Dehydrocoupling Reactions of Organosilanes with Hydrazines

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Phenylsilane reacts spontaneously with hydrazine to give a soluble oligomer, [PhSi(NHNH)$_2$SiPhNHNH]$_n$, **1**, while in the presence of dimethyltitanocene (DMT) as catalyst, rapid coupling took place to give an insoluble gel. The dehydrocoupling reactions of phenylsilane with methylhydrazines (1-methyl-, 1,1-dimethyl-, and 1,2-dimethylhydrazine) are effectively catalyzed by DMT. Phenylsilane reacts with 1-methylhydrazine to give poly((phenylsilyl)-*N*-(methylamino)azane), **2**, and poly[phenyl(methylhydrazyl)silane], **3**. In the reaction with 1,1-dimethylhydrazine, homocoupling of phenylsilane competes effectively with the cross-coupling reaction with the hydrazine, to give diphenyldisilane and triphenyltrisilane in about the same amount as the oligomeric silylhydrazines (**4** and **5**, the analogs of **2** and **3**, respectively). The reaction with 1,2-dimethylhydrazine gives simple silylhydrazines PhSiH$_2$(NMeNHMe), **6**, and PhSiH(NMeNHMe)$_2$, **7**, without homocoupling. The cyclic compound Ph$_2$Si(NHNH)$_2$SiPh$_2$, **8**, was obtained in 40% yield from the reaction of diphenylsilane with hydrazine. The reaction of diphenylsilane with 2 equiv of methylhydrazine gave Ph$_2$Si(NHNHMe)$_2$, **13**, in 70% yield, by the stepwise replacement of the Si–H groups of diphenylsilane with hydrazyl groups. A strong inhibiting effect of methyl substitution was evident in the reactions of diphenylsilane with 1,1-dimethyl- and 1,2-dimethylhydrazine. The crystal structure of **8** reveals a chairlike conformation of the Si$_2$N$_4$ ring [a = 29.683(5) Å, b = 5.8972(17) Å, c = 39.038(7) Å, β = 105.492(14)°; monoclinic, $A2/a$; two independent molecules in one unit cell, Z = 12], in which each NHNH unit contains one planar nitrogen and one pyramidal nitrogen atom. The structure of **13** [a = 7.7725(5) Å, b = 9.1289(9) Å, c = 21.2624(17) Å, β = 91.814(7)°; monoclinic, $P2_1/c$; Z = 4] is also reported.

Introduction

Dehydrocoupling of covalent hydrides represents an interesting route to the formation of element–element bonds for a number of reasons. Most importantly, this chemistry has provided routes to hitherto unknown compounds, but it is also environmentally attractive in that it does not produce side products that are difficult and costly to dispose of.[1] The group 4 metallocene catalyzed dehydrocoupling of silanes, and germanes, to give either simple oligomers, or relatively long chains, has been extensively investigated by several groups.[2–7] Catalyzed heterodehydrocoupling has also been reported for SiH/NH,[8,9] SiH/CH,[10] and SiH/OH,[11] as well as BH/NH, reactions.[12]

Poly(organosilazanes) have recently attracted interest as potential polymer precursors to Si$_3$N$_4$.[9,13,14] We have studied the catalyzed reactions of organosilanes with

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Table 1. Some Data for Uncatalyzed Reactions of Phenylsilane with Hydrazine

[$PhSiH_3$], M	[H_2NNH_2], M	T, °C	t, min	conv,[a] mol %	M_w[b]
4.3	12.9	90	100	100	840
5.5	8.2	90	120	94	910
6.0	6.0	100	90	83	780
6.0	6.0	25	950	35	

[a] Based on silane consumption. [b] M_w/M_n ca. 1.1–1.2; monomodal distribution. n.b. calibation of GPC vs polystyrene.

primary amines, and with ammonia, with a view to synthesizing poly(organosilazanes).[9] A problem with the simple polysilazanes as precursors for Si_3N_4 is that the polymer is nitrogen deficient with respect to the Si/N stoichiometry of the product. A possible way of redressing this nitrogen deficiency would be to incorporate some –NH–NH– units into the polysilazane.[15] We have therefore undertaken a study of the dehydrocoupling chemistry of some hydrazines with organosilanes.

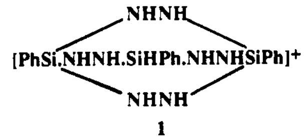
Although silylhydrazine chemistry has been well developed since the 1950s[16] and has found a number of uses in organic synthesis,[17] apart from the thoroughly studied anionic rearrangements of silylhydrazines,[18] surprisingly little is known of the chemical behavior of these interesting molecules and only a few molecular structures containing the Si–N–N– unit have been previously described in the literature.[19–21] The most widely used synthesis of silylhydrazines, originally developed and extensively studied by Wannagat et al.,[22] is the elimination of HCl between a chlorosilane and a hydrazine. To our knowledge, there is only a single previous report of a catalyzed dehydrocoupling between a silane and a hydrazine.[23]

Results

Reaction of Phenylsilane. Uncatalyzed Reactions of Phenylsilane. Phenylsilane reacts slowly with hydrazine at room temperature. With equimolar reactants, a third of the silane is consumed in 15 h of reaction. At elevated temperatures the rates are much faster and some results are summarized in Table 1. A striking feature of the reaction is the essentially complete disappearance of Si–H, monitored by both IR (ν_{Si-H}: 2140 cm^{-1} for $PhSiH_3$; 2148 cm^{-1} for Si(H)N) and ^{1}H NMR (δ_{Si-H}: 4.2 ppm for $PhSiH_3$; 5.2–5.4 ppm for Si(H)N). Despite the fact that the $PhSiH_3$ is a trifunctional reactant, the product of the reaction, a glassy white solid, remains soluble in organic solvents, indicating that the reaction is not taking place by a random branched polymerization. Further, the molecular weight of the product of the reaction is more or less independent of the reaction conditions.

In the course of the reaction, a group of three proton resonances at 5.23, 5.26, and 5.28 ppm, whose total integral never exceeds 6% of the phenyl proton integral, are assigned to intermediates containing the Si(H)–N function. In addition, the hydrazine proton resonance at 2.5 ppm broadens considerably and diminishes in intensity to about half its original integral relative to the phenyl protons, while the peak maximum shifts to 3.05 ppm. ^{15}N NMR revealed a single broad resonance at –338.0 ppm (relative to $MeNO_2$), which an INEPT pulse sequence confirmed to be due to NH. The ^{15}N chemical shift of compound **8**, described below, was measured to be –337.2 ppm. This evidence shows that the nitrogen is largely present in the form of NHNH groups and most likely in rings analogous to **8**.

The most intense and highest mass peak in the mass spectrum of the product was at m/e = 436. An exact mass determination showed this peak to be due to a species of formula $C_{18}H_{24}N_8Si_3$. The fragmentation of this species was dominated by loss of N_nH_m and phenyl radicals. The formula, and its general fragmentation behavior point to a structure for this ion of the kind



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The molecular weight of the product, obtained by GPC, was between 60 and 90% higher than that of the heaviest ion in the MS. The significance of this must be viewed with caution, since the calibration was carried out with polystyrene, which may not be a very good calibrant in this case. In contrast to the calibrant, the hydrazine reaction product may have a closed, cagelike structure and a high polarity. Both of these effects would tend to increase the elution volume and the molecular weight value based on polystyrene represents a lower limit.

