Silylene- and Germylene-Mediated C−H Activation: Reaction with Alkanes, Ethers, and Amines

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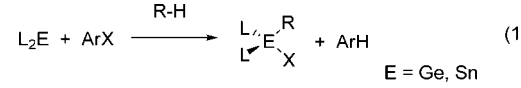
The reaction of silylene $Si[N_2(^tBu)_2C_2H_2]$ and Ph−X (X = I, Br) in alkane and ethereal solvents results in the formation of C−H activation product $[C_2H_2(^tBu_2)N_2]SiRI$ and an equivalent of benzene or oxidative-addition product $[C_2H_2(^tBu_2)N_2]SiPhI$. The ratio of products obtained is dependent upon substrate and concentration. This class of reaction has been extended for $Si[N_2(^tBu)_2C_2H_2]$ and $Ge[CH(SiMe_3)_2]_2$ to alkylamines. The primary kinetic isotope effect has been measured for the reaction of $Si[N_2(^tBu)_2C_2H_2]$ with Et_2O and determined to be $k_H/k_D = 5.1 \pm 0.1$. The reaction of $Ge[CH(SiMe_3)_2]_2$ and Ph−Br with THF was determined to be second order. A large isotope effect ranging from 1.8 to 1.1 was measured for a variety of deuterated aryl halides, consistent with an initial electron transfer to the aryl halide.

Introduction

Several methods for the direct formation of Ge−C and Sn−C bonds from C−H bonds have been reported. It is now possible to form these bonds concomitant with activation of the C−H bond in alkanes, alkenes, and alkynes and to regioselectively activate the α-C−H bond in ethers and nitriles.[1−6] $Ge[CH(SiMe_3)_2]_2$ undergoes salt-catalyzed insertions into the α-C−H bond of nitriles.[2] $Ge[CH(SiMe_3)_2]_2$, $Ge[N(SiMe_3)_2]_2$, $Sn[N(SiMe_3)_2]_2$, and $Sn[C_2(SiMe_3)_4C_2H_4]$ form an active complex in the presence of Ar−X (X = Br, I) that is capable of C−H activating alkanes, alkenes, alkynes, and ethers, resulting in the formation of Ge−C or Sn−C bonds and 1 equiv of aromatic hydrocarbon.[1,3−5] Labeling studies indicate that the origin of the hydrogen atom transferred to Ar−X is the activated hydrocarbon (eq 1). Intramolecular insertion of germylenes into C−H bonds has also been reported[7−9] as well as electrophilic arene activation for Sn.[10] Although substantial progress is needed to make these chemistries of practical utility, the published reports have provided intriguing proofs of principle.

Direct activation of the C−H bond to form a new Si−C bond is rare. The most important example of Si−C bond formation



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is the Direct Process used on an industrial scale to form $(CH_3)_xSiCl_{4-x}$ ($x = 1-3$) from elemental silicon and methyl chloride.[11] A more flexible and generally applicable approach for forming Si−C bonds involves nucleophilic substitution by a carbanion at a silicon with a good leaving group such as a halogen.[12−14] Hydrosilylation is a powerful method for forming Si−C bonds from carbon−carbon double bonds.[15−19] Silylenes can insert into the terminal C−H bonds of alkynes.[20] C−H activation of the methyl group on the backbone of β-diketiminato ligands has also been observed.[21] In recent years, the chemistry of the Si−C bond has been extensively developed for applications in organic synthesis.[22−24] These developments are significant both for the development of novel chemical transformations and because they provide a more environmentally friendly alternative to tin-based coupling chemistry. Given

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the growing importance of silicon to the synthetic chemist's toolkit, we endeavored to develop direct methods for forming Si−C bonds with alkanes and ethers in analogy to our previously reported germanium and tin chemistries.[1,3−5] We have also expanded the chemistry for both Si and Ge to C−H activation of alkyl amines.

Silylene Si[N_2(^{t}Bu)$_2$$C_2H_2$] (**1**), originally reported by West and Denk in 1994,[25−28] has been shown to undergo a variety of reaction chemistry including addition of R−X bonds to give oxidative-addition products and/or disilanes in which a Si−Si bond has formed and RX has formally performed an oxidative-addition reaction across the Si−Si bond vector.[29] **1** has also been shown to react with radicals to yield a stable, three-coordinate silicon radical (lifetime 1−7 days at 298 K).[30] We now report that **1** also forms an activated complex in the presence of Ar−X that is capable of C−H activating alkanes and ethers, forming a Si−C bond along with 1 equiv of aromatic hydrocarbon. We also report the C−H activation reaction with alkyl amines including a surprising and dramatic difference in reaction pathway for silylenes and germylenes. Finally, we present a set of experiments exploring isotope effects upon reaction rate.

Experimental Section

All manipulations were performed using dry solvents and air-free techniques. Tetrahydrofuran (THF), diethyl ether (Et_2O), cyclopentane, cyclohexane, 1,4-dioxane, *N*,*N*,*N*-triethylamine (Et_3N), *N*,*N*,*N*-tripropylamine (Pr_3N), *N*,*N*-dimethyl-*tert*-butylamine (Me_2N^tBu), *N*-methylpiperidine, *N*,*N*-dimethylaniline (Me_2NPh), *N*,*N*-dimethylbenzylamine (Me_2NCH_2Ph), *N*,*N*,*N*′,*N*′-tetramethylmethanediamine, toluene, benzene-d_6, Et_2O-d_{10}, and THF-d_8 were degassed and dried over sodium benzophenone ketyl. Acetonitrile (CH_3CN) was dried over P_2O_5 and stored over 4 Å sieves. Aryl halides were passed through a plug of $MgSO_4$ and then degassed before use. Si[N_2^{t}Bu$_2$$(CH)_2$] (**1**)[25] and Ge[$CH(SiMe_3)_2$]$_2$ (**15**)[31] were synthesized according to literature procedures. GC-MS was performed using a HP 5890A GC connected to a Finnegan MS or a Shimadzu GC-17A connected to a GCMS-QP5000. A Razel syringe pump, model A-99, was used for syringe pump additions. ^{1}H and ^{13}C NMR spectra were acquired on Varian 500, 400, or 300 MHz instruments and referenced to residual solvent peaks. Mass spectra (MS) were acquired on a VG (Micromass) 70−250-S magnetic sector mass spectrometer. Time of flight (TOF) electrospray ionization (ESI) mass spectra were acquired on a MicroMass LCT operating in positive or negative ion mode. IR spectra were acquired on a Perkin-Elmer Spectrum BX. Compounds **5**, **6**, **7**, and **9** contained oxidative-addition product **2** as an impurity. We were unable to separate the mixture using fractional crystallization or sublimation. The compounds were not stable toward chromatography. Infrared spectra for all species containing the ^{t}BuNCHCHN^{t}Bu backbone exhibited characteristic absorptions at roughly 3105, 2970, 2870, 1620, and 1590 cm^{-1}. Additional infrared data are provided in cases where specific functional groups of interest are present.

[$(CH)_2$^{t}Bu$_2$$N_2$]SiI($C_6H_5$) (2). A 50 mL round-bottom flask was charged with 126 mg (0.64 mmol, 1 equiv) of **1** and 1.160 g (5.69 mmol, 8.9 equiv) of iodobenzene (Ph−I), resulting in the formation of a gold-colored solution. After 1 h, all volatiles were removed, resulting in a golden oil. Upon exposure to dynamic vacuum for over 12 h, a white, feathery, crystalline solid formed. ^{1}H and ^{13}C NMR spectra are given for both benzene and chloroform solvents due to the benzene obscuring one of the carbon signals for **2** at 128 ppm. This is a revision of the original ^{1}H and ^{13}C assignments made for this molecule.[29] ^{1}H NMR (C_6D_6): δ 8.05 (br, *o*-Ph, 2H), 7.09 (m, *m*,*p*-Ph, 3H), 5.91 (s, =C*H*, 2H), 1.15 (s, CH_3, 18H); ($CDCl_3$) δ 7.97 (d, $^3J_{H-H}$ = 4 Hz, *o*-Ph, 2H) 7.47 (m, *m*,*p*-Ph, 3H), 6.02 (s, =C*H* 2H), 1.21 (s, CH_3, 18H); ^{13}C NMR (C_6D_6) δ 137.21 (*ipso*-Ph), 135.35 (*o*-Ph), 131.32 (Ph), 128 (Ph), 113.59 (CH=*C*H-N), 52.82 (^{t}Bu*C*-N), 30.53 (*C*H_3); ($CDCl_3$) δ 136.51 (*ipso*-Ph), 135.21 (*o*-Ph), 131.34 (Ph), 127.95 (Ph), 113.37 (*C*H-N), 52.95 (^{t}Bu*C*-N), 30.65 (*C*H_3); MS (EI) *m*/*z* (relative intensity) 400.1 (100), 161.0 (83.4), 273.2 (67.9), 287.9 (45.3), 286.9 (36.4), 344.0 (32.1), 401.1 (28.0), 329.0 (27.1), 217.1 (27.0); HRMS 400.0832 predicted, 400.0831 found.

[$(CH)_2$^{t}Bu$_2$$N_2$]SiI($C_5H_9$) (3). A 50 mL two-neck round-bottom flask was charged with 314 mg (1.54 mmol, 1.2 equiv) of Ph−I and 10 mL of cyclopentane. A solution consisting of 248 mg (1.26 mmol, 1.0 equiv) of **1** in 7.8 mL of cyclopentane was transferred to an airtight syringe. The solution containing **1** was added to the Ph−I solution at a rate of 2.0 mL/h. Upon completion of the addition, the yellow solution was stirred for 1 h and the volatiles were removed. This resulted in 450 mg of a golden oil containing a mixture of **3** (52%) and **2** (48%). Alternate method for synthesis of **3**: A 100 mL round-bottom flask was charged with 834 mg (4.25 mmol, 2.2 equiv) of cyclopentyl iodide and 10.263 g of cyclopentane. A solution containing 387 mg (1.97 mmol, 1 equiv) of **1** dissolved in 2.5 mL of cyclopentane was added dropwise to the cyclopentyliodide solution using a Pasteur pipet. The reaction was stirred for 24 h and all volatiles were removed. The golden oil was distilled *in vacuo* using a 90 °C oil bath, resulting in 370 mg of an analytically pure colorless oil (47.8% yield). ^{1}H NMR (C_6D_6) δ 5.80 (s, =C*H*, 2H), 2.0−1.86 (m, cy, 3H), 1.75−1.62 (m, cy, 2H), 1.62−1.49 (m, cy, 2H), 1.49−1.38 (m, cy, 2H), 1.26 (s, CH_3, 18H); ^{13}C NMR (C_6D_6) δ 114.0 (CH=*C*H-N), 52.4 (^{t}Bu*C*-N), 36.6 (CH_2-*C*H-Si), 30.9 (*C*H_3), 28.8 (*C*H_2), 27.0 (*C*H_2); MS (EI) *m*/*z* (relative intensity) 392.1 (100), 265.2 (48.9), 336.0 (39.6), 280.0 (37.8), 153.1 (31.4), 393.1 (26.4), 210.9 (25.0). Anal. Calcd for $C_{15}H_{29}N_2ISi$: C: 45.91, H: 7.45, N: 7.14. Found: C: 45.86, H: 7.27, N: 6.90.

[$(CH)_2$^{t}Bu$_2$$N_2$]SiI($C_6H_{11}$) (4). A 100 mL two-necked round-bottom flask was charged with 268 mg (1.31 mmol, 1.1 equiv) of Ph−I and 15.020 g of cyclohexane. A solution consisting of 244 mg (1.24 mmol, 1 equiv) of **1** in 10.2 mL of cyclohexane was transferred to an airtight syringe. The solution containing **1** was added to the solution containing Ph−I at a rate of 3.17 mL/h. Upon completion of the addition, the yellow solution was stirred for 1 h and the volatiles were removed. The resulting golden oil contained a 3:1 mixture of **4** and **2**. Alternate method for synthesis of **4**: A 50 mL round-bottom flask was charged with 727 mg (3.46 mmol, 2.2 equiv) of cyclohexyl diodide and 10.35 g of cyclohexane. To this flask was added a solution of 310 mg (1.58 mmol, 1 equiv) of **1** in 1.65 g of cyclohexane. The reaction was allowed to stir overnight before removal of volatiles. The resulting golden oil was distilled onto an isopropyl alcohol/dry ice cooled probe *in vacuo* using a 90 °C oil bath. An analytically pure colorless oil was recovered (477 mg. 74.3% yield). ^{1}H NMR (C_6D_6) δ 5.79 (s, =C*H*, 2H), 2.19 (pseudo-d, $^3J_{H-H}$ = 13.6 Hz, 2H), 1.70 (m, CH_2, 2H), 1.6−1.5 (m, CH_2, 2H), 1.28 (obscured-m, CH_2, 2H), 1.27 (s, CH_3, 18H) 1.15−1.05 (m, C*H* and CH_2, 3H); ^{13}C NMR (C_6D_6) δ 114.0 (CH=*C*H-N), 52.4 (^{t}Bu*C*-N), 37.3 (CH_2-*C*H−Si), 30.9 (*C*H_3), 28.5, 28.4, 27.1 (*C*H_2); MS (EI) *m*/*z* (relative intensity) 406.1 (100), 279.2 (55.5), 350.1 (37.4), 294.0 (33.3), 167.1 (29.8), 407.1 (28.0), 210.9

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(26.3). Anal. Calcd for $C_{16}H_{31}N_2ISi$: C: 47.28, H: 7.69, N: 6.89. Found: C: 47.45, H: 7.66, N: 6.85.

