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C−H Activation of Alkanes, Alkenes, Alkynes, Arenes, and Ethers Using a Stannylene/Aryl Halide Mixture†

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The reaction of $\overline{SnC(SiMe_3)_2CH_2CH_2C(SiMe_3)_2}$/ArI (Ar = Ph, 2,4,6-triisopropylphenyl) with cyclohexane, diethyl ether, tetrahydrofuran (THF), toluene, and mesitylene yields C−H activation products in which a new Sn−C bond is formed at the location of the weakest C−H bond. The regioselectivity of this reaction with *trans*-4-methyl-2-pentene and 4-methyl-2-pentyne was explored as a function of aryl halide for PhI, 2,4,6-trimethyliodobenzene, 2,4,6-triisopropyliodobenzene, 4-iodoanisole, 4-iodobenzonitrile, and 2,6-mesityliodobenzene. A degree of regiochemical control could be obtained as highlighted by increased amounts of primary activation. The use of 2,4,6-*tert*-butyliodobenzene resulted in C−H activation of the *ortho tert*-butyl groups in all solvents tried. The primary kinetic isotope effect for the reaction of $\overline{SnC(SiMe_3)_2CH_2CH_2C(SiMe_3)_2}$/2,4,6-triisopropyliodobenzene with toluene/toluene-d_7 was found to be 4.9 ± 0.5.

Introduction

C−H activation is one of the important goals of synthetic and mechanistic chemists. These reactions promise increased synthetic efficiency, waste reduction, and utilization of inexpensive source materials such as petroleum or methane gas.[1,2] C−H activation reactions are performed for the purposes of direct functionalization or carbon−carbon bond formation.[3] Designing reagents and conditions that exhibit selective reactivity with only one type of C−H bond in an organic compound is essential.[4] Successful approaches include the use of directing groups, chelation assistance, and exploitation of differential homolytic strengths of C−H bonds.[5,6] In the literature, a general distinction is made between radical, σ bond metathesis, and electrophilic pathways.[7,8] Competition between radical and electrophilic pathways has been observed.[9] Although a comprehensive treatment of radical methods is available elsewhere,[10] notable recent advances include an environmentally friendly variant of the traditional bromination reaction and an enantioselective variant of the Kharasch−Sosnovsky reaction.[11,12] Generation of methyl or ethyl radicals from Me_2Zn/air or Et_3B/air has been used for hydrogen abstraction of C−H bonds α to the ethereal oxygen for hydroxyalkylation of ethers and acetals.[13]

Our lab has published a series of papers on the C−H activation of alkanes, ethers, alkenes, alkynes, and amines utilizing stable, heavy, divalent group 14 EL_2 species (E = Si, Ge, Sn) in combination with an aryl halide.[14−18] Involvement of an EL_2/PhX radical intermediate that abstracts the homolytically weakest hydrogen from the substrate has been implicated in the reaction manifold (Scheme 1).[18] Oxidative addition products, which can be minimized by carrying out the reaction under high dilution conditions, are formed in competition with C−H activation products. The effect of

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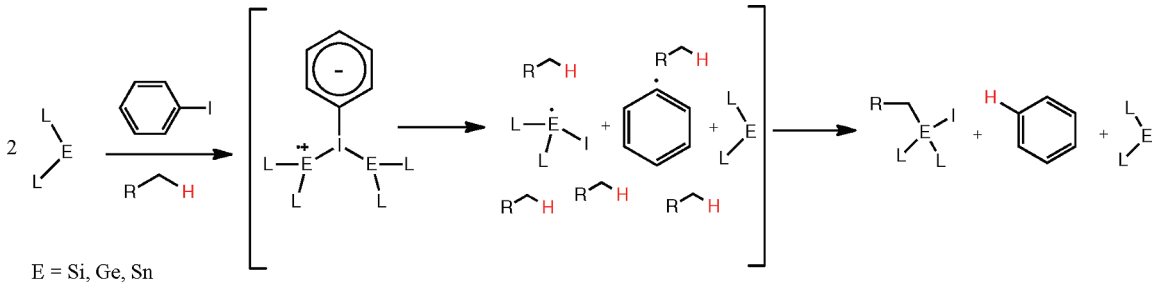
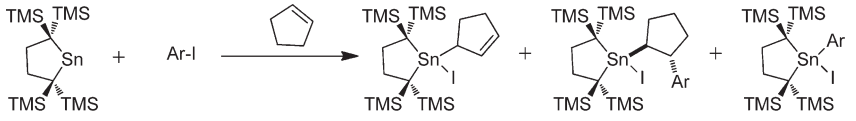
Scheme 1. C−H Activation Reaction Is Believed to Occur via the Formation of an Active Intermediate Involving Two Equivalents of EL_2 and One Equivalent of Aryl Halide[a]



[a] Electron transfer from EL_2 to the aryl ring initiates the breaking of the Ar−I bond. Abstraction of the hydrogen atom and recombination of the $R'CH_2^{\bullet}$ and $L_2IE^{\bullet}$ radicals occurs within the solvent cage.