The low molecular weight, the narrow polydispersity ($M_w/M_n \sim 1.1$–1.2), and the simple MS behavior all point toward the product being a relatively simple molecular species. On the other hand, the amorphous nature of the solid and the very broad resonances in the NMR spectra are more typical of a mixture of polymeric species.

Attempts to react n-hexylsilane with hydrazine, in the absence of a catalyst, were unsuccessful up to temperatures of 120 °C for periods of several days.

Catalyzed Reactions of Hydrazine with Phenylsilane. We have previously reported on the catalytic activity of dimethyltitanocene (DMT) in the reactions of silanes with amines and ammonia.[9] The reaction of phenylsilane with hydrazine is greatly accelerated at room temperature by catalytic amounts of DMT. The reaction is quite violent and leads to a complex mixture of products and, eventually, intractable gels which were not studied further.

Reactions of Phenylsilane with Methylhydrazines. The rate of spontaneous reaction of phenylsilane with methylhydrazine is very slow under ambient conditions. The presence of 1 mol % of DMT greatly accelerates the rate of reaction. With equimolar reactants, about 90% of phenylsilane was converted into silylhydrazine oligomer

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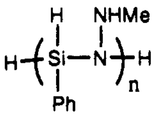
Table 2. Dehydrocoupling Reactions between Diphenylsilane and Hydrazines[a]

reaction	temp, °C	time	conv, %[b]	products
$Ph_2SiH_2 + H_2N\text{-}NH_2$ (1:1 mole) (neat)	25	5 days	75	$Ph_2Si(NHNH)_2SiPh_2$ (**8**) (15%) $Ph_2Si(H)NHNH_2$ (**9**) (20%) $Ph_2Si(NHNH_2)_2$ (**10**) (25%) and higher oligomers
(1:1 mole) (in 65 vol % toluene)	120	24 h	100	**8** (40%) $Ph_2Si[NHNHSiPh_2H]_2$ **11** (15%) $[Ph_2SiNH]_3$ (**12**) (10%) **9** (5%) **10** (5%) and higher oligomers
$Ph_2SiH_2 + 2H_2N\text{-}NHMe$ (1:2 mole) (neat)	25	2 days	70	$Ph_2Si(NHNHMe)_2$ (**13**) (25%) $Ph_2Si(H)NHNHMe$ (**14**) (35%) $HPh_2SiSiPh_2H$ (**15**) (5%) and higher oligomers
(neat)	80	20 h	100	**13** (70%) **14** (15%) **15** (<5%) and higher oligomers
$Ph_2SiH_2 + H_2N\text{-}NMe_2$ (1:1) (in 40 vol % hexane)	70	20 h	36	**15** (16%) $Ph_2SiH(NHNMe_2)$ (**16**) (13%) $(Ph_2SiH)_2NNMe_2$ (**17**) (7%)

[a] Catalyst: 1 mol % DMT. [b] Based on diphenylsilane consumption as measured by ^1H NMR.

at ambient temperature in 44 h. At 75 °C, 94% conversion was achieved in 12 h. The molecular weight of the product of this reaction, measured by GPC, was $M_n = 550$ ($M_w = 614$). The formation of the oligomer was monitored by ^1H NMR. Coupling between the proton and the methyl groups in the moieties –NHMe was observed by ^1H NMR throughout the course of the reaction, indicating the presence of SiNNHMe groups in the product. This means that the further dehydrocoupling of Si–H with N–H of the –NHMe groups can be excluded. The ^{29}Si NMR spectrum showed a broad peak from −19.0 to −36.0 ppm. A DEPT (^{29}Si) experiment illustrated that the product contains Si–H and $Si–H_2$ species, suggesting the presence of unit **2**. However, the integral ratios of (Ph–Si):(H–SiN):(Me–N + H–N) were observed to be roughly equal to 8:1:7 in the ^1H NMR spectrum of the product. This means that the composition of the product has more than one structural unit, i.e., **2**. One rationalization is that the product contains a mixture of **2** and **3** in a proportion of ca. 3:2. Only a small amount of diphenyldisilane (less than 4%) is formed in the product, as determined by ^1H and ^{29}Si NMR.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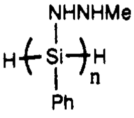
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The rate of reaction of 1,1-dimethylhydrazine with phenylsilane is very slow in the absence of catalyst. In the presence of 1 mol % of DMT the reaction proceeds at a reasonable rate at 70 °C, but homocoupling of silane to oligophenylsilanes competes effectively with the hydrazine reaction, to give 1,2-diphenyldisilane and 1,2,3-triphenyltrisilane in about the same amount as oligomeric silylhydrazines. The composition of the silylhydrazine products was deduced from ^1H NMR to be a mixture of poly((phenylsilyl)-*N*-(dimethylamino)azane), **4**, and poly[phenyl(dimethylhydrazyl)silane], **5**. the analogs of **2** and **3**. From the relative sharpness of the NMR resonances, the degree of polymerization does not appear to be very high. The combination of overall low activity, homopolymerization of silane, and aminolysis of backbone Si–H groups is reminiscent of the reactions of ammonia with primary silanes.[9a]

The rate of the DMT catalyzed reaction of 1,2-dimethylhydrazine with phenylsilane is quite a bit faster than that of the 1,1-dimethylhydrazine, and the homocoupling reaction of the silane does not compete. In this case the products are simple silylhydrazines, $PhSiH_2(NMeNHMe)$, **6**, and $PhSiH(NMeNHMe)_2$, **7**, resulting from the stepwise replacement of the Si–H groups of the phenylsilane by hydrazyl groups.

Reactions of Diphenylsilane. Reaction of Diphenylsilane with Hydrazine. Diphenylsilane does not react spontaneously with hydrazine at temperatures up to 120 °C. In the presence of 1 mol % of DMT, an equimolar mixture of diphenylsilane and hydrazine reacts slowly at room temperature and quite rapidly at 80 °C and above. The results of the two reactions are summarized in Table 2. In both cases the NH region of the ^1H NMR spectra contained many peaks between 2.2 and 3.4 ppm. However, the resonances of compounds **8**–**12** were easily identified and their integrals were measurable. In both the low temperature and high temperature reactions these small molecules accounted for about 65–70% of the NMR measurable NH species. The remainder is assumed to be due to higher molecular weight oligomers.

Compound **8** was successfully crystallized from the product mixture, and its structure was determined by single crystal X-ray diffraction. An ORTEP diagram is shown in Figure 1, and some selected bond parameters are listed in Table 3. The structures of **9**–**11** were deduced from their NMR spectra and **12** was identified by comparison of its properties to those of an authentic sample.