[(CH)$_2$(^{t}Bu$_2$N$_2$]SiI(CH(CH$_3$)OCH$_2$CH$_3$) (5). A 100 mL round-bottom flask was charged with 121 mg (0.593 mmol, 1.1 equiv) of Ph−I and 25 mL of Et_2O. A solution consisting of 103 mg (0.525 mmol, 1.0 equiv) of **1** dissolved in 10.2 mL of Et_2O was transferred to an airtight syringe. The solution containing **1** was added to the Ph−I solution at a rate of 3.17 mL/h. After addition of **1** was completed, volatiles were removed from the pale yellow solution. The resulting golden oil contained a mixture of **5** (76%) and **2** (15%). Spectroscopic data were obtained on this mixture. ^{1}H NMR (C_6D_6) δ 5.78 (d, =C*H*, $^3J_{H-H}$ = 4.4 Hz, 1H), 5.76 (d, $^3J_{H-H}$ = 4.4 Hz, 1H), 3.52 (q, $^3J_{H-H}$ = 7.3 Hz, C*H*, 1H), 3.45 (m, CH_2, 2H), 1.33 (d, $^3J_{H-H}$ = 7.3 Hz, CHCH_3, 3H), 1.32 (s, C(CH_3)$_3$, 9H), 1.26 (s, C(CH_3)$_3$, 9H), 1.10 (t, $^3J_{H-H}$ = 7.0 Hz, CH$_2$CH_3, 3H); ^{13}C NMR (C_6D_6) δ 113.9 (CH=*C*H-N), 113.6 (CH=*C*H-N), 73.3 (CH$_3$-*C*H(Si)-O) [$^1J_{C-Si}$ = 52 Hz], 67.6 (CH$_3$-*C*H$_2$-O), 52.5 ((CH$_3$)$_3$-*C*-N), 52.3 ((CH$_3$)$_3$-*C*-N), 30.7 (C-(*C*H$_3$)$_3$), 30.3 (C-(*C*H$_3$)$_3$), 16.9 (CH-*C*H$_3$), 15.8 (CH$_2$-*C*H$_3$); HRMS calcd ($C_{14}H_{29}N_2OSiI$) 396.1094, found 396.1089; MS (EI) *m*/*z* (relative intensity) 396.2 (100%), 157.1 (49.5%) 196.2 (35.6%), 211.0 (35.1%), 213.2 (20.4%), 267.1 (21.8%), 267.1 (21.8%), 269.0 (23.4%), 269.3 (27.5%), 283.1 (22.1%), 284.1 (22.0%).

[(CH)$_2$(^{t}Bu$_2$N$_2$]SiI(C$_4$H$_7$O$_2$) (6). A 100 mL round-bottom flask was charged with 120 mg (0.588 mmol, 1.1 equiv) of Ph−I and 25 mL of 1,4-dioxane. A solution consisting of 103 mg (0.525 mmol, 1.0 equiv) of **1** dissolved in 10.0 mL of 1,4-dioxane was transferred to an airtight syringe. The solution containing **1** was added to the Ph−I solution at a rate of 3.17 mL/h. After addition of **1** was completed, the volatiles were removed. The resulting golden oil contained a mixture of **6** (67%) and **2** (17%). Spectroscopic data were obtained on this mixture. ^{1}H NMR (C_6D_6) δ 5.74 (d, $^3J_{H-H}$ = 4.0 Hz, =C*H*, 1H), 5.68 (d, $^3J_{H-H}$ = 4.0 Hz, =C*H*,1H), 3.96 (m, C*H* and CHCH_2, 2H), 3.76 (pseudo t, *J* = 11.2 Hz, CHCH_2, 1H), 3.48−3.38 (m, CH_2CH_2, 4H), 1.33 (s, 9H), 1.20 (s, 9H); ^{13}C NMR (C_6D_6) δ 114.3 (CH=*C*H-N), 113.6 (CH=*C*H-N), 75.7 (O-CH$_2$-*C*H(Si)-O) [$^1J_{C-Si}$ = 50 Hz], 69.5 (O-CH$_2$-*C*H$_2$-O), 67.9 (O-(Si)CH-*C*H$_2$-O), 67.1 (O-*C*H$_2$CH$_2$−O), 52.6 (^{t}Bu*C*-N), 52.5 (^{t}Bu*C*-N), 31.1 (*C*H$_3$), 30.7 (*C*H$_3$); HRMS calcd ($C_{14}H_{27}N_2O_2SiI$) 410.0886, found 410.0883; MS (EI) *m*/*z* (relative intensity) 410.3 (100%), 105.1 (24.0%) 127.1 (26.9%), 143.1 (21.8%), 144.1 (55.9%), 161.1 (77.1%), 171.1 (56.4%), 211.0 (34.0%), 217.2 (21.2%), 273.1 (44.4%), 287.1 (22.0%), 288.1 (29.0%), 298.1 (32.8%), 354.2 (52.4%).

[(CH)$_2$(^{t}Bu$_2$N$_2$]SiI[CH(CH$_3$)N(CH$_2$CH$_3$)$_2$] (7). A 100 mL round-bottom flask was charged with 119 mg (0.583 mmol, 1.1 equiv) of Ph−I and 25 mL of Et_3N. A solution consisting of 102 mg (0.519 mmol, 1.0 equiv) of **1** dissolved in 9.6 mL of Et_3N was transferred to an airtight syringe. The solution containing **1** was added to the Ph−I solution at a rate of 3.17 mL/h. After addition of **1** was completed, volatiles were removed. The resulting golden semisolid contained a mixture of **7** (80%), **2** (10%), and **8** (10%). Spectroscopic data were obtained on this mixture. ^{1}H NMR (C_6D_6) δ 5.88 (d, $^3J_{H-H}$ = 4.4 Hz, =CH, 1H), 5.77 (d, $^3J_{H-H}$ = 4.4 Hz, =CH, 1H), 3.14 (q, $^3J_{H-H}$ = 7.3 Hz, C*H*, 1H), 2.63 (qd, $^2J_{HH}$= 13.0 Hz, $^3J_{H-H}$ = 7.2 Hz, CH_2, 2H), 2.26 (qd, $^2J_{H-H}$ = 13.0 Hz, $^3J_{H-H}$ = 7.2 Hz, CH_2, 2H), 1.38 (s, CH_3, 9H), 1.29 (d, $^3J_{H-H}$ = 7.3 Hz, CHCH_3, 3H) 1.28 (s, CH_3, 9H), 0.90 (br t, $^3J_{H-H}$ = 7.2 Hz, CH$_2$CH_3, 6H); ^{13}C NMR (C_6D_6) δ 114.5 (CH=*C*H-N), 113.0 (CH=*C*H-N), 58.2 (*C*H, $^1J_{C-Si}$ = 48 Hz), 52.9 (^{t}Bu*C*-N), 52.3 (^{t}Bu*C*-N), 47.0 (CH$_3$CH$_2$N), 30.9 (C-(*C*H$_3$)$_3$), 30.2 (C-(*C*H$_3$)$_3$), 14.8 (CH$_2$CH$_3$), 8.0 (CH*C*H$_3$); HRMS calcd ($C_{16}H_{34}N_3SiI$) 423.1567, found 423.1578; MS (EI) *m*/*z* (relative intensity) 100.1 (100%), 125.0 (6.5%) 127.9 (6.7%), 196.1 (7.3%), 210.9 (7.1%), 423.1 (5.1%).

[(CH)$_2$(^{t}Bu$_2$N$_2$]SiH[N(CH$_2$CH$_3$)$_2$] (8). This product is present in ∼10% yield as indicated by ^{1}H NMR spectroscopy using the reaction conditions given for compound **7**. Synthesis of **8** was independently carried out by reaction of **1** with [HNEt$_3$]I. A 100 mL round-bottom flask was charged with [HNEt$_3$]I (148 mg, 0.646 mmol, 1.0 equiv), **1** (121 mg, 0.616 mmol, 1.0 equiv), and 15.94 g of Et_3N. The flask was capped and allowed to stir overnight. Removal of volatiles produced 239 mg of a white solid and an amber oil (154 mg). Filtration with pentane separated the white solid and amber oil. The white solid recovered was [HNEt$_3$]I. ^{1}H NMR spectroscopy indicated that ∼30% of the amber oil was **8**. ^{1}H NMR (C_6D_6) δ 5.82 (s, *H*-C=C, 2H), 5.70 (br s, Si-*H*, 1H), 2.84 (q, $^3J_{H-H}$ = 7.1 Hz, CH_2, 4H), 1.25 (s, C(CH_3)$_3$, 18H), 0.99 (t, $^3J_{H-H}$ = 7.1 Hz, CH$_2$CH_3, 6H); ^{13}C NMR (C_6D_6) δ 111.8 (CH=*C*H-N), 51.0 (^{t}Bu*C*-N), 38.3 (N*C*H$_2$), 30.9 (C(*C*H$_3$)$_3$), 14.8 (CH$_2$*C*H$_3$); GC-MS *m*/*z* (relative intensity) 269.30 (53.02%), 270.30 (11.27%) 72.10 (100.00%), 84.05 (24.95%), 85.05 (72.22%), 156.05 (23.21%), 183.20 (14.81%), 198.25 (24.20%), 212.25 (24.15%), 254.25 (26.04%); IR (neat on NaCl plate) 2132 cm^{-1} (ν Si−H).

[(CH)$_2$(^{t}Bu$_2$N$_2$]SiI[CH(CH$_2$CH$_3$)N(CH$_2$CH$_2$CH$_3$)$_2$] (9). A 100 mL round-bottom flask was charged with 122 mg (0.598 mmol, 1.2 equiv) of Ph−I and 25 mL of Pr_3N. A solution containing 102 mg (0.519 mmol, 1.9 equiv) of **1** dissolved in 10.4 mL of Pr_3N was transferred to an airtight syringe. The solution containing **1** was added at a rate of 3.17 mL/h to the Ph−I solution. After addition of **1** was completed, volatiles were removed from the pale yellow solution. The resulting golden oil was a mixture of **9** (77%), **2** (2%), and **10** (3%). Spectroscopic data were obtained on this mixture. ^{1}H NMR (C_6D_6) δ 5.83 (d,$^3J_{H-H}$ = 4.0 Hz, =C*H*, 1H), 5.76 (d, $^3J_{H-H}$ = 4.0 Hz, =C*H*, 1H), 2.76−2.68 (m, NCH_2 and NC*H*CH$_2$, 3H), 2.48 (m, NCH_2, 2H), 2.35 (dqd, NCHCH_2, $^2J_{H-H}$ = 14.2 Hz, $^3J_{H-H}$ = 7.2, 2.5 Hz, 1H), 1.60 (ddq, NCHCH_2, $^2J_{H-H}$ = 14.2 Hz, $^3J_{H-H}$ = 9.8, 7.2 Hz, 1H), 1.50−1.33 (m, NCH$_2$CH_2CH$_3$, 4H), 1.37 (s, C(CH_3)$_3$, 9H), 1.29 (s, C(CH_3)$_3$ 9H), 1.10 (t, $^3J_{H-H}$ = 7.2 Hz, CHCH$_2$CH_3, 3H), 0.81 (br t, $^3J_{H-H}$ = 7.4 Hz, NCH$_2$CH$_2$CH_3, 6H); ^{13}C NMR (C_6D_6) δ 114.3 (CH=*C*H-N), 113.5 (CH=*C*H-N), 64.1 (Si*C*H, $^1J_{C-Si}$ = 45 Hz), 56.2 (N*C*H$_2$), 53.3 (^{t}Bu*C*-N), 52.6 (^{t}Bu*C*-N), 30.8 (C(*C*H$_3$)$_3$), 30.3 (C(*C*H$_3$)$_3$), 23.2 (CH$_2$*C*H$_2$CH$_3$), 21.1 (CH*C*H$_2$CH$_3$), 16.0 (CHCH$_2$*C*H$_3$), 11.9 (CH$_2$CH$_2$*C*H$_3$); HRMS calcd ($C_{19}H_{40}N_3SiI$) 465.2036, found 465.2046; MS (EI) *m*/*z* (relative intensity) 196.2 (100%), 84.0 (58.1%) 84.1 (75.4%), 112.1 (48.3%), 125.1 (41.8%), 141.2 (26.2%) 142.2 (93.9%), 161.1 (%), 181.1 (33.7%), 335.3 (38.0%), 450.0 (2.2%), 465.3 (1.7%).