Scheme 2. Steric Bulk at the *ortho* Position of the Aryl Halide Changes the Distribution of C−H Activation, Double-Bond Addition, and Oxidative Addition Products[a]



[a] The selectivities indicated were determined by ^{1}H NMR spectroscopy.

steric bulk in the *ortho* positions of the aryl halide has not been systematically explored to date. An interesting example of such an effect is the reaction of $\overline{SnC(SiMe_3)_2CH_2CH_2C(SiMe_3)_2}$ (**1**) with cyclopentene, which resulted in a mixture of products including the C−H activation product (**2**), the product derived from the addition of stannylene and aryl halide across the double bond (**3**), and a trace amount of oxidative addition product (**4**) (Scheme 2).[16,19] When 2,4,6-trimethyliodobenzene was used, pure C−H activation product was obtained. We note that the use of high dilution to obtain greater yields of the C−H activation products is counterintuitive given a proposed intermediate containing two molecules of EL_2 and one molecule of aryl halide as illustrated in Scheme 1.

Regioselective C−H activation of alkanes has been a long-standing goal.[20] In terms of regiochemical preference, transition metal mediated pathways generally give products of less hindered functionalization, i.e., primary > secondary > tertiary.[1] To date, our chemistry has consistently yielded products derived from C−H activation of the thermodynamically weaker bonds, i.e., tertiary > secondary > primary or activation next to an activating group such as an ether oxygen.[14,16,18] We now report how the product distribution in C−H activation reactions with stannylene/aryl halide is dependent on the electronic and steric substitution of the aryl halide. The stereoelectronic properties of the aryl halide have been used to control the amount of oxidative addition product and to effect a degree of regioselectivity for substrates containing different C−H bonds. For the first time, we have demonstrated a degree of kinetic control of the C−H activation reaction by manipulating the steric bulk of the aryl halide.

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Experimental Section

Manipulations involving $\overline{SnC(SiMe_3)_2CH_2CH_2C(SiMe_3)_2}$ (**1**) were performed using inert-atmosphere techniques. Solvents were dried over sodium benzophenone ketyl and degassed. PhI was purchased from Aldrich Chemicals and degassed. 2,4,6-Triisopropyliodobenzene was synthesized according to literature procedures.[21] 2,4,6-Tri-*tert*-butylbromobenzene was borrowed from Arthur Ashe III lab, who prepared it by bromination of 2,4,6-tri-*tert*-butylbenzene.[22] Compound **1** and $Sn[N(SiMe_3)_2]_2$ (**11**) were synthesized according to literature procedures.[23,24] ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were acquired on a Varian 500 MHz instrument (499.904, 125.714, and 186.417 MHz, respectively). ^{1}H and ^{13}C were referenced according to residual proton (δ 7.15) and solvent carbons (δ 128.0), respectively. ^{119}Sn spectra were referenced to the ^{1}H signal of internal tetramethylsilane using a Ξ of 37.290632 for Me_4Sn.[25] All coupling constants listed are for ^{119}Sn satellites. Mass spectra were acquired on a VG (Micromass) 70-250-S magnetic sector mass spectrometer. IR spectra were acquired on a Perkin-Elmer Spectrum BX. Reactions typically were performed using a syringe pump (Razel R-99) inside an inert-atmosphere box.

