Halogenodisilanes: Precursors for New Disilane Derivatives[†]

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Starting from hexachloro- or hexabromodisilane a wide variety of 1,2-disubstituted tetrachlorodisilanes ($RSiCl_2$-$SiCl_2R$) [R = Cp* **(2a)**, 4-*i*$PrC_6H_4(SiMe_3)N$ **(2b)**, 2,6-*i*$Pr_2C_6H_3(SiMe_3)N$ **(2c)**, $(Me_3Si)_2CH$ **(2d)** $(Me_3Si)_3C$ **(2e)**, $(Me_3Si)_3Si$ **(2f)**], tetrabromodisilanes ($RSiBr_2SiBr_2R$) [R = Cp* **(3a)**, 4-*i*$PrC_6H_4(SiMe_3)N$ **(3b)**, $(Me_3Si)_3Si$ **(3f)**] and the monosubstituted pentahalogenodisilanes $Cp^*SiX_2SiX_3$ [X = Cl **(4)**, Br **(5)**] were prepared. The tetrachlorodisilanes **2a−e** are converted to various functionalized disilanes. Ammonolysis of **2a−e** leads to the tetraaminodisilanes [$RSi(NH_2)_2Si(NH_2)_2R$] **6a−e**. A reduction of **2d** with $LiAlH_4$ resulted in the formation of the disilane $RSiH_2SiH_2R$ [R = $(Me_3Si)_2CH$] **7** and the metathesis with Me_3SnF yielded the tetrafluorodisilane $RSiF_2$-SiF_2R [R = $(Me_3Si)_2CH$] **8**. Treatment of **6d** with reagents containing H acidic protons (HX) [X = Br, I and OH] leads under elimination of NH_3 to the tetrabromo- $R_2SiBr_2SiBr_2R$ **(3d)** tetraiodo- $RSiI_2SiI_2R$ **(9)** and the tetrahydroxodisilane $RSi(OH)_2Si(OH)_2R$ **(10)** [R = $(Me_3Si)_2CH$]. Single-crystal X-ray structural analysis of **2d**, **6a**, **6d**, and **9** are reported.

Introduction

Silicon compounds are materials with high thermal stability and especially silicon−nitrogen compounds have gained increasing industrial importance. In recent years Schnick et al. reported on nitridosilicates synthesized by using silicondiimide [$Si(NH)_2$] and a series of metals at elevated temperatures.[1] Promising starting materials for a large variety of silicon compounds are chlorosilanes, chlorodisilanes, and chloropolysilanes.[2] Organic ligands can be easily attached to silicon by employing the reaction of chlorosilanes with the lithium or potassium salts of the ligands. In most of the cases the resulting organochlorosilanes can be easily transformed to the corresponding organoaminosilanes by ammonolysis. Using this method several triaminosilanes and tetraaminodisilanes have been prepared.[3−5] The aminosilanes are starting materials for preparing metalasilazanes containing the metals aluminum, gallium, indium, and titanium.[4−8] Moreover trihydroxosilanes were used for the preparation of metalasiloxanes with aluminum and titanium.[9−14]

Herein we report on various transformations using the tetrachlorodisilanes $R_2Si_2Cl_4$ [R = Cp* **(2a)**, 4-*i*$PrC_6H_4(SiMe_3)N$ **(2b)**, 2,6-*i*$Pr_2C_6H_3(SiMe_3)N$ **(2c)**, $(Me_3Si)_2CH$ **(2d)**, $(Me_3Si)_3C$ **(2e)**] and ammonia to yield the respective tetraaminodisilanes **(6a−e)**. Recently, Malisch et al. demonstrated that $LiAlH_4$ is a good metathesis reagent for chlorine atoms bonded on silicon;[15] therefore, this method was used here starting from **2d** to generate the disilane $R_2Si_2H_4$ [R = $(Me_3Si)_2CH$ **(7)**]. For the metathesis

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[†] Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 60th birthday.

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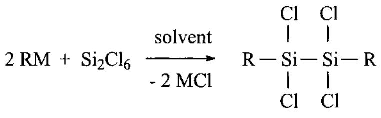
Scheme 1



$$2\,RM + Si_2Cl_6 \xrightarrow[-\,2\,MCl]{solvent} R-\underset{Cl}{\overset{Cl}{Si}}-\underset{Cl}{\overset{Cl}{Si}}-R$$

2a-f

2	RM	solvent	condition
a	Cp*K	THF	reflux
b	4-*i*Pr$C_6H_4(Me_3Si)NLi$	toluene	reflux
c	2,6-*i*$Pr_2C_6H_3(Me_3Si)NLi$	toluene	reflux
d	$(Me_3Si)_2CHLi$	toluene	reflux
e	$(Me_3Si)_3CLi$	toluene	reflux
f	$(Me_3Si)_3SiK$	toluene	20 °C

of chloro compounds to the corresponding fluoro derivatives, we employed in recent years Me_3SnF[16] as a powerful reagent. This fluorination method is facile due to the generation of Me_3SnCl that can be easily removed under vacuum. Consequently, **2d** was transformed into the tetrafluorodisilane $R_2Si_2F_4$ [R = $(Me_3Si)_2CH$ **(8)**]. Furthermore, **6d** reacted with acidic protons containing reagents such as HBr and HI to yield the tetrahalogenodisilanes $R_2Si_2X_4$ [R = $(Me_3Si)_2CH$; X = Br **(3d)**, I **(9)**]. The latter compounds are interesting for further reactions due to the higher reactivity of the bromo and iodo derivatives compared to the chloro ones. A formation of **3d** using the reaction between Si_2Br_6 and the lithium salt of the ligand was not successful. The conversion of **6d** with water resulted in the tetrahydroxodisilane $R_2Si_2(OH)_4$ [R = $(Me_3Si)_2CH$ **(10)**]. To our surprise the silicon−silicon bonds were not cleaved under these conditions.

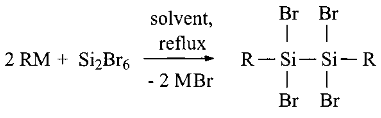
Results and Discussion

A general route for the synthesis of the tetrahalogenodisilanes (**2a**−**f**, **3a**−**b**, **3f**) is the use of a solution or a suspension of the lithium or potassium salt of the ligand in a suitable solvent followed by the addition of a solution of hexahalogenodisilane in the same solvent. However for a complete conversion it is necessary to reflux the solution for several hours under stirring (Schemes 1 and 2).

As a result of using Cp*Li (Cp* = C_5Me_5) instead of Cp*K as a starting material, the formation of the respective mono(pentamethylcyclopentadienyl)pentahalogenodisilane (**4**, **5**) has been observed (Scheme 3). Not even an excess of the lithium salt, or an exchange of the solvent or an increase of the reaction temperature and time, led to the 1,2-disubstituted tetrahalogenodisilanes.

The preparation of the tetraaminodisilanes (**6a**−**e**) was accomplished by three different routes (Scheme 4). First, a solution of the tetrachlorodisilane in toluene was added to a solution of sodium in liquid ammonia at −78 °C, giving the tetraaminodisilanes **6a** and **6d**, respectively. Second, the ammonolysis of the tetrachlorodisilanes **2b**,**c** using ammonia without sodium results in higher yields of the products. However, the tetrachlorodisilane **2e** did not react using either the first or second route. Therefore, liquid ammonia was condensed at −78 °C in an autoclave containing **2e**. Stirring the mixture for 7 days at 80 °C leads to **6e**.

Scheme 2

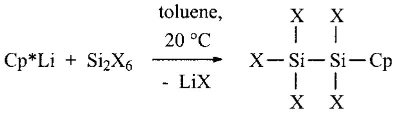


$$2\,RM + Si_2Br_6 \xrightarrow[-\,2\,MBr]{solvent,\ reflux} R-\underset{Br}{\overset{Br}{Si}}-\underset{Br}{\overset{Br}{Si}}-R$$

3a-b, 3f

3	RM	solvent
a	Cp*K	THF
b	4-*i*Pr$C_6H_4(Me_3Si)NLi$	toluene
f	$(Me_3Si)_3SiLi$	toluene

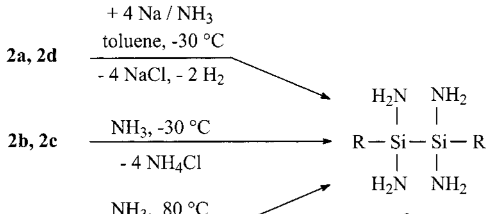
Scheme 3



$$Cp^*Li + Si_2X_6 \xrightarrow[-\,LiX]{toluene,\ 20\ °C} X-\underset{X}{\overset{X}{Si}}-\underset{X}{\overset{X}{Si}}-Cp$$

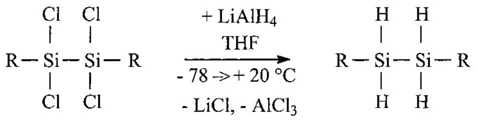
	4	**5**
X	Cl	Br

Scheme 4



6a-e

Scheme 5

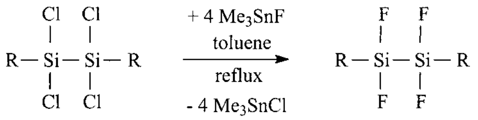


$$R-\underset{Cl}{\overset{Cl}{Si}}-\underset{Cl}{\overset{Cl}{Si}}-R \xrightarrow[-78 \to +20\ °C;\ -LiCl,\ -AlCl_3]{+LiAlH_4,\ THF} R-\underset{H}{\overset{H}{Si}}-\underset{H}{\overset{H}{Si}}-R$$

2d **7**

R = $CH(SiMe_3)_2$

Scheme 6



$$R-\underset{Cl}{\overset{Cl}{Si}}-\underset{Cl}{\overset{Cl}{Si}}-R \xrightarrow[reflux;\ -4\,Me_3SnCl]{+4\,Me_3SnF,\ toluene} R-\underset{F}{\overset{F}{Si}}-\underset{F}{\overset{F}{Si}}-R$$

2d **8**

R = $CH(SiMe_3)_2$

The metathesis of **2d** with $LiAlH_4$ in tetrahydrofuran at room temperature gave the colorless disilane **7** with four hydrogen atoms bonded to the central silicon atoms as shown in Scheme 5.

