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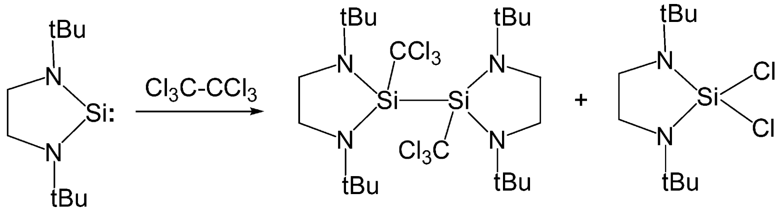

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ARTICLES

Formation of Disilanes in the Reaction of Stable Silylenes with Halocarbons

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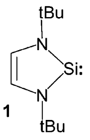
Abstract: Reactions of stable silylenes **1** and **2** with a variety of halogenated organic compounds have been studied. Depending on the nature of the halocarbon, the products can be disilanes, LSiX−LSiR, or monosilanes, LSiXR, or a mixture of both types of products. Hexachloroethane reacts with the silylenes to give mainly the dichlorodisilane, LSiX−LSiX. The experimental results are rationalized in terms of several related free-radical chain mechanisms.

The chemistry of room-temperature stable silylenes, of which **1**−**4** are the best known, has been investigated in numerous studies since their discovery 11 years ago.[1−4] These silylenes are potent Lewis bases, acting as donors in the formation of many transition metal and lanthanide complexes. They are oxidized by chalcogens, form complexes with boranes and carbenes, and take part in many insertion reactions, for instance into Si−Cl, C−Li, and O−H bonds.[3,4]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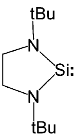
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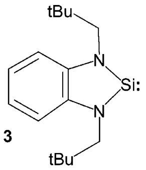
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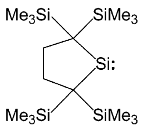
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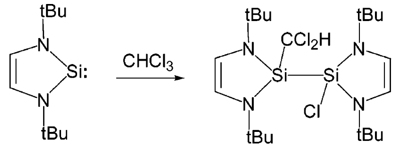
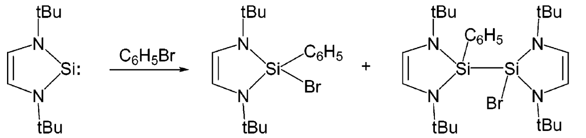
In 2002, we described the reaction of stable silylene **1** with several halogenated hydrocarbons, which proceeded in unprecedented fashion to yield disilane products.[5] The reaction of **1** with trichloromethane is shown in eq 1 as an example. With other halocarbons a 1:1 adduct and a 1:2 product were obtained, as shown in eq 2 for bromobenzene.


(1)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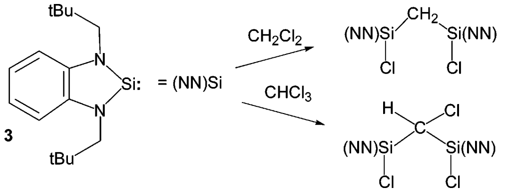
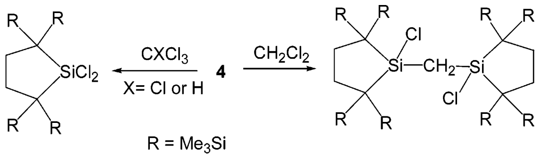
Scheme 1. Reaction of **3** with Chloromethanes



Scheme 2. Reaction of **4** with Chloromethanes



Two other groups have looked at the reaction of stable silylenes with halocarbons. The team of Lappert and Gehrhus[2] found that addition of stable silylene **3** to chloroform and methylene chloride resulted in the formation of the double insertion product (Scheme 1).

Kira and co-workers[6,7] have studied the reaction of dialkylsilylene **4** with a variety of haloalkanes. With carbon tetrachloride or chloroform, the silylene abstracted chlorine atoms to yield the dichlorosilane, while with dichloromethane a double insertion product was obtained, similar to that of Gehrhus and Lappert (Scheme 2). Kira proposed that the reaction proceeds through a more conventional acid−base complex intermediate, with a chlorine atom donating a lone pair of electrons to silicon.

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(1) Haaf, M.; Schmedake, T. A.; West, R. *Acc. Chem. Res.* **2000**, *33*, 704.

(2) Gehrhus, B.; Lappert, M. F. *J. Organomet. Chem.* **2001**, *617*, 209.

(3) Hill, N. J.; West, R. *J. Organomet. Chem.* **2004**, *689*, 4165.

(4) Gaspar, P. P.; West, R. In *The Chemistry of Organosilicon Compounds*; Rappoport. Z., Apeloig, Y., Eds.; Wiley: New York 1998; Vol. 2, Chapter 43, part 3.

(5) Moser, D. F.; Bosse, T.; Olson, J.; Moser, J. L.; Guzei, I. A.; West, R. *J. Am. Chem. Soc.* **2002**, *124*, 4186.

(6) Ishida, S.; Iwamoto, T.; Kabuto, C.; Kira, M. *Chem. Lett.* **2001**, 1102. A more complicated product was obtained in a reaction of **4** with chloromethylcyclopropane.

(7) Ishida, S.; Iwamoto, T.; Kabuto, C.; Kira, M. *Silicon Chem.* **2003**, *2*, 137.

10.1021/ja052584g CCC: $30.25

Table 1. Yields of Products from Reaction of Silylenes with Halocarbons

RX	LSiRX	LSiX-LSiR
A. Unsaturated Silylene, **1**		
CCl_4		>98 (**5**)
$CHCl_3$		>98 (**6**)
CH_2Cl_2		>98 (**7**)
$CHBr_3$	>98 (**8**)	
$PhCH_2Cl$		>98 (**9**)
n-BuCl		>90 (**10**)
n-HexBr	35 (**11a**)	65 (**11b**)
i-PrCl	50 (**12a**)	50 (**12b**)
i-PrBr	50 (**13a**)	50 (**13b**)
t-BuCl	>98 (**14**)	
PhCl	(no reaction)	
PhBr	67 (**15a**)	33 (**15b**)
p-$CF_3C_6H_4Br$	85 (**16a**)	15 (**16b**)
p-t-BuC_6H_4Br	80 (**17a**)	20 (**17b**)
p-$CH_3OC_6H_4Br$	>98 (**18**)	
PhI	>98 (**19**)	
2-Br-$C_{10}H_7$[a]	>98 (**20**)	
9-Br-$C_{11}H_9$[b]	>98 (**21**)	
C_6F_5Cl		>98 (**22**)
C_6F_5Br		>98 (**23**)
C_6F_5I		>98 (**24**)
B. Saturated Silylene, **2**		
CCl_4		>98 (**25**)
$CHCl_3$		>98 (**26**)
CH_2Cl_2		>98 (**27**)
$PhCH_2Cl$		>98 (**28**)
n-BuCl	30 (**29a**)	70 (**29b**)
i-PrCl	50 (**30a**)	50 (**30b**)
n-HexBr	50 (**31a**)	50 (**31b**)
i-PrBr		75 (**32**)
t-BuCl	67 (**33a**)	33 (**33b**)
PhBr	33 (**34a**)	67 (**34b**)

[a] 2-Bromonaphthalene. [b] 9-Bromofluorene.

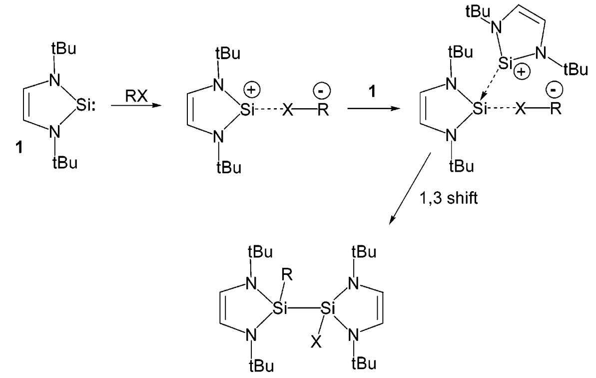
We have now extended this study to include reactions of the saturated silylene **2**, as well as **1**, with a variety of halogenated organic compounds. The results of these experiments are displayed in Table 1. As seen from the table, many halogenated organic compounds react with **1** and **2** to give the disilane as the predominant product. Other halocarbons react to give the simple insertion product LSi(X)R, (LSi = silylene), and for still others a mixture of both types of compounds is formed. The results of these reactions will be discussed in greater detail after a brief consideration of the reaction mechanism leading to the disilanes.

Reaction Mechanism

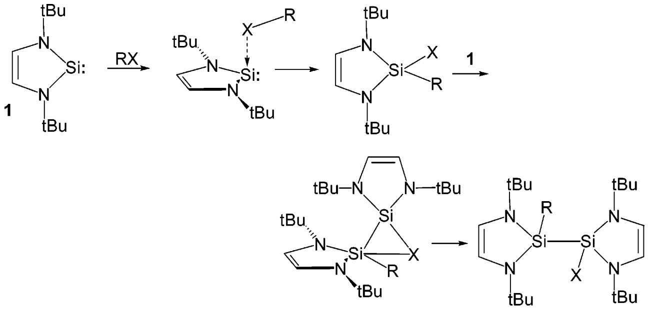
From our early results, it appeared that halocarbons that could provide a stable anion after removal of halogen were most likely to yield the disilane product. Partly for this reason we initially proposed, though we no longer favor, a halophilic mechanism for the reaction leading to the disilanes (Scheme 3).[5] In this mechanism, electron donation from a silicon lone pair into an antibonding orbital of the halogen takes place to give a weak acid−base complex. Next, a second silylene molecule donates its electron pair into the vacant p orbital of the (now more electrophilic) silylene silicon. A simple 1,3 shift would then lead to the disilane product.

The mechanism of Scheme 3 was strongly criticized by Su, partly on the basis that the first step, complexation between the silylene as a donor atom and a chlorine atom, is strongly endothermic. Su proposed instead a two-step mechanism illustrated in Scheme 4, based on density functional calculations.[8,9]

Scheme 3. Halophilic Mechanism for Disilane Formation



Scheme 4. Stepwise Mechanism for Disilane Formation



In this mechanism, a halogen atom binds to the vacant orbital of the silylene silicon, followed by insertion to give the stable 1:1 product. The disilane product then arises from insertion of another silylene silicon into the Si−X bond.

We had previously considered, and rejected, this mechanism on several grounds. First, silylene **1** shows essentially no Lewis acid behavior, even to bases as strong as pyridine. Thus the first step of the mechanism seemed unlikely. And indeed, theoretical calculations show that the activation barrier for the first step is about 50 kcal mol^{-1}. This is inconsistent with the rapid rate for the reaction, which takes place promptly at room temperature for many halocarbons.

Second, in the reaction of **1** with bromobenzene, which produces both the 1:1 and 2:1 products, we were able to separate the 1:1 compound and treat it with additional silylene **1**. No reaction took place, even under forcing conditions, showing that the pathway in Scheme 4 cannot be correct.