Reaction of Diphenylsilane with 1-Methyl-, 1,2-Dimethyl-, and 1,1-Dimethylhydrazine. Methylhydrazine does not react spontaneously with diphenylsilane. No reaction was detected after 4 h at 80 °C. In the presence of 1 mol % of DMT, about 99% of the silane had reacted under these conditions. The products of the two reactions are listed in Table 2. Compound **13** was isolated as a crystalline product. Its structure was determined by X-ray

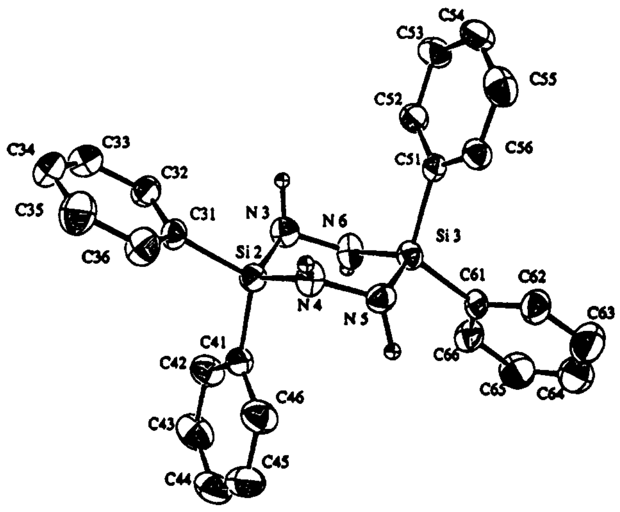


Figure 1. ORTEP view of 8, showing the atom numbering scheme. Selected bond distances (Å) and angles (deg) are given in Table 3.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound 8

Si2–N3	1.739(5)	Si3–N5	1.742(5)
Si2–N4	1.718(5)	Si3–N6	1.716(5)
Si2–C31	1.875(4)	Si3–C51	1.884(3)
Si2–C41	1.886(3)	Si3–C61	1.878(4)
N3–N6	1.463(6)	N4–N5	1.452(6)
N3–Si2–N4	110.67(24)	Si2–N3–N6	111.3(3)
N3–Si2–C31	107.34(20)	Si2–N3–HN3	114.7(3)
N3–Si2–C41	107.77(21)	N6–N3–HN3	110.0(4)
N4–Si2–C31	109.50(21)	Si2–N4–N5	116.8(3)
N4–Si2–C41	109.11(21)	Si2–N4–HN4	131.9(4)
C31–Si2–C41	112.42(18)	N5–N4–HN4	111.3(4)
N5–Si3–N6	111.19(23)	Si3–N5–N4	112.9(3)
N5–Si3–C51	107.26(20)	Si3–N5–HN5	114.6(3)
N5–Si3–C61	106.22(20)	N4–N5–HN5	117.3(4)
N6–Si3–C51	109.75(21)	Si3–N6–N3	118.2(3)
N6–Si3–C61	109.37(21)	Si3–N6–HN6	135.0(4)
C51–Si3–C61	113.00(17)	N3–N6–HN6	105.9(4)

crystallography, and an ORTEP diagram is shown in Figure 2. Some selected bond parameters are listed in Table 4.

The structure of compound 14 was determined from its ^{1}H NMR and mass spectra. The course of the reaction was followed by ^{1}H NMR, and the results of one such reaction are summarized in Figure 3. From this figure it is clear that the reactivities of the two Si–H functions are very similar and that the reaction proceeds in a stepwise manner. Attempts to cyclize 13 by extended reaction with excess diphenylsilane under forcing conditions were unsuccessful.

The reaction of diphenylsilane with 1,1-dimethylhydrazine took place slowly in the presence of DMT at 70 °C. The results are listed in Table 2. The product distribution shows that competition of homocoupling and heterodehydrocoupling occurs during this reaction, in a manner similar to the results described above for phenylsilane.

The strong inhibiting effect of methyl substitution, as reflected in the preceding result, was also evident in the complete failure of 1,2-dimethylhydrazine to react under any conditions with diphenylsilane.

Discussion

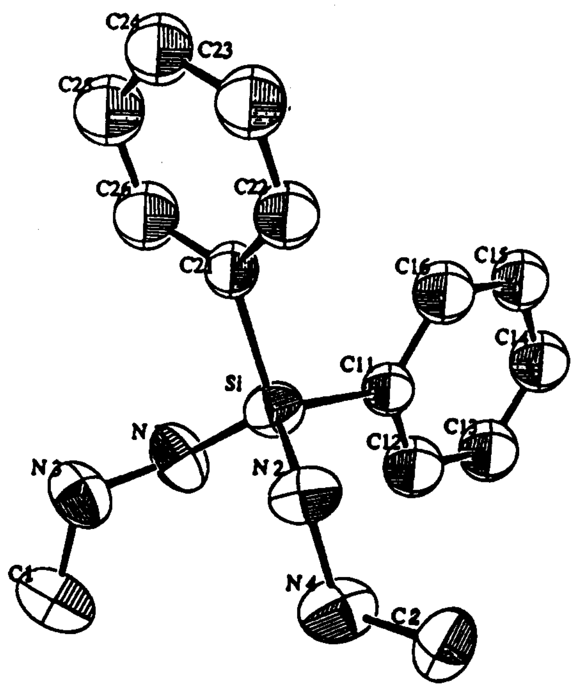


Figure 2. ORTEP view of 13, showing the atom numbering scheme. Selected bond distances (Å) and angles (deg) are given in Table 4.

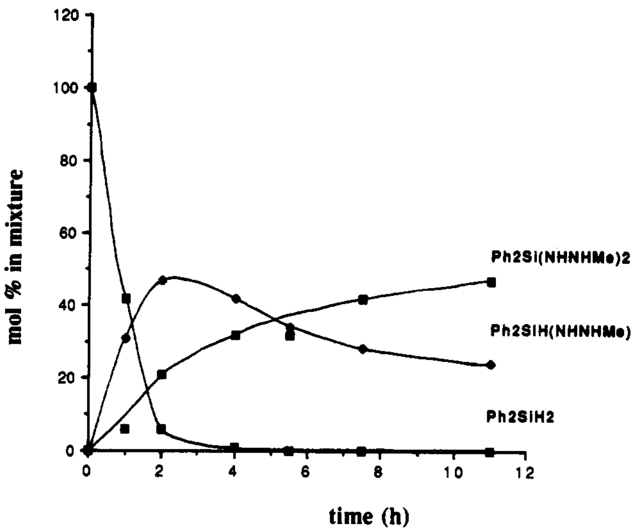


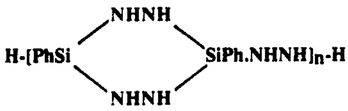
Figure 3. Course of a dehydrocoupling of diphenylsilane with methylhydrazine: Ph_2SiH_2, 4.00 mL; $MeHNNH_2$, 2.24 mL; DMT, 93 mg.

Table 4. Selected Bond Distances (Å) and Angles (deg) for Compound 13

Si–N1	1.710(4)	N1–N3	1.421(5)
Si–N2	1.690(4)	N2–N4	1.439(5)
Si–C11	1.874(5)	N3–C1	1.454(6)
Si–C21	1.874(4)	N4–C2	1.439(6)
N1–Si–N2	114.18(18)	C11–Si–C21	111.02(19)
N1–Si–C11	110.89(19)	Si–N1–N3	119.3(3)
N1–Si–C21	103.17(18)	Si–N2–N4	117.3(3)
N2–Si–C11	104.78(19)	N1–N3–C1	110.2(3)
N2–Si–C21	112.98(18)	N2–N4–C2	111.6(3)

Uncatalyzed Reactions of Phenylsilane. The facts that all three hydrogens of $PhSiH_3$ react with hydrazine and that only traces of intermediate $PhSiH_n(NHNH_2)_{3-n}$ species are observed during the spontaneous reaction strongly suggest that replacement of Si–H by Si–N results in activation of the remaining Si–H's. On the other hand, substitution of N–H by either Si or C strongly suppresses reaction of the second N–H.