The tetrafluorodisilane **8** was generated by the reaction of **2d** with trimethyltin fluoride in boiling toluene, as a colorless liquid with melting point close to 0 °C (Scheme 6).

The conversion of the tetraaminodisilane **6d** with reagents containing H acidic protons such as HBr, HI, and H_2O,

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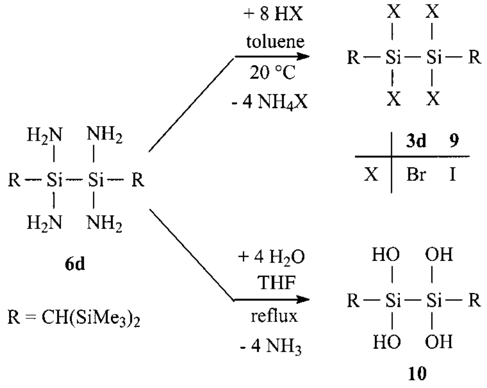
Scheme 7



respectively, was successful for the preparation of compounds **3d**, **9**, and **10** under elimination of ammonia (Scheme 7). The reaction with HBr and HI was carried out at room temperature by passing a gas stream of HBr and HI, respectively, through a solution of **6d** in toluene. NH_4Br and NH_4I, respectively, were generated as a byproduct. As far as the reaction with water is concerned, the temperature of refluxing tetrahydrofuran is necessary to eliminate the ammonia formed during the reaction.

Structural Investigations

All compounds were characterized by standard spectroscopic techniques such as NMR, MS, and IR as well as by elemental analysis.

The NMR chemical shifts for the organic ligands are in the typical range. For the discussion here only the resonances of the central disilane units with four functional groups are recorded. In the ^1H NMR the protons of the amino groups of the compounds **6a**−**e** give broad nonresolved resonances (0.3 to 2.0 ppm), and the hydroxo group in **10** displayed a resonance at 3.55 ppm. The hydrogen atoms which are directly bonded to silicon in compound **7** give a multiplet (3.96 ppm). The Si_2H_4 hydrogen atoms are not magnetically equivalent, and therefore a complex non-first-order splitting pattern appeared in the ^1H NMR spectrum. In the ^{19}F NMR the fluorine atoms of **8** resonate at 43.9 ppm. The chemical values of the central silicon atoms of compounds $R_2Si_2X_4$ and $R_2Si_2X_5$ are summarized in Table 1. The most upfield resonance (−59.9 ppm) was observed for **7**. The solid-state IR vibrational spectra of the tetrachlorodisilanes **2a**−**f** have absorptions between 446 and 503 cm^{-1} and in the range of 538 to 588 cm^{-1} which can be tentatively assigned to the Si−Cl stretching modes. The $\tilde{\nu}$ (Si−Br) bands of the corresponding tetrabromodisilanes (**3a**−**b**,**d**,**f**) are tentatively assigned between 310 and 375 cm^{-1} and additionally in the range of 423 to 435 cm^{-1}. For the pentahalogenodisilanes (**4**, **5**), the $\tilde{\nu}$ (Si−Cl) bands have been found between 381 and 582 cm^{-1}, whereas in the Si−Br system they are in the range 291 to 460 cm^{-1}. All these absorptions are in agreement with the literature.[17] The $\tilde{\nu}$ (NH_2) stretching bands of the tetraaminodisilanes are observed in the range 3364−3495 cm^{-1}, and the deformation bands are found in the area ranging from 1533 to 1538 cm^{-1}. The IR spectrum of compound **7** contains $\tilde{\nu}$ (Si−H) at 2117 cm^{-1}, and in **8** the $\tilde{\nu}$ (Si−F) stretching bands are at 875 and 995 cm^{-1}. The corresponding $\tilde{\nu}$ (Si−I) bands in **9** appear in the range 359−383 cm^{-1}. In the IR spectrum of the tetrahydroxo compound **10** a band for the $\tilde{\nu}$ (OH) is found at 3361 cm^{-1}. The broadening of this absorption indicates intermolecular hydrogen bonds comparable to those in $2,4,6\text{-}Me_3C_6H_2N(SiMe_3)Si(OH)_3$ and $[2,6\text{-}Me_2C_6H_3N(SiMe_3)\text{-}Si(OH)_2]_2O$.[18] The Si−O bands are observed at 850 cm^{-1}. For the compounds reported, the mass spectra show the molecular ions [M^+] or half of the molecular ions [$M^+/2$] and fragment peaks after elimination of one or two small groups, and thus this reflects that the compounds in the gas phase are kinetically quite stable.

Table 1. ^{29}Si NMR Data of the Central Silicon Atoms of $R_2\mathbf{Si_2}X_4$ (**2a**−**f**, **3a**−**b**, **3d**, **3f**, **6a**−**e**, **7**−**10**) and $R\mathbf{Si_2}X_5$ (**4**, **5**)

	R	X	ppm[a]
2a	Cp*	Cl	0.9
2b	4-*i*$PrC_6H_4(SiMe_3)N$	Cl	−21.1
2c	2,6-*i*$Pr_2C_6H_3(SiMe_3)N$	Cl	−27.5
2d	$(Me_3Si)_2CH$	Cl	18.0
2e	$(Me_3Si)_3C$	Cl	3.6
2f	$(Me_3Si)_3Si$	Cl	−8.1
3a	Cp*	Br	−12.9
3b	4-*i*$PrC_6H_4(SiMe_3)N$	Br	−37.2
3d	$(Me_3Si)_2CH$	Br	4.1
3f	$(Me_3Si)_3Si$	Br	−23.7
4	Cp*	Cl	0.5 ($SiCl_2$) −8.1 ($SiCl_3$)
5	Cp*	Br	−18.9 ($SiBr_2$) −30.8 ($SiBr_3$)
6a	Cp*	NH_2	−16.6
6b	4-*i*$PrC_6H_4(SiMe_3)N$	NH_2	−28.2
6c	2,6-*i*$Pr_2C_6H_3(SiMe_3)N$	NH_2	−41.1
6d	$(Me_3Si)_2CH$	NH_2	−15.2
6e	$(Me_3Si)_3C$	NH_2	−18.9
7	$(Me_3Si)_2CH$	H	−59.9
8	$(Me_3Si)_2CH$	F	4.5
9	$(Me_3Si)_2CH$	I	−50.3
10	$(Me_3Si)_2CH$	OH	−7.4

[a] Relative to $SiMe_4$.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for **2d**, **2d*** (X = Cl) and **9** (X = I)

	2d	**2d***	**9**
Si(5)−Si(6)	2.380(2)	2.3702(9)	2.423(2)
Si(5)−X(1)	2.0627(9)	2.0521(11)	2.4722(13)
Si(5)−X(2)	2.0700(9)	2.0668(8)	2.5036(12)
Si(5)−C(1)	1.837(2)	1.843(2)	1.866(4)
X(1)−Si(5)−X(2)	103.91(5)	104.25(4)	105.75(4)
X(1)−Si(5)−Si(6)	105.55(4)	105.32(5)	112.87(5)
X(2)−Si(5)−Si(6)	109.09(4)	108.58(3)	99.50(5)
C(1)−Si(5)−Si(6)	114.97(7)	114.54(6)	116.7(2)
C(1)−Si(5)−X(1)	113.19(6)	113.05(7)	109.4(2)
C(1)−Si(5)−X(2)	109.49(6)	110.45(7)	111.77(13)

Single crystals suitable for the X-ray structural analysis of the compounds **2d**, **6d** and **9** were grown from *n*-hexane while single crystals of compound **6a** were obtained from toluene.