We then considered the possibility that the reaction might follow a radical rather than a polar pathway. A careful study of the minor products in the reaction of carefully purified trichloromethane with **1** showed that $Cl_2CH-CHCl_2$ was formed in 1.3% yield. We interpret this as a radical coupling product, indicating that $\bullet CCl_2H$ radical was present at some point in the reaction.

Of the several possible radical pathways, we favor the radical chain mechanism outlined in Scheme 5. The initiation step is the reaction of silylene with halocarbon to give a halosilyl radical and a carbon radical. (This might be preceded by a single-electron transfer from the silylene to the halocarbon.[10]) Reaction of the carbon-centered radical with a second silylene molecule to give a organosilylene radical represents the first propagation

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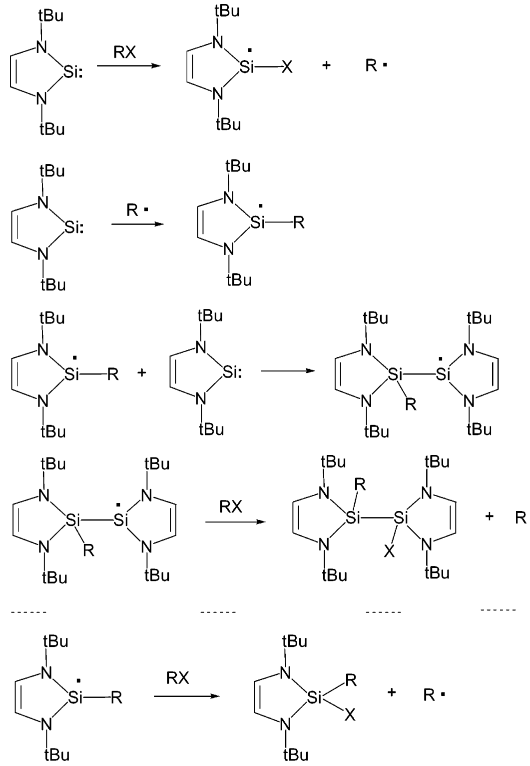
(8) Su, M.-D. *J. Am. Chem. Soc.* **2003**, *125*, 1714.
(9) Su, M.-D. *Chem. Phys. Lett.* **2003**, *374*, 385.
(10) Mikami, T.; Narasaka, K. *Adv. Free Radical Chem.* **1999**, *2*, 45.

Scheme 5. Radical Chain Mechanism for Reaction of Silylenes To Yield 2:1 and 1:1 Products[a]



[a] Equations are shown for **1** but apply equally to **2**.

step. In a second propagation step, the resulting silyl radical reacts with another silylene molecule to give a disilanyl radical. Abstraction of halogen from the starting halo compound yields the 2:1 product and a carbon radical, continuing the radical chain.

At first we were doubtful about this mechanism, because model density functional theory (DFT) calculations for the first step required an activation energy of about 40 kcal mol^{-1}, which again seemed inconsistent with the rapid rates of the reaction. More detailed calculations by Joo and McKee, however, now show that the activation barrier is much less than originally thought and thus is not inconsistent with the rapid reaction rates.[11]

The mechanism outlined in Scheme 5 could also lead to the 1:1 products. As shown at the bottom of Scheme 5, the first silyl radical could abstract a halogen atom from the halocarbon. This would constitute an alternate propagation step.

Results and Discussion

Yields of the monosilane and disilane products from the reactions of **1** and **2** with halocarbons are summarized in the Table 1A,B. In general the yields are reported for reactions in which the silylene was added to an equimolar amount of the halocarbon in hexane solution. For some of the reactions, the results are independent of the ratios of reactants. For example, **1** reacts with $CHCl_3$ to produce the disilane **6** in >98% yield, even when **1** is added to a 100-fold excess of $CHCl_3$. However in reactions where the monosilane and disilane products are both produced, the relative yields may depend on the ratios of reactants. This is clearly true for the bromobenzenes, as will be discussed below.

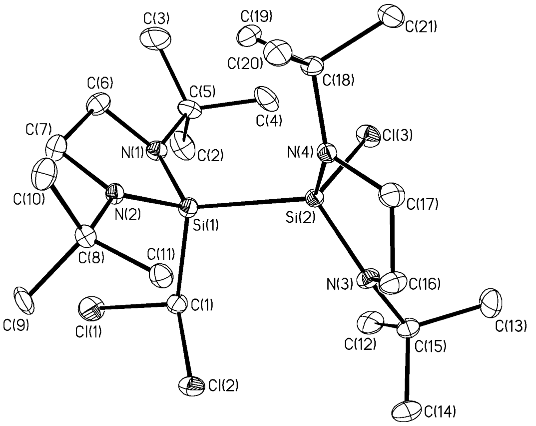


Figure 1. Molecular structure of **26**. Thermal ellipsoids are shown at the 30% probability level. Selected bond distances (Å) and angles (deg): Si(1)−Si(2), 2.3732(9); Si(1)−N(1), 1.7200(18), Si(1)−N(2), 1.700(2); Si(2)−N(3), 1.712(2); Si(2)−N(4), 1.720(2); Si(2)−Cl(3), 2.1161(10); Si(1)−C(1), 2.025(3); Cl(3)−Si(2)−Si(1), 106.64(4); C(1)−Si(1)−Si(2), 108.75(9); N(2)−Si(1)−N(1), 96.61(10); N(3)−Si(2)−N(4), 96.26(12).

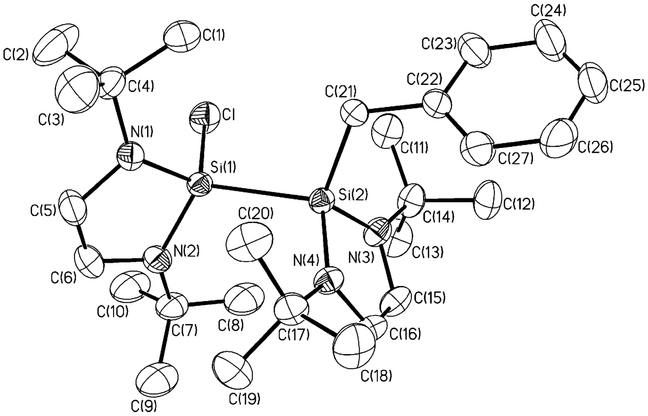


Figure 2. Molecular structure of **9**. Thermal ellipsoids are shown at the 30% probability level. Selected bond distances (Å) and angles (deg): Si(1)−Si(2), 2.4315((8); Si(1)−N(1), 1.734(2); Si(1)−N(2), 1.730(2); Si(2)−N(3), 1.736(2); Si(2)−N(4), 1.7447(18); Si(1)−Cl, 2.1370(9); Si(2)−C(21), 1.888(2); N(2)−Si(1)−N(1), 93.14(10); N(3)−Si(2)−N(4), 92.86(9); Cl−Si(1)−Si(2), 107.06(3); C(21)−Si(2)−Si(1), 107.48(7).

The highly chlorinated alkanes, CCl_4, $CHCl_3$, and CH_2Cl_2, react with both **1** and **2** to produce exclusively the 1:2 adducts. Earlier we reported the crystal structure for the disilane **6**, produced from **1** and $CHCl_3$. We have now determined the crystal structure of **26**, the corresponding disilane from **2** and $CHCl_3$ (Figure 1). The Si−Si bond length is shorter in **26** (2.37 Å) than in **6** (2.42 Å). This can be explained by the twisting of the five-membered rings in **26**, which reduces the steric repulsion between the two halves of the molecule and allows a closer approach of the silicon atoms.

Reaction of $CHBr_3$ with **1** proceeded smoothly, but gave entirely the 1:1 adduct, **8**. This difference in product is also explainable in terms of the mechanism of Scheme 3. The crucial second propagation step may be inhibited by the large $CHBr_2$ substituent on silicon, preventing the approach of a second silylene molecule. Instead, abstraction of a bromine atom could take place, leading to the alternate radical chain.

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[11] Joo, H.; McKee, M. L. *J. Phys. Chem.* **2005**, *109*, 3728.

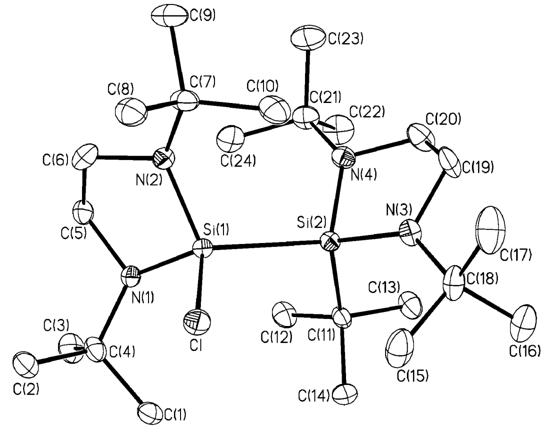


Figure 3. Molecular structure of **33b**. Selected bond distances (Å) and angles (deg): Si(1)−Si(2), 2.4705(12); Si(1)−N(1), 1.727(3); Si(1)−N(2), 1.729(3); Si(2)−N(3), 1.759(3); Si(2)−N(4), 1.750(3); Si(1)−Cl, 2.1278(11); Si(2)−C(11), 1.926(4); N(1)−Si(1)−N(2), 95.64(14); N(4)−Si(2)−N(3), 93.73(14); Cl−Si(1)−Si(2), 111.03(5); C(11)−Si(2)−Si(1), 110.34(11).

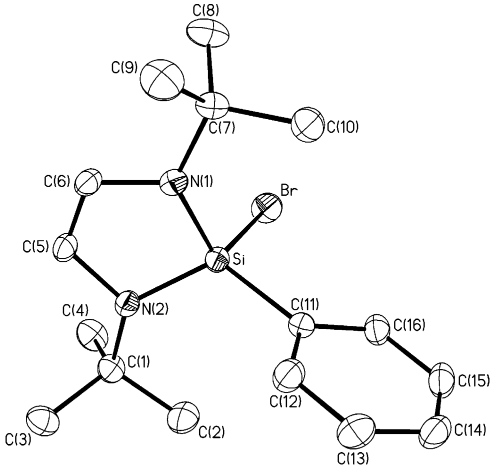


Figure 4. Molecular structure of **15a**. Thermal ellipsoids are shown at the 30% probability level. Selected bond distances (Å) and angles (deg): Si−N(1), 1.716(2); Si−N(2), 1.714(2); Si−Br, 2.2959(7); Si−C(11), 1.863(2); N(2)−Si−N(1), 94.08(10); N(2)−Si−C(11), 118.36(10); N(1)−Si−C(11), 118.12(10); N(2)−Si−Br, 109.80(7); N(1)−Si−Br, 110.32(8); C(11)−Si−Br, 105.81(8).

Benzyl chloride also reacts with both **1** and **2** to yield entirely the 2:1 adducts, **9** and **28** (Table 1). We obtained the crystal structure of disilane **9**, the product of reaction of benzyl chloride with **1**. The thermal ellipsoid diagram is displayed in Figure 2. The crystal structure shows that the chlorine atom on silicon (1) and the carbon atom C21 on Si(2) are in a gauche conformation; this is similar to the structure of **6**.