[(CH)$_2$(^{t}Bu$_2$N$_2$]SiH[N(CH$_2$CH$_2$CH$_3$)$_2$] (10). This product is present in ∼3% yield as indicated by ^{1}H NMR spectroscopy using the reaction conditions given for compound **9**. Synthesis of **10** was independently carried out by reaction of **1** with [HNPr$_3$]I. A 100 mL round-bottom flask was charged with 140 mg (0.516 mmol, 1.0 equiv) of [HNPr$_3$]I, 98 mg (0.499 mmol, 1 equiv) of **1**, and 15 mL of Pr_3N. The solution was allowed to stir for 24 h. Removal of volatiles afforded a white solid with a goldish-colored oil. The white solid was removed via filtration with pentane. Then 148 mg of a goldish-colored oil was recovered, by ^{1}H NMR; 23% of the oil was **10**. The white solid remaining after filtration was 114 mg of [HNPr$_3$]I (81% recovery). ^{1}H NMR (C_6D_6) δ 5.83 (s, *H*-C=C, 2H), 5.73 (br s, Si-*H*, 1H), 2.77 (m, N-CH_2, 4H), 1.49 (m, CH_2-CH$_3$, 4H), 1.27 (s, C(CH_3)$_3$, 18H), 0.79 (t, ^3J = 7.2 Hz CH$_2$-CH_3), 6H); ^{13}C NMR (C_6D_6) δ 111.9 (CH=*C*H-N), 51.0 (^{t}Bu*C*-N), 47.9 (N*C*H$_2$), 30.9 (C(*C*H$_3$)$_3$), 23.2 (CH$_2$*C*H$_2$CH$_3$), 12.1 (CH$_2$*C*H$_3$); GC-MS *m*/*z* (relative intensity) 297.35 (49.34%), 298.35 (11.70%), 84.00 (36.55%), 85.00 (100.00%), 86.00 (17.03%), 100.10 (91.56%), 184.20 (25.25%), 240.25 (20.03%), 282.30 (18.75%); IR (neat on NaCl plate) 2199 cm^{-1} (ν Si−H).

[(CH)$_2$(^{t}Bu$_2$N$_2$]SiI[CH$_2$N(CH$_3$)^{t}Bu] (11). A two-neck 100 mL round-bottom flask was charged with 254 mg (1.24 mmol, 1.2 equiv) of Ph−I and 7.750 g of Me$_2$N^{t}Bu. A solution containing 200 mg (1.02 mmol, 1 equiv) of **1** in 4 mL of Me$_2$N^{t}Bu was transferred to an airtight syringe. The solution containing **1** was added to the Ph−I solution at a rate of 1.19 mL/h. After addition of **1** was completed, the solution was stirred for 16 h, after which

Table 1. Summary of Crystallographic data

	13	**16**	**20**
empirical formula	$C_{16}H_{32}IN_3Si$	$C_{22}H_{48}GeINSi_4$	$C_{14}H_{39}GeISi_4$
fw	421.44	638.46	519.30
temperature	85(2) K	118(2) K	150(2) K
cryst syst, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	monoclinic, *Cc*
unit cell dimens	a = 9.4165 (4) Å	a = 9.5644 (18) Å	a = 9.2067(10) Å
	b = 9.5587 (4) Å	b = 10.362 (2) Å	b = 21.527(2) Å
	c = 12.2601 (5) Å	c = 16.856 (3) Å	c = 13.1974(14) Å
	α = 96.403(1)°	α = 102.125(4)°	α = 90°
	β = 95.239(1)°	β = 93.528(4)°	β = 110.055(2)°
	γ = 118.010(1)°	γ = 109.538(3)°	γ = 90°
volume	955.11(7) A^3	1523.4(5) A^3	2457.0(4) A^3
Z, calcd density	2, 1.465 mg/m^3	2, 1.392 mg/m^3	4, 1.404 mg/m^3
absorp coeff	1.739 mm^{-1}	2.186 mm^{-1}	2.692 mm^{-1}
Λ	0.71073 Å	0.71073 Å	0.71073 Å
final R indices $[I > 2\sigma(I)]$	R1 = 0.0193	R1 = 0.0311	R1 = 0.0189
	wR2 = 0.0491	wR2 = 0.0808	wR2 = 0.0502
R indices (all data)	R1 = 0.0198	R1 = 0.0400	R1 = 0.0192
	wR2 = 0.0494	wR2 = 0.0850	wR2 = 0.0504

time all volatiles were removed. The crude material was composed of 6% **2**, 67% **11**, and 4% **12**. Crude material containing **11**, **2**, and **12** was dissolved in 5 mL of pentane and filtered, yielding 17 mg of **12** (6% yield based upon Ph−I) as a white solid. Analytically pure **11** was obtained as a white solid after three recrystallizations from pentane at −78 °C (45 mg, 10% yield based upon **1**). ^{1}H NMR (C_6D_6) δ 5.82 (s, =C*H*, 2H), 2.92 (s, CH_2, 2H), 2.20 (s, NCH_3, 3H) 1.38 (s, C(CH_3)$_3$, 18H), 0.89 (s, NCH$_2$C(CH_3)$_3$, 9H); ^{13}C NMR (C_6D_6) δ 113.4 (=*C*H), 54.8 (^{t}Bu*C*NCH$_3$), 52.7 (^{t}Bu*C*N-Si), 52.5 (*C*H$_2$), 37.5 (*C*H$_3$N), 30.3 (SiNC(*C*H$_3$)$_3$), 25.4 (CH$_2$NC(*C*H$_3$)$_3$); MS (EI) *m*/*z* (relative intensity) 100.1 (100), 44.0 (45.1), 57.1 (17.2), 423.2 (14.3); HRMS 423.1567 calcd, 423.1561 found. Anal. Calcd for $C_{16}H_{34}IN_3Si$: C: 45.38, H: 8.09, N: 9.92. Found: C: 45.67, H: 8.25, N: 9.68.

[(CH)$_2$(^{t}Bu$_2$N$_2$]SiI[(CH(CH$_2$)$_4$)NCH$_3$] (13). A 100 mL round-bottom flask was charged with 231 mg (1.13 mmol, 1.1 equiv) of Ph−I and 20 mL of *N*-methylpiperidine. A solution containing 211 mg (1.07 mmol, 1 equiv) of **1** in 26 mL of *N*-methylpiperidine was transferred to an airtight syringe. The solution containing **1** was added to the solution containing Ph−I at a rate of 2.85 mL/h. After addition of **1** the solution was colorless and appeared to contain a colloid. Upon removal of volatiles, a pink-colored solid remained. ^{1}H NMR spectroscopy revealed that the crude reaction mixture contained less than 0.5% of **2** and 85% of the desired C−H activation product. Twenty milliliters of Et$_2$O was used for filtering the solution, and all volatiles were subsequently removed, yielding a pink solid. The solid was dissolved and filtered using 10 mL of hexanes, and volatiles were subsequently removed, yielding a slightly tan solid. Recrystallization from hexanes provided 265 mg (56.5%) of an off-white solid. Material suitable for X-ray analysis was grown via slow evaporation of hexanes. ^{1}H NMR (C_6D_6) δ 5.82 (d, $^3J_{H-H}$ = 4.2 Hz, 1H, C*H*=CH), 5.78 (d, $^3J_{H-H}$ = 4.2 Hz, 1H, C*H*=CH), 2.67 (br d, $^3J_{H-H}$ = 11.2 Hz, 1H, CH_2), 2.41 (br d, $^3J_{H-H}$ = 13.2 Hz, 1H, CH_2), 2.26 (dd, $^3J_{H-H}$ = 12.8, 2.8 Hz, 1H, C*H*), 2.14 (s, 3H, CH_3), 1.79−1.64 (m, 3H), 1.58−1.25 (m, 2H), 1.38 (s, 9H, C(CH_3)$_3$), 1.08 (s, 9H, C(CH_3)$_3$)), 0.98 (m, 1H, CH_2); ^{13}C NMR (C_6D_6) δ 113.5 (=*C*H), 113.3 (=*C*H), 60.9 (N-*C*H$_2$), 60.9 (N-*C*H), 52.8 (^{t}Bu*C*-N), 52.1 (^{t}Bu*C*-N), 47.3 (N-*C*H$_3$), 31.0 (C-(*C*H$_3$)$_3$), 30.6 (*C*H$_2$), 30.4 (C-(*C*H$_3$)$_3$), 26,0 (*C*H$_2$), 25.8 (*C*H$_2$); HRMS (ESI with Na^+) calcd ($C_{16}H_{33}IN_3Si^+$) 422.1489, found 422.1471; MS (ESI) *m*/*z* (relative intensity) 326.2 (100%), 191.1 (19.6%) 327.2 (24.8%), 409.3 (11.3%), 422.1 (10.21%). Anal. Calcd for $C_{16}H_{32}N_3ISi$: C: 45.60, H: 7.65, N: 9.97. Found: C: 45.88, H: 7.68, N: 9.88.

Structural Determination of [(CH)$_2$(^{t}Bu$_2$N$_2$]SiI[(CH(CH$_2$)$_4$)-NCH$_3$] (13). Colorless blocks of **13** were grown from hexanes at 20 °C. A crystal of dimensions 0.33 × 0.32 × 0.22 mm was cut from a larger mass and mounted on a Bruker SMART APEX CCD-based X-ray diffractometer equipped with a low-temperature device and fine-focus Mo-target X-ray tube (λ = 0.71073 A) operated at 1500 W power (50 kV, 30 mA). The X-ray intensities were measured at 85(1) K; the detector was placed at a distance of 5.055 cm from the crystal. A total of 4095 frames were collected with a scan width of 0.5° in ω and 0.45° in ϕ with an exposure time of 5 s/frame. The integration of the data yielded a total of 42 226 reflections to a maximum 2θ value of 66.44°, of which 7220 were independent and 7053 were greater than 2σ(*I*). The final cell constants (Table 1) were based on the *xyz* centroids of 9947 reflections above 10σ(*I*). Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 6.12) software package, using the space group $P\bar{1}$ with Z = 2 for the formula $C_{16}H_{32}N_3SiI$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file.

[(Me$_3$Si)$_2$CH]$_2$GeI[(CH$_2$)N(CH$_3$)(Ph)] (16). A 100 mL flask was charged with 301 mg (0.796 mmol, 1.0 equiv) of **15**, 163 mg (0.799 mmol, 1.0 equiv) of Ph−I, and 70.5 mL of *N*,*N*-dimethylaniline (Me$_2$NPh). The contents were stirred for 72 h, over which time the solution changed from orange-yellow to very pale yellow. The volatiles were removed to give a yellow solid containing only **16** as indicated by ^{1}H NMR. ^{1}H NMR (C_6D_6) δ 7.20 (pseudo t, $^3J_{H-H}$ = 7.7 Hz, *m*-Ph, 2H), 6.87 (d, $^3J_{H-H}$ = 8.0 Hz, *o*-Ph, 2H), 6.78 (t, *p*-Ph, $^3J_{H-H}$ = 7.3 Hz 1H), 3.81 (s, CH_2, 2H), 3.00 (s, NCH_3, 3H), 0.64 (s, C*H*, 2H), 0.36 (s, Si(CH_3)$_3$, 18H), 0.23 (Si(CH_3)$_3$, 18H); ^{13}C NMR (C_6D_6) δ 152.7 (*ipso*-Ph), 129.4 (*m*-Ph), 119.0 (*p*-Ph), 115.9 (*o*-Ph), 53.1 (*C*H$_2$), 43.9 (N*C*H$_3$), 12.6 (*C*H), 4.2 (*C*H$_3$Si), 4.1 (*C*H$_3$Si); EI/MS [M − CH$_3$]$^+$ = 623.8 amu. Anal. Calcd for $C_{22}H_{48}GeINSi_4$: C: 41.39, H: 7.58 N: 2.19. Found: C: 41.49, H: 7.70, N: 1.81.