$(C_4H_7O)\overline{ISnC(SiMe_3)_2CH_2CH_2C(SiMe_3)_2}$ (5). A one-necked 100 mL flask fitted with a rubber septum was charged with 165 mg of 2,4,6-trimethyliodobenzene (0.67 mmol, 1.1 equiv) and 5 mL of THF. A solution containing 300 mg of **1** (0.65 mmol, 1 equiv) and 10 mL of THF was placed in a gastight syringe equipped with a 20-gauge needle. A 5 mL amount of the red stannylene solution was added to the iodomesitylene/THF

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solution at a rate of 8 mL/h using a syringe pump. The last 5 mL was added at 2 mL/h. The solution was stirred for 8 h, yielding a cloudy, white solution containing only the C−H activation product by ^{1}H NMR spectroscopy. The volatiles were removed *in vacuo*, resulting in a white powder (110 mg, 25.7% yield). ^{1}H NMR (C_6D_6): δ 4.23 (dd, $^3J_{H-H}$ = 2.00 Hz, $^3J_{H-H}$ = 7.21 Hz, 1H, Sn-C*H*), 3.74 (pseudoquartet, J_{H-H} = 7.21 Hz, 1H, O-CH_2), 3.46 (dt, $^3J_{H-H}$ = 8.0 Hz, $^2J_{H-H}$ = 4.8 Hz, 1H, O-CH_2), 2.42 (m, 1H, Sn-CH-CH_2), 2.26−1.80 (m, 4H, Sn-C(SiMe$_3$)$_2$-CH_2-CH_2), 2.09 (m, 1H, Sn-CH-CH_2), 1.64 (m, 1H, O-CH$_2$-CH_2), 1.38 (m, 1H, O-CH$_2$-CH_2), 0.43 (s, 9H, Si(CH_3)$_3$), 0.38 (s, 9H, Si(CH_3)$_3$), 0.30 (s, 9H, Si(CH_3)$_3$), 0.15 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR (C_6D_6): δ 81.95 (Sn-*C*H), 70.04 (O-*C*H$_2$), 35.24 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 35.02 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 32.89 (Sn-CH-*C*H$_2$), 26.62 (O-CH$_2$-*C*H$_2$), 4.70 (Si(*C*H$_3$)$_3$), 4.61 (Si(*C*H$_3$)$_3$), 4.52 (Si(*C*H$_3$)$_3$), 4.37 (Si(*C*H$_3$)$_3$). ^{119}Sn NMR (C_6D_6): δ 133.4. MS CI with methane *m*/*z*: 647.1 (M − CH$_3$). IR (film) cm^{-1}: ν 2920, 1462, 1377, 1251, 1036, 901, 848, 754, 653, 607

(C$_6$H$_{11}$)ISnC(SiMe$_3$)$_2$CH$_2$CH$_2$C(SiMe$_3$)$_2$ (6). A one-necked 100 mL flask fitted with a rubber septum was charged with 236 mg of 2,4,6-triisopropyliodobenzene (0.71 mmol, 1 equiv), and 5 mL of cyclohexane. A solution containing 300 mg of **1** (0.65 mmol, 1 equiv) and 10 mL of cyclohexane was placed in a gastight syringe equipped with a 20-gauge needle. A 5 mL amount of the red stannylene solution was added to the 2,4,6-triisopropyliodobenzene/alkane solution at a rate of 8 mL/h using a syringe pump. The last 5 mL was added at 2 mL/h. The solution was stirred for 8 h, yielding a cloudy, white solution containing only the C−H activation product by ^{1}H NMR spectroscopy. The volatiles were removed *in vacuo*, and column chromatography was performed to give a white powder (398.2 mg, 91.3% yield). ^{1}H NMR (C_6D_6): δ 2.14−1.92 (m, 8H, Sn-C(SiMe$_3$)$_2$-CH_2-CH_2 and SnCHCH_2), 1.77 (tt, $^3J_{H-H}$ = 12.5 Hz, $^3J_{H-H}$ = 3.5 Hz, 1H, Sn-C*H*), 1.68 (m, 2H, SnCHCH$_2$CH_2), 1.52 (m, 1H, SnCHCH$_2$CH$_2$CH_2), 1.27 (m, 3H, SnCHCH$_2$CH_2 and SnCHCH$_2$CH$_2$CH_2), 0.39 (s, 18H, Si(CH_3)$_3$), 0.18 (s, 18H, Si(CH_3)$_3$). ^{13}C NMR (C_6D_6) δ 42.19 (Sn-*C*H), 35.73 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 31.79 (SnCH*C*H$_2$), 29.17 (SnCHCH$_2$*C*H$_2$), 26.91 (SnCHCH$_2$CH$_2$*C*H$_2$), 4.55 (Si(*C*H$_3$)$_3$), 4.48 (Si(*C*H$_3$)$_3$). ^{119}Sn (C_6D_6): δ 166.8. MS EI *m*/*z*: 659.4 (M-CH$_3$). IR (film) cm^{-1}: ν 2920, 1458, 1377, 1251, 897, 848. Anal. Calc'd for $C_{22}H_{51}ISi_4Sn$: C: 39.23; H: 7.63. Found: C: 39.53; H: 7.84.