Primary and secondary chlorides and bromides react with both silylenes to give mixtures of the 1:1 and 1:2 products. The yields in Table 1A,B are those obtained under the experimental conditions given but should be regarded as approximate since the relative amounts of the products depend on the ratios of silylene to halocarbon and on the overall concentration of reactants. A large excess of halo compound favors the formation of the 1:1 product, whereas excess silylene yields more of the disilane. Among these compounds, the results for *tert*-butyl chloride are revealing. With **1**, only the monosilane product **14** is produced, but with **2**, a mixture of the 1:1 and 1:2 products is obtained. We rationalize this difference as a result of the twisting of the rings in the intermediates from **2**, reducing steric hindrance just enough so that some Si−Si bond formation can take place in the crucial second propagation step. The crystal structure for the disilane product **33b** from the reaction of *tert*-butyl chloride with **2** is shown in Figure 3. Significant steric hindrance in this molecule is evidenced by the strongly elongated Si−Si bond, 2.47 Å.[12]

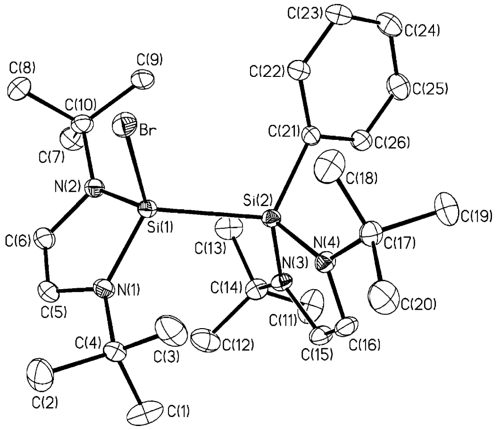


Figure 5. Molecular structure of **15b**. Selected bond distances (Å) and angles (deg): Si(1)−Si(2), 2.4267(9); Si(1)−Br, 2.3263(6); Si(1)−N(1), 1.7359(19); Si(1)−N(2), 1.7453(19); Si(2)−N(3), 1.7466(18); Si(2)−N(4), 1.7532(19); N(1)−Si(1)−N(2), 92.95(9); N(3)−Si(2)−N(4), 92.58(9); Br−Si(1)−Si(2), 109.35(3); C(21)−Si(2)−Si(1), 113.55(8).

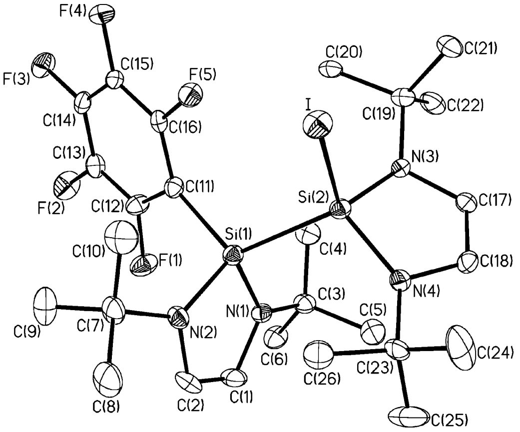
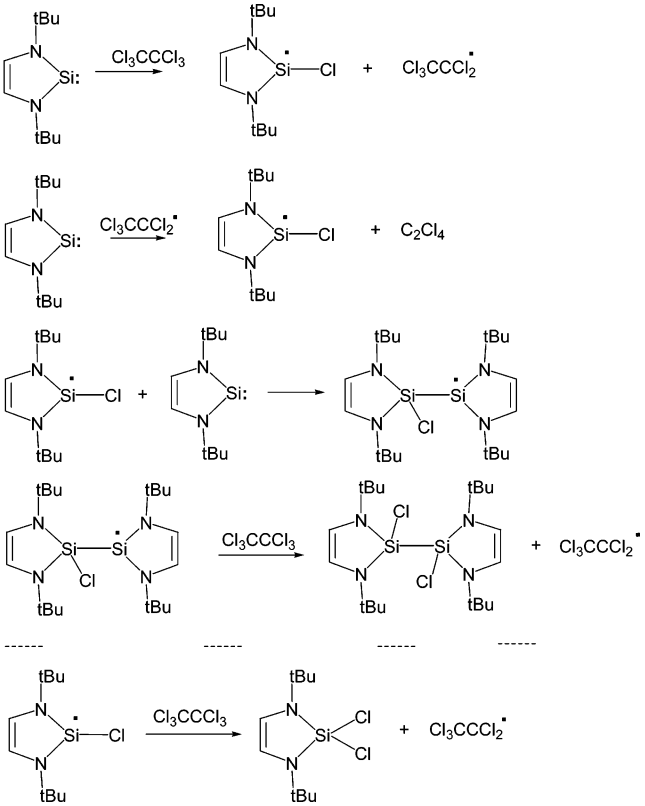


Figure 6. Molecular structure of **24**. Selected bond distances (Å) and angles (deg): Si(1)−Si(2), 2.4427(18); I−Si(2), 2.5720(13); Si(1)−N(1), 1.737(4); Si(1)−N(2), 1.739(4); Si(1)−C(11), 1.931(4); Si(2)−N(3), 1.728(4); Si(2)−N(4); 1.730(4); I−Si(2)−Si(1), 114.32(6); C(11)−Si(1)−Si(2), 115.92(15); N(2)−Si(1)−N(1), 93.35(18); N(3)−Si(2)−N(4), 93.07(18).

For the aryl halides, the reaction course depends on the nature of the halogen. No reaction was observed between **1** or **2** and chlorobenzene, even after heating a mixture of the reactants to reflux in toluene. Iodobenzene reacted promptly with silylene **1**, yielding exclusively the 1:1 monosilane adduct, **19**.

The bromoaromatic compounds reacted slowly, over several hours at room temperature. Bromobenzene yielded a mixture of the 1:1 to 1:2 products with both silylenes, as shown in eq 3 for the reaction with **1**. If a large excess of bromobenzene is present, the product is almost entirely the 1:1 adduct. X-ray structures were determined for both the monosilane (**15a**) and disilane (**15b**) adducts and are displayed in Figures 4 and 5. Disilane **15b** also contains a rather long Si−Si bond, 2.43 Å. Silylene **2** reacted in a similar fashion with bromobenzene, yielding a mixture of **35a** and **35b**.

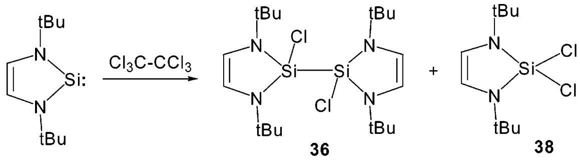
Scheme 6. Radical Chain Mechanism for the Reaction of Hexachloroethane with Stable Silylenes



Bromobenzenes with para-substituents, CF_3 or t-Bu, gave slightly increased yields of the 1:1 adducts with **1**. Para substitution with the strongly electron releasing *p*-methoxy substituent, however, led exclusively to the monosilane product, **18**. Reaction of **1** with the more hindered bromoaromatics, 2-bromonaphthalene and 9-bromofluorene, also gave only the 1:1 products, **20** and **21**. The latter results are again understandable because of the large bulk of these substituents, blocking silicon−silicon bond formation.

The stable carbene with structure analogous to **1** is known to react with iodopentafluorobenzene reversibly, to form a halophilic complex in which the divalent carbon atom serves as an electron donor to the iodine atom.[13] With **1**, however, pentafluorophenyl iodide, bromide, and chloride all reacted to yield exclusively the disilanes. In this series we determined the crystal structure for the iodo compound, **24**, shown in Figure 6. Once again we find for this molecule a relatively long Si−Si bond, 2.44 Å.

Both **1** and **2** react with hexachloroethane by a strikingly different pathway, to yield the dimeric dichloro compounds **36** and **37** (eq 3), along with about 10% of the monomeric dichloro compounds, **38** and **39** (eq 4). X-ray crystal structures were determined for both **36** and **37** and are given in the Supporting Information.



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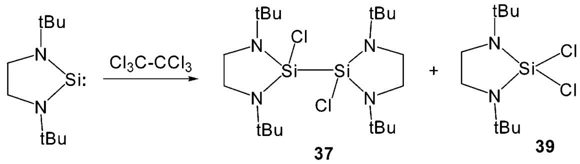

(4)

We rationalize these results in terms of the strong tendency of the radical $CCl_3CCl_2\bullet$ to give up a chlorine atom, with formation of a C=C double bond. The radical chain mechanism now becomes that shown in Scheme 6. Here also, as in Scheme 5, there is an alternate chain pathway leading to the monosilane products, shown at the bottom of the scheme.

Conclusion

We have found that a wide variety of halogenated organic compounds react with N-heterocyclic stable silylenes to give either disilane or monosilane products, or a mixture of both, depending on the nature of the halocarbon. The results are explicable in terms of related free-radical chain mechanisms. Further study of the reaction mechanisms is warranted and awaits investigation of the reaction kinetics, which we plan to carry out.

Other reactions of stable silylenes leading to disilane products have not yet been reported, but it seems likely that these may be observed in the future.

Experimental Section

Synthesis. All manipulations were performed using standard Schlenk techniques under an atmosphere of nitrogen or argon or handled under an atmosphere of nitrogen in a glovebox. All solvents were distilled from sodium benzophenone ketyl and used immediately. CH_2Cl_2 and $CHCl_3$ were purchased from Fisher Chemical and distilled from CaH_2 and stored over 4 Å molecular sieves. All other reagents used were purchased from Aldrich Chemical Co. and were dried over CaH_2 immediately before use. Both silylene compounds, **1** and **2**, were prepared according to literature methods.[16]

Instrumentation. ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 NMR at room temperature, and chemical shifts are reported in parts per million downfield from an internal tetramethylsilane (TMS) standard. ^{29}Si NMR spectra were recorded on a Varian 500 NMR spectrometer at room temperature. Melting points were performed using a Mel-Temp apparatus and are uncorrected. Mass spectra were obtained on a Shimadzu QP 5000. Elemental analyses were performed at Chemisar Laboratories Inc., Guelph, ON. Crystal structures were obtained on a Bruker CCD-1000 diffractometer with Mo Kα (λ = 0.710 73 Å) radiation. The data were refined using the SHELXTL (v. 5.1) program library.[17]

Reaction of 1 with CCl_4. A solution of **1** (0.199 g, 1.02 mmol) in 10 mL of hexane was added to a solution of CCl_4 (0.157 g, 1.02 mmol) in 10 mL of hexane. The solution immediately turned bright yellow. The solution was concentrated in vacuo and refrigerated at −10 °C for

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(12) The range of normal silicon−silicon single bond lengths is 2.33−2.37 Å. See: Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Part 1, pp 249−284.