Structural Determination of [(Me$_3$Si)$_2$CH]$_2$Ge[I][(CH$_2$)N-(CH$_3$)(Ph)] (16). Colorless plates were grown from a pentane solution at 22 °C. A crystal of dimensions 0.60 × 0.22 × 0.08 mm was mounted on a standard Bruker SMART CCD-based X-ray diffractometer equipped with a LT-2 low-temperature device and normal-focus Mo-target X-ray tube (λ = 0.71073 A) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 118(2) K; the detector was placed at a distance 4.950 cm from the crystal. A total of 2837 frames were collected with a scan width of 0.2° in ω and phi with an exposure time of 20 s/frame. The integration of the data yielded a total of 14 401 reflections to a maximum 2θ value of 56.79°, of which 7426 were independent and 6274 were greater than 2σ(*I*). The final cell constants (Table 1) were based on the *xyz* centroids of 4518 reflections above 10σ(*I*). Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 5.10) software package, using the space group $P\bar{1}$ with Z = 2 for the formula $C_{22}H_{48}Si_4NGeI$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0311 and wR2 = 0.0808 [based on $I > 2\sigma(I)$], R1 = 0.0400 and wR2 = 0.0850 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file.

[(Me$_3$Si)$_2$CH]$_2$GeI[CH$_2$N(CH$_3$)(C(CH$_3$)$_3$)] (17). A 100 mL flask was charged with **15** (351 mg, 0.897 mmol, 1 equiv), Ph−I (210 mg, 1.03 mmol, 1.1 equiv), and 12.5 mL of Me$_2$N^{t}Bu. The contents were stirred for 37 h, over which time the solution changed from orange-yellow to very pale yellow. The volatiles were removed

and the solid was recrystallized from Et_2O/acetonitrile (CH_3CN) to yield a fine, white powder (257 mg, 46% yield). ^1H NMR (C_6D_6) δ 3.11 (s, CH_2N, 2H), 2.36 (s, $CH_2N(CH_3)(C(CH_3)_3)$, 3H), 0.98 (s, $N(CH_3)(C(CH_3)_3)$, 9H), 0.66 (s, 2H, C*H*Si, 2H), 0.40 (s, $Si(CH_3)_3$, 18H), 0.32 (s, $Si(CH_3)_3$, 18H); ^{13}C NMR (C_6D_6) δ 4.34 (Si*C*H_3), 4.51 (Si*C*H_3), 12.19 (*C*H(TMS)$_3$), 25.84 ((*C*H_3)$_3$), 39.67 (N*C*H_3), 53.63 (*C*$(CH_3)_3$), 55.59 (CH_2); EI/MS $[M - CH_3]^+ = 603.9$ amu.

$[(Me_3Si)_2CH]_2GeI[CH_2N(CH_3)(C(CH_3)_3)]$ (**17**) was synthesized using high-dilution conditions. A 100 mL flask was charged with 88 mg (0.431 mmol, 1.1 equiv) of Ph−I and 20 mL of Me_2N^tBu. A 25 mL airtight syringe filled with 20 mL of a Me_2N^tBu solution containing 154 mg (0.393 mmol, 1.0 equiv) of **15** was added to the Ph−I solution at an rate of 3.02 mL/h. After the addition was completed, the solution was stirred for 12 h, resulting in a colorless solution containing a white precipitate. Removal of volatiles resulted in formation of a white solid, containing a 1:10 ratio of **12**:**17** (ratio determined by ^1H NMR with $CDCl_3$ as the solvent). The $[HNMe_2{}^tBu]I$ salt (**12**) was isolated (9 mg, 10% yield based on **15**) by filtration from pentane; 193 mg (79% yield based on **15**) of **17** was isolated as a white solid from the filtrate by removal of volatiles.

$[(Me_3Si)_2CH]_2GeI[(PhCH)N(CH_3)_2]$ (18a) and $[(Me_3Si)_2CH]_2GeI[(PhCH_2)N(CH_2)(CH_3)]$ (18b). A 100 mL flask was charged with 124 mg (0.317 mmol, 1 equiv) of **15**, 25 mL of *N*,*N*-dimethylbenzylamine (Me_2NCH_2Ph), and 105 mg of Ph−I (0.515 mmol, 1.6 equiv). The solution was left to stir until colorless. Volatiles were removed under dynamic vacuum. ^1H NMR of the crude reaction mixture showed three products present in a 2:2:1 ratio: 40% **18a**, 40% **18b**, and 20% $[(Me_3Si)_2CH]_2GeI(Ph)$. We were unable to separate **18a** from **18b**, and we were unable to obtain a ratio of **18a**:**18b** that was not 1:1. ^1H NMR (C_6D_6) δ 7.53 (d, $^3J_{H-H}$ = 7.0 Hz, 2H, *o*-Ph), 7.41 (d, $^3J_{H-H}$ = 7.1 Hz, 2H, *o*-Ph), 7.20 (t, $^3J_{H-H}$ = 7.7 Hz, 2H, *m*-Ph), 7.18−7.14 (m, 2H, *p*-Ph), 7.10 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, *m*-Ph), 4.04 (s, 1H, NC*H*, **18a**), 3.60 (s, 2H, CH_2, **18b**), 2.92 (s, 2H, CH_2, **18b**), 2.27 (s, 3H, CH_3, **18b**), 2.17 (s, 6H, CH_3, **18a**), 0.98 (s, 1H, C*H*(TMS)$_3$, **18a**), 0.59 (s, 2H, C*H*(TMS)$_3$, **18b**), 0.58 (s, 1H, C*H*(TMS)$_3$, **18a**), 0.46 (s, 9H, Si(CH_3)$_3$, **18a**), 0.40 (s, 9H, Si(CH_3)$_3$, **18a**), 0.39 (s, 18H, Si(CH_3)$_3$, **18b**), 0.29 (s, 18H, Si(CH_3)$_3$, **18b**), 0.25 (s, 9H, Si(CH_3)$_3$, **18a**), 0.10 (s, 9H, Si(CH_3)$_3$. **18a**); ^{13}C NMR (C_6D_6) δ 138.7 (*ipso*-Ph), 133.5 (*ipso*-Ph), 132.5 (*o*-Ph, ^1H 7.53 ppm), 129.6 (*o*-Ph, ^1H 7.41 ppm), 128.5 (*m*-Ph, ^1H 7.20 ppm), 128.3 (*p*-Ph, ^1H 7.18−7.14 ppm), 127.8 (*p*-Ph, ^1H 7.18−7.14 ppm), 127.4 (*m*-Ph, ^1H 7.10 ppm), 69.0 (N*C*H, **18a**), 66.8 (*C*H_2, **18b**), 57.3 (CH_2, **18b**), 45.5 (CH_3, **18b**), 44.8 (CH_3, **18a**), 13.7 (*C*H(TMS)$_3$, **18a**), 13.4 (*C*H(TMS)$_3$, **18a**), 12.7 (*C*H-(TMS)$_3$, **18b**), 4.9 (Si*C*H_3, **18a**), 4.8 (Si*C*H_3, **18a**), 4.6 (Si*C*H_3, **18a**), 4.4 (Si*C*H_3, **18a**), 4.2 (Si*C*H_3, **18b**), 4.1 (Si*C*H_3, **18b**); EI/MS $[M - CH_3]^+ = 638.0$ amu. Anal. Calcd for $C_{23}H_{50}GeINSi_4$: C: 42.34, H: 7.72 N: 2.15. Found: C: 42.45, H: 7.85, N: 1.84.

$[(Me_3Si)_2CH]_2GeI[CH_2N(CH_3)(CH_2N(CH_3)_2)]$ (19). A 100 mL flask was charged with 248 mg (0.634 mmol, 1 equiv) of **15**, 20 mL of *N*,*N*,*N*′,*N*′-tetramethylmethanediamine, and 171 mg (0.838 mmol, 1.3 equiv) of Ph−I. The amber-colored solution was allowed to stir for 12 h, at which time the reaction was colorless and contained a white precipitate. Removal of volatiles afforded a white oily solid. The white solid was removed via filtration with pentane solvent. Then 374 mg (0.604 mmol, 95% yield based on **15**) of a clear oil was recovered, corresponding to **19**. The white solid remaining after filtration was 39 mg of $[Me_2N{=}CH\text{-}NMe_2]I$ (0.171 mmol, 26% yield based on **13**). ^1H NMR (C_6D_6) δ 2.90 (s, N-CH_2-N, 2H), 2.77 (s, Ge-CH_2-N, 2H), 2.56 (s, N-CH_3, 3H), 2.19 (s, N-$(CH_3)_2$, 6H), 0.63 (s, 2H, C*H*(TMS)$_2$), 0.40 (s, 18H, Si(CH_3)$_3$), 0.30 (s, 18H, Si(CH_3)$_3$); ^{13}C NMR (C_6D_6) δ 85.6 (N-*C*H_2-N), 55.3 (N-CH_2-Ge), 44.0 (N*C*H_3), 43.8 (N*C*H_3), 12.5 (*C*H(TMS)$_3$), 4.2 (Si*C*H_3), 4.1 (Si*C*H_3).

$[(Me_3Si)_2CH]_2Ge[H][I]$ (20). A 100 mL flask was charged with 350 mg (0.894 mmol, 1 equiv) of **15**, 200 mg of Ph−I (0.983 mmol, 1.1 equiv), and 18.5 mL of Et_3N. The contents were allowed to stir for 13 h, over which time the solution changed from orange-yellow to almost colorless, faint yellow to eventually a darker brownish-yellow. Then the volatiles were pumped off under dynamic vacuum for 2 h. Approximately an hour later the oil began to crystallize. Three successive recrystallizations out of THF/CH_3CN gave 0.065 g of white solid. ^1H NMR (C_6D_6) δ 0.17 (s, 18H, Si*Me*$_3$), 0.31 (s, 18H, Si*Me*$_3$), 0.38 (d, $^3J_{HH}$ = 2.8 Hz, 2H, GeC*H*Si), 5.17 (t, $^3J_{HH}$ = 2.8, 1H, Ge*H*); ^{13}C NMR (C_6D_6) δ 9.14 (GeCHSi), 3.27 and 2.4 (Si(*C*H_3)$_3$); IR (cm^{-1}) 2031 ν(Ge−H); EI/MS $[M - CH_3]^+$ = 505.0 amu. Anal. Calcd for $C_{14}H_{39}GeISi_4$: C 32.38, H 7.57. Found: C 32.59, H 7.70.

Structural Determination of 20. Colorless blocks were grown from a Et_3N solution at 22 °C. A crystal of dimensions 0.38 × 0.32 × 0.20 mm was mounted the same as crystal **3**. The X-ray intensities were measured at 150(2) K; the detector was placed at a distance of 4.950 cm from the crystal. A total of 3267 frames were collected with a scan width of 0.2° in ω and phi with an exposure time of 20 s/frame. The integration of the data yielded a total of 12 948 reflections to a maximum 2θ value of 56.58°, of which 5928 were independent and 5726 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the *xyz* centroids of 5555 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 5.10) software package, using the space group *Cc* with $Z = 4$ for the formula $C_{14}H_{39}Si_4GeI$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0189 and wR2 = 0.0502 [based on $I > 2\sigma(I)$], R1 = 0.0192 and wR2 = 0.0504 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file.

General Procedure for Independent Preparation of $[HNR_3]I$ Salts. A 4 mL amount of HI(aq) acid was added to a 20 mL scintillation vial, followed by 8 mL of R_3N. The solution was stirred for 30 min in a water bath. If a biphasic solution was not present after 30 min, an additional 2 mL of R_3N was added and solution allowed to stir an additional 30 min. Volatiles were removed and the resulting solution was placed under vacuum to remove residual water and R_3N. A white solid soluble in $CDCl_3$ was obtained in all cases.

$[HNEt_3]I$: ^1H NMR ($CDCl_3$) δ 10.06 (br, 1 H, *H*N), 3.19 (qd, $^3J_{H-H}$ = 7.4, 5.1 Hz, 6H, CH_2), 1.43 (br t, $^3J_{H-H}$ = 7.4 Hz, 9H, CH_3); ^{13}C NMR ($CDCl_3$) δ 46.3 (*C*H_2), 8.6 (*C*H_3); MS (ESI) positive ion 331.2; negative ion 126.9.