Crystallographic data for compounds **2d**, **6a**, **6d**, and **9** are summarized in Table 4. In Table 2 selected bond lengths and angles of **2d** and **9** are given. Compound **2d** crystallizes in the monoclinic space group $P2_1/n$ with two molecules (**2d** and **2d***) in the asymmetric unit and **9** crystallizes in the monoclinic space group $P2_1/c$. A Si_2X_4 core is the central unit of both compounds [**2d** (X = Cl) and **9** (X = I)]. The tetrahedral coordination sphere of each of the silicon centers is completed by one $CH(SiMe_3)_2$ group. The stuctures are shown in Figures 1 (**2d**) and 2 (**9**). In either case the molecules show an anticlinal conformation. The bond length of the two central silicon atoms in **9** (2.423 Å) is

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Table 3. Selected Bond Lengths [Å] and Angles [deg] for **6a**, **6d**, and **6d***

	6a	**6d**	**6d***
Si(1)−Si(2)	2.3693(14)	2.3727(18)	2.3852(16)
Si(1)−N(1)	1.732(2)	1.726(4)	1.723(4)
Si(1)−N(2)	1.712(2)	1.739(4)	1.722(4)
Si(1)−C(1)	1.929(3)	1.897(4)	1.905(4)
N(1)−Si(1)−N(2)	106.23(13)	108.1(2)	106.25(19)
N(1)−Si(1)−Si(2)	117.41(10)	104.15(14)	117.13(14)
N(2)−Si(1)−Si(2)	107.57(10)	105.76(15)	101.93(14)
N(1)−Si(1)−C(1)	105.70(12)	110.59(19)	106.42(17)
N(2)−Si(1)−C(1)	109.91(12)	109.8(2)	114.78(19)
Si(2)−Si(1)−C(1)	109.86(9)	117.89(13)	110.55(12)

slightly longer than that in **2d** (av 2.375 Å). The big difference in the atomic radii of the halogen atoms is the reason that the X−Si−X angles in **2d** are somewhat smaller (av 103.02°) than in **9** (av 104.68°). Remarkable are the I−Si−Si angles in **9** on both sides of the molecule. One of the angles is relatively small (av 99.64°), whereas the other one is significantly bigger (av 113.05°). The conformation of the molecule with the direct neighborhood of the iodo atoms I(1) and I(3) might be the reason for this phenomenon (Figure 3).

Selected bond distances and angles for **6a** and **6d** are given in Table 3. The single-crystal X-ray analyses show **6a** to crystallize in the monoclinic space group $P2_1/n$ with half a molecule in the asymmetric unit and **6d** to crystallize in the triclinic space group $P\bar{1}$ with six molecules in the asymmetric unit. Compounds **6a** and **6d** consist of a $Si_2(NH_2)_4$ core, linked to two Cp* **(6a)** or $CH(SiMe_3)_2$ groups **(6d)** which leads to a tetrahedral coordination sphere for both silicon atoms. The structure of **6a** is shown in Figure 4, the molecule exhibits an anticlinal conformation and the Cp* moiety is bonded in an η^1-fashion to the silicon. Four of the independent molecules of **6d** are conformed synperiplanar (**6d**) and two of them possess the anticlinal (**6d***) conformation. Figure 5 shows the two molecules from the asymmetric unit possessing the two different conformations present in the crystal. In the lattice of **6d** the molecules are linked via a net of eight crystallographically independent N−H−N hydrogen bonds (H···N distances range from 2.38(2) to 2.57(2) Å). Three of the six independent molecules are pairwise related to the other three molecules via noncrystallographic symmetry in the form of one pseudo inversion center and two pseudo 2-fold axes. One of these axes is only partially fulfilled. The eight highest residual electron density maxima (1.24 to 0.98 e/Å^3) are significantly higher than the others (next highest: 0.47 e/Å^3) and correspond to the four silicon atoms of the $SiMe_3$ ligands of two slightly disordered molecules. However, the refinement of two discrete positions for the $CH(SiMe_3)_2$ ligands was not stable. The average Si−N distances (1.722 Å (**6a**), 1.728 Å (**6d**)) and the Si−Si bond lengths (2.369 (2) Å (**6a**), av 2.377 Å (**6d**)) are nearly the same.

The Si−Si bond lengths of all molecules are in the same range. Compounds **6a** and **6d** are the first structurally characterized tetraaminodisilanes.

Experimental Section

General Information. All reactions were performed under dry nitrogen conditions using standard Schlenk and syringe techniques. The solvents were dried according to literature methods[19] and freshly distilled and saturated with nitrogen prior to use. Melting points were measured on a Bühler SPA-1 or a Büchi B-540 melting point apparatus (uncorrected), IR spectra were recorded using a BIO-RAD FTS 7 spectrophotometer and mass spectra (MS) were obtained with a Finnigan MAT 8200 or a Finnigan MAT 95 spectrometer using EI technique. NMR spectra were recorded with a Bruker AM 200, a Bruker AC 250, a Bruker MSL 400, or a Bruker Avance 500 spectrometer. Chemical shifts are reported in ppm relative to external $SiMe_4$ (^1H, ^{13}C, ^{29}Si) or C_6F_6 (^{19}F). Elemental analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry at the University of Göttingen. The salts of the ligands **1a**, **1c−f**, Cp*Li, Si_2Cl_6, and the Si_2Br_6 were prepared by literature methods.[20−27] **1b** was synthesized using a new route.

(*N*-(4-Isopropylphenyl)-*N*-(trimethylsilyl)amino)lithium (1b). 4-iPr$C_6H_4NH_2$ (11.0 g, 50.1 mmol) was dissolved in diethyl ether (20 mL), and at −78 °C a solution of *n*-butyllithium (3.46 g, 54 mmol) in *n*-hexane (35 mL) was added. The mixture was stirred for 1 h at −78 °C and for additional 2 h at room temperature. The suspension was cooled to −78 °C again, and trimethylchlorosilane (6.2 g, 57 mmol) was added. Under continuous stirring, the mixture was slowly brought to room temperature over a period of 12 h. The generated LiCl was removed by filtration, and a solution of 3.85 g (60 mmol) *n*-butyllithium in *n*-hexane (40 mL) was added to the filtrate. The reaction mixture was refluxed for 5 h, and after cooling to room temperature the solvents were removed in vacuo. To the residue was added *n*-pentane (50 mL), and the solution was stored at −30 °C for 2 days. The precipitated colorless solid was separated by filtration and was dried under vacuum. 9.35 g (41.5 mmol, 83%) of pure **1b** was obtained. Decomp 126 °C. ^1H NMR (200 MHz, C_6D_6): δ 0.10 (s, Si(CH_3)$_3$), 1.23 (d, $^3J_{HH} = 6.9$ Hz, CH(CH_3)$_2$), 2.77 (sept, $^3J_{HH} = 6.9$ Hz, C*H*Me$_2$), 6.55−6.61, 7.00−7.15 (m, arom-*H*). ^{13}C NMR (125 MHz, C_6D_6): δ 2.0 (Si(CH_3)$_3$), 24.5 (CH(CH_3)$_2$), 33.6 (*C*HMe$_2$), 123.0, 128.7, 137.7, 154.5 (arom-*C*). ^{29}Si NMR (100 MHz, C_6D_6): δ −7.0 (*Si*Me$_3$) ppm. IR (KBr, Nujol): $\tilde{\nu}$ 1884 (w), 1603 (m), 1515 (m), 1296 (w), 1251 (s), 1242 (s), 1189 (m), 1176 (m), 1120 (w), 1101 (w), 1053 (w), 942 (m), 923 (s), 906 (s), 835 (vs), 823 (vs), 767 (w), 740 (m), 669 (m), 567 (m), 544 (m), 479 (w), 454 (w) cm^{-1}. MS (EI, *m*/*z*, (%)): 206 (5) [M$^+$ − Li], 73 (100) [SiMe$_3$]. Anal. Calcd for $C_{12}H_{20}LiNSi$ (213.32): C, 67.6; H, 9.5; N, 6.6; Si, 13.2. Found: C, 67.8; H, 9.6; N, 6.4; Si, 13.0.

Synthesis of the Tetrahalogenodisilanes 2a, 3a. A solution of the respective hexahalogenodisilane (25 mmol) was added to a suspension of Cp*K (8.7 g, 50 mmol) in THF (200 mL) over a period of 15 min. The reaction mixture was subsequently heated under reflux for 6 h. After cooling to room-temperature, all volatiles were stripped off. The residue was extracted with hot diethyl ether (3 × 50 mL) and filtered. The filtrate was concentrated to 50 mL and kept at 0 °C for 24 h to afford the respective pure tetrahalogenodisilane.

1,2-Bis(pentamethylcyclopentadienyl)tetrachlorodisilane (2a). Yield 8.9 g (19 mmol, 76%). Mp 218 °C. ^1H NMR (200 MHz, C_6D_6): δ 1.35 (m, 1-C*H*$_3$), 1.82 (m, 2-C*H*$_3$, 3-C*H*$_3$, 4-C*H*$_3$, 5-C*H*$_3$). ^{13}C NMR (125 MHz, C_6D_6): δ 12.6 (*C*H$_3$), 58.7 (*C*-1), 135.2, 142.0 (*C*-2, *C*-3, *C*-4, *C*-5). ^{29}Si NMR (50 MHz, C_6D_6): δ 0.9 (*Si*Cl$_2$) ppm. IR (KBr, Nujol): $\tilde{\nu}$ 1627 (m), 1229 (s), 1134 (s), 1074 (m), 1040 (m), 1008 (w), 833 (m), 791 (m), 742 (s), 538 (vs), 446 (vs) cm^{-1}. MS (EI, *m*/*z*, (%)): 468 (17) [M$^+$], 333 (71) [M$^+$ − Cp*], 233 (100) [$^1/_2$ M$^+$]. Anal. Calcd for $C_{20}H_{30}Cl_4Si_2$ (468.44): C, 51.3; H, 6.5; Cl, 30.3; Si, 12.0. Found: C, 51.3; H, 6.5; Cl, 30.2; Si, 12.1.