All attempts to detect $PhSi(NHNH)_3SiPh$ met with failure. This observation is in accord with the anticipated difficulty that $PhSi(H)(NHNH)_2SiPh(NHNH_2)$, **18**, would have in achieving the boat conformation necessary for closure of the third ring to a completely closed structure. At this point, it appears that **18** reacts by linear polymerization to give a structure of the type **19**. Despite the superficial resemblance between **19** and **1** (the heaviest species observed in the MS), it is not clear how the observed cation could be produced from **19** by a simple process.



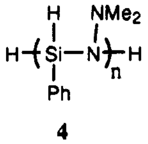
19

Catalyzed Reactions of Phenylsilane with Hydrazines. DMT dramatically increases the rate of the reaction of phenylsilane with hydrazine, but the product is a complex mixture of compounds which was not successfully characterized. The product quickly gels to a three dimensional network. This may be attributed to the fact that the steric requirements of the catalyst-containing transition state disfavor the closure of the six membered ring, relative to the spontaneous reaction, and hence increases the potential for cross-linking.

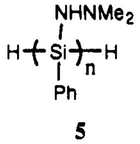
The DMT-catalyzed reaction of methylhydrazine with phenylsilane proceeded rapidly to give a mixture of polymeric products, from which no simple molecules were isolated or identified. Replacement of two of the hydrogens of hydrazine by methyl groups, either 1,1- or 1,2-, considerably reduces the rate of reaction and the complexity of the products.

In all of these reactions both steric and electronic effects will be important and the present database is insufficient to separate the two with any precision. The difference in behavior between the 1,1- and the 1,2-dimethylhydrazines may be sought in the differing properties of the two intermediates $PhSiH_2NHNMe_2$, **20**, and $PhSiH_2NMeNHMe$, **6**, which are the anticipated first reaction products for the two cases. The presence of the methyl group on the α-nitrogen of **6** increases the steric encumbrance of the transition states for both homo- and heterodehydrocoupling. This results in essentially complete suppression of the former but does not prevent the substitution of a second Si–H by heterodehydrocoupling to give $PhSiH(NMeNMeH)_2$, **7**. This is attributed in part to the fact that the increased Si–H reactivity, induced by Si–N formation, partly overrides the negative effect of steric encumbrance. Compound **6** does not, however, react significantly via the β-NH to give the 1,2-bis(phenylsilyl) derivative because the reactivity of the β-NH is reduced by the electronic effect of the first silyl group. Substitution of the third Si–H group is negligibly slow due to the excessive steric encumbrance of the two α-NMe substituents.

Compound **20** can further undergo another heterodehydrocoupling step to produce a second Si–N bond, on the way to giving the oligosilazane structure **4**, or homodehydrocoupling of Si–H to give the hydrazyl substituted poly(phenylsilane) **5** ($n > 1$). This pattern of behavior follows that previously observed for the DMT-catalyzed dehydrocoupling of primary silanes with ammonia.[9a]



4



5

Reactions of Diphenylsilane with Hydrazine and Methylhydrazines. The DMT-catalyzed reaction of diphenylsilane with hydrazine proceeds in a stepwise manner, with each of the Si–H bonds reacting in sequence with a similar reactivity, but with only one of the NH bonds of each nitrogen reacting. The formation of large amounts of **8** shows that once the species $Ph_2Si(NHNH_2)(NHNHSiHPh_2)$ is formed, ease of ring closure by intramolecular dehydrocoupling is greater than that of further extension of the chain by intermolecular coupling. This behavior parallels that described above for the uncatalyzed reaction of phenylsilane with hydrazine.

The reaction of diphenylsilane with methylhydrazine is similar to that with hydrazine, except that the NHMe is essentially unreactive toward dehydrocoupling. This is reflected in the accumulation of high yields of **13** and essentially no cyclic product, even under forcing conditions. The overall lower reactivity of the methylhydrazine also results in the appearance of some tetraphenyldisilane, **15**, since the rate of homodehydrocoupling is competitive with that of heterodehydrocoupling.

Structures of the Silylhydrazines. Compound **8** crystallizes with two independent molecules in the unit cell, one at a general position and the other with the Si_2N_4 ring centered about an inversion center (see Figure 4). Both molecules possess the same chairlike conformation of the Si_2N_4 ring. The ORTEP plot shows only the molecule at the general position. The distances of the Si2 and Si3 atoms to the least-squares plane (N3N4N5N6) are −0.624(6) and +0.624(6) Å, respectively. An interesting aspect of the structure is the coordination geometries about the N atoms. A planar environment is found about both N4 and N6 (angle sums: 360.0(4)° at N4, 359.1(4)° at N6), and pyramidal about both N3 and N5 (angle sums: 336.0(3)° at N3, 344.8(3)° at N5).

Only six crystal structures have been previously reported for compounds containing the Si–N–N– bond system.[20,21] One of these compounds, 3,3,6,6-tetrafluoro-1,2,4,5-tetrakis(*tert*-butyldimethylsilyl)-1,2,4,5-tetraaza-3,5-disilacyclohexane, **21**,[21a] is analogous to **8**, but the substitution pattern is radically different. It is no surprise, therefore, that there are important differences in the structure of the six membered ring. Particularly noteworthy are the facts that (i) the ring of **21** has a twisted-boat conformation while that of **8** is close to a chair conformation and (ii) the coordination geometries of all four N atoms in **21** are equivalent and close to trigonal-planar (sum of bond angles 357.6(9)°) while in **8** each NHNH unit contains one planar nitrogen and one pyramidal nitrogen.

The structure of compound **13** is the first reported for an open-chain silylhydrazine with two hydrazyl groups. The hydrogens on the nitrogens were not located in this structure; however, the angle value of Si–N1–N3 (or Si–N2–N4), 117.3° (or 119.3°), close to 120°, suggests a planar geometry at N1 (or N2), and the angle value of N1–N3–C1 (or N2–N4–C2), 110.2° (or 111.6°), close to 109°, suggests pyramidal geometry at N3 (or N4). This conclusion is supported by the observation of planar α-N and pyramidal β-N in 1,3-bis(methylhydrazyl)tetraphenyldisiloxane, **22**.[24] In the structure of **22**, the hydrogens on the nitrogens of

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[24] He, J.; Harrod, J. F. Manuscript in preparation.