(C$_4$H$_9$O)ISnC(SiMe$_3$)$_2$CH$_2$CH$_2$C(SiMe$_3$)$_2$ (7). A one-necked 100 mL flask fitted with a rubber septum was charged with 175.2 mg of 2,4,6-trimethyliodobenzene (0.71 mmol, 1.1 equiv) and 5 mL of diethyl ether. A solution containing 300 mg of **1** (0.65 mmol, 1 equiv) and 10 mL of diethyl ether was placed in a gastight syringe equipped with a 20-gauge needle. A 5 mL amount of the red stannylene solution was added to the iodomesitylene/diethyl ether solution at a rate of 8 mL/h using a syringe pump. The last 5 mL was added at 2 mL/h. The solution was stirred for 8 h, yielding a cloudy, white solution containing only the C−H activation product by ^{1}H NMR spectroscopy. The volatiles were removed *in vacuo*, and the resulting solid was column chromatographed to give elementally pure material. (200 mg, 46.6% yield). ^{1}H NMR (C_6D_6): δ 4.12 (q, $^3J_{H-H}$ = 6.8 Hz, 1H, Sn-C*H*), 3.41 (pseudo-p, J_{H-H} = 6.8 Hz, 1H, O-CH_2-CH$_3$), 2.98 (pseudo-p, J_{H-H} = 6.8 Hz, 1H, O-CH_2-CH$_3$), 2.21−1.83 (m, 4H, Sn-C(SiMe$_3$)$_2$-CH_2-CH_2), 1.72 (d, $^3J_{H-H}$ = 6.8 Hz, 3H, Sn-CH-CH_3), 1.03 (t, $^3J_{H-H}$ = 7.2 Hz, 3H, O-CH$_2$-CH$_3$), 0.40 (s, 9H, Si(CH_3)$_3$), 0.39 (s, 9H, Si(CH_3)$_3$), 0.25 (s, 9H, Si(CH_3)$_3$), 0.18 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR (C_6D_6): δ 81.90 (Sn-*C*H), 65.9 (O-*C*H$_2$-CH$_3$), 35.25 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 35.10 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 19.66 (Sn-CH*C*H$_3$), 15.62 (O-CH$_2$-*C*H$_3$), 4.78 (Si(*C*H$_3$)$_3$), 4.60 (Si(*C*H$_3$)$_3$), 4.57 (Si(*C*H$_3$)$_3$), 4.49 (Si(*C*H$_3$)$_3$). ^{119}Sn NMR (C_6D_6): δ 117.68. MS CI with methane *m*/*z*: 649.4 (M − CH$_3$). IR (film) cm^{-1}: ν 2919, 1250, 899, 843 Anal. Calcd for $C_{20}H_{49}IOSi_4Sn$: C: 36.20; H: 7.44. Found: C: 37.10; H: 7.64.

(C$_7$H$_7$)ISnC(SiMe$_3$)$_2$CH$_2$CH$_2$C(SiMe$_3$)$_2$ (8). A one-necked 100 mL flask fitted with a rubber septum was charged with 157 mg of 2,4,6-triisopropyliodobenzene (0.48 mmol, 1.1 equiv) and 5 mL of toluene. A solution containing 200 mg of **1** (0.43 mmol, 1 equiv) and 10 mL of toluene was placed in a gastight syringe equipped with a 20-gauge needle. Then 5 mL of the red stannylene solution was added to the 2,4,6-triisopropyliodobenzene/alkane solution at a rate of 8 mL/h using a syringe pump. The last 5 mL was added at 2 mL/h. The solution was stirred for 8 h, yielding a cloudy, white solution containing only the C−H activation product by ^{1}H NMR spectroscopy. The volatiles were removed *in vacuo*, and the resulting solid was recrystallized from pentane at −78 °C to give a white powder (120 mg, 41% yield). ^{1}H NMR (C_6D_6): δ 7.38 (pseudo-d, 7.2 Hz, 3H, *ortho*-Ph and *para*-Ph), 7.0 (pseudo-*t*, J_{H-H} = 7.6 Hz, 2H, *meta*-Ph), 3.25 (s with br Sn satellites, $^2J_{Sn-H}$ = 22.8 Hz, 2H, Sn-CH_2), 2.04 (m, 2H, SnC(Si(CH$_3$)$_2$CH_2), 1.89 (m, 2H, SnC(Si(CH$_3$)$_2$CH_2), 0.32 (s, 18H, Si(CH_3)$_3$), 0.13 (s, 18H, Si(CH_3)$_3$). ^{13}C NMR (C_6D_6): δ 139.0 (*ipso*-Ph), 129.8 (*ortho*-Ph), 128.97 (*meta*-Ph), 126.32 (*para*-Ph), 34.90 (Sn-*C*H$_2$), 34.21 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$-*C*H$_2$), 4.60 (Si(*C*H$_3$)$_3$), 4.47 (Si(*C*H$_3$)$_3$). ^{119}Sn NMR (C_6D_6): δ 118.86. MS CI with methane *m*/*z*: 667.2 (M-CH$_3$). IR (film) cm^{-1}: ν 2921, 2854, 1461, 1377, 1260, 1251, 900, 847, 755, 721, 654. Anal. Calcd for $C_{23}H_{47}ISi_4Sn$ C: 40.53; H: 6.95. Found: C: 40.84; H: 7.22.