$[HN^iPr_3]I$: ^1H NMR ($CDCl_3$) δ 10.14 (br, 1 H, *H*N), 3.01 (dt, $^3J_{H-H}$ = 12.3, 4.6 Hz, 6H, N-CH_2), 1.89 (m, 6H, CH_2-CH_3), 1.01 (t, $^3J_{H-H}$ = 7.4 Hz, 9H, CH_3); ^{13}C NMR ($CDCl_3$) δ 54.2 (N-*C*H_2), 16.8 (*C*H_2-CH_3), 11.2 (*C*H_3); MS (ESI) positive ion 144.2; negative ion 126.9.

$[HN(CH_3)_2{}^tBu]I$ (12): ^1H NMR ($CDCl_3$) δ 10.25 (br, N-*H*, 1H), 2.72 (s, N-CH_3, 6H), 1.51 (s, (C(CH_3)$_3$), 9H); ^{13}C NMR ($CDCl_3$) δ 63.1 (*C*-$(CH_3)_3$), 38.2 (N-*C*H_3), 25.1 (C-(*C*H_3)$_3$); MS (ESI) positive ion 331.1; negative ion 126.9.

$[HNMe(C_5H_{10})]I$ (14): ^1H NMR δ ($CDCl_3$) 9.6 (br, N-H, 1H), 3.42 (d, $^3J_{H-H}$ = 10.8 Hz, N-CH_2, 2H), 3.00 (t, $^3J_{H-H}$ = 11.8 Hz, N-CH_2, 2H), 2.76 (s, N-CH_3, 3H), 2.14 (br d, $^3J_{H-H}$ = 12.8 Hz, NCH_2-CH_2-CH_2, 2H), 1.87 (br d, $^3J_{H-H}$ = 14.0 Hz, NCH_2-CH_2-CH_2, 3H), 1.52 (br d, $^3J_{H-H}$ = 12.4 Hz, NCH_2CH_2-CH_2, 1H); ^{13}C NMR ($CDCl_3$) δ 54.96 (N-*C*H_2), 44.08 (N-*C*H_3), 22.73 (NCH_2-*C*H_2), 20.99 (NCH_2CH_2-*C*H_2); MS (ESI) positive ion 327.1 (100%), 100.1 (34.5%), 328.2 (13.4%); negative ion 126.9 (100%).

Measurement of Primary Kinetic Isotope Effects. Primary isotope effect for reaction of **15** or $Ge[N(SiMe_3)_3]_2$ (**21**) with Ph−I/THF: A vial was charged with THF (0.50 mL, 6.17 mmol), THF-d_8 (0.50 mL, 6.61 mmol), and **15** (22 mg, 0.056 mmol). Ph−I (9.0

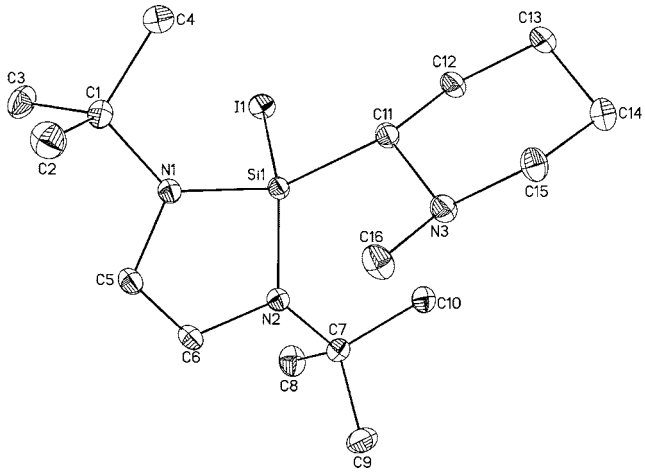


Figure 1. ORTEP representation of $[(CH)_2{}^tBu_2N_2]SiI[(CH(CH_2)_4)NCH_3]$ (**13**) (50% probability). Selected bond distances (Å) and angles (deg): Si−C11, 1.9130(11); Si−N1, 1.7266(10); Si−N2, 1.7205(10); Si−I, 2.5521(3); C11−C12, 1.5330(15); C11−N3, 1.4781 (14); N1−Si−N2, 94.14(4); I−Si−N1, 111.01(3); I−Si−N2, 109.58(3); I−Si−C11, 107.33(3); C11−Si−N1, 115.15(5); C11−Si−N2, 119.13(5); Si−C11−C12, 114.64(7); Si−C11−N3, 110.94(7); C12−C11−N3, 111.34(9).

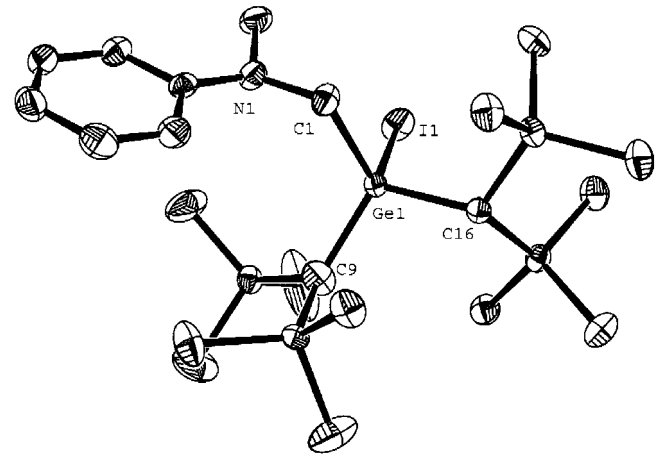


Figure 2. ORTEP representation of $[(Me_3Si)_2CH]_2Ge[I][(CH_2)N(CH_3)(Ph)]$ (**16**) (50% probability). Selected bond distances (Å) and angles (deg): N1−C1, 1.1.449(4); N1−C2, 1.452(4), N1−C3, 1.385(4); C1−Ge, 1.999(3); Ge−I, 2.5839(5); Ge−C9, 1.984(4); Ge−C16(1.973(3); C9−Ge−C16, 108.55(14); C16−Ge−I, 103.93(7); C16−Ge−C1, 113.38(11); C9−Ge−C1, 117.63(15); C1−Ge−I, 101.69(10); C1−N−C2, 116.8(3); C1−N−C3, 121.5(2); C2−N−C3, 118.4(2); Ge−C1−N, 116.67(19).

μL, 0.064 mmol) was added, and the contents were mixed. After completion of the reaction at 20 °C, as monitored by color and ^{1}H NMR spectroscopy, all volatiles were transferred. GC-MS was used for separating the volatiles into a THF fraction and a benzene fraction, and the ratio of C_6H_6/C_6H_5D was determined using MS data. An analogous procedure was used for **21**. The k_H/k_D ratio was determined to be 6.5 ± 0.2 for **15** and 5.6 ± 0.2 for **21**. The primary isotope effect for **15**/PhCl/THF was measured in a similar fashion with the exception that the sealed vial containing the mixture was heated for 1 week at 70 °C. Over this time period the reaction color varied from orange to brown to green to colorless. The k_H/k_D ratio was determined to be 5.2 ± 0.2.

Primary Isotope Effect for Reaction of 1/Ph−I/Et_2O/Et_2O-d_{10}. A 1 dram GC-MS vial was charged with **1** (16 mg, 0.081 mmol), Et_2O (0.5 mL, 4.76 mmol), Et_2O-d_{10} (0.5 mL, 4.76 mmol), and Ph−I (20 μL, 0.18 mmol). The solution immediately turned a golden color upon addition of Ph−I. Vials were capped immediately after addition of Ph−I and shaken to ensure complete mixing. GC-MS analysis was used to determine the ratio of C_6H_6/C_6H_5D. The k_H/k_D ratio was measured to be 5.7 ± 0.1.

Measurement of Order in [Ge(CH(SiCH$_3$)$_2$)$_2$] (15) and Kinetic Measurement of $k_{Ph\text{-}Br}/k_{Ph\text{-}Br\text{-}d5}$ Ratio. A 0.025 M stock solution (A) was prepared by dissolving **15** (225 mg, 0.575 mmol) in THF (20.070 g, 22.51 mL). A dilution was made by extracting 0.813 g of stock solution A (9.1 mg **15**, 0.023 mmol) and adding THF to give a total weight of 2.711 g and a final concentration of 0.0076 M for stock solution B. A concentration of **15** in THF suitable for UV−vis spectroscopy was obtained by taking 0.550 g of B (1.88 mg **15**, 0.0048 mmol) and diluting it with THF to give 3.483 g (3.91 mL). The final concentration of **15** in THF is 0.0012 M. The sample was placed in a quartz cuvette capable of being sealed by a Teflon stopcock. The initial spectrum of **15** in THF was obtained. The sample was returned to the drybox, where Ph−Br (10.0 μL, 0.092 mmol, 19.2 equiv) was added. Spectra were acquired for 32 min, until the absorption at 420 nm was barely visible. The reaction mixture was then transferred to a flask, and volatiles were removed. ^{1}H NMR spectroscopy revealed only the formation of C−H activation product. No trace of oxidative addition product was observed. A second-order plot of the data resulted in the best fit (R^2 = 0.992, Figure 4). Zero-order, first-order, and third-order plots gave R^2 values of 0.587, 0.888, and 0.975, respectively.

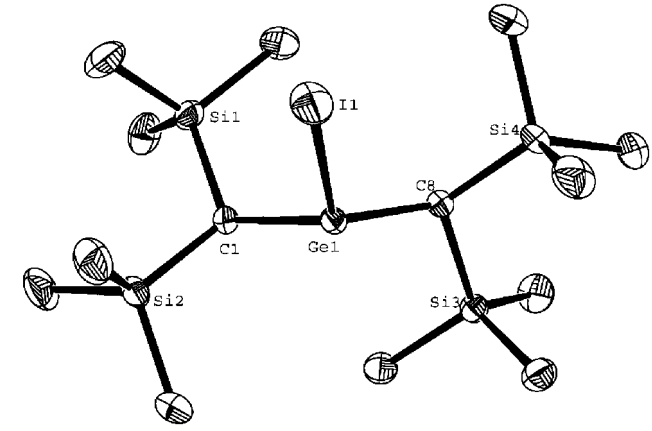


Figure 3. ORTEP representation of $[(Me_3Si)_2CH]_2Ge[I][H]$ (**20**) (50% probability). Selected bond distances (Å) and angles (deg): Ge−C1, 1.9587(19); Ge−C8, 1.958(2), Ge−I, 2.5709(3); C1−Ge−C8, 116.08(8); C1−Ge−I, 106.89(6); C8−Ge−I, 113.89(6).

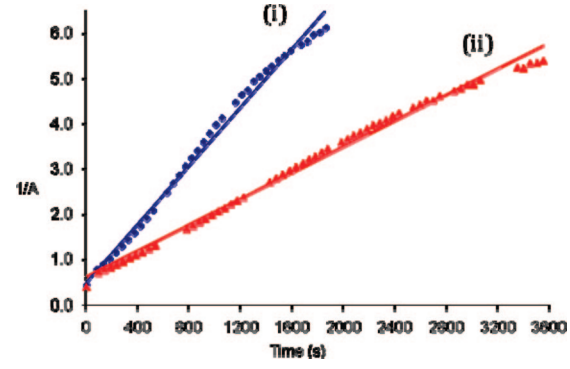


Figure 4. Second-order plot of concentration of Ge[CH(SiMe$_3$)$_2$]$_2$ (**15**) vs time for C−H activation of THF using (i) C_6H_5Br and (ii) C_6D_5Br.

Additionally, the zero-, first-, and third-order plots exhibited systematic, consistent deviation from linearity across the full data set.

This reaction was also performed using C_6D_5Br instead of C_6H_5Br. A 0.0013 M solution of **15** in THF was prepared by taking

Table 2. Product Distribution of 16 as a Function of Equivalents of Dimethylaniline per $Ge[CH(SiMe_3)_2]_2$ (15)[a]

equivalents dimethylaniline	% C−H activation	% oxidative addition	% CH_3Si activation
1	12	57	31
5	31	43	26
20	37	27	17
50	56	16	5
790	100	0	0
neat dimethylaniline			

[a] All reactions were performed using 50 μM **1** and 56 μM Ph−I in tetramethylsilane. Product percentages were determined by integration of ^{1}H NMR spectra.