1,2-Bis(pentamethylcyclopentadienyl)tetrabromodisilane (3a). Yield: 11.5 g (17.8 mmol, 71%). Mp 257 °C. ^1H NMR (200 MHz, C_6D_6): δ 1.62−1.76 (m, C*H*$_3$). ^{13}C NMR (125 MHz, C_6D_6): δ 13.2 (*C*H$_3$), 128.5 (*C*$_5$Me$_5$). ^{29}Si NMR (79 MHz, C_6D_6): δ −12.9 (*Si*Br$_2$) ppm. IR (CsI, Nujol): $\tilde{\nu}$ 1629 (m), 1557 (w), 1227 (m), 1133 (m), 1076 (m), 790 (w), 590 (m), 535 (w), 435 (vs), 341 (vs), 297 (m) cm^{-1}.

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Table 4. Crystal Data and Structure Refinement Details for **2d**, **6a**, **6d**, and **9**

	2d	**6a**	**6d**	**9**
empirical formula	$C_{14}H_{38}Cl_4Si_6$	$C_{20}H_{38}N_4Si_2$	$C_{14}H_{46}N_4Si_6$	$C_{14}H_{38}I_4Si_6$
formula weight	516.78	390.72	439.09	882.58
temperature [K]	203(2)	203(2)	133(2)	133(2)
crystal system	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a [Å]	12.672(2)	7.7197(8)	15.198(3)	18.971(4)
b [Å]	13.035(3)	11.638(2)	25.390(5)	9.720(2)
c [Å]	33.87(3)	12.952(2)	25.527(5)	17.396(4)
α [deg]	90	90	115.07(3)	90
β [deg]	94.02(2)	103.717(9)	106.12(3)	103.01(3)
γ [deg]	90	90	96.71(3)	90
volume [Å^3]	5581(4)	1130.4(3)	8254(3)	3125.3(11)
z	8	2	12	4
density (calculated) [Mg/m^3]	1.230	1.148	1.060	1.876
absorption coefficient [mm^{-1}]	0.682	0.168	0.309	4.219
F(000)	2192	428	2904	1672
crystal size [mm^3]	0.80 × 0.80 × 0.60	0.70 × 0.60 × 0.40	0.30 × 0.30 × 0.10	0.90 × 0.30 × 0.30
θ range for data collection	3.52 to 24.92°	3.68 to 22.60°	1.65 to 23.26°	2.54 to 27.58°
limiting indices	$-14 \le h \le 14$	$-8 \le h \le 8$	$-16 \le h \le 16$	$-24 \le h \le 24$
	$-15 \le k \le 15$	$-12 \le k \le 12$	$-28 \le k \le 25$	$0 \le k \le 12$
	$-40 \le l \le 40$	$-14 \le l \le 14$	$0 \le l \le 28$	$0 \le l \le 22$
reflections collected	19248	3794	81603	47812
independent reflections	9666 [R_{int} = 0.0697]	1486 [R_{int} = 0.0202]	23689 [R_{int} = 0.0646]	7157 [R_{int} = 0.0677]
data/restraints/parameters	9644/0/458	1485/0/123	23689/503/1435	7157/0/229
final R indices [$I > 2\sigma(I)$]^a	$R1 = 0.0279$	$R1 = 0.0479$	$R1 = 0.0538$	$R1 = 0.0342$
	$wR2 = 0.0684$	$wR2 = 0.1217$	$wR2 = 0.1317$	$wR2 = 0.0726$
R indices (all data)	$R1 = 0.0349$	$R1 = 0.0517$	$R1 = 0.0931$	$R1 = 0.0455$
	$wR2 = 0.0759$	$wR2 = 0.1276$	$wR2 = 0.1530$	$wR2 = 0.0757$
goodness-of-fit on F^2 ^{b}	1.137	1.065	1.013	1.068
largest diff peak and hole [eÅ^{-3}]	0.301 and −0.244	0.463 and −0.488	1.242 and −0.357	0.569 and −1.172

^{a} $R1 = \Sigma|F_o - F_c|/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$. ^{b} Goodness of fit $S = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(n - p)]^{1/2}$.

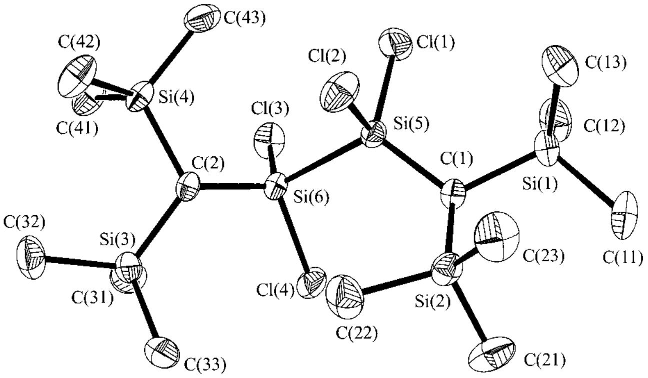

Figure 1. Crystal structure of **2d** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

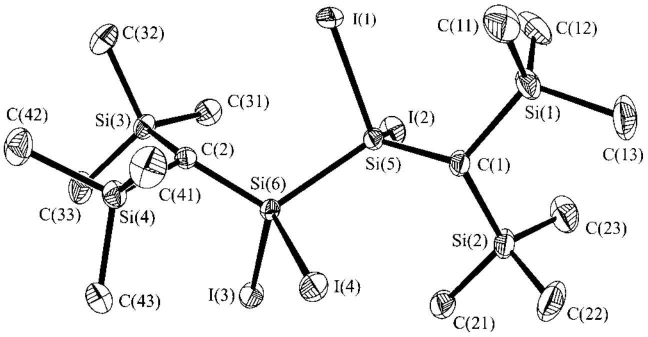

Figure 2. Crystal structure of **9** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

MS (EI, *m/z* (%)): 646 (6) [M$^+$], 567 (11) [M$^+$ − Br], 323 (36) [$^1/_2$ M$^+$], 135 (100) [$C_5Me_5^+$]. Anal. Calcd for $C_{20}H_{30}Br_4Si_2$ (646.25): C, 37.2; H, 4.7; Br, 49.5; Si, 8.7. Found: C, 37.2; H, 4.6; Br, 49.7; Si, 8.5.

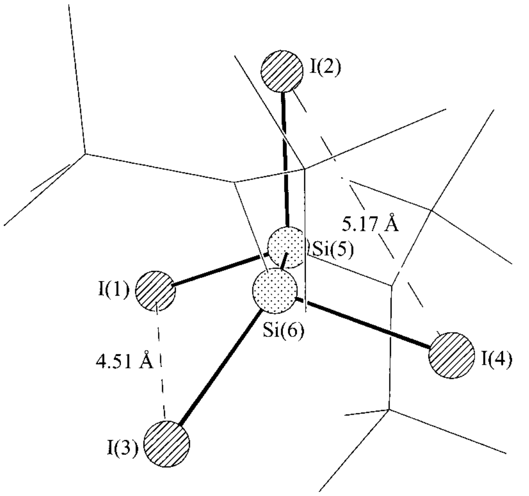

Figure 3. Conformation of **9** showing the neighborhood relation of the iodine atoms.

Synthesis of the Tetrahalogenodisilanes 2b−e, 3b, 3f. To a solution of the respective lithium salts (50 mmol) in toluene (100 mL) was added dropwise a solution of the respective hexahalogenodisilane (25 mmol) in toluene (50 mL) with constant stirring. After the addition was complete, the reaction mixture was heated under reflux for 6 h and cooled to room temperature. The lithium halogenide formed was removed by filtration through Celite. All volatiles were removed in vacuo, and the residue was dissolved in *n*-hexane (30 mL) and stored at −20 °C. **2b−e**, **3b**, and **3f** precipitated as colorless solids.

1,2-Bis(*N*-(4-isopropylphenyl)-*N*-(trimethylsilyl)amino)tetrachlorodisilane (2b). Yield: 12.7 g (20.7 mmol, 83%). Mp 75 °C. ^{1}H NMR (200 MHz, C_6D_6): δ 0.15 (s, Si(CH_3)$_3$), 1.12 (d, $^3J_{H-H}$ = 6.9 Hz, CH(CH_3)$_2$), 2.68 (sept, $^3J_{H-H}$ = 6.9 Hz, CHMe$_2$), 6.79−7.09 (m, arom-H). ^{13}C NMR (50 MHz, C_6D_6): δ 1.9 (Si(CH$_3$)$_3$), 24.1 (CH(CH$_3$)$_2$), 33.9 (CHMe$_2$), 127.5, 130.8, 139.7, 147.0 (arom-C). ^{29}Si NMR (100 MHz, C_6D_6): δ −21.1 (SiCl$_2$), 13.2 (SiMe$_3$) ppm. IR (KBr, Nujol):

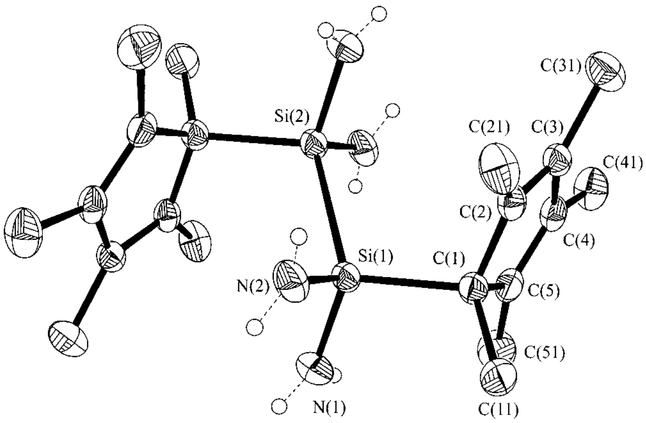

Figure 4. Crystal structure of **6a** showing 50% probability ellipsoids. Hydrogen atoms bonded to carbon are omitted for clarity.