(C$_9$H$_{11}$)ISnC(SiMe$_3$)$_2$CH$_2$CH$_2$C(SiMe$_3$)$_2$ (9). A one-necked 100 mL flask fitted with a rubber septum was charged with 157 mg of 2,4,6-triisopropyliodobenzene (0.48 mmol, 1.1 equiv) and 5 mL of mesitylene. A solution containing 200 mg of **1** (0.43 mmol, 1 equiv) and 10 mL of toluene was placed in a gastight syringe equipped with a 20-gauge needle. Then 5 mL of the red stannylene solution was added to the 2,4,6-triisopropyliodobenzene/mesitylene solution at a rate of 8 mL/h using a syringe pump. The last 5 mL was added at 2 mL/h. The solution was stirred for 8 h, yielding a cloudy, white solution containing only the C−H activation product by ^{1}H NMR spectroscopy. The volatiles were removed and heated to 80 °C *in vacuo* to remove the impurities. The remaining white solid was elementally pure (390 mg, 84.9% yield). ^{1}H NMR (C_6D_6): δ 7.14 (s, 2H, *ortho*-Ph), 6.69 (s, 1H, *para*-Ph), 3.33 (s with Sn satellites, $^2J_{Sn-H}$ = 30.0 Hz, 2H, Sn-CH_2), 2.21 (s, 6H, ArCH_3), 2.07 (m, 2H, Sn-C(SiMe$_3$)$_2$-CH_2), 1.90 (m, 2H, Sn-C(SiMe$_3$)$_2$-CH_2), 0.33 (s, 18H, Si(CH_3)$_3$), 0.14 (s, 18H, Si(CH_3)$_3$). ^{13}C NMR (C_6D_6): δ 138.78 (*ipso*-Ph), 137.77 (*meta*-Ph), 127.40 (*ortho*-Ph), 114.94 (*para*-Ph), 36.01 (Sn-*C*H$_2$), 34.64 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$-*C*H$_2$), 21.37 (Ar*C*H$_3$), 4.14 (Si(*C*H$_3$)$_3$), 4.04 (Si(*C*H$_3$)$_3$). ^{119}Sn NMR (C_6D_6): δ 96.59. MS EI *m*/*z*: 695.5 (M − CH$_3$). IR (film) cm^{-1}: ν 2925, 1598, 1463, 1377, 1245, 902, 844. Anal. Calcd for $C_{25}H_{51}$-ISi_4Sn: C: 42.31; H: 7.24. Found: C: 42.31; H: 7.17.