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24 h, yielding yellow crystals. Successive recrystallizations from hexane resulted in 0.239 g (86.0%) of **5**. Mp 153 °C. ^{1}H NMR (300 MHz, 298 K, C_6D_6): δ 5.79 (s, 2H, CH), 5.75 (s, 2H, CH), 1.38 (s, 18H, $C(CH_3)_3$), 1.36 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, 298 K, C_6D_6): δ 116.0 (s, *C*H), 115.3 (s, *C*H), 75.3 (s, *C*Cl$_3$), 53.7 (s, *C*(CH$_3$)$_3$), 53.3 (s, *C*(CH$_3$)$_3$), 31.4 (s, C(*C*H$_3$)$_3$), 31.3 (s, C(***C***H$_3$)$_3$). ^{29}Si NMR (99 MHz, 298 K, C_6D_6): δ −35.3, −35.5. Anal. Calcd (found) for $C_{21}H_{40}Cl_4N_4Si_2$: C, 46.15 (46.40); H, 7.38 (7.66); N, 10.25 (10.01).

Reaction of 1 with CH_2Cl_2. A solution of **1** (0.100 g, 0.509 mmol) in 10 mL of hexane was added to a stirring solution of CH_2Cl_2 (0.043 g, 0.510 mmol) in 10 mL of hexane. The solution turned pale yellow immediately. Partial removal of solvent in vacuo, followed by refrigeration for 24 h at −10 °C, resulted in 0.114 g (94.0%) of **7**. Mp 150 °C. ^{1}H NMR (300 MHz, 298 K, C_6D_6): δ 5.77 (s, 2H, CH), 5.72 (s, 2H, CH), 3.23 (s, 2H, CH_2Cl), 1.32 (s, 18H, $C(CH_3)_3$), 1.27 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, 298 K, C_6D_6): δ 114.9 (s, ***C***H), 114.1 (s, ***C***H), 52.7 (s, ***C***(CH3)3), 52.1 (s, ***C***(CH3)3), 36.0 (s, ***C***H$_2$Cl), 31.0 (s, C(***C***H$_3$)$_3$), 30.9 (s, C(***C***H$_3$)$_3$). ^{29}Si NMR (99 MHz, 298 K, C_6D_6): δ −22.8, −33.6. Anal. Calcd (found) for $C_{21}H_{42}Cl_2N_4Si_2$: C, 52.80 (53.25); H, 8.86 (9.26); N, 11.73 (11.49).

Reaction of 1 with $CHBr_3$. Bromoform (0.120 mL, 1.34 mmol) was added to a stirring solution of **1** (0.250 g, 1.27 mmol) in hexane. The mixture immediately turned clear brown, but after stirring 20 min at room temperature, turned deep red. The mixture was stirred 1 h, and then all solvent was removed in vacuo, yielding a deep red oil. The oil was distilled under vacuum at 40 °C and 0.1 Torr, resulting in 0.536 g (94.1%) of **8**. ^{1}H NMR (300 MHz, 298 K, C_6D_6): δ 5.75 (s, 2H, CH), 5.35 (s, 1H, $CHBr_2$), 1.22 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, 298 K, C_6D_6): δ 109.9 (s, ***C***H), 84.0 (s, ***C***HBr$_2$), 55.9 (s, ***C***(CH$_3$)$_3$), 30.9 (s, C(***C***H$_3$)$_3$). ^{29}Si NMR (99 MHz, 298 K, C_6D_6): δ −56.4. MS (EI) *m/z* (%): 449.2 (50) (M^+), 369.0 (67) ($M^+ - Br$).

Reaction of 1 with Benzyl Chloride. A solution of **1** (0.167 g, 0.850 mmol) in 10 mL of hexane was added to a solution of benzyl chloride (0.108 g, 0.850 mmol) in 10 mL of hexane. The solution immediately turned yellow, and the solvent was partially removed in vacuo. The saturated solution was refrigerated at −10 °C for 14 h, producing rectangular yellow crystals. Recrystallization from hexane yielded 0.214 g (97.1%) of **9**. Mp 109 °C. ^{1}H NMR (300 MHz, 298 K, C_6D_6): δ 7.30 (d, 2H, J_{HH} = 7.8 Hz), 7.19 (t, 2H, J_{HH} = 7.8 Hz), 7.04 (t, 1H, J_{HH} = 7.2 Hz), 5.86 (s, 2H, CH), 5.69 (s, 2H, CH), 2.88 (s, 2H, CH_2), 1.42 (s, 18H, $C(CH_3)_3$), 1.19 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, 298 K, C_6D_6): δ 138.6 (s), 130.7 (s,), 128.5 (s,), 125.6 (s), 114.8 (s, ***C***H), 114.2 (s, ***C***H), 52.8 (s, ***C***(CH$_3$)$_3$), 52.0 (s, ***C***(CH$_3$)$_3$), 32.9 (s, ***C***H$_2$), 31.3 (s, C(***C***H$_3$)$_3$), 30.8 (s, C(***C***H$_3$)$_3$). ^{29}Si NMR (99 MHz, 298 K, C_6D_6): δ −18.0, −32.0. Anal. Calcd (found) for $C_{27}H_{47}ClN_4Si_2$: C, 62.45 (62.14); H, 9.12 (9.59); N,10.79 (10.80).

Reaction of 1 with *n*-BuCl. To a solution of **1** (0.066 g, 0.336 mmol) in 5 mL of hexane was added 0.033 g (0.356 mmol) of 1-chlorobutane. The mixture was stirred for 12 h at room temperature. NMR spectrum showed one major product, 1:2 adduct **10** (90% NMR yield), in addition to a small amount of unidentified products. The oily mixture was vacuum distilled at 120 °C and 0.1 Torr, and the remaining crude solid was dissolved in a minimum amount of hexane and recrystallized at −20 °C, resulting (0.114 g, 70%) in colorless solid **10**. MS (M^+) 484. ^{1}H NMR (C_6D_6): δ 0.92 (t, 3H, CH_3, *J* = 7 Hz), 1.10 (br, 6H, CH_2), 1.33 (s, 18H, t-Bu), 1.41 (s, 18H, t-Bu), 5.68 (s, 2H, =CH), 5.85 (s, 2H, CH). ^{13}C NMR (C_6D_6): δ 14.0 (CH_3), 25.6, 25.8, 26.5 (CH_2), 31.1, 31.2 (Me_3C), 51.8, 52.7 (N−CMe_3), 114.0, 114.7 (=CH). ^{29}Si NMR (C_6D_6): δ −31.5, −13.6. MS (EI) *m/z* (%): 485.1 (55) (M^+), 449.6 (67) ($M^+ - Cl$), 427.3 (86) ($M^+ - C_4H_9$).

Reaction of 1 with *n*-Hexyl Bromide. To a solution of silylene (0.126 g, 0.642 mmol) in 10 mL of hexane was added 0.106 g (0.642 mmol) of 1-bromohexane. The mixture was stirred for 12 h at room temperature. The solvent was removed in vacuo, and the NMR spectrum showed two products, the 1:1 adduct **11a** and 1:2 adduct **11b** in a ratio of 1:1.8. The mixture was vacuum distilled at 120 °C and 0.1 Torr, and 0.058 g (25%) of the colorless oil **11a** was isolated. The remaining crude solid was dissolved in a minimum amount of hexane and recrystallized at −20 °C, resulting (0.175 g, 49%) in colorless solid **11b**.

(a) For 11a. MS (M^+) 360. ^{1}H NMR (C_6D_6): δ 0.85 (t, 3H, CH_3, *J* = 7 Hz), 1.27 (s, 18H, t-Bu), 1.29−1.63 (m, 10H, CH_2), 5.77 (s, 2H, =CH). ^{13}C NMR (C_6D_6): δ 14.2 (CH_3), 22.9, 24.8, 27.1 (CH_2), 30.4 (Me_3C), 31.7, 32.2 (CH_2), 52.1 (N−CMe_3), 113.2 (=C). ^{29}Si NMR (C_6D_6): δ −18.8.

(b) For 11b. MS (M^+) 556. ^{1}H NMR (C_6D_6): δ 0.88 (t, 3H, CH_3, *J* = 7 Hz), 1.21−1.65 (br, 10H, CH_2), 1.35 (s, 18H, t-Bu), 1.44 (s, 18H, t-Bu), 5.68 (s, 2H, =CH), 5.87 (s, 2H, =CH). ^{13}C NMR (C_6D_6): δ 14.3 (CH_3), 23.0, 23.6, 25.8 (CH_2), 31.1, 31.2 (Me_3C), 32.1, 33.3 (CH_2), 51.9, 53.1 (N−CMe_3), 114.3, 114.9 (=C). ^{29}Si NMR (C_6D_6): δ −35.8, −12.6. Anal. Calcd for $C_{26}H_{53}Si_2N_4Br$ (found): C, 54.99 (54.60); H, 9.58 (9.92); N, 10.04 (9.56).

Reaction of 1 with Isopropyl Chloride. To a solution of **1** (0.107 g, 0.545 mmol) in 5 mL of dry hexane was added 0.043 g (0.547 mmol) of 2-chloropropane. The mixture was stirred for 12 h at room temperature. The NMR spectrum showed two products, 1:1 adduct **12a** and 1:2 adduct **12b**. The ratio of **12a**:**12b** was determined to be 1:1 by ^{1}H NMR spectrometric analysis. The oily mixture was vacuum distilled at 120 °C and 0.1 Torr, and 0.037 g (25%) of the colorless oil **12a** was isolated. The remaining crude solid was dissolved in a minimum amount of hexane and recrystallized at −20 °C, resulting (0.089 g, 35%) in colorless solid **12b**.

(a) For 12a. MS (M^+) 274. ^{1}H NMR (C_6D_6): δ 1.14 (d, 6H, CH_3, *J* = 8 Hz), 1.22 (s, 18H, t-Bu), 1.50 (sep, 1H, HC, *J* = 8 Hz), 5.76(s, 2H, =CH). ^{13}C NMR (C_6D_6): δ 17.7 (CH_3), 21.5 (CH), 30.9 (Me_3C), 51.6 (N−CMe_3), 113.2 (=C). ^{29}Si NMR (C_6D_6): δ −10.2.

(b) For 12b. MS (M^+) 470. ^{1}H NMR (C_6D_6): δ 1.29 (d, 6H, CH_3, *J* = 8 Hz), 1.30 (s, 18H, t-Bu), 1.38 (s, 18H, t-Bu), 1.51 (sep, 1H, CH, *J* = 8 Hz), 5.70 (s, 2H, =CH), 5.82 (s, 2H, =CH). ^{13}C NMR (C_6D_6): δ 18.6 (CH_3), 22.4 (CH), 31.1, 31.6 (Me_3C), 51.6, 52.8 (N−CMe_3), 114.3, 114.6 (=C). ^{29}Si NMR (C_6D_6): δ −30.3, −10.1.

Reaction of 1 with Isopropyl Bromide. To a solution of silylene (0.110 g, 0.560 mmol) in 5 mL of dry hexane was added 0.070 g (0.569 mmol) of 2-bromopropane. The mixture was stirred for 2 h at room temperature. NMR spectrum showed two products, 1:1 adduct **13a** and 1:2 adduct **13b**, in a 1:1 ratio. The oily mixture was vacuum distilled at 120 °C at 0.1 Torr, and 0.039 g (22%) of the colorless oil **13a** was isolated. The remaining crude solid was dissolved in a minimum amount of hexane and recrystallized at −20 °C, yielding 0.115 g (40%) of colorless solid **13b**.

