int.): 345 (1 M$^+$), 330 (3 M$^+$–CH$_3$), 314 (100 M$^+$–SiH$_3$), 298 (21 M$^+$–CH$_3$SiH$_4$). IR (cm^{-1}, rel. Int.): 2141 vs, 1300 w, 1256 s, 1189 w, 1113 s, 1065 m, 998 w, 940 s, 920 s, 893 m, 831 m, 801 s, 725 m, 700 m, 667 w, 648 w, 619 w, 596 w, 528 m, 493 w, 471 m, 407 m, 358 w.

3.12. 1-t-butyl-2-chlorodisilane (12)

Anhydrous HCl was slowly passed through a solution of 3 g (0.01 mol) of **8** in 20 ml of pentane at room temperature until the starting material completely had been consumed as shown by GC analysis. After filtration and removal of the solvent at 100 mbar the resulting colorless liquid was distilled at reduced pressure to give 1.3 g (= 80%) of pure **12**.

B.p.: 65–66°C (100 mbar). Anal. Found: C, 31.63; H, 8.52%. $C_4H_{13}ClSi_2$ (152.77) calcd.: C, 31.45; H, 8.58%. ^{29}Si-NMR (ext. TMS, ppm): Tables 1 and 2. ^{1}H NMR (ext. TMS, ppm) δ: 0.96 (s, 9H, –CMe$_3$); 3.63 (m, 2H, –SiH$_2$C); 4.74 (t, 2H, –SiH$_2$Cl). MS (70 eV) m/e (rel. Int.): 152 (4 M$^+$), 120 (12 M$^+$–SiH$_4$), 109 (8 M$^+$–C$_3$H$_7$), 93 (8 M$^+$–C$_4$H$_{11}$), 63 (29 SiCl), 57 (100 CMe$_3$). IR (cm^{-1}, rel. Int.): 2130 s, 1012 m, 934 s, 911 s, 859 w, 821 m, 770 s, 738 s, 684 w, 530 s, 413 w, 331 w.

3.13. Reaction of 6 and 7 with HCl

Five grams of anhydrous HCl were condensed onto 0.005 mol of **6** or **7** at −196°C. After the reaction

mixture had been stirred for one hour at $-90°C$ excess HCl was allowed to evaporate at atmospheric pressure and $-30°C$. Repeated fractional condensation of the liquid residue at $-50°C$ and 0.05 mbar afforded $ClSiH_2SiH_3$ or $ClSiH_2SiH_2Cl$, respectively, containing up to 10% of Me_3SiCl. ^1H and ^{29}Si NMR spectra of the products are consistent with literature data [15].

3.14. Reaction of 10 with HCl

Ten grams of anhydrous HCl (10 fold excess) were condensed onto 4 g (0.01 mol) of **10** at $-196°C$. After the reaction mixture had been stirred for one hour at $-90°C$ excess HCl was allowed to evaporate at atmospheric pressure. Fractional condensation of the liquid residue at $0°C$ and 0.05 mbar afforded 1.5 g ($= 94\%$) of pure 1,1,1-trichlorodisilane. ^1H-, ^{29}Si-NMR and MS spectra of the product are consistent with literature data [8,15].

3.15. Reaction of 11 with HCl

Four grams of anhydrous HCl (10 fold excess) were condensed onto 1.4 g (0.004 mol) of **11** at $-196°C$. After the reaction mixture had been stirred for 30 min at $-90°C$ excess HCl was allowed to evaporate at atmospheric pressure at $-30°C$. Fractional condensation of the liquid residue at $-50°C$ and 0.05 mbar afforded 0.37 g ($= 95\%$) of pure chlorodisilane. ^1H and ^{29}Si NMR spectra of the product are consistent with literature data [15].

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