(C$_{15}$H$_{23}$)ISnC(SiMe$_3$)$_2$CH$_2$CH$_2$C(SiMe$_3$)$_2$ (10). A one-necked 100 mL flask fitted with a rubber septum was charged with 156.7 mg (0.47 mmol, 1.1 equiv) of 2,4,6-tri-isopropyliodobenzene and 10 mL of benzene. Stannylene (**1**) (200 mg, 0.43 mmol, 1 equiv) was added in one portion, and the red solution was stirred overnight until the red color disappeared completely. Volatiles were removed *in vacuo*, and the flask was heated to 80 °C via a Kugel-Rohr apparatus to obtain a white solid. (340 mg, 99.3% yield). ^{1}H NMR (C_6D_6): δ 7.17 (s, 2H, *meta*-Ph), 3.05 (m, 2H, *ortho*-C*H*(CH$_3$)$_2$, 2.73 (septet, $^3J_{H-H}$ = 7.0 Hz, *para*-C*H*(CH$_3$)$_2$), 2.23−2.00 (m, 4H, SnC(Si(CH$_3$)$_2$CH_2-CH_2), 1.42 (d, $^3J_{H-H}$ = 6.5 Hz, 6H, *para*-CH(CH_3)$_2$), 1.15 (d, $^3J_{H-H}$ = 7.0 Hz, 12H, *ortho*-CH(CH_3)$_2$, 0.50 (s, 18H, Si(CH_3)$_3$), 0.20 (s, 18H, Si(CH_3)$_3$). ^{13}C NMR (C_6D_6): δ 153.8 (*ipso*-Ph), 151.0 (*ortho*-Ph), 150.2 (*meta*-Ph), 123.6 (*para*-Ph), 38.56 (*ortho*-*C*H(CH$_3$)$_2$), 36.83 (SnC(Si(CH$_3$)$_2$CH_2-*C*H$_2$), 34.53 (*para*-*C*H(CH$_3$)$_2$), 26.20 (*para*-CH(*C*H$_3$)$_2$), 24.33 (*ortho*-CH(*C*H$_3$)$_2$), 5.16 (Si(*C*H$_3$)$_3$), 4.40 (Si(*C*H$_3$)$_3$). ^{119}Sn NMR (C_6D_6): δ −28.67. MS EI *m*/*z*: 779.8 (M − CH$_3$). IR (film)

cm^{-1}: ν 2920, 1461, 1377, 1249, 896, 845. Anal. Calcd for $C_{31}H_{63}ISi_4Sn$: C: 46.91; H: 8.00. Found: C: 46.88; H: 8.01.

(C_6H_{11})ISnC(SiMe$_3$)$_2$CH$_2$CH$_2$C(SiMe$_3$)$_2$ (15 and 16). A one-necked 100 mL flask fitted with a rubber septum was charged with 157 mg of 2,4,6-triisopropyliodobenzene (0.48 mmol, 1.1 equiv) and 5 mL of *trans*-4-methyl-2-pentene. A solution containing 200 mg of **1** (0.43 mmol, 1 equiv) and 10 mL of *trans*-4-methyl-2-pentene was placed in a gastight syringe equipped with a 20-gauge needle. Then 5 mL of the red stannylene solution was added to the 2,4,6-triisopropyliodobenzene/*trans*-4-methyl-2-pentene solution at a rate of 8 mL/h using a syringe pump. The last 5 mL was added at 2 mL/h. The solution was stirred for 8 h, yielding a cloudy, white solution. The volatiles were removed *in vacuo*, and the ^{1}H NMR of the crude mixture indicated 71% primary carbon C−H activation product, 24% tertiary C−H activation product, and 5% oxidative addition product. The resulting solid was recrystallized from pentane at −78 °C to give a white powder (220 mg, 76% yield). **15** ^{1}H NMR (C_6D_6): δ 5.82 (pseudo-dt, 2H, J_{H-H} = 11.5 Hz, J_{H-H} = 1.6 Hz, *H*C═C*H*), 2.81 (m, 3H, C*H*$_3$CH═CH), 2.19 (m, 2H, SnC-(Si(CH$_3$)$_2$C*H*$_2$), 1.82 (m, 2H, SnC(Si(CH$_3$)$_2$C*H*$_2$), 1.65 (s with br Sn satellites, $^3J_{Sn-H}$ = 9.19 Hz, 6H, Sn-C(C*H*$_3$)$_2$), 0.40 (9H, Si(C*H*$_3$)$_3$), 0.39 (9H, Si(C*H*$_3$)$_3$), 0.21 (9H, Si(C*H*$_3$)$_3$), 0.13 (9H, Si(C*H*$_3$)$_3$). ^{13}C NMR (C_6D_6): δ 128.94 (H*C*═*C*H), 35.78 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 35.74 (*C*H$_3$-HC═C), 34.8 ((Sn-*C*(CH$_3$)$_2$), 26.2 (Sn-C(*C*H$_3$)$_2$) 4.78 (Si(*C*H$_3$)$_3$), 4.37 (Si(*C*H$_3$)$_3$), 4.28 (Si(*C*H$_3$)$_3$), 4.25 (Si(*C*H$_3$)$_3$). ^{119}Sn NMR (C_6D_6): δ 169.2. MS EI *m*/*z*: 659.1 (M − CH$_3$). **16** ^{1}H NMR (C_6D_6): δ 5.77 (m, 1H, *H*C═C), 5.56 (m, 1H, C═C*H*), 2.58 (d with Sn satellites, $^3J_{H-H}$ = 8.4 Hz, $^2J_{Sn-H}$ = 23.6 Hz, 2H, Sn-C*H*$_2$), 2.32 (septet, $^3J_{H-H}$ = 6.8 Hz, (CH$_3$)$_2$-C*H*), 2.10 (m, 2H, SnC(Si(CH$_3$)$_2$C*H*$_2$), 1.86 (m, 2H, SnC(Si(CH$_3$)$_2$C*H*$_2$), 1.1 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, (C*H*$_3$)$_2$-CH), 0.37 (s, 18H, Si(C*H*$_3$)$_3$), 0.15 (s, 18H, Si(C*H*$_3$)$_3$). ^{13}C NMR (C_6D_6): δ 139.6, 123.5 (H*C*═CH), 35.0 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$-*C*H$_2$), 32.1 (Sn-*C*H$_2$), 23.9 ((CH$_3$)*C*H), 23.2 ((*C*H$_3$)CH), 4.51 (Si(*C*H$_3$)$_3$), 4.49 (Si(*C*H$_3$)$_3$) ^{119}Sn NMR (C_6D_6): δ 132.0. MS EI *m*/*z* of mixture: 659.1 (M − CH$_3$). IR (film) of mixture cm^{-1}: ν 2954, 2866, 1464, 1406, 1251, 901, 843. Anal. Calcd for the mixture of $C_{22}H_{51}ISi_4Sn$: C: 39.23; H: 7.63. Found: C: 38.97; H: 7.74.