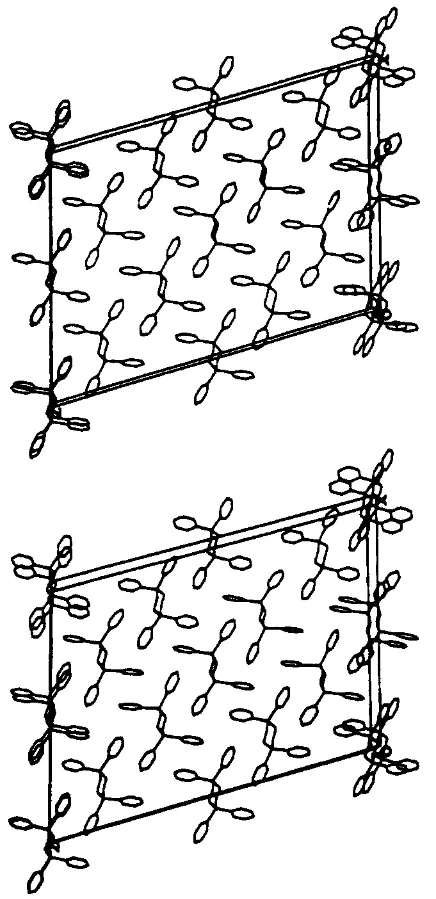

Figure 4. Packing diagram for 8, showing two crystallographically independent molecules.

the hydrazyl groups were located, and the sums of bond angles are 360.0(3)° at the α-N atoms and 330.7(4)° at the β-N atoms.

The average Si–N bond length of 1.695(4) Å in 13 is the shortest distance found in silylhydrazine compounds so far, and 0.036 Å shorter than that in 8. The average N–N bond length in 13 is 0.025 Å shorter than that in 8. This is attributed to more steric crowding of the phenyl groups in 8 than in 13.

Experimental Section

All manipulations were performed under a dry nitrogen or argon atmosphere, using Schlenk techniques. Glassware was oven-dried before use. ^{1}H NMR spectra were recorded on a Varian XL-200 FT-NMR (200 MHz) or a Varian XL-300 FT-NMR (300 MHz) spectrometer at 20 °C. Benzene-d_6 was used as solvent and the chemical shift of the residual protons was set as the reference (δ 7.15 ppm). ^{29}Si (*^{15}N*) NMR spectra were measured on a Varian XL-300 FT-NMR spectrometer operating at 59.6 (*30.4*) MHz in C_6D_6 at 20 °C. An external standard of TMS (*$MeNO_2$*) (0.00 ppm) was used. Low resolution mass spectra were obtained on a DuPont 21-492b spectrometer with an ion source temperature of 25 °C and an ionizing energy of 70 eV. IR spectra were recorded, under a dry air purge, on a Bruker IFS-88 FT spectrometer at a resolution of 4 cm^{-1} and using an MCT detector. Samples were prepared as a thin film on a KBr plate. The molecular weights of the polymers were measured on a Varian 5000 gel permeation chromatograph, equipped with a Waters Ultrastyragel 1000-Å column, or 500- and 100-Å columns in tandem at 35 °C, and with THF as solvent. Polystyrene standards were used for calibration. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Preparation and Purification of Materials. Organosilanes were prepared from the corresponding chlorosilanes (Aldrich) by reduction with $LiAlH_4$.[25] Cp_2TiMe_2 was prepared according to literature procedures.[26] Dry, oxygen-free solvents were employed throughout.

Hydrazine (anhydrous, 97%, Anachemia Canada Inc.) was purified by double distillation from crushed BaO.[27] The sample to be purified was refluxed *in vacuo* with 5 times its weight of BaO at 70 °C and distilled. The process was repeated with half the original amount of BaO.

Methylhydrazine (Eastman Kodak Co.) was purified by fractional distillation from CaH_2 after refluxing for 3 h under 1 atm of N_2. The distillate was collected over the range 88.0–88.1 °C.

1,1-Dimethylhydrazine (anhydrous, 98%, Anachemia Canada Inc.), was refluxed under vacuum at 50–60 °C for 1 h with 5 times its weight of crushed BaO and then distilled.

1,2-Dimethylhydrazine dihydrochloride (Aldrich Chemical Co., Inc.) was treated with crushed reagent grade NaOH pellets *in vacuo* to obtain free MeNHNHMe. The material so obtained was dried over NaOH pellets and distilled three times. Finally, CaH_2 was added to remove the last traces of moisture, and the material was fractionally distilled at atmospheric pressure. The fraction to be used was collected over the range 81.0–82.0 °C.

Dehydrocoupling of Phenylsilane with Hydrazine. Both catalytic and noncatalytic reactions were carried out under argon in stirred Schlenk flasks equipped with a reflux condenser. After evacuation, the flask was charged with 10 mL of toluene, followed by 1.7 mL of $PhSiH_3$ (0.014 mol) and 0.44 mL of hydrazine (0.014 mol). After mixing, the dehydrocoupling reaction took place with the evolution of hydrogen gas at ambient temperature. The solution became gradually more viscous as the reaction progressed. The course of reaction was followed by ^{1}H NMR. After 6 h at 100 °C, the reaction was stopped and the solvent was removed under reduced pressure. A white, amorphous oligomer was obtained in 83% yield. ^{1}H NMR: δ 2.2–3.5 (br, 1 H, NH), 6.5–8.0 (br, 1.8 H, Ph). ^{15}N NMR (INEPT), δ −338.0. EI-MS (*m/e*, abundance, fragmentation): 436 (100) [$C_{18}H_{24}N_8Si_3$, $M^{\bullet+}$], 406 (6.5) [$M^{\bullet+} - N_2H_2$], 375 (60) [$M^{\bullet+} - N_4H_5$], 358 (34) [$M^{\bullet+} - C_6H_6$], 343 (23) [$M^{\bullet+} - NH - C_6H_6$], 299 (17) [$M^{\bullet+} - PhSi - N_2H_4$]. GPC: $M_n = 710$, $M_w/M_n = 1.1$.

For the catalytic reaction, 1.0 mol % of DMT (58 mg) was added into the above mixture. The reaction took place violently and produced gelled material in 5 h.

The results of other experiments under a variety of conditions are summarized in Table 1.

Dehydrocoupling of Phenylsilane with Methylhydrazine. A typical catalytic experiment is as follows. Phenylsilane (2.50 mL, 0.020 mol), methylhydrazine (1.07 mL, 0.020 mol), toluene (8 mL), and DMT (82 mg, 1 mol %) were charged into a Schlenk flask (25 mL), equipped with a stirring bar, a rubber septum, and condenser. The reaction took place at ambient temperature. The course of the reaction was monitored by following the disappearance of the Si–H resonance of $PhSiH_3$ by ^{1}H NMR. After 44 h, 90% of the phenylsilane was converted. A similar reaction at 75 °C for 12 h gave 94% conversion. A polymeric product was obtained after the removal of toluene. GPC: $M_n = 550$, $M_w/M_n = 1.1$. ^{1}H NMR: δ 2.10–3.30 (br, 7H, NH + NMe), 5.00–5.40 (br, 1H, NSiH), 7.00–8.30 (br, 8H, Ph). ^{29}Si NMR (DEPT): δ −19.0 to −32.0 (br, SiH), −31.0 to −36.0 (br, SiH_2).