Table 3. Summary of Kinetic Isotope Data for Reactions of $Si[N_2(^tBu)_2C_2H_2]$ (1), $Ge[CH(SiMe_3)_2]_2$ (15), and $Ge[N(SiMe_3)_2]_2$ (21) with THF and Et_2O

	substrate	Ar−X	k_H/k_D
$Ge[N(SiMe_3)_2]_2$ (**21**)	THF/THF-d_8	C_6H_5I	4.1 ± 0.2
$Ge[CH(SiMe_3)_2]_2$ (**15**)	THF/THF-d_8	C_6H_5I	5.0 ± 0.2
	THF	C_6H_5Br/C_6D_5Br	1.8 ± 0.1
	Et_2O	C_6H_5I/C_6D_5I	1.6 ± 0.1
		C_6H_5I/p-C_6H_4DI	1.3 ± 0.1
		C_6H_5I/m-C_6H_4DI	1.3 ± 0.1
		C_6H_5Br/C_6D_5Br	1.7 ± 0.2
$Si[N_2(^tBu)_2C_2H_2]$ (**1**)	Et_2O/Et_2O-d_{10}	C_6H_5I	5.7 ± 0.1
	Et_2O	C_6H_5I/C_6D_5I	1.3 ± 0.1
		C_6H_5I/p-C_6H_4DI	1.1 ± 0.1
		C_6H_5I/m-C_6H_4DI	1.1 ± 0.1
		C_6H_5Br/C_6D_5Br	1.3 ± 0.2

0.675 g of solution B (2.3 mg **15**, 0.0059 mmol) and diluting with THF to a final weight of 4.085 g (4.59 mL). To this solution in the quartz cuvette was added C_6D_5Br (10.0 μL, 0.092 mmol, 15.6 equiv), and the reaction was monitored via UV−vis spectroscopy for over 1 h. Once again, ^{1}H NMR spectroscopy indicated only C−H activation product was formed. A second-order plot gave the best fit to the data ($R^2 = 0.994$). The $k_{Ph\text{-}Br}/k_{Ph\text{-}Br\text{-}d5}$ ratio measured kinetically was 2.3.

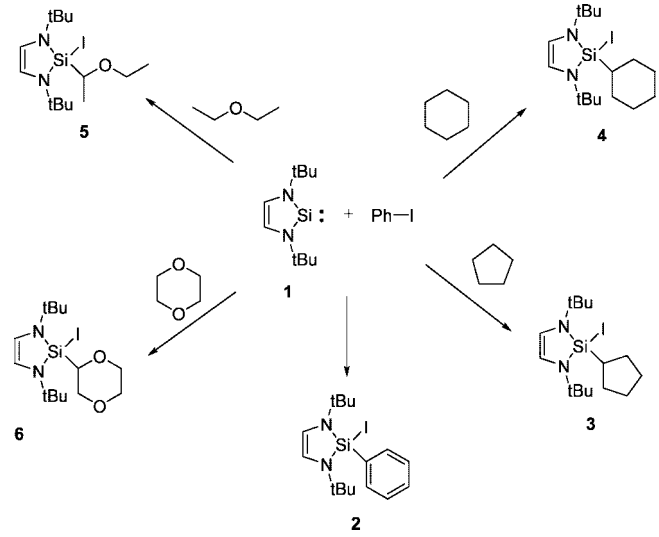
Measurement of Isotope Effects Arising from Deuteration of the Aromatic Ring of the Aryl Halide Using GC-MS Analysis of the Resulting Ratio of Benzenes. (a) Measurement of the $k_{Ph\text{-}Br}/k_{Ph\text{-}Br\text{-}d5}$ ratio for $Ge[CH(SiMe_3)_2]_2$ (**15**)/THF: A stock solution of **15** was prepared by adding 192 mg of **15** to 20 mL of THF. A 1.0 mL amount of the stock solution of **15** and 75 μL of C_6H_5Br/C_6D_5Br were added to a 1 dram GC-MS vial. The vial was capped and left at room temperature until colorless ($2^1/_2$ days). Employing a 70 °C hold for 2 min followed by a 70−250 °C ramp at 20 °C/min using a DB-5 equivalent column, the C_6H_6/C_6HD_5 mixture was separated from the other materials present and analyzed by mass spectrometry. All reactions were repeated in quadruplicate, and each sample was injected on the GC-MS in triplicate to generate the data presented in Table 3. For all methods (a, b, and c), the exact ratio of deuterated to nondeuterated aryl halide present in the initial reaction mixture was determined by an independent MS measurement of the prepared stock solution containing a nominal 1:1 ratio of the aryl halides.

(b) Measurement of ratios for $Ge[CH(SiMe_3)_2]_2$ (**15**)/Et_2O: A stock solution of **15** was prepared by adding 33 mg of **15** to 16.0 mL of Et_2O. A 1.0 mL amount of the stock solution of **15** and 25 μL of C_6H_5Br/C_6D_5Br (20 equiv of each aryl halide) were added to a 1 dram GC-MS vial. The vial was capped and left at room temperature until colorless (this time varies with aryl halide). Employing a 40 °C hold for 2.5 min followed by a 40−200 °C ramp at 20 °C/min using a DB-5 equivalent column, the C_6H_6/C_6HD_5 mixture was separated from the other materials present and analyzed by mass spectrometry. All reactions were repeated in quadruplicate, and each sample was injected on the GC-MS in quadruplicate to generate the data presented in Table 3. All other ratios reported for **15** in Et_2O were collected using a similar method.

Table 4

1-X-4-iodobenzene	% of C−H activation	$\log(K/K_0)$	σ_I	σ_m	σ_p	σ_R
H	65	0.0000	0.00	0.00	0.00	0.00
CH_3	67	0.0132	0.01	−0.06	−0.14	−0.11
I	77	0.0736	0.42	0.034	0.28	−0.16
Cl	83	0.1062	0.47	0.37	0.24	−0.23
F	82	0.1009	0.52	0.34	0.15	−0.32
CN	82	0.1009	0.57	0.62	0.71	0.13

Scheme 1. C−H Activation of Alkanes and Ethers Using 1/Ph−I



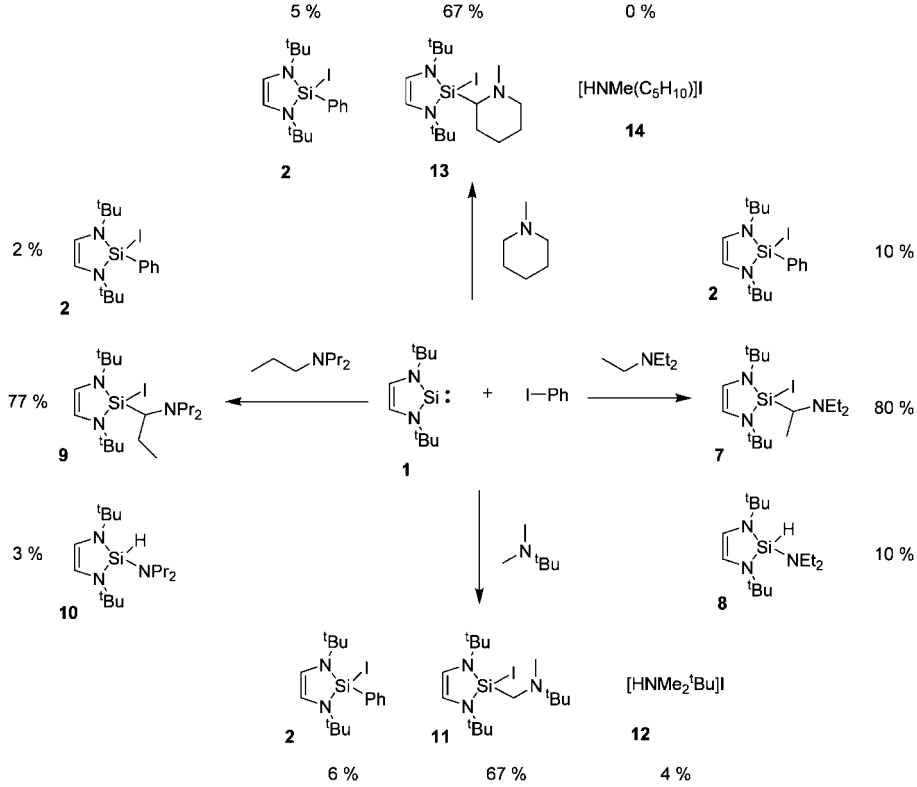
(c) Measurement of ratios for $Si[N_2(^tBu)_2C_2H_2]$ (**1**)/Et_2O: A stock solution of **1** was prepared by adding 16 mg of **1** to 16.0 mL of Et_2O. A 1.0 mL amount of the stock solution of **1** and the amount of a stock solution of C_6H_5Br/C_6D_5Br required to give 20 equiv of each aryl halide were added to a 1 dram GC-MS vial. The vial was capped and left at room temperature until colorless (this time varies with aryl halide). Employing a 40 °C hold for 2.5 min followed by a 40−200 °C ramp at 20 °C/min using a DB-5 equivalent column, the C_6H_6/C_6HD_5 mixture was separated from the other materials present and analyzed by mass spectrometry. All reactions were repeated in quadruplicate, and each sample was injected on the GC-MS in quadruplicate to generate the data presented in Table 3. All other ratios reported for **1** in Et_2O were collected using a similar method.

General Reaction Conditions for Determining Aryl Halide Substituent Effects. To a 25 mL round-bottom flask was added 25 mg (0.064 mmol, 1.0 equiv) of $[(Me_3Si)_2N]_2Ge$, 2.5 g of THF, and then 21 mg (0.064 mmol, 1.0 equiv) of *para*-diiodobenzene. Solutions were allowed to stir for 24 h, at which time volatiles were removed. ^{1}H NMR was used for obtaining the percentages of C−H activation product and oxidative-addition product formation. The percentage of C−H activation product was used as the K values, with K_o being the percentage of C−H activation product from the reaction of iodobenzene as the aryl iodide source.

Results and Discussion

C−H Activations Employing Silylene $Si[N_2(^tBu)_2C_2H_2]$ (1). Slow addition of a clear, colorless solution of **1** (1.0 equiv) dissolved in cyclopentane to a solution of Ph−I (1.2 equiv) in cyclopentane resulted in the formation of a clear, golden yellow solution containing a mixture of $[C_2H_2(^tBu_2)N_2]Si(C_6H_5)I$ (**2**), $[C_2H_2(^tBu_2)N_2]Si(C_5H_9)I$ (**3**), and benzene. Removal of volatiles resulted in the formation of a golden oil containing a 1:1 mixture of **2** and **3**. The reaction of **1** with cyclohexane was performed in a similar fashion to yield $[C_2H_2(^tBu_2)N_2]Si(C_6H_{11})I$ (**4**) and

Scheme 2. C−H Activation of Amines Using 1/Ph−I



2, although the **4**:**2** ratio obtained was 3:1 (Scheme 1). We were unable to separate **3** or **4** from **2** by fractional crystallization or sublimation. Pure **3** and **4** were synthesized as golden oils by the reaction of C_5H_9I and $C_6H_{11}I$, respectively, with **1**. Characteristic features for the NMR spectrum (C_6D_6) include the =CH protons of the five-membered ring, which appear at δ = 5.80 ppm for both **3** and **4**. The methyl protons of the ^{t}Bu groups appear at δ = 1.26 and 1.28 ppm for **3** and **4**, respectively. The =CH and ^{t}Bu protons for **2** come at δ = 5.91 and 1.15 ppm, respectively. The *ortho* protons on the phenyl ring (δ = 8.05 ppm) also provide a convenient diagnostic for the presence of **2**.

Slow addition of a clear, colorless solution of **1** (1.0 equiv) dissolved in Et_2O to a solution of Ph−I (1.1 equiv) in Et_2O resulted in a clear, pale yellow solution containing a mixture of $[C_2H_2(^tBu_2)N_2]Si[CH(CH_3)OCH_2CH_3]I$ (**5**) and **2** in a 4:1 ratio along with benzene. Similarly, slow addition of a solution of **1** (1.0 equiv) dissolved in 1,4-dioxane to a Ph−I solution (1.1 equiv) in 1,4-dioxane resulted in a clear, pale yellow solution containing a mixture of $[C_2H_2(^tBu_2)N_2]Si[C_4H_7O_2]I$ (**6**) and **2** in a 12:1 ratio along with benzene. Similarly to the case for the alkanes, we were unable to separate **5** or **6** from **2** by fractional crystallization or sublimation. The ether substrates exhibited a high degree of regioselectivity presumably arising from the presence of weaker C−H bonds on the carbon alpha to the oxygen. This observation suggested that alkyl amines would also be interesting substrates to explore.