(a) For 13a. MS (M^+) 318. ^{1}H NMR (C_6D_6): δ 1.15 (d, 6H, CH_3, *J* = 7 Hz), 1.23 (s, 18H, t-Bu), 1.59 (sep, 1H, CH, *J* = 7 Hz), 5.77 (s, 2H, =CH). ^{13}C NMR (C_6D_6): δ 17.8 (CH_3), 23.1 (CH), 30.9 (Me_3C), 51.9 (N−CMe_3), 113.5 (HC=). ^{29}Si NMR (C_6D_6): δ −14.1.

(b) For 13b. MS (M^+) 514. ^{1}H NMR (C_6D_6): δ 1.28 (d, 6H, CH_3, *J* = 7 Hz), 1.30 (s, 18H, t-Bu), 1.41 (s, 18H, t-Bu), 1.46 (sep, 1H, CH, *J* = 7 Hz), 5.71 (s, 2H, =CH), 5.86 (s, 2H, =CH). ^{13}C NMR (C_6D_6): δ 18.7 (CH_3), 22.2 (CH), 31.1, 31.8 (Me_3C), 51.7, 53.1 (N−CMe_3), 114.6, 114.8 (HC=). ^{29}Si NMR (C_6D_6): δ −35.7, −9.7. Anal. Calcd for $C_{23}H_{47}Si_2N_4Br$ (found): C, 53.57 (53.40); H, 9.19 (9.66); N, 10.54 (10.86).

Reaction of 1 with *tert*-Butyl Chloride. To a solution of **1** (0.338 g, 1.72 mmol) in 10 mL of hexane was added *tert*-butyl chloride (0.200 g, 2.16 mmol) in 5 mL of hexane. The solution was stirred for 10 h at room temperature. Solvent was removed in vacuo to yield a colorless oil, which was vacuum distilled at 55 °C and 0.1 Torr to give 0.432 g (87.0%) of **14**. ^{1}H NMR (300 MHz, 298 K, C_6D_6): δ 5.77 (s, 2H, CH), 1.27 (s, 18H, $C(CH_3)_3$), 1.10 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, 298 K, C_6D_6): δ 115.0 (s, ***C***H), 52.7 (s, ***C***(CH$_3$)$_3$), 31.0 (s, C(***C***H$_3$)$_3$), 29.3 (s, ***C***(CH$_3$)$_3$), 27.2 (s, C(***C***H$_3$)$_3$). ^{29}Si NMR (99 MHz, 298 K, C_6D_6): δ −5.5. M. S. (EI) *m/z* (%): 288.6 (60) (M^+), 253.0 (65) ($M^+ - Cl$).

Reaction of 1 with Bromobenzene. A solution of **1** (0.320 g, 1.63 mmol) in 10 mL of hexane was added to a solution of bromobenzene (0.256 g, 1.63 mmol) in 10 mL of toluene. The mixture was stirred for 5 h and monitored by ^{1}H NMR until all silylene was consumed. Two products, **15a** and **15b**, were identified in the NMR spectrum. The solvent was removed from the mixture, yielding a yellow oil. The oil was vacuum distilled carefully at 40 °C and 0.1 Torr. The 1:1 adduct, **15a**, was separated from the 2:1 adduct, and the solid was dissolved in a minimum amount of hexane and refrigerated at -10 °C for 24 h. Large, colorless, rectangular crystals of the 1:1 adduct were isolated (0.123 g, 63.9%). The 2:1 adduct was also dissolved in a minimum amount of hexane and stored in the refrigerator at -10 °C for 24 h. Small yellow needles of **15b** were isolated (0.0872 g, 29.2%).

(a) For 15a. Mp 61−63 °C. ^{1}H NMR (300 MHz, 298 K, C_6D_6): δ 8.00 (m, 2H), 7.10 (m, 3H), 5.90 (s, 2H, CH), 1.16 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, 298 K, C_6D_6): δ 136.9 (s), 130.4 (s), 127.4 (s), 120.0 (s), 113.0 (s, ***C***H), 52.2 (s, ***C***$(CH_3)_3$), 31.46 (s, C(***C***$H_3)_3$). ^{29}Si NMR (99 MHz, 298 K, C_6D_6): δ -28.1. Anal. Calcd (found) for $C_{16}H_{25}BrN_2Si$: C, 54.38 (53.97); H, 7.13 (7.63); N, 7.93 (7.92).

(b) For 15b. Mp 118 °C dec. ^{1}H NMR (300 MHz, 298 K, C_6D_6): δ 8.24 (m, 5H), 5.89 (s, 2H, CH), 5.81 (s, 2H, CH), 1.40 (s, 18H, $C(CH_3)_3$), 1.22 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, 298 K, C_6D_6): δ 135.4 (s), 131.0 (s), 128.1 (s), 115.0 (s, ***C***H), 114.6 (s, ***C***H), 113.5 (s), 53.1 (s, ***C***$(CH_3)_3$), 52.4 (s, ***C***$(CH_3)_3$), 31.5 (s, C(***C***$H_3)_3$), 30.7 (s, C(***C***$H_3)_3$). ^{29}Si NMR (99 MHz, 298 K, C_6D_6): δ -24.2, -37.6. Anal. Calcd (found) for $C_{26}H_{45}BrN_4Si_2$: C, 56.81 (56.38); H, 8.25 (8.28); N, 10.19 (9.77).

Reaction of 1 with *p*-(Trifluoromethyl)bromobenzene. A solution of **1** (0.180 g, 0.917 mmol) in 10 mL of hexane was added to a solution of *p*-(trifluoromethyl)bromobenzene (0.206 g, 0.918 mmol) in 10 mL of hexane. The reaction mixture was stirred for 8 h at room temperature until all silylene was consumed. ^{1}H NMR revealed the appearance of the 1:1 adduct, **16a** (85%), and the 2:1 adduct, **16b** (15%). All solvent was removed in vacuo to yield an oil. The mixture of products was distilled under vacuum (65 °C and 0.1 Torr) to yield the 1:1 adduct as a colorless oil (0.085 g, 66.3%). The 2:1 adduct was isolated as a yellow oil (0.017 g, 9.15%).

(a) For 16a. ^{1}H NMR (300 MHz, 298 K, C_6D_6): δ 7.87 (d, 2H, $J_{HH} = 8.4$ Hz), 7.32 (d, 2H, $J_{HH} = 8.4$ Hz), 5.84 (s, 2H, CH), 1.15 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, 298 K, C_6D_6): δ 161.1 (s), 137.0 (s), 135.7 (s), 124.7 (s), 113.1 (s, ***C***H), 69.9 (s, ***C***F_3), 52.6 (s, ***C***$(CH_3)_3$), 30.6 (s, C(***C***$H_3)_3$). ^{29}Si NMR (99 MHz, 298 K, C_6D_6): δ -30.1. MS (EI) *m/z* (%): 422.0 (96) (M^+), 312.3 (60) ($M^+ - Br$).

(b) For 16b. ^{1}H NMR (300 MHz, 298 K, C_6D_6): δ 8.17 (d, 2H, $J_{HH} = 7.5$ Hz), 7.35 (d, 2H, $J_{HH} = 7.5$ Hz), 5.86 (s, 2H, CH), 5.76 (s, 2H, CH), 1.34 (s, 18H, $C(CH_3)_3$), 1.29 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, 298 K, C_6D_6): δ 157.6 (s), 137.2 (s), 130.0 (s), 124.6 (s), 115.0 (s, ***C***H), 114.6 (s, ***C***H), 70.1 (s, ***C***F_3), 53.1 (s, ***C***$(CH_3)_3$), 52.2 (s, ***C***$(CH_3)_3$), 31.4 (s, C(***C***$H_3)_3$), 29.3 (s, C(***C***$H_3)_3$). ^{29}Si NMR (99 MHz, 298 K, C_6D_6): $\delta - 25.77$, -38.77.

Reaction of 1 with *p-tert*-Butylbromobenzene. A solution of **1** (0.125 g, 0.637 mmol) in 10 mL of hexane was added to a solution of *p*-*tert*-butylbromobenzene (0.136 g, 0.637 mmol) in 10 mL of hexane. The mixture was stirred for 8 h, and ^{1}H NMR showed that all of **1** was consumed. The spectrum revealed the presence of both the 1:1 adduct, **17a**, and the 2:1 adduct, **17b**, in a 4:1 ratio. The 1:1 adduct was vacuum distilled from the 2:1 adduct (65 °C, 0.1 Torr) to yield a colorless oil (0.0613 g, 70.9%). The 2:1 adduct was isolated as a pale yellow oil (0.020, 15.0%).

(a) For 17a. ^{1}H NMR (300 MHz, 298 K, C_6D_6): δ 8.04 (d, 2H, $J_{HH} = 8.4$ Hz), 7.31 (d, 2H, $J_{HH} = 8.4$ Hz), 5.92 (s, 2H, CH), 1.19 (s, 18H, $C(CH_3)_3$), 1.14 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, 298 K, C_6D_6): δ 154.2 (s), 135.6 (s), 125.2 (s), 124.4 (s), 113.0 (s, ***C***H), 52.5 (s, ***C***$(CH_3)_3$), 31.2 (s, C(***C***$H_3)_3$) 30.7 (s, C(***C***$H_3)_3$), 29.3 (s, ***C***$(CH_3)_3$). ^{29}Si NMR (99 MHz, 298 K, C_6D_6): δ -27.9. MS (EA) *m/z* (%): 408.0 (65) (M^+), 393.2 (86) ($M^+ - CH_3$), 329.3 (100) ($M^+ - Br$).

(b) For 17b. ^{1}H NMR (300 MHz, 298 K, C_6D_6): δ 8.22 (d, 2H, $J_{HH} = 8.7$ Hz), 7.30 (d, 2H, $J_{HH} = 8.7$ Hz), 5.90 (s, 2H, CH), 5.83 (s, 2H, CH), 1.42 (s, 18H, $C(CH_3)_3$), 1.25 (s, 18H, $C(CH_3)_3$), 1.20 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, 298 K, C_6D_6): δ 153.6 (s), 142.6 (s), 136.9 (s), 134.2 (s), 115.0 (s, ***C***H), 114.6 (s, ***C***H), 53.1 (s, ***C***$(CH_3)_3$), 52.2 (s, ***C***$(CH_3)_3$), 34.6 (s, C(***C***$H_3)_3$), 31.5 (s, C(***C***$H_3)_3$), 31.1 (s, C(***C***$H_3)_3$), 27.2 (s, ***C***$(CH_3)_3$). ^{29}Si NMR (99 MHz, 298 K, C_6D_6): δ -19.0, -37.3.