Dehydrocoupling of Phenylsilane with 1,1-Dimethylhydrazine. A typical experimental procedure is as follows: Phenylsilane (1.7 mL, 0.014 mol), 1,1-dimethylhydrazine (1.06 mL, 0.014 mol), hexane (8 mL), and DMT (58 mg, 1 mol %) were charged into a Schlenk flask (25 mL), equipped with a stirring bar, a rubber septum, and condenser. The reaction mixture was heated to 70 °C. The course of the reaction was monitored by following the disappearance of the Si–H resonance of $PhSiH_3$ by ^{1}H NMR. After 20 h, the reaction was stopped by cooling to ambient temperature and removing the solvent under reduced

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(25) Benkeser, R. A.; Landesman, H.; Foster, D. *J. Am. Chem. Soc.* **1952**, *74*, 648.

(26) Claus, K.; Bestian, H. *Justus Liebigs Ann. Chem.* **1962**, *654*, 8.

(27) Hale, C. C.; Shetterly, F. F. *J. Am. Chem. Soc.* **1911**, *33*, 1071.

pressure. The conversion of phenylsilane was 90%. The products consisted of 1,2-diphenyldisilane (7%), 1,2,3-triphenyltrisilane (37%), and the oligomeric products **4** and **5** (46%). ^{1}H NMR: 1,2-diphenyldisilane δ 4.48 (s, 4H, SiH), 6.95–7.90 (m, 10H, Ph); 1,2,3-triphenyltrisilane δ 4.60 (br, 5H, SiH), 6.95–7.90 (m, 15H, Ph); **4** and **5** δ 2.15–2.60 (m, NH + NMe), 5.03–5.40 (m, NSiH), 6.95–7.90 (m, Ph).

Dehydrocoupling of Phenylsilane with 1,2-Dimethylhydrazine. A typical procedure using DMT catalysis is the following: Phenylsilane (1.7 mL, 0.014 mol), 1,2-dimethylhydrazine (1.02 mL, 0.014 mol), hexane (8 mL), and DMT (58 mg, 1 mol %) were charged into a Schlenk flask (25 mL), equipped with stirring bar, a rubber septum, and condenser. The course of the reaction was followed by ^{1}H NMR. After 20 h at ambient temperature, phenylsilane was completely converted. ^{1}H NMR analysis showed the product to contain about 65% $PhSiH_2(NMeNHMe)$ and 18% $PhSiH(NMeNHMe)_2$. ^{1}H NMR: $PhSiH_2(NMeNHMe)$ δ 2.25, 2.23 (d, 3H, β-NCH), 2.37 (m, 1H, β-NH), 2.48 (s, 3H, α-NCH), 5.16 (s, 2H, SiH), 7.20, 7.62 (m, 5H, Ph). CI-MS (*m/e*): 166. ^{1}H NMR: $PhSiH(NMeNHMe)_2$ δ 2.33, 2.31 (d, 6H, β-NCH), 2.44 (m, 2H, β-NH), 2.56 (s, 6H, $SiNCH_3$), 5.14 (s, 1H, SiH), 7.20, 7.80 (m, 5H, Ph). CI-MS (*m/e*): 224. When a mixture with a 1:2 molar ratio of phenylsilane to 1,2-dimethylhydrazine was heated for 15 h at 70 °C, 72% of $PhSiH(NMeNHMe)_2$ and 14% of $PhSiH_2(NMeNHMe)$ were obtained. The remaining product was a viscous oligomer. Pure $PhSiH(NMeNHMe)_2$ can be obtained by fractional distillation at 65 °C (0.25 mmHg).

Catalytic Dehydrocoupling of Diphenylsilane with Hydrazine. A Schlenk flask was charged with Ph_2SiH_2 (5.0 mL, 27 mmol), N_2H_4 (0.85 mL, 27 mmol), and toluene (12 mL), followed by the addition of DMT (98 mg, 0.47 mmol). The solution changed from orange to dark brown within 10 min. The mixture was refluxed at 120 °C and periodically sampled and analyzed by ^{1}H NMR. Gas(es) evolved vigorously in the first 2 h, and no further gas was observed after 12 h. The solution became gradually viscous as the reaction proceeded. Stirring was continued for 24 h. The yields of the several products formed in the reaction were roughly measured from their ^{1}H NMR spectra. $Ph_2SiH(NHNH_2)$ (ca. 5% yield): ^{1}H NMR δ 2.43 (br, 2H, β-NH), 2.87 (br, 1H, α-NH), 5.545 (d, $^3J_{HSiNH}$ = 2 Hz, 1H, HSi), 7.0–8.2 (m, 10H, Ph). $Ph_2Si(NHNH_2)_2$ (ca. 5%): ^{1}H NMR δ 2.77 (br, 4H, β-NH), 3.16 (br, 2H, α-NH), 7.0–8.2 (m, 10H, Ph). $Ph_2Si(NHNH_2)_2$ (ca. 5%): ^{1}H NMR δ 2.77 (br, 4H, β-NH), 3.16 (br, 2H, α-NH), 7.0–8.2 (m, 10H, Ph). $Ph_2Si(NHNHSiPh_2H)_2$ (ca. 15%): ^{1}H NMR δ 2.94 (s, 4H, NH), 5.63 (s, 2H, SiH), 7.0–8.2 (m, 30H, Ph). $[Ph_2SiNH]_3$ (ca. 10%): ^{1}H NMR δ 2.63 (s, 3H, NH), 7.0–8.2 (m, 30H, Ph). $Ph_2Si[NHNH]_2SiPh_2$ (2.3 g, 40% yield) was crystallized out by the addition of a minimum amount of hexane to the reaction mixture in toluene: ^{1}H NMR δ 3.31 (s, 4H, NH), 7.20, 7.65 (m, 20H, Ph); ^{29}Si NMR δ −19.89 (ppm); ^{15}N NMR δ −337.22 (ppm); IR (neat, γ, cm^{-1}) 428 (m), 462 (s), 488 (vs), 529 (w), 552 (vs, N—Si), 610 (w), 621 (m), 697 (vs), 717 (vs), 737 (s), 800 (vs, N—H), 922 (w), 997 (m, N—Si), 1029 (w), 1066 (s, N—N), 1113 (vs, Ph—Si), 1122 (vs, Ph—Si), 1185 (w), 1263 (m), 1305 (w), 1346 (w), 1376 (m), 1427 (vs, Ph—Si), 1482 (m), 1586 (m, N—H), 2915 (w, C═C), 2998 (m, Ar—H), 3026 (m, Ar—H), 3051 (w, Ar—H), 3065 (m, Ar—H), 3342 (s, N—H); EI-MS (*m/e*, abundance, fragmentation) 424 (100) [$M^{\bullet+}$], 393 (6) [$M^{\bullet+} - NHNH_2$], 378 (20) [$M^{\bullet+} - HNNH_2 - NH$], 364 (5) [$M^{\bullet+} - 2NHNH$], 317 (33) [$M^{\bullet+} - Ph - NHNH$], 285 (4) [$M^{\bullet+} - Ph - 2NHNH_2$], 158 (24) [$M^{\bullet+} - 3PhH - H_2NNH_2$]; mp 162.5–164.5 °C (uncalibrated). Anal. Calcd: C, 67.88; H, 5.69; N, 13.19. Found: C, 66.43; H, 5.65; N, 12.10.