Examples of amine C−H activation in the literature remain rare, and none of the examples reported to date represent a general method that can be implemented on a broad class of typical alkyl amines. The basic nitrogen functional group is reactive, even as a two-electron donor ligand, and undergoes undesired side reactions with many of the Lewis-acidic metal complexes typically employed for C−H activation. Most examples to date derive from C−H activation of an *ortho* aromatic proton in a substituted phenyl amine.[32−34] Reversible C−H activation of an N-methyl group has been achieved using Cp_2Zr=NR(THF).[35] Activation of N-alkyl groups, forming a proposed η^2-imine complex, followed by olefin hydroaminoalkylation has been achieved with tantalum complexes.[36] Activation of N-boc-protected amines with rhodium[37] and imines with Wilkinson's catalyst[38] and C−H activation via cyclopalladation[39] have also been reported.

Slow addition of a solution of **1** (1.0 equiv) dissolved in Et_3N to a solution of Ph−I (1.1 equiv) in Et_3N resulted in a golden solution containing a mixture of $[C_2H_2(^tBu_2)N_2]Si[CH(CH_3)NEt_2]I$ (**7**), **2**, and $[C_2H_2(^tBu_2)N_2]SiH(NEt_2)$ (**8**) in an 8:1:1 ratio, respectively. Similarly, slow addition of a solution of **1** (1.0 equiv) dissolved in Pr_3N to a solution of Ph−I (1.1 equiv) in Pr_3N resulted in a pale yellow solution containing a mixture of $[C_2H_2(^tBu_2)N_2]Si[CH(CH_2CH_3)NPr_2]I$ (**9**), **2**, and $[C_2H_2(^tBu_2)N_2]Si(NPr_2)H$ (**10**) in 38:1:1.5 ratio, respectively (Scheme 2). For both of these cases, excellent conversion to **7** and **9**, 85% and 66%, respectively, can also be obtained by simple mixing of **1** and Ph−I employing the amine as solvent. Under the conditions of simple mixing of

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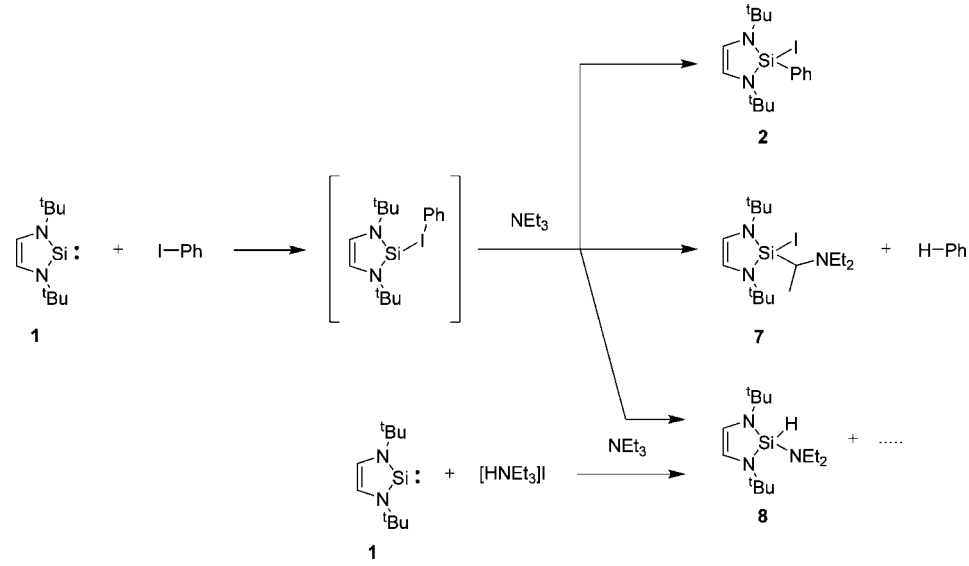
Scheme 3. Reaction of Triethylamine with 1 and Phenyl Iodide: Formation of 2, 7, and 8 and the Possible Role of HEt_3NI



reagents, compounds **8** and **10** were not detected via ^{1}H NMR spectroscopy.

Slow addition of a solution of **1** (1.0 equiv) dissolved in Me_2N^tBu to a solution of Ph−I (1.1 equiv) in Me_2N^tBu resulted in a colorless solution with a white precipitate containing a mixture of $[C_2H_2(^tBu_2)N_2]Si[CH_2(CH_3)N^tBu]I$ (**11**), **2**, and $[HNMe_2{}^tBu]I$ (**12**) in an 11:1:0.6 ratio, respectively. Slow addition of a solution of **1** (1.0 equiv) dissolved in *N*-methylpiperidine to a solution of Ph−I (1.1 equiv) in *N*-methylpiperidine resulted in a colorless solution containing a mixture of $[(CH)_2{}^tBu_2N_2]SiI[(CH(CH_2)_4)NCH_3]$ (**13**) and $[C_2H_2(^tBu_2)N_2]Si(C_6H_5)I$ (**2**), in an 13.4:1 ratio, respectively. In this case, the corresponding ammonium salt, $[HNMe(C_5H_{10})]I$ (**14**), was not detected. Simple mixing of **1** and Ph−I in Me_2N^tBu or *N*-methylpiperidine gives 81% **11** and 72% **13**, respectively, with no observable formation of **12** or **14**. A single-crystal X-ray structure analysis of **13** was carried out using a crystal grown from hexanes (Figure 1). The six-membered piperidine ring adopts a chair confirmation with the silicon moiety and the methyl nitrogen occupying adjacent axial sites.

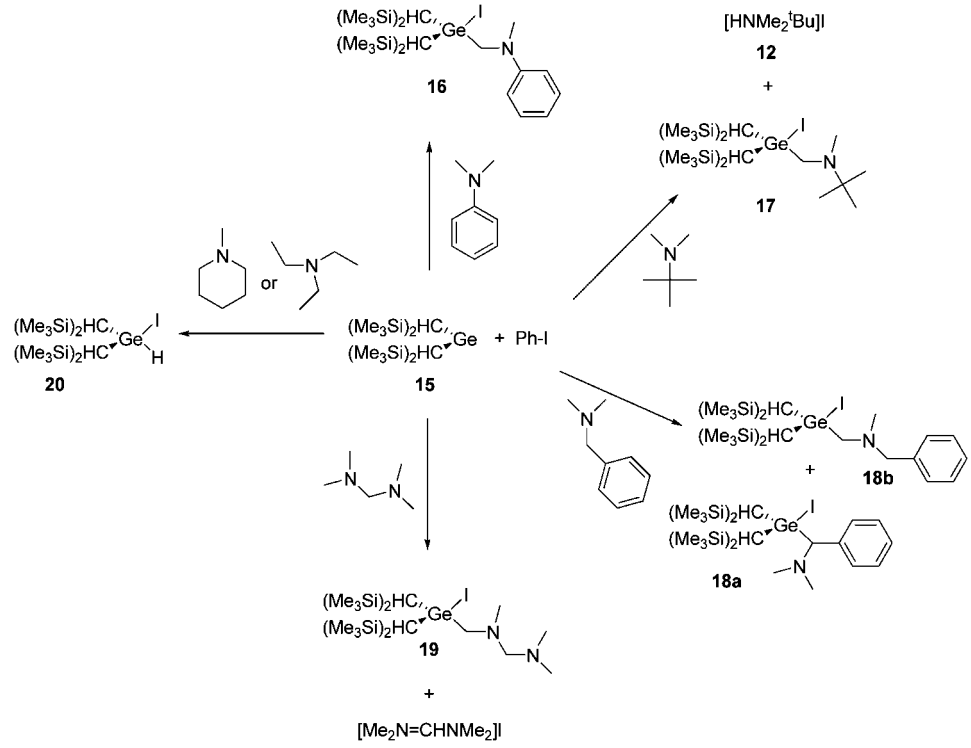
The formation of ammonium iodide salt **12** was unexpected, as was the formation of hydrido-amide complexes **8** and **10**. The role of ammonium iodides in the formation of C−H activation products was immediately of great interest, especially since previous germylene C−H insertion chemistry was shown to be catalyzed by the presence of salts.[2,8] However, addition of 0, 0.2, and 1.1 equiv of $[HNEt_3]I$ had no effect on the amount of C−H activation product **7** formed. Additional **8** was formed when $[HNEt_3]I$ was added; however, the relative amount of **8** was similar for both the 0.2 and 1.1 equiv reactions.

The reaction of **1** and $[HNEt_3]I$ in Et_3N did yield **8** at a kinetically competent rate (Scheme 3). Interestingly, no **8** was formed for the reaction of **1** and $[HNEt_3]I$ in THF, and **1** and $HNEt_2$ did not react over a period of 4 h at 20 °C. However, the addition of 0.1 equiv of LiI to a mixture of **1** and Et_3N also yielded **8**, although addition of LiCl did not. The sum of these results suggests that **8** is formed via an I^--mediated reaction between **1** and Et_3N and not by a direct reaction of **1** and $[HNEt_3]^+$. The role of the cation remains important, as $[Et_4N]I$ in NEt_3 also did not give any conversion of **1** to **8**. No reaction was observed between **1** and $[HNMe_2{}^tBu]I$ (**12**) in Me_2N^tBu, and no hydrido-amide species is observed for the reaction of **1** and Me_2N^tBu. Thus although the pathway to form **12** is present, the more sterically bulky **12** does not react to form a hydrido-amide analogous to **8** or **10**. The ammonium halide salt **14** was not observed as a side-product in the C−H activation reaction, and addition of **14** did not yield a hydrido-amide analogous to **8** or **10**. The presence of **8** and **10** as reaction products appears to be the result of the initial formation of the ammonium iodide salts that are subsequently consumed in the direct reaction with **1**.

The formation of the ammonium iodide salts appears intricately linked to the C−H activation process. The iodide originates on the Ph−I, and the hydrogen must originate on the C−H-activated alkyl amine. Given these sources of H and I, the corresponding alkyl amine radical and phenyl radical remain unaccounted for in the reaction mixture. We have been unable to find evidence for biphenyl, R−R coupling, or R−Ph coupling products by NMR spectroscopy or GC-MS studies. Interestingly, ammonium iodide salts also appear to play an important role in the reaction of $Ge[CH(SiMe_3)_2]_2$ (**15**) with alkyl amines although with a strikingly different outcome.

C−H Activations of Tertiary Amines Employing Germylene $Ge[CH(SiMe_3)_2]_2$ (15). The C−H activation chemistry of tertiary amines was also explored using $Ge[CH(SiMe_3)_2]_2$ (**15**). This germylene, originally synthesized by Lappert et al.,[31] proved most effective in our earlier studies of alkane and ether C−H activation.[1] As was noted for the silylene chemistry, high yields of C−H activation products could often be obtained upon simple mixing of **15** and Ph−I in the desired amine substrate. Addition of 1 equiv of **15** and 1.1 equiv of Ph−I to either Me_2NPh or Me_2N^tBu resulted in a clear orange solution that faded to colorless as **15** was consumed. The products $[(Me_3Si)_2CH]_2Ge[(CH_2)N(CH_3)(Ph)]$ (**16**) and $[(Me_3Si)_2CH]_2$-$Ge[I][CH_2N(CH_3)(C(CH_3)_3)]$ (**17**) were characterized by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and mass spectrometry. The structure of compound **16** was also verified by X-ray crystallography, confirming the presence of the Ge−C bond (1.999(3) Å) in the product (Figure 2). For both of these amines, C−H activation occurred exclusively at methyl groups containing C−H bonds α to nitrogen (Scheme 4). Similar regioselectivity, attributed to the difference in bond strengths, was previously observed for activation of ethers by germylene **15**.[1] The exclusive formation of C−H activation product in both cases was surprising since reactions of **15** with ethers or alkanes performed by simply mixing the reagents together typically

Scheme 4. C−H Activation of Amines Using 15/Ph−I



produces >50% of the Ph−I oxidative-addition product $[(Me_3Si)_2CH]_2GePhI$. Furthermore, for the reaction with Me_2N^tBu, oxidative addition to form $[(Me_3Si)_2CH]_2GePhI$ and **12** is not observed, so the reaction products are not directly analogous to those seen for silylene **1**. When the reactions of **15**/Ph−I with Me_2N^tBu were run under slow addition conditions using a syringe pump, the ammonium salt **12** was observed.