Reaction of 1 with *p*-Bromoanisole. A solution of **1** (0.174 g, 0.886 mmol) in 10 mL of hexane was added all at once to a solution of *p*-bromoanisole (0.166 g, 0.886 mmol) in 5 mL of hexane. After stirring 10 h at room temperature, the solution was bright yellow and all silylene had been consumed. Hexane was removed in vacuo, and the bright yellow oil that remained was vacuum distilled at 55 °C and 0.1 Torr, to yield solid **18**. The solid was dissolved in a minimum amount of hexane and successive crystallizations at -10 °C resulted in 0.292 g (87.9%) of **18**. Mp 102−104 °C. ^{1}H NMR (300 MHz, 298 K, C_6D_6): δ 7.95 (d, 2H, $J_{HH} = 9.0$ Hz), 6.75 (d, 2H, $J_{HH} = 9.0$ Hz), 5.92 (s, 2H, CH), 3.20 (s, 3H, OCH_3), 1.21 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, 298 K, C_6D_6): δ 162.4 (s), 137.2 (s), 116.0 (s), 114.0 (s), 112.9 (s, ***C***H), 54.5 (s, ***C***$(CH_3)_3$), 52.4 (s, O***C***H_3), 30.7 (s, C(***C***$H_3)_3$). ^{29}Si NMR (99 MHz, 298 K, C_6D_6): δ -28.0. Anal. Calcd (found) for $C_{17}H_{27}BrN_2OSi$: C, 53.26 (53.74); H, 7.10 (7.40); N, 7.31 (7.34).

Reaction of 1 with Iodobenzene. A solution of **1** (0.075 g, 0.382 mmol) in 10 mL of hexane was added to a solution of iodobenzene (0.0779 g, 0.382 mmol) in 10 mL of hexane. The solution was stirred at room temperature for 10 h, resulting in a bright yellow solution. The solvent was removed in vacuo to give an oil. The oil was vacuum distilled at 50 °C and 0.1 Torr to yield 0.145 g (95.0%) of **19**. ^{1}H NMR (300 MHz, 298 K, C_6D_6): δ 7.09 (m, 5H), 5.91 (s, 2H, CH), 1.15 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, 298 K, C_6D_6): δ 137.2 (s), 131.3 (s), 127.2 (s), 118.8 (s), 113.6 (s, ***C***H), 52.8 (s, ***C***$(CH_3)_3$), 30.5 (s, C(***C***$H_3)_3$). ^{29}Si NMR (99 MHz, 298 K, C_6D_6): δ -40.5. MS (EI) *m/z* (%): 399.8 (65) (M^+), 273.2 (83) ($M^+ - I$).

Reaction of 1 with 2-Bromonaphthalene. To a stirring solution of **1** (0.199 g, 1.01 mmol) in 10 mL of hexane was added 0.140 mL (1.01 mmol) of 2-bromonaphthalene. The solution immediately turned bright yellow, and a ^{1}H NMR of the solution revealed all silylene was consumed and **20** was formed. The solution was concentrated under vacuum, and the saturated solution of **20** was refrigerated overnight at -10 °C. Successive crystallizations resulted in a total yield of 0.387 g (95.1%) of **20**. Mp 159−161 °C. ^{1}H NMR (300 MHz, 298 K, C_6D_6): δ 8.70 (d, 1H, $J_{HH} = 8.7$ Hz), 8.06 (d, 1H, $J_{HH} = 8.7$ Hz), 7.64 (d, 1H, $J_{HH} = 8.1$ Hz), 7.58 (d, 1H, $J_{HH} = 8.1$ Hz), 7.27 (m, 3H), 6.03 (s, 2H, CH), 1.08 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, 298 K, C_6D_6): δ 137.9 (s), 137.4 (s), 134.0 (s), 133.7(s), 132.4 (s), 129.1 (s), 128.7 (s), 126.5 (s), 126.1(s), 125.6 (s), 113.0 (s, ***C***H), 52.4 (s, ***C***$(CH_3)_3$), 30.4 (s, $C(CH_3)_3$). ^{29}Si NMR (99 MHz, 298 K, C_6D_6): δ -29.7. Anal. Calcd (found) for $C_{20}H_{27}BrN_2Si$: C, 59.54 (59.22); H, 6.75 (6.99); N, 6.94 (6.95).

Reaction of 1 with 9-Bromofluorene. To a suspension of 9-bromofluorene (0.258 g, 1.05 mmol) in 5 mL of hexane was added a solution of 0.207 g of **1** (1.05 mmol) in 10 mL of hexane. The mixture was stirred 14 h at room temperature, and ^{1}H NMR of an aliquot of the yellow solution revealed that all the silylene had been consumed. The solvent was removed to concentrate the solution, which was then refrigerated at -10 °C overnight. Successive crystallizations resulted in 0.403 g (86.9%) of **21**. Mp 127−129 °C. ^{1}H NMR (300 MHz, 298 K, C_6D_6): δ 7.99 (br, 2H), 7.71 (m, 2H), 7.25 (m, 4H), 5.77 (s, 2H, CH), 4.41 (s, 1H), 0.97 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, 298 K, C_6D_6): δ 143.1 (s), 141.5 (s), 141.2 (s), 126.9 (s), 126.6 (s), 126.3 (s), 120.1 (s), 114.0 (s, ***C***H), 47.2 (s, ***C***$(CH_3)_3$), 30.3 (s, C(***C***$H_3)_3$). ^{29}Si NMR (99 MHz, 298 K, C_6D_6): δ -28.4. Anal. Calcd (found) for $C_{23}H_{29}BrN_2Si$: C, 62.57 (62.75); H, 6.62 (6.58); N, 6.35 (5.98).

Reaction of 1 with Chloropentafluorobenzene. A solution of **1** (0.236 g, 1.20 mmol) in 10 mL of hexane was added to a solution of chloropentafluorobenzene (0.245 g, 1.20 mmol) in 10 mL of hexane. The mixture was brought to reflux for 36 h after which all silylene had been consumed. The solvent was removed in vacuo from the bright orange solution of **22**, yielding bright orange oil. The oil was vacuum distilled at 50 °C and 0.1 Torr, yielding 0.279 g (78.2%) of **22**. ^{1}H NMR (300 MHz, 298 K, C$_6$D$_6$): δ 5.81 (s, 2H, CH), 5.74 (s, 2H, CH), 1.32 (s, 18H, C(CH$_3$)$_3$), 1.15 (s, 18H, C(CH$_3$)$_3$). ^{13}C NMR (75 MHz, 298 K, C$_6$D$_6$): δ 159.2 (s), 158.6 (s), 146.0 (s), 132.5 (s), 115.0 (s, CH), 114.5 (s, CH), 52.7 (s, C(CH$_3$)$_3$), 52.1 (s, C(CH$_3$)$_3$), 31.0 (s, C(CH$_3$)$_3$), 30.5 (s, C(CH$_3$)$_3$). ^{29}Si NMR (99 MHz, 298 K, C$_6$D$_6$): δ −32.6, −36.4. MS (EI) *m*/*z* (%): 595.2 (71) (M$^+$), 559.1 (84) (M$^+$ − Cl).

Reaction of 1 with Bromopentafluorobenzene. A solution of **1** (0.160 g, 0.815 mmol) in 10 mL of hexane was added to a solution containing bromopentafluorobenzene (0.201 g, 0.815 mmol) in 10 mL of hexane. The mixture immediately turned bright orange, and the solvent was removed in vacuo to yield a bright orange oil. The oil was vacuum distilled at 65 °C and 0.1 Torr to yield 0.198 g (76%) of pure **23**. ^{1}H NMR (300 MHz, 298 K, C$_6$D$_6$): δ 5.83 (s, 2H, CH), 5.74 (s, 2H, CH), 1.34 (s, 18H, C(CH$_3$)$_3$), 1.15 (s, 18H, C(CH$_3$)$_3$). ^{13}C NMR (75 MHz, 298 K, C$_6$D$_6$): δ 164.2 (s), 150.1 (s), 143.2 (s), 134.4 (s), 115.2 (s, ***C***H), 114.8 (s, ***C***H), 53.0 (s, ***C***(CH$_3$)$_3$), 52.2 (s, ***C***(CH$_3$)$_3$), 31.1 (s, C(***C***H$_3$)$_3$), 30.8 (s, C(***C***H$_3$)$_3$). ^{29}Si NMR (99 MHz, 298 K, C$_6$D$_6$): δ −36.5, −39.5. MS (EI) *m*/*z* (%): 638.8 (75) (M$^+$), 559.0 (100) (M$^+$ − Br).

Reaction of 1 with Iodopentafluorobenzene. A solution of **1** (0.157 g, 0.769 mmol) in 10 mL of hexane was added to a solution containing iodopentafluorobenzene (0.228 g, 0.769 mmol) in 10 mL of hexane. The solution immediately turned bright orange. It was concentrated under vacuum and the saturated hexane solution was stored for 15 h at −10 °C. Successive crystallizations resulted in 0.241 g (91.3%) of **24**. Mp 111−113 °C. ^{1}H NMR (300 MHz, 298 K, C$_6$D$_6$): δ 5.86 (s, CH), 5.74 (s, CH), 1.36 (s, 18H, C(CH$_3$)$_3$), 1.15 (s, 18H, C(CH$_3$)$_3$). ^{13}C NMR (75 MHz, 298 K, C$_6$D$_6$): δ 165.1 (s), 154.4 (s), 146.3 (s), 132.5 (s), 116.6 (s, ***C***H), 115.7 (s, ***C***H), 53.4 (s, ***C***(CH$_3$)$_3$), 52.2 (s, ***C***(CH$_3$)$_3$), 31.3 (s, C(***C***H$_3$)$_3$), 30.5 (s, C(***C***H$_3$)$_3$). ^{29}Si NMR (99 MHz, 298 K, C$_6$D$_6$): δ −22.7, −38.0. Anal. Calcd (found) for C$_{26}$H$_{40}$F$_5$IN$_4$Si$_2$: C, 45.48 (45.22); H, 5.87 (6.06); N, 8.16 (7.65).

Reaction of 2 with CCl$_4$. A 5 mL aliquot of a 0.28 M solution of CCl$_4$ (1.40 mmol) in hexane was added to a pale red solution of **2** (0.280 g, 1.41 mmol) in 10 mL of hexane. The mixture immediately turned colorless and after 1 h; ^{1}H NMR revealed all silylene had reacted to produce **25**. The solution was concentrated in vacuo and refrigerated at −10 °C for 24 h. Successive crystallizations resulted in 0.298 g (76.8%) of colorless crystals of **25**. Mp 155−156 °C. ^{1}H NMR (300 MHz, 298 K, C$_6$D$_6$): δ 3.15 (m, 4H, CH$_2$), 2.92 (m, 4H, CH$_2$), 1.42 (s, 18H, C(CH$_3$)$_3$), 1.35 (s, C(CH$_3$)$_3$). ^{13}C NMR (75 MHz, 298 K, C$_6$D$_6$): δ 93.1 (s, ***C***Cl$_3$), 53.0 (s, ***C***(CH$_3$)$_3$), 52.8 (s, ***C***(CH$_3$)$_3$), 45.1 (s, ***C***H$_2$), 43.7 (s, ***C***H$_2$), 30.5 (s, C(***C***H$_3$)$_3$), 30.0 (s, C(***C***H$_3$)$_3$). ^{29}Si NMR (99 MHz, 298 K, C$_6$D$_6$): δ −25.5, −26.7. Anal. Calcd (found) for C$_{21}$H$_{44}$Cl$_4$N$_4$Si$_2$: C, 45.81 (45.37); H, 8.05 (8.45); N, 10.18 (9.80).