Table 5. Summary of the Crystal Structure Data for $Ph_2Si(NHNH)_2SiPh_2$ and $Ph_2Si(NHNHMe)_2$

formula	$Si_2C_{24}H_{24}N_4$	$SiC_{14}H_{20}N_4$
fw	424.65	272.42
cryst size, mm	0.5 × 0.15 × 0.10	0.5 × 0.5 × 0.45
cryst syst	monoclinic	monoclinic
space	*A*2/*a*	*P*2$_1$/*c*
a, Å	29.683(5)	7.7725(5)
b, Å	5.8972(17)	9.1289(9)
c, Å	39.038(7)	21.2624(17)
β, deg	105.492(14)	91.814(7)
V, Å^3	6585.2(25)	1507.90(21)
Z	12	4
d_{calcd}, g cm^{-3}	1.285	1.200
temp, °C	20	20
radiation	graphite monochromator, Mo Kα (λ = 0.709 30 Å)	
2θ range, deg	25.00–30.00	40.00–45.00
scan type	2θ/θ	2θ/θ
no. of reflcts collcd	4422	2140
no. of unique reflcts	4314	1971
R	0.054	0.054
R_w	0.056	0.056
gof	1.65	2.67

Catalytic Dehydrocoupling of Diphenylsilane with Methylhydrazine. The experimental procedure for the catalytic reaction of diphenylsilane with methylhydrazine was similar to the previous reaction. Ph_2SiH_2 (4.0 mL, 22.4 mmol), $MeHNNH_2$ (2.24 mL, 44.8 mmol), and DMT (93 mg, 0.44 mmol) were charged into a 50-mL Schlenk flask, equipped with condenser, stir bar, and a rubber septum. Reaction took place immediately after mixing, but the gas evolution was slower than that in the case of hydrazine. The mixture was heated to 80 °C and periodically sampled and measured by ^{1}H NMR. After 20 h, the reaction was cooled down to ambient temperature and $Ph_2Si(NHNHMe)_2$ crystallized out (3.8 g; 65%). It was purified by recrystallization from toluene/hexane (5:2). The residual brown oil was distilled in vacuo. The distillate collected over the range of 80–90 °C (0.25 mmHg) was found to be $Ph_2Si(H)NHNHMe$, a colorless oil (15%, 0.87 g). $Ph_2Si(NHNHMe)_2$: ^{1}H NMR δ 2.32, 2.35 (d, $^3J_{HNCH}$ = 6 Hz, 6H, β-NCH), 2.55, 2.58, 2.61, 2.64 (q, $^3J_{HNCH}$ = 6 Hz, 2H, β-NH), 2.91 (br, 2H, α-NH), 7.25–7.85 (m, 10H, Ph); ^{29}Si NMR δ −29.51 (ppm); ^{15}N NMR (HMQC) δ −305.43 (SiNH), −327.35 (NHMe); IR (neat, γ, cm^{-1}) 499 (s), 552 (s, N—Si), 701 (vs), 742 (s), 838 (w, N–H), 870 (m), 996 (m, br, N–Si), 1014 (w), 1101 (w, N–N), 1120 (vs, Ph–Si), 1187 (m), 1260 (w), 1363 (w), 1427 (s, Ph–Si), 1478 (m, C–N), 1590 (m, N–H), 2783 (m, br), 2837 (w), 2858 (w), 2931 (s, C–H), 2976 (m, C–H), 3016 (w, C–H), 3049 (m, Ar–H), 3066 (s, Ar–H), 3273 (w, N–H), 3282 (s, N–H), 3327 (m, N–H); EI-MS (*m/e*, abundance, fragmentation) 272 (71) [$M^{\bullet+}$], 226 (73) [$M^{\bullet+} - H_2NNHMe$], 198 (93) [$M^{\bullet+} - H_2NNHMe - N_2$], 183 (55) [$M^{\bullet+} - H_2NNHMe - N_2 - CH_3$], 149 (100) [$M^{\bullet+} - Ph - H_2NNHMe$]; mp 95 °C. Anal. Calcd: C, 61.72; H, 7.39; N, 20.56. Found: C, 61.36; H, 7.47; N, 20.96. $Ph_2Si(H)NHNHMe$: ^{1}H NMR δ 2.23, 2.26 (d, 3H, β-NCH), 2.55–2.70 (br, 2H, SiNHNHC), 5.61, 5.62 (d, $^3J_{HSiNH}$ = 1.5 Hz, 1H, SiH), 7.0–8.2 (m, 10H, Ph); EI-MS (*m/e*, abundance, fragmentation): 228 (21) [$M^{\bullet+}$], 198 (49) [$M^{\bullet+} - NHMe$], 183 (71) [$M^{\bullet+} - NHNHMe$], 150 (19) [$M^{\bullet+} - PhH$], 120 (100) [$M^{\bullet+} - NHMe - Ph$], 105 (69) [$M^{\bullet+} - NHNHMe - PhH$].

Catalytic Dehydrocoupling of Diphenylsilane with 1,1-Dimethylhydrazine. The above procedure was followed. Ph_2SiH_2 (2.5 mL, 14 mmol), Me_2NNH_2 (1.06 mL, 14 mmol), hexane (8.0 mL), and DMT (58 mg, 0.28 mmol) were charged into a 25-mL Schlenk flask. The dehydrocoupling of diphenylsilane with 1,1-dimethylhydrazine did not occur at ambient temperature, but the dimerization of diphenylsilane took place very slowly with 10% conversion of diphenylsilane after 3 days. When the mixture was refluxed at 70 °C for 20 h, 36% of the diphenylsilane was converted to $H(Ph_2Si)_2H$ (16%), $Ph_2SiH(NHNMe_2)$ (13%), and $(Ph_2SiH)_2NNMe_2$ (7%). ^{1}H NMR: $H(Ph_2Si)_2H$ δ 5.49 (s, 2H, SiH), 7.0–7.6 (m, 20H, Ph). ^{1}H NMR: $Ph_2SiH(NHNMe_2)$ δ 2.22 (s, 6H, NMe), 5.62 (s, 1H, SiH), 7.2–8.0 (m, 10H, Ph). CI-MS (*m/e*): 242. ^{1}H NMR: $(Ph_2SiH)_2NNMe_2$ δ 2.53 (s, 6H, NMe), 5.63 (s, 2H, SiH), 7.2–8.0 (m, 20H, Ph). CI-MS (*m/e*): 424.