(C_6H_9)ISnC(SiMe$_3$)$_2$CH$_2$CH$_2$C(SiMe$_3$)$_2$ (17 and 18). A one-necked 100 mL flask fitted with a rubber septum was charged with 235.1 mg of 2,4,6-triisopropyliodobenzene (0.71 mmol, 1.1 equiv) and 2 mL of 4-methyl-2-butyne. A solution containing 300 mg of **1** (0.43 mmol, 1 equiv) and 10 mL of 4-methyl-2-butyne was placed in a gastight syringe equipped with a 20-gauge needle. Then 5 mL of the red stannylene solution was added to the 2,4,6-triisopropyliodobenzene/mesitylene solution at a rate of 8 mL/h using a syringe pump. The last 5 mL was added at 2 mL/h. The solution was stirred for 8 h, yielding a cloudy, white solution containing only the C−H activation products. The volatiles were removed and heated to 80 °C *in vacuo* to remove the impurities. The remaining white solid was elementally pure (420 mg, 96.6% yield). Column chromatography was performed with hexane to yield pure tertiary product (140 mg, 32.2% yield). The primary C−H activation product decomposed on the column. **17** ^{1}H NMR (C_6D_6): δ 2.20 (s with br Sn satellites, $^2J_{Sn-H}$ = 29.6 Hz, 3H, C≡C-C*H*$_3$), 2.11 (m, 2H, SnC(Si(CH$_3$)$_2$C*H*$_2$), 1.97 (m, 2H, SnC(Si(CH$_3$)$_2$C*H*$_2$), 1.59 (s with br Sn satellites, $^3J_{Sn-H}$ = 17.6 Hz, 6H, Sn-C-(C*H*$_3$)$_2$), 0.42 (s, 18H, Si(C*H*$_3$)$_3$), 0.22 (s, 18H, Si(C*H*$_3$)$_3$). ^{13}C NMR (C_6D_6): δ 98.1 (Sn-C(CH$_3$)$_2$-*C*≡C), 91.7 (Sn-C-C≡*C*), 35.0 (Sn-C-(SiMe$_3$)$_2$-*C*H$_2$-*C*H$_2$), 22.2 (Sn-*C*(CH$_3$)$_2$), 21.6 (C≡*C*CH$_3$), 21.1 ((*C*H$_3$)$_2$*C*-C≡C), 4.49 (Si(C*H*$_3$)$_3$), 4.28 (Si(C*H*$_3$)$_3$). ^{119}Sn NMR (C_6D_6): δ 57.9. MS EI *m*/*z*: 658.0 (M − CH$_3$). Anal. Calcd for $C_{22}H_{49}ISi_4Sn$: C: 39.35 ; H: 7.35. Found: C: 39.32; H: 7.44.