Reaction of 2 with CHCl$_3$. A pale red solution of **2** (0.101 g, 0.504 mmol) in 10 mL of hexane was added to 5 mL of 0.101 M solution of chloroform (0.505 mmol). The solution became colorless after 2 min, and ^{1}H NMR revealed all silylene had been consumed. Solvent was removed in vacuo, yielding a saturated solution of **26** that was refrigerated for 15 h. Successive crystallizations resulted in 0.118 g (90.8%) of colorless crystals of **26**. Mp 151−152 °C. ^{1}H NMR (300 MHz, 298 K, C$_6$D$_6$): δ 5.59 (s, 1H, CHCl$_2$), 3.13 (m, 4H, CH$_2$), 2.80 (m, 4H, CH$_2$), 1.38 (s, 18H, C(CH$_3$)$_3$), 1.28 (s, 18H, C(CH$_3$)$_3$). ^{13}C NMR (75 MHz, 298 K, C$_6$D$_6$): δ 67.4 (s, ***C***HCl$_2$), 52.5 (s, ***C***(CH$_3$)$_3$), 51.9 (s, ***C***(CH$_3$)$_3$), 44.7 (s, ***C***H$_2$), 43.9 (s, ***C***H$_2$), 30.1 (s, C(***C***H$_3$)$_3$), 29.6 (s, C(***C***H$_3$)$_3$). ^{29}Si NMR (99 MHz, 298 K, C$_6$D$_6$): δ −25.6, −37.7. Anal. Calcd (found) for C$_{21}$H$_{45}$Cl$_3$N$_4$Si$_2$: C, 48.87 (48.65); H, 8.79 (9.14); N, 10.85 (10.37).

Reaction of 2 with CH$_2$Cl$_2$. A pale red solution of **2** (0.280 g, 1.41 mmol) in 10 mL of hexane was added all at once to a solution of CH$_2$Cl$_2$ (0.100 mL, 1.56 mmol) in 10 mL of hexane at room temperature. After 15 min, ^{1}H NMR of the colorless mixture revealed that all silylene was consumed. Solvent was removed in vacuo, and the resulting saturated solution was refrigerated at −10 °C for 24 h. Successive crystallizations resulted in 0.316 g (92.9%) of colorless crystals of **27**. Mp 145−146 °C. ^{1}H NMR (300 MHz, 298 K, C$_6$D$_6$): δ 3.22 (s, 2H, CH$_2$Cl), 2.89 (m, 4H, CH$_2$), 2.74 (m, 4H, CH$_2$), 1.34 (s, 18H, C(CH$_3$)$_3$), 1.23 (s, 18H, C(CH$_3$)$_3$). ^{13}C NMR (75 MHz, 298 K, C$_6$D$_6$): δ 52.3 (s, ***C***(CH$_3$)$_3$), 51.7 (s, ***C***(CH$_3$)$_3$), 44.2 (s, ***C***H$_2$), 44.0 (s, ***C***H$_2$), 37.9 (s, ***C***H$_2$Cl), 30.0 (s, C(***C***H$_3$)$_3$), 29.8 (s, C(***C***H$_3$)$_3$). ^{29}Si NMR (99 MHz, 298 K, C$_6$D$_6$): δ −20.5, −24.4. Anal. Calcd (found) for C$_{21}$H$_{46}$Cl$_2$N$_4$Si$_2$: C, 52.36 (51.90); H, 9.62 (10.01); N, 11.63 (11.14).

Reaction of 2 with Benzyl Chloride. To a solution of **2** (0.061 g, 0.307 mmol) in 10 mL of hexane was added 0.040 g (0.316 mmol) of benzyl chloride. The mixture was stirred for 30 min at room temperature. The solvent was removed in vacuo, and the NMR spectrum showed a product, the 1:2 adduct **28**. The mixture was vacuum distilled at 120 °C and 0.1 Torr. The remaining crude solid was dissolved in a minimum amount of hexane and recrystallized at −20 °C, yielding 0.113 g (70%) of colorless solid **28**. MS (M$^+$) 522. ^{1}H NMR (C$_6$D$_6$): δ 1.18 (s, 9H, t-Bu), 1.22 (s, 9H, t-Bu), 1.26 (s, 9H, t-Bu), 1.37 (s, 9H, t-Bu), 2.73−3.01 (m, 10H, CH$_2$), 7.04−7.09 (m, 1H, phenyl ring protons), 7.18−7.24 (m, 2H, phenyl ring protons), 7.43−7.47 (m, 2H, phenyl ring protons). ^{13}C NMR (C$_6$D$_6$): δ 29.4, 29.5, 29.6, 30.4 (Me$_3$C), 31.8, 42.3, 42.7, 45.2, 50.5 (CH$_2$), 51.1, 51.9, 54.8, 56.3 (N−CMe$_3$), 125.0, 127.5, 130.7, 139.0 (phenyl ring carbons). ^{29}Si NMR (C$_6$D$_6$): δ −36.6, −5.1. HRMS. Exact mass calcd (found) for C$_{27}$H$_{51}$Si$_2$N$_4$Cl: *m*/*z* 522.3341 (522.3331).

Reaction of 2 with *n*-Butyl Chloride. To a solution of **2** (0.070 g, 0.353 mmol) in 10 mL of hexane was added 0.036 g (0.389 mmol) of 1-chlorobutane. The mixture was stirred for 12 h at room temperature. The solvent was removed in vacuo, and the NMR spectrum showed two products, the 1:1 adduct **29a** and 1:2 adduct **29b**, in a ratio of 3:7. The oily mixture was vacuum distilled at 120 °C and 0.1 Torr, and 0.020 g (20%) of **29a** was isolated as a colorless oil. The remaining crude solid was dissolved in a minimum amount of hexane and recrystallized at −20 °C, yielding 0.095 g, (55%) of colorless solid **29b**.

(a) For 29a. MS (M$^+$) 290. ^{1}H NMR (C$_6$D$_6$): δ 0.87 (t, 3H, CH$_3$, $J = 7$ Hz), 1.21 (s, 18H, t-Bu), 1.17−1.33 (m, 6H, CH$_2$), 2.71−2.86 (m, 4H, CH$_2$). ^{13}C NMR (C$_6$D$_6$): δ 13.9 (CH$_3$), 24.0, 25.9, 26.1 (CH$_2$), 29.2 (Me$_3$C), 43.0 (CH$_2$), 51.3 (N−CMe$_3$). ^{29}Si NMR (C$_6$D$_6$): δ −11.4. HRMS. Exact mass calcd (found) for C$_{14}$H$_{31}$SiN$_2$Cl: *m*/*z* 290.1945 (290.1940). Anal. Calcd (found) for C$_{14}$H$_{31}$SiN$_2$Cl: C, 57.79 (57.69); H, 10.74 (10.44); N, 9.63 (9.60).

(b) For 29b. MS (M$^+$) 488. ^{1}H NMR (C$_6$D$_6$): δ 0.97 (t, 3H, CH$_3$, $J = 7$ Hz), 1.35 (s, 18H, t-Bu), 1.36 (s, 18H, t-Bu), 1.19−1.40 (m, 6H, CH$_2$), 2.82−3.02 (m, 8H, CH$_2$). ^{13}C NMR (C$_6$D$_6$): δ 14.1 (CH$_3$), 26.1, 26.3, 26.7 (CH$_2$), 29.9, 30.7 (Me$_3$C), 44.2 (CH$_2$), 51.5, 52.3 (N−CMe$_3$). ^{29}Si NMR (C$_6$D$_6$): δ −22.2, −12.4. HRMS. Exact mass calcd (found) for C$_{24}$H$_{53}$Si$_2$N$_4$Cl: *m*/*z* 488.3497 (488.3514). Anal. Calcd (found) for C$_{24}$H$_{53}$Si$_2$N$_4$Cl: C, 58.91 (58.81); H, 10.92 (10.87); N, 11.45 (11.10).

Reaction of 2 with Isopropyl Chloride. To a solution of **2** (0.117 g, 0.590 mmol) in 10 mL of hexane was added 0.046 g (0.590 mmol) of 2-chloropropane. The mixture was stirred for 5 h at room temperature. The solvent was removed in vacuo, and the NMR spectrum showed two products, the 1:1 adduct **30a** and 1:2 adduct **30b** in a ratio of 1:1. The oily mixture was vacuum distilled at 120 °C and 0.1 Torr, and 0.065 g (40%) of the colorless oil **30a** was isolated. The remaining crude solid was dissolved in a minimum amount of hexane and recrystallized at −20 °C, resulting in 0.107 g (38%) of colorless solid **30b**.

(a) For 30a. MS (M$^+$) 276. ^{1}H NMR (C$_6$D$_6$): δ 1.16 (d, 6H, CH$_3$, $J = 7$ Hz), 1.18 (s, 18H, t-Bu), 1.49 (sep, 1H, HC, $J = 7$ Hz), 2.71−2.89 (m, 4H, CH$_2$). ^{13}C NMR (C$_6$D$_6$): δ 17.9 (CH$_3$), 20.5 (CH), 29.7

(Me_3C), 43.5 (CH_2), 51.1 ($N-CMe_3$). ^{29}Si NMR (C_6D_6): δ −8.0. HRMS. Exact mass calcd (found) for $C_{13}H_{29}SiN_2Cl$ [M^+]: *m/z* 276.1789 (276.1784). Anal. Calcd (found) for $C_{13}H_{29}SiN_2Cl$: C, 52.87 (52.80); H, 9.71 (9.70); N, 7.71 (7.60).

(b) For 30b. MS (M^+) 474. ^{1}H NMR (C_6D_6): δ 1.29 (d, 6H, CH_3, $J = 7$ Hz), 1.33 (s, 18H, t-Bu), 1.36 (s, 18H, t-Bu), 1.43 (sep, 1H, CH, $J = 7$ Hz), 2.88−2.97 (m, 8H, CH_2). ^{13}C NMR (C_6D_6): δ 19.5 (CH_3), 21.8 (CH), 29.9, 30.1 (Me_3C), 44.3, 44.8 (CH_2), 51.4, 52.6($N-CMe_3$). ^{29}Si NMR (C_6D_6): δ −20.5, −8.3. HRMS. Exact mass calcd (found) for $C_{23}H_{51}Si_2N_4Cl$: *m/z* 474.3341 (474.3336). Anal. Calcd (found) for $C_{23}H_{51}Si_2N_4Br$: C, 53.15 (52.99); H, 9.89 (9.80); N, 10.78 (10.70).

Reaction of 2 with *n*-Hexyl Bromide. To a solution of **2** (0.068 g, 0.343 mmol) in 10 mL of hexane was added 0.057 g (0.345 mmol) of 1-bromohexane. The mixture was stirred for 12 h at room temperature. The solvent was removed in vacuo, and the NMR spectrum showed two products, the 1:1 adduct **31a** and 1:2 adduct **31b** in a ratio of 1:1. The oily mixture was vacuum distilled at 120 °C and 0.1 Torr, and 0.044 g (35%) of the colorless oil **31a** was isolated. The remaining crude solid was dissolved in a minimum amount of hexane and recrystallized at −20 °C, resulting (0.057 g, 30%) in colorless solid **31b**.