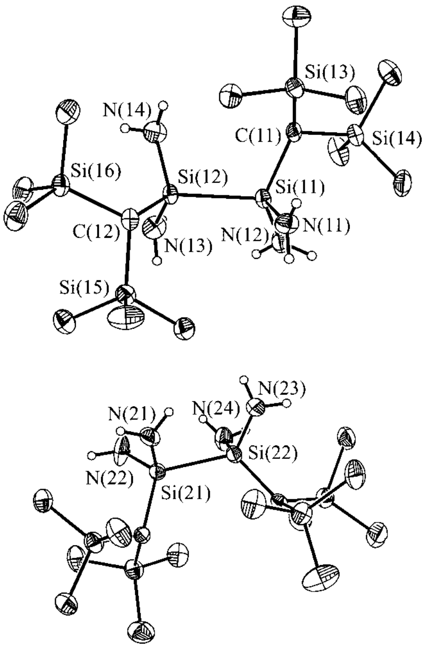

Figure 5. Crystal structure of **6d** (top: anticlinal, bottom synperiplanar conformation) showing 50% probability ellipsoids. Hydrogen atoms bonded to carbon are omitted for clarity.

$\tilde{\nu}$ 1898 (w), 1662(w), 1606 (w), 1572 (w), 1505 (s), 1417 (m), 1261 (m), 1253 (vs), 1208 (vs), 1178 (m), 1118 (w), 1096 (w), 1001 (vs), 983 (s), 879 (vs), 844 (vs), 761 (s), 728 (s), 690 (m), 639 (w), 589 (m), 549 (s), 544(vs), 508 (m), 468 (m), 415 (w), 400 (w) cm^{-1}. MS (EI, *m*/*z*, (%)): 610 (8) [M^+], 595 (2) [$M^+ - Me$], 304 (4) [1/2 M^+], 120 (100) [$C_9H_{12}{}^+$]. Anal. Calcd for $C_{24}H_{40}Cl_4N_2Si_4$ (610.75): C, 47.2; H, 6.6; Cl, 23.2; N, 4.6; Si, 18.4. Found: C, 47.3; H, 6.6; Cl, 23.1; N, 4.6; Si 18.2.

1,2-Bis(*N*-(2,6-diisopropylphenyl)-*N*-(trimethylsilyl)amino)tetrachlorodisilane (2c). Yield: 10.9 g (15.7 mmol, 63%). Mp 121 °C. ^{1}H NMR (200 MHz, C_6D_6): δ 0.13, 0.18 (s, Si(C*H*$_3$)$_3$), 1.16, 1.20, 1.25 (d, $^3J_{H-H} = 6.8$ Hz, CH(C*H*$_3$)$_2$), 3.45, 3.53 (sept, $^3J_{H-H} = 6.8$ Hz, C*H*Me$_2$), 6.95−7.08 (m, arom-*H*). ^{13}C NMR (63 MHz, C_6D_6): δ 1.4 (Si(*C*H$_3$)$_3$), 2.7 (Si(*C*H$_3$)$_3$), 25.2 (CH(*C*H$_3$)$_2$), 27.8 (*C*HMe$_2$), 124.0 (arom-*C*-4), 125.0 (arom-*C*-3, arom-*C*-5), 143.3 (arom-*C*-2, arom-*C*-6), 147.1 (arom-*C*-1). ^{29}Si NMR (50 MHz, C_6D_6): δ −27.5 (*Si*Cl$_2$), 4.3, 12.2 (*Si*Me$_3$) ppm. IR (KBr, Nujol): $\tilde{\nu}$ 1255 (vs), 1169 (s), 1102 (s), 980 (vs), 871 (vs), 840 (vs), 609 (s), 588 (s), 571 (vs) cm^{-1}. MS (EI, *m*/*z*, (%)): 694 (2) [M^+], 346 (17) [$^1/_2M^+$], 311 (100) [$^1/_2M^+ -$ Cl]. Anal. Calcd for $C_{30}H_{52}Cl_4N_2Si_4$ (694.91): C, 51.9; H, 7.5; N, 4.0; Cl, 30.3. Found: C, 51.8; H, 7.9; N, 4.0; Cl, 30.3.

1,2-Bis[bis(trimethylsilyl)methyl]tetrachlorodisilane (2d). Yield: 6.9 g (13.4 mmol, 53%). Mp 105 °C. ^{1}H NMR (200 MHz, C_6D_6): δ 0.28 (s, Si(C*H*$_3$)$_3$), 0.61 (s, C*H*(SiMe$_3$)$_2$). ^{13}C NMR (100 MHz, C_6D_6): δ 3.2 (Si(*C*H$_3$)$_3$), 10.2 (*C*H(SiMe$_3$)$_2$). ^{29}Si NMR (50 MHz, C_6D_6): δ 1.1 (*Si*Me$_3$), 18.0 (*Si*Cl$_2$) ppm. IR (KBr, Nujol): $\tilde{\nu}$ 2101 (w), 1937 (w), 1900 (w), 1864 (w), 1404 (s), 1307 (m), 1267 (s), 1255 (vs), 1170 (w), 1027(vs), 987 (vs), 828 (vs), 770 (s), 719 (s), 682 (s), 616 (m), 580 (s), 545 (s), 518 (s), 469 (s), 372 (s) cm^{-1}. MS (EI, *m*/*z*, (%)): 501 (20) [$M^+ - Me$], 257 (100) [1/2 M^+]. Anal. Calcd for $C_{14}H_{38}Cl_4Si_6$ (516.78): C, 32.5; H, 7.4; Cl, 27.4; Si, 32.6. Found: C, 32.4; H, 7.5; Cl, 26.9; Si 32.1.

1,2-Bis[tris(trimethylsilyl)methyl]tetrachlorodisilane (2e). Yield: 11.9 g (18.0 mmol, 72%). Mp >300 °C. ^{1}H NMR (200 MHz, C_6D_6): δ 0.32 (s, Si(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz, C_6D_6): δ 4.6 (Si(*C*H$_3$)$_3$), 3.4 (*C*(SiMe$_3$)$_3$). ^{29}Si NMR (50 MHz, C_6D_6): δ −0.3 (*Si*Me$_3$), 3.6 (*Si*Cl$_2$) ppm. IR (KBr-pellet): $\tilde{\nu}$ 1410 (s), 1300 (w), 1274 (vs), 1259 (vs), 1094 (w), 1058 (w), 1024 (w), 1011 (s), 883 (w), 854 (w), 835 (m), 793 (w), 756 (m), 704 (w), 679 (vs), 549 (vs), 503 (vs) cm^{-1}. MS (EI, *m*/*z*, (%)): 643 (0.5) [$M^+ - Me$], 351 (100) [$M^+ - 4SiMe_3 - Me$], 329 (5) [$^1/_2M^+$]. Anal. Calcd for $C_{20}H_{54}Cl_4Si_8$ (661.14): C, 36.3; H, 8.2; Cl, 21.4. Found: C, 35.9; H, 7.9; Cl, 21.2.

1,2-Bis(*N*-(4-isopropylphenyl)-*N*-(trimethylsilyl)amino)tetrabromodisilane (3b). Yield: 15.4 g (19.5 mmol, 78%). Mp 243 °C. ^{1}H NMR (250 MHz, C_6D_6): δ 0.17 (s, 18 H, SiC*H*$_3$), 1.14 (d, $^3J_{HH} = 6.9$ Hz, 12 H, CH(C*H*$_3$)$_2$), 2.73 (sept, $^3J_{HH} = 6.9$ Hz, 2 H, C*H*Me$_2$), 6.72−7.01 (m, 8 H, arom. *H*). ^{13}C NMR (125 MHz, C_6D_6): δ 1.7 (Si*C*H$_3$), 25.3 (CH(*C*H$_3$)$_2$), 33.7 (*C*HMe$_2$), 127.4, 131.2, 139.6, 147.7 (arom-*C*). ^{29}Si NMR (79 MHz, C_6D_6): δ −37.2 (*Si*Br$_2$), 12.9 (*Si*Me$_3$) ppm. IR (CsI, Nujol): $\tilde{\nu}$ 1594 (w), 1450 (s), 1383 (m), 1371 (s), 1298 (vs), 1253 (vs), 1185 (s), 1143 (w), 1057 (w), 907 (vs), 841 (vs), 822 (vs), 781 (w), 750 (m), 688 (w), 639 (w), 609 (w), 548 (m), 431 (vs), 375 (s), 263 (s) cm^{-1}. MS (EI, *m*/*z* (%)): 773 (5) [$M^+ - Me$], 709 (9) [$M^+ - Br$], 394 (36) [$^1/_2M^+$], 73 (100) [Me_3Si^+]. Anal. Calcd for $C_{24}H_{40}Br_4N_2Si_4$ (788.55): C, 36.6; H, 5.1; Br, 40.5; N, 3.6; Si, 14.3. Found: C, 36.6; H, 5.2; Br, 40.2; N, 3.5; Si, 14.0.