Catalytic Dehydrocoupling of Diphenylsilane with 1,2-Dimethylhydrazine. The above procedure was followed. Ph_2SiH_2 (2.5 mL, 14 mmol), Me_2NNH_2 (1.06 mL, 14 mmol), hexane (8.0 mL), and DMT (58 mg, 0.28 mmol) were charged into a 25-mL Schlenk flask. The cross-dehydrocoupling of diphenyl-

Table 6. Atomic Parameters *x*, *y*, and *z* and B_{eq} for Compound 8[a]

	x	*y*	*z*	B_{eq}, Å^2
Si1	0.05518(6)	0.4980(3)	0.50389(5)	2.42(8)
Si2	0.10983(6)	0.0471(3)	0.33099(5)	2.47(8)
Si3	0.22030(6)	0.0156(3)	0.34316(4)	2.44(8)
N1	0.02266(17)	0.7409(9)	0.50188(13)	2.9(3)
N2	0.01906(17)	0.2716(9)	0.48537(12)	2.6(3)
N3	0.14668(17)	0.2617(8)	0.35275(12)	2.8(3)
N4	0.13953(17)	–0.2054(9)	0.33398(13)	2.9(3)
N5	0.18286(17)	–0.2032(9)	0.32341(12)	2.7(3)
N6	0.19040(17)	0.2655(8)	0.34221(13)	2.9(3)
C11	0.08387(13)	0.4224(7)	0.55152(8)	2.4(3)
C12	0.08491(14)	0.5850(6)	0.57767(11)	3.4(3)
C13	0.10784(15)	0.5386(7)	0.61308(10)	4.3(4)
C14	0.12974(14)	0.3297(9)	0.62233(9)	4.0(4)
C15	0.12870(14)	0.1671(6)	0.59618(13)	3.8(4)
C16	0.10576(15)	0.2134(6)	0.56078(11)	3.1(3)
C21	0.09779(12)	0.5381(8)	0.47643(10)	2.7(3)
C22	0.09668(14)	0.7327(7)	0.45589(12)	3.9(4)
C23	0.12938(17)	0.7612(7)	0.43638(10)	4.4(4)
C24	0.16320(14)	0.5952(9)	0.43740(10)	4.2(4)
C25	0.16431(13)	0.4007(8)	0.45794(12)	4.6(4)
C26	0.13160(15)	0.3721(6)	0.47745(10)	3.7(4)
C31	0.06147(12)	0.0187(8)	0.35330(10)	2.6(3)
C32	0.05272(14)	0.1968(6)	0.37414(11)	3.4(3)
C33	0.01652(16)	0.1796(7)	0.39060(10)	4.1(4)
C34	–0.01092(13)	–0.0158(9)	0.38621(12)	4.7(4)
C35	–0.00216(15)	–0.1940(7)	0.36537(12)	4.7(4)
C36	0.03403(16)	–0.1767(6)	0.34892(10)	3.8(4)
C41	0.08769(15)	0.1299(7)	0.28273(8)	2.7(3)
C42	0.06841(15)	0.3435(6)	0.27282(11)	3.8(4)
C43	0.04914(15)	0.3943(7)	0.23699(13)	4.7(4)
C44	0.04915(15)	0.2315(9)	0.21107(9)	4.7(4)
C45	0.06843(16)	0.0179(8)	0.22098(10)	4.7(4)
C46	0.08770(15)	–0.0330(6)	0.25681(11)	3.9(4)
C51	0.24798(13)	–0.0698(7)	0.39063(8)	2.5(3)
C52	0.24995(13)	0.0890(6)	0.41748(11)	3.0(3)
C53	0.27296(15)	0.0361(7)	0.45263(10)	4.1(4)
C54	0.29400(14)	–0.1756(8)	0.46093(9)	4.2(4)
C55	0.29203(14)	–0.3344(6)	0.43409(12)	3.8(4)
C56	0.26902(14)	–0.2815(6)	0.39894(10)	3.1(3)
C61	0.26385(13)	0.0472(7)	0.31634(10)	2.6(3)
C62	0.29637(15)	–0.1258(6)	0.31781(10)	3.9(4)
C63	0.32844(13)	–0.1108(7)	0.29749(12)	5.1(4)
C64	0.32798(14)	0.0772(9)	0.27571(11)	5.1(4)
C65	0.29546(16)	0.2502(7)	0.27425(10)	4.8(4)
C66	0.26340(13)	0.2352(6)	0.29456(11)	3.8(4)

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid. Phenyl rings were constrained to idealized geometry and refined as rigid groups. (Estimated standard deviations in parentheses.)

Table 7. Atomic Parameters *x*, *y*, and *z* and B_{eq} for Compound 13[a]

	x	*y*	*z*	B_{eq}, Å^2
Si	0.64324(16)	0.35956(14)	0.09176(6)	3.71(6)
N1	0.4892(5)	0.2259(4)	0.09331(16)	4.39(18)
N2	0.6909(5)	0.4162(4)	0.1865(16)	4.29(18)
N3	0.3312(5)	0.2467(4)	0.05904(18)	4.69(19)
N4	0.7483(5)	0.3070(4)	–0.02473(18)	5.13(21)
C1	0.2938(7)	0.1204(6)	0.01927(24)	6.0(3)
C2	0.9020(6)	0.3525(6)	–0.05528(23)	6.0(3)
C11	0.5699(5)	0.5290(5)	0.13286(19)	3.53(21)
C12	0.4325(6)	0.5202(5)	0.17304(22)	4.80(24)
C13	0.3728(7)	0.6426(7)	0.20412(23)	6.1(3)
C14	0.4488(8)	0.7771(6)	0.1963(3)	5.9(3)
C15	0.5846(7)	0.7876(5)	0.1572(3)	5.5(3)
C16	0.6444(6)	0.6654(5)	0.12595(22)	4.6(3)
C21	0.8312(5)	0.2738(5)	0.13515(19)	3.65(20)
C22	0.8894(6)	0.1338(5)	0.12161(22)	4.8(3)
C23	1.0286(7)	0.0725(5)	0.1544(3)	5.9(3)
C24	1.1141(6)	0.1513(7)	0.2011(3)	5.6(3)
C25	1.0602(6)	0.2897(6)	0.21605(22)	5.1(3)
C26	0.9202(6)	0.3503(5)	0.18307(21)	4.46(22)

[a] See Table 6.

silane with 1,2-dimethylhydrazine did not occur either at ambient temperature or at 70 °C, but the dimerization of diphenylsilane took place slowly at 70 °C with about 20% conversion of diphenylsilane after 20 h.

Crystal Structure Determinations. Crystals of $Ph_2Si(NHNH)_2SiPh_2$ (*$Ph_2Si(NHNHMe)_2$*) were sealed in a thin-walled capillary under argon and mounted on a Rigaku diffractometer, controlled by TEXRAY software.[28] Cell dimensions were obtained from 24 (*25*) reflections with 2θ in the range 25.00–30.00° (*40.00–45.00°*). The intensity data were collected by using the $\theta/2\theta$ scan mode. The last least squares cycle was calculated with 81 (*39*) atoms, 298 (*173*) parameters, and 2216 (*1469*) out of 4314 (*1971*) reflections. Weights based on counting statistics were used. The weight modifier K in KF_o^2 is 0.000 100 (*0.000 050*). Standard intensities varied 2.6% (*1.2%*) over the course of collection. Merging R for 108 (*169*) pairs of symmetry related reflections was 1.0% (*1.4%*). The structures were solved by direct methods.[29] Hydrogen atoms were included in calculated positions. All non-hydrogen atoms were refined anisotropically. Computations were performed using the NRCVAX system[30] of crystallographic software.

Hydrogens on nitrogen in the compound $Ph_2Si(NHNH)_2SiPh_2$ were located in a d-map which was then normalized to an N–H distance of 1.08 Å and not refined.

Crystal data and collection parameters are listed in Table 5. Further detailed information, atomic coordinates, and the mean of the principal axes of the thermal ellipsoids are listed in Tables 6 and 7, respectively.

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Supplementary Material Available: Complete tables of H atom parameters, bond distances, bond angles, and anisotropic thermal parameters for 8 and 13 (6 pages). Ordering information is given on any current masthead page.

OM9306281

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