(a) For 31a. MS (M^+) 362. ^{1}H NMR (C_6D_6): δ 0.87 (t, 3H, CH_3, $J = 7$ Hz), 1.23 (s, 18H, t-Bu), 1.20−1.23 (br, 10H, CH_2), 2.74−2.85 (m, 4H, CH_2). ^{13}C NMR (C_6D_6): δ 14.2 (CH_3), 22.9, 24.0, 26.8 (CH_2), 29.1 (Me_3C), 31.8, 32.5, 43.1 (CH_2), 51.6 ($N-CMe_3$). ^{29}Si NMR (C_6D_6): δ −15.6. HRMS. Exact mass calcd (found) for $C_{15}H_{32}SiN_2Br$ [$M^+ - Me$]: *m/z* 347.1518 (347.1529).

(b) For 31b. MS (M^+) 560. ^{1}H NMR (C_6D_6): δ 0.92 (t, 3H, CH_3, $J = 7$ Hz), 1.20−1.24 (br, 10H, CH_2), 1.31 (s, 18H, t-Bu), 1.47 (s, 18H, t-Bu), 2.82−2.98 (m, 8H, CH_2). ^{13}C NMR (C_6D_6): δ 14.3 (CH_3), 23.0, 24.8, 27.0 (CH_2), 29.1, 29.7, 29.8, 30.0 (Me_3C), 32.2, 33.6, 42.4, 42.5, 44.5, 50.7 (CH_2), 51.4, 51.8, 54.9, 56.7 ($N-CMe_3$). ^{29}Si NMR (C_6D_6): δ −37.6, −0.9. HRMS. Exact mass calcd (found) for $C_{26}H_{57}Si_2N_4Br$: *m/z* 560.3305 (560.3289).

Reaction of 2 with Isopropyl Bromide. To a solution of **2** (0.151 g, 0.756 mmol) in 10 mL of hexane was added 0.100 g (0.813 mmol) of 2-bromopropane. The mixture was stirred for 12 h at room temperature. The solvent was removed in vacuo, and the NMR spectrum showed a product, 1:2 adduct **32** (75% NMR yield) in addition to some unidentified products. The mixture was distilled at 120 °C and 0.1 Torr, and the remaining crude solid was dissolved in a minimum amount of hexane and recrystallized at −20 °C, yielding 0.255 g (65%) of colorless solid **32**. MS (M^+) 518. ^{1}H NMR (C_6D_6): δ 1.227 (s, 9H, t-Bu), 1.231 (s, 9H, t-Bu), 1.31 (d, 3H, CH_3, $J = 7$ Hz), 1.32 (s, 9H, t-Bu), 1.461 (d, 3H, CH_3, $J = 7$ Hz), 1.463 (s, 9H, t-Bu), 1.62 (sep, 1H, CH, $J = 7$ Hz), 2.76−3.03 (m, 8H, CH_2). ^{13}C NMR (C_6D_6): δ 20.0 (CH_3), 20.3 (CH), 21.6 (CH_3), 29.5, 29.7, 29.8, 29.9 (Me_3C), 42.4, 42.5, 43.8, 50.9 (CH_2), 51.4, 51.8, 55.05, 56.2 ($N-CMe_3$). ^{29}Si NMR (C_6D_6): δ −38.1, 6.0. HRMS. Exact mass calcd (found) for $C_{23}H_{51}Si_2N_4Br$: *m/z* 518.2836 (518.2812). Anal. Calcd (found) for $C_{23}H_{51}Si_2N_4Br$: C, 53.15 (53.03); H, 9.89 (9.70); N, 10.78 (11.01).

Reaction of 2 with *tert*-Butyl Chloride. To a solution of **2** (0.117 g, 0.590 mmol) in 10 mL of hexane was added 0.046 g (0.590 mmol) of 2-chloropropane. The mixture was stirred for 5 h at room temperature. The solvent was removed in vacuo, and the NMR spectrum showed two products, the 1:1 adduct **33a** and 1:2 adduct **33b** in a ratio of 1:1. The oily mixture was vacuum distilled at 120 °C and 0.1 Torr, and 0.065 g (40%) of the colorless oil **33a** was isolated. The remaining crude solid was dissolved in a minimum amount of hexane and recrystallized at −20 °C, yielding 0.107 g (38%) of colorless solid **33b**.

(a) For 33a. MS (M^+) 276. ^{1}H NMR (C_6D_6): δ 1.16 (d, 6H, CH_3, $J = 7$ Hz), 1.18 (s, 18H, t-Bu), 1.49 (sep, 1H, HC, $J = 7$ Hz), 2.71−2.89 (m, 4H, CH_2). ^{13}C NMR (C_6D_6): δ 17.9 (CH_3), 20.5 (CH), 29.7 (Me_3C), 43.5 (CH_2), 51.1 ($N-CMe_3$). ^{29}Si NMR (C_6D_6): δ −8.0. HRMS. Exact mass calcd (found) for $C_{13}H_{29}SiN_2Cl$ [M^+]: *m/z* 276.1789 (276.1784). Anal. Calcd (found) for $C_{13}H_{29}SiN_2Cl$: C, 52.87 (52.80); H, 9.71 (9.70); N, 7.71 (7.60).

(b) For 33b. MS (M^+) 474. ^{1}H NMR (C_6D_6): δ 1.29 (d, 6H, CH_3, $J = 7$ Hz), 1.33 (s, 18H, t-Bu), 1.36 (s, 18H, t-Bu), 1.43 (sep, 1H, CH, $J = 7$ Hz), 2.88−2.97 (m, 8H, CH_2). ^{13}C NMR (C_6D_6): δ 19.5 (CH_3), 21.8 (CH), 29.9, 30.1 (Me_3C), 44.3, 44.8 (CH_2), 51.4, 52.6($N-CMe_3$). ^{29}Si NMR (C_6D_6): δ −20.5, −8.3. HRMS. Exact mass calcd (found) for $C_{23}H_{51}Si_2N_4Cl$: *m/z* 474.3341 (474.3336). Anal. Calcd (found) for $C_{23}H_{51}Si_2N_4Br$: C, 53.15 (52.99); H, 9.89 (9.80); N, 10.78 (10.70).

Reaction of 2 with Bromobenzene. To a solution of **2** (0.070 g, 0.353 mmol) in 10 mL of hexane was added 0.054 g (0.344 mmol) of bromobenzene. The mixture was stirred for 12 h at room temperature. The solvent was removed in vacuo, and the NMR spectrum showed two products, the 1:1 adduct **34a** and 1:2 adduct **34b** in a ratio of 1:2. The mixture was vacuum distilled at 120 °C and 0.1 Torr, and 0.028 g (22%) of the colorless oil **34a** was isolated. The remaining crude solid was dissolved in a minimum amount of hexane and recrystallized at −20 °C, resulting (0.097 g, 50%) in colorless solid **34b**.

(a) For 34a. MS (M^+) 354. ^{1}H NMR (C_6D_6): δ 1.09 (s, 18H, t-Bu), 2.95 (s, 4H, CH_2), 7.11−7.17 (m, 3H, phenyl ring protons), 7.95−7.97 (m, 2H, phenyl ring protons). ^{13}C NMR (C_6D_6): δ 29.3 (Me_3C), 43.2 (CH_2), 51.9 ($N-CMe_3$), 127.5, 130.4, 135.0, 139.4 (phenyl ring carbons). ^{29}Si NMR (C_6D_6): δ −24.8. HRMS. Exact mass calcd (found) for $C_{16}H_{27}SiN_2Br$: *m/z* 354.1128 (354.1129).

(b) For 34b. MS (M^+) 552. ^{1}H NMR (C_6D_6): δ 1.22 (s, 18H, t-Bu), 1.38 (s, 18H, t-Bu), 2.84−3.03 (m, 8H, CH_2), 7.15−7.21 (m, 3H, phenyl ring protons), 8.23−8.27 (m, 2H, phenyl ring protons). ^{13}C NMR (C_6D_6): δ 30.0, 30.2 (Me_3C), 44.4, 44.6 (CH_2), 51.9, 52.9 ($N-CMe_3$), 127.1, 129.9, 137.0, 141.0 (phenyl ring carbons). ^{29}Si NMR (C_6D_6): δ −27.4, −22.8. HRMS. Exact mass calcd (found) for $C_{26}H_{49}Si_2N_4Br$: *m/z* 552.2679 (552.2662). Anal. Calcd (found) for $C_{26}H_{49}Si_2N_4Br$: C, 56.39 (56.47); H, 8.92 (9.27); N, 10.12 (9.88).

Reaction of 1 with Hexachloroethane. To a solution of **1** (0.300 g, 1.53 mmol) in 5 mL of dry hexane was added 0.362 g (1.52 mmol) of hexachloroethane. The mixture was stirred for 30 min at room temperature. NMR spectrum showed that one major product, **35**, was formed in addition to a small amount of the known[14] dichloromonosilane. The ratio of **1**:dichloro derivative was determined to be 6:1 by ^{1}H NMR spectrometric analysis. Recrystallization from hexane solution gave pure **35** (0.560 g, 79% isolated yield). Tetrachloroethene was detected by ^{13}C NMR. Major product **35**. MS (M^+) 462. ^{1}H NMR (C_6D_6): δ 1.20−1.46 (br s, 36H, t-Bu), 5.79 (s, 4H, $=CH$). ^{13}C NMR (C_6D_6): δ 30.4−31.4 (Me_3C), 52.4−53.0 ($N-CMe_3$), 114.1 ($=C$). ^{29}Si NMR (C_6D_6): δ −34.6. HRMS. Exact mass calcd (found) for $C_{20}H_{40}Si_2N_4Cl_2$: *m/z* 462.2169 (462.2149).

Reaction of 2 with Hexachloroethane. To a solution of **2** (0.222 g, 1.12 mmol) was added 0.270 g (1.14 mmol) of hexachloroethane. The mixture was stirred for 2 h at room temperature. The solvent was removed in vacuo, and the NMR spectrum showed that one major product, **36**, was formed, in addition to a small amount of the dichloro derivative.[15] The ratio of **36**:dichloro derivative was determined to be 7:1 by ^{1}H NMR spectrometric analysis. Recrystallization from hexane gave pure **36** (0.419 g, 80% isolated yield). MS (M^+) 466. ^{1}H NMR (C_6D_6): δ 1.38 (s, 36H, t-Bu), 2.81−2.99 (s, 8H, CH_2). ^{13}C NMR (C_6D_6): δ 29.7 (Me_3C), 43.5 (CH_2), 52.3 ($N-CMe_3$). ^{29}Si NMR (C_6D_6): δ −26.5. HRMS. Exact mass calcd (found) for $C_{20}H_{44}Si_2N_4Cl_2$: *m/z* 466.2482 (466.2479).

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Supporting Information Available: Crystallographic data for **9**, **15a**, **15b**, **24**, **26**, **33b**, **35**, and **36**. This material is available free of charge via the Internet at http://pubs.acs.org.

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