1,2-Bis[tris(trimethylsilyl)silyl]tetrabromodisilane (3f). Yield: 14.6 g (16.8 mmol, 67%). Mp >290 °C. ^{1}H NMR (250 MHz, C_6D_6): δ 0.23 (s, C*H*$_3$). ^{13}C NMR (125 MHz, C_6D_6): δ 2.3 (*C*H$_3$). ^{29}Si NMR (50 MHz, C_6D_6): δ −99.8 (*Si*Si$_4$), −23.7 (*Si*Br$_2$), −12.4 (*Si*Me$_3$) ppm. IR (CsI, Nujol): $\tilde{\nu}$ 1441 (m), 1312 (w), 1085 (s), 860 (vs), 831 (vs), 819 (s), 745 (m), 692 (s), 623 (s), 517 (m), 501 (m), 423 (vs), 310 (s), 251 (s) cm^{-1}. MS (EI, *m*/*z* (%)): 871 (4) [M^+], 791 (8) [$M^+ - Br$], 435 (19) [$^1/_2M^+$], 73 (100) [Me_3Si^+]. Anal. Calcd for $C_{18}H_{54}Br_4Si_{10}$ (871.10): C, 24.8; H, 6.3; Br, 36.7; Si, 32.2. Found: C, 24.6; H, 6.2; Br, 36.9; Si, 32.0.

1,2-Bis[tris(trimethylsilyl)silyl]tetrachlorodisilane (2f). A solution of hexachlorodisilane (2.7 g, 10 mmol) in toluene (30 mL) was cooled to −78 °C. $(Me_3Si)_3SiK{\cdot}2THF$ (7.2 g, 20 mmol), dissolved in toluene (50 mL), was added dropwise with constant stirring. The reaction mixture was allowed to warm to room temperature over a period of 15 h, and the formed potassium chloride was removed by filtration through Celite. All volatiles were stripped off in vacuo. The residue was dissolved in *n*-hexane (20 mL) and stored at −20 °C. **2f** precipitated as a colorless solid. Yield: 5.8 g (6.0 mmol, 60%). Mp >300 °C. ^{1}H NMR (200 MHz, C_6D_6): δ 0.40 (s, C*H*$_3$). ^{13}C NMR (125 MHz, C_6D_6): δ 3.0 (*C*H$_3$). ^{29}Si NMR (50 MHz, C_6D_6): δ −107.8 (*Si*Si$_4$), −8.1 (*Si*Cl$_2$), 3.0 (*Si*Me$_3$) ppm. IR (KBr, Nujol): $\tilde{\nu}$ 2050 (w), 1928 (w), 1398 (m), 1309 (w), 1258 (m), 1245 (vs), 1082 (m), 1057 (m), 973 (w), 838 (vs), 748 (m), 738 (m), 689 (s), 623 (s), 554 (w), 525 (s), 510 (m), 441 (w), 423 (m). MS (EI, *m*/*z* (%)): 678 (3) [$M^+ - Me$], 642 (5) [$M^+ - Me - Cl$], 345 (38) [$^1/_2M^+$], 73 (100) [Me_3Si^+]. Anal. Calcd for $C_{18}H_{54}Cl_4Si_{10}$ (693.29): C, 31.2; H, 7.9; Cl, 20.5; Si, 40.5. Found: C, 31.4; H, 7.8; Cl, 20.3; Si, 40.3.

Synthesis of the Pentahalogenodisilanes 4, 5. A solution of the respective hexahalogenodisilane (10 mmol) in toluene (20 mL) was added dropwise to a suspension of Cp*Li (1.8 g, 13 mmol) in toluene (50 mL). After stirring at room temperature over a period of 15 h, the formed lithium halogenide was removed by filtration over Celite. All volatiles were removed in vacuo. The residue was purified by distillation **(4)** or recrystallization from *n*-pentane (10 mL) at 0 °C **(5)**.

Pentamethylcyclopentadienylpentachlorodisilane (4). Yield: 3.1 g (8.5 mmol, 85%). Bp 55 °C/0.005 mbar. ^{1}H NMR (200 MHz, C_6D_6): δ 1.61 (s, C*H*$_3$). ^{13}C NMR (125 MHz, C_6D_6): δ 11.9 (*C*H$_3$), 133.5 (*C*$_5$Me$_5$). ^{29}Si NMR (50 MHz, C_6D_6): δ −8.1 (*Si*Cl$_3$), −0.5 (*Si*Cl$_2$) ppm. IR (KBr, Nujol): $\tilde{\nu}$ 1621 (m), 1553 (w), 1261 (m), 1240 (m), 1165 (w), 1137 (s), 1079 (vs), 975 (w), 820 (m), 792 (m), 746 (s), 724 (w), 611 (m), 582 (vs), 545 (vs), 452 (vs), 381 (vs) cm^{-1}. MS (EI, *m*/*z*, (%)): 368 (12) [M$^+$], 333 (5) [M$^+$ − Cl], 135 (100) [$C_{10}H_{15}{}^+$]. Anal. Calcd for $C_{10}H_{15}Cl_5Si_2$ (368.66): C, 32.6; H, 4.1; Cl, 48.1; Si, 15.2. Found: C, 32.2; H, 4.2; Cl, 47.9; Si, 15.2.

Pentamethylcyclopentadienylpentabromodisilane (5). Yield: 5.2 g (8.8 mmol, 88%). Mp 169 °C. ^{1}H NMR (250 MHz, C_6D_6): δ 1.63 (s, C*H*$_3$). ^{13}C NMR (50 MHz, C_6D_6): δ 12.6 (*C*H$_3$), 130.8 (*C*$_5$Me$_5$). ^{29}Si NMR (50 MHz, C_6D_6): δ −30.8 (*Si*Br$_3$), −18.9 (*Si*Br$_2$) ppm. IR (CsI, Nujol): $\tilde{\nu}$ 1622 (w), 1554 (w), 1234 (w), 1135 (m), 1074 (m), 790 (w), 740 (m), 592 (w), 571 (w), 561 (w), 534 (w), 496 (s), 460 (vs), 448 (vs), 330 (vs), 291 (w) cm^{-1}. MS (EI, *m*/*z* (%)): 591 (14) [M$^+$], 511 (3) [M$^+$ − Br], 135 (100) [$C_5Me_5{}^+$]. Anal. Calcd for $C_{10}H_{15}Br_5Si_2$ (590.92): C, 20.3; H, 2.6; Br, 67.6; Si, 9.5. Found: C, 20.2; H, 2.5; Br, 67.2; Si, 9.4.

1,2-Bis(pentamethylcyclopentadienyl)tetraaminodisilane (6a). A solution of **2a** (4.68 g, 10.0 mmol) in toluene (100 mL) was added slowly at −78 °C to a solution of sodium (0.92 g, 40 mmol) in ammonia (30 mL). The mixture was heated to the boiling temperature of the ammonia and was stirred at this temperature for 1 h. After heating to room temperature, whereby the ammonia vaporized, the precipitate was removed by filtration and extracted twice with boiling toluene (20 mL). The solvent was removed under vacuum, and 3.68 g (9.42 mmol, 94%) **6a** was obtained as colorless solid. Mp 193 °C. ^{1}H NMR (200 MHz, C_6D_6): δ 0.38 (br s, N*H*$_2$), 0.87−1.39 (m, 1-C*H*$_3$), 1.74−1.93 (m, 2-C*H*$_3$, 3-C*H*$_3$, 4-C*H*$_3$, 5-C*H*$_3$). ^{13}C NMR (100 MHz, C_6D_6): δ 11.5, 12.7, 13.4 (*C*H$_3$), 57.2 (*C*-1), 134.5, 139.5 (*C*-2, *C*-3, *C*-4, *C*-5). ^{29}Si NMR (50 MHz, C_6D_6): δ −16.6 (*Si*(NH$_2$)$_2$) ppm. IR (KBr, Nujol): $\tilde{\nu}$ 3440 (s), 3364 (s), 3347 (m), 1625 (w), 1533 (s), 1262 (w), 1231 (m), 1131 (m), 1075 (w), 1061 (w), 1034 (w), 953 (w), 861 (s), 835 (s), 821 (s), 794 (s), 763 (m), 594 (w), 574 (w), 461 (s) cm^{-1}. MS (EI, *m*/*z*, (%)): 390 (0.03) [M$^+$], 255 (60) [M$^+$ − Cp*], 195 (100) [$^1/_2$M$^+$]. Anal. Calcd for $C_{20}H_{38}N_4Si_2$ (390,72): C, 61.5; H, 9.8; N, 14.4; Si, 14.3. Found: C, 61.9; H, 9.3; N, 14.1; Si, 14.0.

Synthesis of the Tetraaminodisilanes 6b,**c.** The respective tetrachlorodisilane (5.00 mmol) was dissolved in liquid ammonia (40 mL) at −78 °C. The reaction mixture was slowly warmed, during which it started refluxing at −30 °C. It was maintained at this temperature for 5 h, before allowing to come to room temperature over a period of 14 h, during which ammonia evaporated. To the resulting residue *n*-hexane (50 mL) was added, and the formed ammonium chloride was removed by filtration. At −20 °C a colorless microcrystalline solid was obtained from the filtrate over a period of 48 h.