Addition of 1 equiv of $Ge[CH(SiMe_3)_2]_2$ (**15**) and 1.1 equiv of Ph−I to Me_2NCH_2Ph resulted in C−H activation at the methyl and the benzylic C−H bonds, resulting in $[(Me_3Si)_2CH]_2Ge[I][(CH_2)N(CH_2Ph)(CH_3)]$ (**18a**) and $[(Me_3Si)_2CH]_2Ge[I][(CHPh)N(CH_3)_2]$ (**18b**), respectively. The relative ratio of products as determined by ^1H NMR was 1:1. This indicates that activation of the benzylic secondary C−H bonds α to nitrogen is favored over activation of the primary C−H bonds α to nitrogen by a 3:1 ratio. The reaction of **15** with $Me_2NCH_2NMe_2$ and 1.1 equiv of Ph−I resulted in the primary C−H activation product $[(Me_3Si)_2CH]_2Ge[I][(CH_2)(CH_3)N(CH_2)N(CH_3)_2]$ (**19**) and the formation of the ammonium salt $[Me_2N{=}CH\text{-}NHMe_2]I$ in a 2.8:1 ratio.

The final class of amines tested, $MeN(C_5H_{10})$ and NEt_3, contain aliphatic C−H bonds β to the amine nitrogen. In both of these cases, the product observed is the formal addition of HI to the germylene to give $[(Me_3Si)_2CH]_2GeHI$ (**20**). Compound **20** has been characterized by ^1H and ^{13}C NMR, elemental analysis, mass spectrometry, and single-crystal X-ray analysis (Figure 3). The reaction of **15** and $[HNEt_3]I$ in Et_3N quantitatively generated **20** in a kinetically competent fashion. **20** is also formed by the reaction of **15** and $[HNEt_3]I$ in THF. Note that these results are quite different from those obtained for **1** and Et_3N, where C−H activation is the primary product, and the reaction with $[HNEt_3]I$ in Et_3N gives hydrido-amide **8** instead of a silicon analogue of **20**.

Previously reported activations of alkanes and ethers utilized the substrate containing the C−H bond as solvent. Attempts to perform the reactions under stoichiometric conditions using benzene or tetramethylsilane as a solvent resulted in high yields of $[(Me_3Si)_2CH]_2GePhI$. The high yields of C−H activation products obtained when using neat Me_2NPh and Me_2N^tBu suggested that the substrate might form a Lewis acid/base adduct with **15**. On the basis of this hypothesis, a number of stoichiometric ratios of Me_2NPh to **15** were tested using tetramethylsilane as the diluent (Table 2). Substantial amounts of C−H activation (12%) were observed for a 1:1 ratio of amine:germylene. Greater than 50% C−H activation product was observed when 50 equiv of amine was employed. In general, as the ratio of amine to germylene approached 1:1, an increasing amount of oxidative addition and competitive C−H activation of the trimethylsilyl groups of the tetramethylsilane occurred.

Attempts to C−H activate toluene using **1** and Ph−I resulted in **2** as the sole product, so toluene was employed as a diluent for a C−H activation reaction using Et_3N as a substrate. Addition of 4.4 equiv of toluene per Et_3N resulted in a 4:1 ratio of **7** to **2**, respectively. Addition of 2.6 equiv of toluene per Et_3N resulted in a 15:1 ratio of **7** to **2**, respectively. The reaction run in pure Et_3N gave a 42:1 ratio of **7**:**2**, respectively.

Studies of Primary Isotope Effects for C−H Activations by Silyenes and Germylenes. We previously reported that the primary isotope effect for the reaction of **15**/Ph−I with THF at 60 °C gave a k_H/k_D ratio of 5.0 ± 0.2.[1] Similarly, the reaction of $Ge[N(SiMe_3)_2]_2$ (**21**) with THF at 60 °C gave a k_H/k_D ratio of 4.1 ± 0.2. The results suggest that breaking the C−H bond of THF is the rate-limiting step of the reaction. Of course, it is also possible that the bond breaking occurs prior to the rate-limiting step. Note also the measurement of two different k_H/k_D values indicates that a common intermediate is not present. This provides evidence that the germylene is present in the complex associated with the C−H bond-breaking step. These reactions were performed at 60 °C to provide convenient comparison to the formation of phenyl radical from phenylazotriphenylmethane (PAT).[40] The k_H/k_D ratio for the

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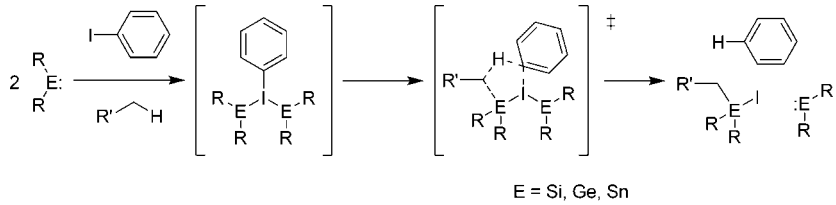

Figure 5. Proposed mechanism for the C−H activation reaction.

C−H abstraction from THF using PAT is 4.2 ± 0.2.[1] The differing k_H/k_D ratios for **15** and PAT indicate a common intermediate is not operative for these reactions and therefore argues against phenyl radical as an intermediate for **15**. Although the k_H/k_D values for $Ge[N(SiMe_3)_2]_2$ and PAT are not statistically different, the differing product ratios observed for cumene/THF competition reactions argue against phenyl radical playing a role for $Ge[N(SiMe_3)_2]_2$ as well.

In order to measure the primary isotope effect for the C−H activation reaction involving silylene **1**, the competition between Et_2O/Et_2O-d_{10} was selected because the reaction with THF does not lead to clean products for the silylene case. The primary isotope effect for the reaction of **1**/Ph−I with Et_2O/Et_2O-d_{10} at 20 °C gave a k_H/k_D ratio of 5.7 ± 0.1. These k_H/k_D ratios for **1**, **15**, and **21** with Ph−I are all consistent with C−H activation occurring prior to or at the rate-limiting step. The sum of the primary isotope effect data is inconsistent with a phenyl radical intermediate and suggests that a complex containing both the silylene or germylene and aryl halide is operative.

Determination of the Reaction Order of $Ge[CH(SiMe_3)_2]_2$ (15) in the Reaction with Ph−Br and THF. The order of the reaction in **15** was obtained for the activation of THF using **15** and Ph−Br. Ph−Br was selected as the aryl halide for these studies because it gives convenient rates for analysis by UV−vis spectroscopy (Figure S1). The reaction was second order in **15** as determined by a best fit to a second-order plot (Figure 4). This result was confirmed by three independent experiments as well as a separate experiment employing Ph−Br-d_5, which exhibited a rate decrease of a factor of 2.3 but was still consistent with a second-order plot. The conclusion from kinetic studies that the reaction was second order in germanium was quite surprising. It is even more surprising when one considers that high-dilution conditions are typically employed to maximize the relative percentage of C−H activation products. In order to further test the conclusion that the reaction was second order in germylene, competition experiments were performed for the C−H activation of toluene using a 50:50 mix of germylenes **15** and **21**. In this instance, **21**, which normally does not C−H activate toluene,[1] does form the C−H activation product in an amount equal to the molar amount of **15** added (i.e., if **15** and **21** are present in a 1:3 ratio, only one-third of **21** is converted to the C−H activation product). This product formation behavior is consistent with the determination that the reaction is second order in germylene.

The observation of a rate ratio of 2.3 based upon the use of C_6H_5Br vs C_6D_5Br was also quite surprising given that no bonds involving these isotopes are broken in the reaction. A GC-MS analysis was designed to independently measure this value and to measure additional aryl halide-based isotope effects.

Studies of Isotope Effects Based upon Deuterium Substitution in the Aryl Halide for C−H Activations by Silyenes and Germylenes: GC-MS Analysis of Resulting Benzenes. The relative rates of C−H activation involving C_6H_6Br and C_6D_5Br were re-examined for the reaction of germylene **15** and THF by employing a GC-MS analysis of the resulting ratio of C_6H_6 and C_6D_5H produced. This analysis method is ideal because the resulting benzenes provide a direct measure of the degree to which the two individual C−H activation pathways were followed. For all of these studies, a nominal 1:1 mixture of the aryl halides was prepared and then measured for the exact ratio of the two species using GC-MS. This exact ratio of input materials was then used in the determination of the relative k_H/k_D rates. The effects of substrate, halide, and substitution by silylene **1** were also explored.

The k_H/k_D ratios measured for germylene **15** and silylene **1** when employing C_6H_5X and C_6D_5X fell in the range 1.3 to 1.8, varying as a function of Si vs Ge, substrate, and halide. Both germylene ratios, 1.8 and 1.6, were substantially larger than the two silylene ratios, which were both 1.3. In both cases, examining the ratios for C_6H_5I and m-C_6DH_4I or p-C_6DH_4I revealed smaller k_H/k_D ratios of 1.3 for **15**/Et_2O and 1.1 for **1**/Et_2O. These values are summarized in Table 3.

The origins of these k_H/k_D ratios were of interest for understanding a potential reaction pathway. Similar k_H/k_D ratios have been reported for the formation of aromatic radical anions.[41,42] For example, k_H/k_D values for formation of benzene radical anions are $k(C_6H_6)/k(C_6H_5D) = 1.16$, $k(C_6H_6)/k(1,2\text{-}C_6H_4D_2) = 1.82$, $k(C_6H_6)/k(1,4\text{-}C_6H_4D_2) = 1.79$, $k(C_6H_6)/k(1,3,5\text{-}C_6H_3D_3) = 2.70$, and $k(C_6H_6)/k(C_6D_6) = 3.85$.[41] The k_H/k_D values observed for the C−H activation reactions are within the range of values reported for the formation of aryl radical anions. Additionally, the reported k_H/k_D values for the thermal decomposition of diazobenzenes range from 1.02 for $(C_6H_5N_2^+)/(4\text{-}C_6H_4DN_2^+)$ to 1.79 for $(C_6H_5N_2^+)/(C_6D_5N_2^+)$.[43] Although the k_H/k_D ratios measured for the C−H activation chemistry might at first seem surprising, they are well within the expected literature values for this type of aryl ring-based isotope effect.

Impact of Subsitutuents on the Aryl Halide for C−H Activations by Germylenes. C−H activation reactions were carried out using $Ge[N(SiMe_3)_2]_2$/THF/IC_6H_4Y (Y = H, CH_3, I, Cl, F, CN) and found to give a good fit ($R^2 = 0.96$) to σ_I, the Hammet parameter developed to be sensitive to inductive effects only (as opposed to the mix of inductive and mesomeric effects that impact σ_p and σ_m).[44] The slope (ρ) obtained of 0.18 is >0, consistent with some buildup of negative charge in the aromatic

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ring in the transition state. Poor fits were obtained for σ_p and σ_R ($R^2 = 0.44$ and 0.08, respectively), although a reasonable correlation was found to σ_m ($R^2 = 0.85$). This was interesting in light of the anticipated buildup of charge *meta* to iodine.

A Proposed Mechanism for C−H Activation. A proposed reaction pathway for the C−H activation reaction is illustrated in Figure 5. The formation of an aryl halide-bridged dimer is proposed on the basis of the observed second-order dependence on germylene and the reactivity behavior of **15/21** mixtures with toluene. An inner-sphere electron transfer from a lone pair on E to form an L_2E: radical cation and an aryl radical ion would facilitate the breaking of the Ph−I bond and initiate the formation of an incipient radical on the *ipso* carbon, which could abstract a hydrogen atom from a proximate solvent molecule. This interaction would generate a transition state with a five-membered ring. The electron transfer proposal is consistent with the measured k_H/k_D ratios, and the location of the transition state in the reaction pathway is consistent with C−H bond breaking as the rate-limiting step. This transition state could also collapse to either L_2E: species, consistent with the reactivity observed for **15/21** mixtures. We note that a variety of previously published observations are consistent with second-order dependence for the oxidative addition of halocarbons to silylenes and germylenes.[29,45−48]

Conclusions

We have developed a direct method of forming Si−C bonds with alkanes and ethers in analogy with our previously reported germanium and tin chemistries. In this work we have demonstrated the expansion of the C−H activation reaction to tertiary amine substrates. C−H activation of N-methyl amines can be achieved, while N-aliphatic tertiary amines give rise to **20** when using **15**/Ph−I. A reaction mechanism is proposed based upon the measurement of the order in L_2E: and the measurement of primary and aryl ring-based isotope effects.

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Supporting Information Available: An X-ray crystallographic file in CIF format for compounds **13**, **16**, and **20**. The UV−vis data for the reaction of $Ge[CH(SiMe_3)_2]_2$ with Ph−Br in THF is also provided. This information is available free of charge via the Internet at http://pubs.acs.org.

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