1,2-Bis(*N*-(4-isopropylphenyl)-*N*-(trimethylsilyl)amino)tetraaminodisilane (6b). Yield: 2.38 g (4.47 mmol, 89%). Mp 72 °C. ^{1}H NMR (200 MHz, C_6D_6): δ 0.20 (s, Si(C*H*$_3$)$_3$), 0.40 (br s, N*H*$_2$), 1.12 (d, $^3J_{H-H}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), 2.74 (sept, $^3J_{H-H}$ = 6.9 Hz, C*H*Me$_2$), 7.00−7.21 (m, arom-*H*). ^{13}C NMR (50 MHz, C_6D_6): δ 2.9 (Si(*C*H$_3$)$_3$), 24.3 (CH(*C*H$_3$)$_2$), 33.8 (*C*HMe$_2$), 126.7, 130.6, 144.2, 145.4 (arom-*C*). ^{29}Si NMR (100 MHz, C_6D_6): δ −28.2 (*Si*(NH$_2$)$_2$), 4.5 (*Si*Me$_3$) ppm. IR (KBr, Nujol): $\tilde{\nu}$ 3464 (m), 3385 (m), 1926 (w), 1887 (w), 1784 (w), 1653 (w), 1606 (m), 1534 (m), 1505 (s), 1415 (w), 1246 (vs), 1229 (vs), 1178 (m), 1139 (m), 1101 (m), 1054 (m), 1017 (m), 960 (s), 928 (vs), 902 (vs), 841 (vs), 755 (m), 737 (m), 684 (m), 637 (w), 578 (m), 562 (m), 484 (w), 456 (w), 427 (w) cm^{-1}. MS (EI, *m*/*z*, (%)): 532 (6) [M$^+$], 249 (100) [$^1/_2$M$^+$ − NH$_2$ − H]. Anal. Calcd for $C_{24}H_{48}N_6Si_4$ (533.03): C, 54.1; H, 9.1; N, 15.8; Si, 21.1. Found: C, 54.2; H, 9.1; N, 15.7; Si, 20.8.

1,2-Bis(*N*-(2,6-diisopropylphenyl)-*N*-(trimethylsilyl)amino)tetraaminodisilane (6c). Yield: 2.53 g (4.10 mmol, 82%). Mp 112−119 °C. ^{1}H NMR (200 MHz, C_6D_6): δ 0.13, 0.20 (s, Si(C*H*$_3$)$_3$), 0.24 (br s, Si(N*H*$_2$)$_2$), 1.13, 1.20, 1.26 (d, $^3J_{H-H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 3.53, 3.64 (sept, $^3J_{H-H}$ = 6.8 Hz, C*H*Me$_2$), 7.00−7.05 (m, arom-*H*). ^{13}C NMR (63 MHz, C_6D_6): δ 2.4, 2.7 (Si(*C*H$_3$)$_3$), 24.6, 25.2, 25.6 (CH(*C*H$_3$)$_2$), 27.8, 28.0 (*C*HMe$_2$), 123.0 (arom-*C*-4), 124.9 (arom-*C*-3, arom-*C*-5), 143.0 (arom-*C*-2, arom-*C*-6), 147.1 (arom-*C*-1). ^{29}Si NMR (50 MHz, C_6D_6): δ −41.1 (*Si*(NH$_2$)$_2$, 3.6 (*Si*Me$_3$), 4.3 (*Si*Me$_3$) ppm. IR (KBr, Nujol): $\tilde{\nu}$ 3495 (s), 3473 (s), 3412 (s), 3393 (s), 1926 (w), 1620 (w), 1537 (m), 1438 (m), 1363 (w), 1315 (m), 1250 (s), 1178 (m), 1105 (m), 1043 (m), 966 (s), 936 (vs), 911 (s), 879 (m), 837 (vs), 802 (m), 753 (w), 685 (m), 678 (w), 543 (w), 446 (w) cm^{-1}. MS (EI, *m*/*z*, (%)): 615 (3) [M$^+$ − H], 307 (59) [$^1/_2$M$^+$ − H], 73 (100) [SiMe$_3$]. Anal. Calcd for $C_{30}H_{60}N_6Si_4$ (617.19): C, 58.4; H, 9.8; Si, 18.2. Found: C, 58.9; H, 9.3; Si, 18.6.

1,2-Bis[bis(trimethylsilyl)methyl]tetraaminodisilane (6d). Sodium (0.93 g, 40 mmol) was dissolved at −78 °C in liquid ammonia (20 mL). A solution of **2d** (3.5 g, 6.7 mmol) in toluene (100 mL) was added dropwise over a period of 30 min. The mixture was heated to the boiling temperature of the ammonia and was stirred at this temperature for 1 h. In addition, the reaction mixture was allowed to warm to room temperature within 3 h, whereby the ammonia vaporized. Precipitated sodium chloride was removed by filtration, and the toluene was removed under vacuum. *n*-Hexane (70 mL) was added to the crude product, and after crystallization at −20 °C 2.4 g (5.5 mmol, 82%) **6d** was obtained as colorless crystals. Mp 64 °C. ^{1}H NMR (200 MHz, C_6D_6): δ −0.37 (s, C*H*(SiMe$_3$)$_2$), 0.25 (s, Si(C*H*$_3$)$_3$), 0.58 (br s, N*H*$_2$). ^{13}C NMR (100 MHz, C_6D_6): δ 3.8 (Si(*C*H$_3$)$_3$), 6.9 (*C*Si(NH$_2$)$_2$). ^{29}Si NMR (50 MHz, C_6D_6): δ −15.2 (*Si*(NH$_2$)$_2$), −1.2 (*Si*Me$_3$) ppm. IR (KBr, Nujol): $\tilde{\nu}$ 3478 (s), 3393 (s), 1535 (vs), 1300 (m), 1262 (s), 1250 (vs), 1169 (w), 1078 (m), 1008(vs), 844 (s), 774 (s), 725 (m), 677 (s), 614 (m), 536 (m) cm^{-1}. MS (EI, *m*/*z*, (%)): 438 (1.5) [M$^+$], 421 (12) [M$^+$ − NH$_3$], 202 (100) [$^1/_2$M$^+$ − NH$_3$]. Anal. Calcd for $C_{14}H_{46}N_4Si_6$ (439.06): C, 38.3; H, 10.6. Found: C, 37.8; H, 10.1.

1,2-Bis[tris(trimethylsilyl)methyl]tetraaminodisilane (6e). At −78 °C **2e** (3.31 g, 5.01 mmol) was dissolved in liquid ammonia (30 mL) using an autoclave. After closing the autoclave the mixture was stirred for 7 days at 80 °C. Subsequently, cooling the autoclave to room temperature the ammonia was released and *n*-hexane (50 mL) was added to the residue. The solution was filtered, and the solvent was removed in vacuo. **6e** (1.34 g, 2.34 mmol, 47%) was obtained as a light yellow oil. Decomp 274 °C. ^{1}H NMR (200 MHz, C_6D_6): δ 0.30 (s, Si(C*H*$_3$)$_3$), 1.95 (br s, N*H*$_2$). ^{13}C NMR (100 MHz, C_6D_6): δ 5.0 (Si(*C*H$_3$)$_3$), 1.5 (*C*SiCl$_2$). ^{29}Si NMR (50 MHz, C_6D_6): δ −0.4 (*Si*Me$_3$), −18.9 (*Si*(NH$_2$)$_2$) ppm. IR (KBr, Nujol): $\tilde{\nu}$ 3492 (m), 3409 (m), 1731 (m), 1538 (s), 1421 (w), 1278 (vs), 1252 (vs), 1200 (w), 1178 (w), 1093 (s), 1012 (s), 870 (vs), 857 (vs), 841 (vs), 806 (s), 720 (m), 676 (m), 617 (m), 550 (w), 514 (w) cm^{-1}. MS (EI, *m*/*z*, (%)): 558 (0.5) [M$^+$ − Me], 286 (65) [$^1/_2$M$^+$], 270 (100) [$^1/_2$M$^+$ − NH$_2$]. Anal. Calcd for $C_{20}H_{52}N_4Si_8$ (573.34): C, 41.9; H, 9.1; N, 9.8. Found: C, 41.8; H, 9.2; N, 9.4.

1,2-Bis[bis(trimethylsilyl)methyl]disilane (7). A solution of **2d** (1.3 g, 2.5 mmol) in THF (30 mL) was added dropwise to a suspension of $LiAlH_4$ (0.42 g, 11.1 mmol) in THF (40 mL) at −78 °C over a period of 15 min. After heating to room temperature within 3 h, the mixture was stirred for 15 h. The solvent was removed in vacuo, and *n*-hexane (80 mL) was added to the residue. After filtration, the clear solution was concentrated under vacuum to 10 mL, and storing at −20 °C for 5 days resulted in 0.72 g (1.9 mmol, 76%) of **7** as colorless solid. Mp 66 °C. ^{1}H NMR (200 MHz, C_6D_6): δ −0.66 (m, C*H*(SiMe$_3$)$_2$), 0.16 (s, Si(C*H*$_3$)$_3$), 3.96 (m, Si*H*$_2$). ^{13}C NMR (125 MHz, C_6D_6): δ −5.4 (*C*H(SiMe$_3$)$_2$), 1.6 (Si(*C*H$_3$)$_3$). ^{29}Si NMR (80 MHz, C_6D_6): δ −59.9 (*Si*H$_2$), 1.1 (*Si*Me$_3$) ppm. IR (KBr, Nujol): $\tilde{\nu}$ 2117 (vs), 1301 (w), 1262 (vs), 1251 (vs), 1095(s), 1012 (vs), 940 (m), 846 (vs), 800 (m), 776 (s), 712 (s), 680 (s), 641 (w) cm^{-1}. MS (EI, *m*/*z*, (%)): 378 (9) [M$^+$], 363 (21) [M$^+$ − Me], 188 (100) [$^1/_2$M$^+$ − H]. Anal. Calcd for $C_{14}H_{42}Si_6$ (379.00): C, 44.4; H, 11.2. Found: C, 43.9; H 10.8.

1,2-Bis[bis(trimethylsilyl)methyl]tetrafluorodisilane (8). To a suspension of Me_3SnF (2.6 g, 14.2 mmol) in toluene (40 mL) was added a solution of **2d** (1.7 g, 3.3 mmol) in toluene (35 mL). The resulting mixture was heated for 15 h under reflux. The solvent and the generated Me_3SnCl were removed in vacuo, and a yellow oil was obtained. After distillation at 15 Torr, 1.26 g (2.8 mmol, 85%) of **8** was obtained as a colorless liquid with a bp of 180 °C (15 Torr). Mp 3 °C. ^{1}H NMR (200 MHz, C_6D_6): δ −0.10 − (−0.22) (m, C*H*(SiMe$_3$)$_2$), 0.18 (s, Si(C*H*$_3$)$_3$). ^{13}C NMR (125 MHz, C_6D_6): δ 2.3 (Si(*C*H$_3$)$_3$), 9.3 (*C*H(SiMe$_3$)$_2$). ^{19}F NMR (188 MHz, C_6D_6): δ 43.89 (t, $^3J_{FF}$ = 5.2 Hz, Si*F*$_2$). ^{29}Si NMR (100 MHz, C_6D_6): δ 0.1 (*Si*Me$_3$), 4.5 (tt, $^1J_{SiF}$ = 342 Hz, $^2J_{SiF}$ = 59 Hz, *Si*F$_2$) ppm. IR (KBr): $\tilde{\nu}$ 2956 (vs), 2902 (s), 2840 (w), 1941 (w), 1433 (m), 1406 (m), 1305 (w), 1268 (vs), 1256 (vs), 1017 (vs), 995 (vs), 875 (vs), 783 (vs), 726 (s), 684 (vs), 652 (w), 617 (m), 538 (s), 493 (m), 417 (vs), 341 (s) cm^{-1}. MS (EI, *m/z*, (%)): 435 (100) [M$^+$ − Me], 225 (20) [$^1/_2$M$^+$]. Anal. Calcd for $C_{14}H_{38}F_4Si_6$ (450.96): C, 37.3; H, 8.5; Si 37.4. Found: C, 37.2; H, 8.4; Si, 37.2.

Synthesis of the Tetrahalogenodisilanes 3d, 9. The tetrahalogenodisilane was prepared from the respective tetraaminodisilane. **6d** (1.0 g, 2.3 mmol) was dissolved in toluene (50 mL), and under continuous stirring HBr and HI gas, respectively, was bubbled slowly through the solution over a period of 15 min. The mixture was stirred for 30 min, and then the insoluble solid was removed by filtration and the toluene was vaporized under vacuum. **3d** was obtained as a colorless solid and **9** gave yellow-white crystals after recrystallization from *n*-hexane (10 mL).

1,2-Bis[bis(trimethylsilyl)methyl]tetrabromodisilane (3d). Yield: 1.2 g (1.7 mmol, 74%). Mp 129 °C. ^{1}H NMR (200 MHz, C_6D_6): δ 0.34 (s, Si(C*H*$_3$)$_3$), 1.11 (s, C*H*(SiMe$_3$)$_2$). ^{13}C NMR (100 MHz, C_6D_6): δ 3.5 (Si(*C*H$_3$)$_3$), 10.4 (*C*H(SiMe$_3$)$_2$). ^{29}Si NMR (100 MHz, C_6D_6): δ 4.1 (*Si*Br$_2$), 2.0 (*Si*Me$_3$) ppm. IR (CsI, Nujol): $\tilde{\nu}$ 1305 (w), 1265 (s), 1255 (vs), 1097 (m), 1027 (s), 983 (m), 843 (vs), 799 (s), 768 (s), 713 (m), 680 (m), 644 (w), 547 (w), 528 (m), 443 (w), 432 (m), 392 (w), 345 (m), 303 (w), 282 (w) cm^{-1}. MS (EI, *m/z*, (%)): 694 (0.1) [M$^+$], 679 (10) [M$^+$ − Me], 347 (100) [$^1/_2$M$^+$]. Anal. Calcd for $C_{14}H_{38}Br_4Si_6$ (694.58): C, 24.2; H, 5.5; Si, 24.3. Found: C, 24.3; H, 5.8; Si, 24.9.

1,2-Bis[bis(trimethylsilyl)methyl]tetraiododisilane (9). Yield: 1.6 g (1.8 mmol, 78%). Mp 142 °C. ^{1}H NMR (200 MHz, C_6D_6): δ 0.42 (s, Si(C*H*$_3$)$_3$), 1.74 (s, C*H*(SiMe$_3$)$_2$). ^{13}C NMR (100 MHz, C_6D_6): δ 4.3 (Si(*C*H$_3$)$_3$), 9.3 (*C*H(SiMe$_3$)$_2$). ^{29}Si NMR (100 MHz, C_6D_6): δ 3.4 (*Si*Me$_3$), −50.3 (*Si*I$_2$) ppm. IR (KBr, Nujol): $\tilde{\nu}$ 1304 (w), 1265 (s), 1254 (vs), 1169 (w), 1096 (m), 1025 (s), 983 (m), 854 (vs), 843 (vs), 807 (m), 768 (m), 723 (m), 711 (m), 679 (m), 642 (w), 532 (w), 523 (m), 472 (w), 383 (s), 359 (s) cm^{-1}. MS (EI, *m/z*, (%)): 867 (2) [M$^+$ − Me], 755 (4) [M$^+$ − I], 441 (100) [$^1/_2$M$^+$]. Anal. Calcd for $C_{14}H_{38}I_4Si_6$ (882.59): C, 19.1; H, 4.3; Si, 19.1. Found: C, 19.3; H, 4.6; Si, 19.1.

1,2-Bis[bis(trimethylsilyl)methyl]tetrahydroxodisilane (10). To a solution of **6d** (0.38 g, 0.87 mmol) in THF (50 mL) was added a solution of water (0.1 mL, 0.1 g, 5.6 mmol) in THF (20 mL) dropwise over 15 min. The mixture was stirred for 20 h at the boiling temperature of the solvent whereby ammonia escaped. After removing the THF under vacuum, diethyl ether (10 mL) was added. Crystallization at −20 °C yields 0.33 g (0.74 mmol, 86%) of **10** as colorless crystals. Mp 145 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ −0.40 (s, C*H*(SiMe$_3$)$_2$), 0.14 (s, Si(C*H*$_3$)$_3$), 3.55 (br s, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 3.1 (Si(*C*H$_3$)$_3$), 8.7 (*C*H(SiMe$_3$)$_2$). ^{29}Si NMR (50 MHz, $CDCl_3$): δ −7.4 (*Si*(OH)$_2$), −0.6 (*Si*Me$_3$) ppm. IR (KBr, Nujol): $\tilde{\nu}$ 3361 (vs), 1302 (w), 1263 (s), 1252 (vs), 1168 (w), 1097 (m), 1012(s), 988 (s), 850 (vs), 841 (vs), 777 (s), 721 (m), 679 (s), 614 (w) cm^{-1}. MS (EI, *m/z*, (%)): 393 (40) [M$^+$ − 2OH − Me], 379 (35) [M$^+$ − 3Me − H$_2$O], 203 (100) [$^1/_2$M$^+$ − H$_2$O]. Anal. Calcd for $C_{14}H_{42}O_4Si_6$ (443.00): C, 38.0; H, 9.6; Si, 38.0. Found: C, 38.0; H, 9.6; Si, 38.5.

X-ray Data Collection, Structure Solution, and Refinement of 2d, 6a, 6d, and 9. The crystals were mounted on a glass fiber in a rapidly cooled perfluoro polyether.[28] Diffraction data were collected on a Stoe−Siemens−Huber four-circle-diffractometer coupled to a Siemens CCD area-detector, with graphite-monochromated Mo−K$_\alpha$ radiation (λ = 0.71073 Å), performing φ- and ω-scans. The structure was solved by direct methods using SHELXS-86 or SHELXS-97[29] and refined against F^2 on all data by full-matrix least squares with SHELXL-93[30] or SHELXL-97.[31] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bonded to carbon atoms were included in the model at geometrically calculated positions and refined using a riding model. The hydrogen atoms bonded to nitrogen were localized in the difference Fourier synthesis and refined freely with the help of distance restraints.

Details of the crystal structure refinement of **2d**, **6a**, **6d**, and **9** are summarized in Table 4. Further details of the crystal structure determination are available on request from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK, on quoting the depository numbers CCDC-153368 for **2d**, CCDC-153369 for **6a**, CCDC-153370 for **6d**, and CCDC-153371 for **9**, the names of the authors, and the full journal citation [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Supporting Information Available: Tables of non-hydrogen coordinates and isotropic thermal parameters, bond distances, bond angles, anisotropic thermal parameters, hydrogen atom positions, and isotropic thermal parameters for **2d**, **6a**, **6d**, and **9**; a plot illustrating the noncrystallographic symmetry elements relating the molecules in the asymmetric unit; and a plot showing the positions of the eight highest residual electron density peaks for **6d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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