18 ^{1}H NMR (C_6D_6): δ 2.56 (m, 1H, (CH$_3$)$_2$-C*H*-C≡C), 2.44 (d with br Sn satellites, $^2J_{H-H}$ = 2.0 Hz, $^2J_{Sn-H}$ = 23.2 Hz, 2H, C*H*$_2$), 2.13−1.85 (m, 4H, SnC(Si(CH$_3$)$_2$C*H*$_2$-C*H*$_2$), 1.18 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 0.39 (s, 18H, Si(C*H*$_3$)$_3$), 0.20 (s, 18H, Si(C*H*$_3$)$_3$). ^{13}C NMR (C_6D_6): δ 88.8 (Sn-CH$_2$-*C*≡C), 77.9 (Sn-CH$_2$-C≡*C*), 34.8 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$-*C*H$_2$), 23.9 (Sn-CH$_2$), 21.9 (*C*H(CH$_3$)$_2$), 21.6 (CH(*C*H$_3$)$_2$), 4.50 (Si(C*H*$_3$)$_3$), 4.33 (Si(C*H*$_3$)$_3$). ^{119}Sn NMR (C_6D_6): δ 104.0. IR of the mixture (film) cm^{-1}: ν 2951, 1941, 1445, 1360, 1320, 1248, 958, 857, 756, 680, 654. Anal. Calcd for mixture of primary and tertiary product for $C_{22}H_{49}ISi_4Sn$: C: 39.35 ; H: 7.35. Found: C: 39.53; H: 7.52. MS CI of **17** and **18** mixture with methane *m*/*z*: 658 (M − CH$_3$)

($C_{18}H_{29}$)BrSnC(SiMe$_3$)$_2$CH$_2$CH$_2$C(SiMe$_3$)$_2$ (19). A one-necked 100 mL flask fitted with a rubber septum was charged with 154.4 mg (0.47 mmol, 1.1 equiv) of 2,4,6-tri-*tert*-butylbromobenzene and 40 mL of pentane. Stannylene (**1**) (200 mg, 0.43 mmol, 1 equiv) was added in one portion, and the red solution was stirred for three days until the red color disappeared completely. Volatiles were removed, and a white solid was recrystallized from pentane at −78 °C (250 mg, 69% yield). ^{1}H NMR (C_6D_6): δ 7.50 (s, 2H, *ortho*-Ar), 7.38 (s, 1H, *para*-Ar), 2.44 (s with br Sn satellites, $^3J_{Sn-H}$ = 15.6 Hz, 2H, Sn-C*H*$_2$), 2.12 (m, 2H, SnC(Si(CH$_3$)$_2$C*H*$_2$), 1.92 (m, 2H, SnC(Si(CH$_3$)$_2$C*H*$_2$), 1.02 (s, 6H, Sn-CH$_2$-C-(C*H*$_3$)$_2$), 1.36 (s, 18H, Ar-(C(C*H*$_3$)$_3$)$_2$, 0.36 (s, 18H, Si(C*H*$_3$)$_3$), 0.18 (s, 18H, Si-(C*H*$_3$)$_3$). ^{13}C NMR (C_6D_6): δ 151.70 (*ipso*-Ar), 150.84 (*meta*-Ar), 120.6 (*ortho*-Ar), 120.3 (*para*-Ar), 44.40 (Sn-*C*H$_2$), 40.68 (Sn-CH$_2$-*C*(CH$_3$)$_2$Ar), 35.61 (Ar-(*C*(CH$_3$)$_3$)$_2$), 34.95 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$-CH$_2$), 32.54 (Sn-CH$_2$-C(*C*H$_3$)$_2$Ar), 32.22 (Ar-(C(*C*H$_3$)$_3$)$_2$), 4.69 (Si(*C*H$_3$)$_3$), 4.61 (Si(*C*H$_3$)$_3$). ^{119}Sn NMR (C_6D_6): δ 175.7. MS CI with methane *m*/*z*: 775.5 (M − CH$_3$).

(C_6H_7O)ISnC(SiMe$_3$)$_2$CH$_2$CH$_2$C(SiMe$_3$)$_2$ (20 and 21). A one-necked 100 mL flask fitted with a rubber septum was charged with 79 mg (0.24 mmol, 1.1 equiv) of 2,4,6-tri-isopropyliodobenzene and 3 mL of 2,3-dimethylfuran. Stannylene (**1**) (100 mg, 0.22 mmol, 1 equiv) dissolved in 2 mL of 2,3-dimethylfuran was added slowly with a syringe, and the red solution was stirred overnight until the red color disappeared completely. Volatiles were removed *in vacuo*, and the flask was heated to 80 °C via a Kugel-Rohr apparatus to obtain a white solid (130 mg, 87% yield) composed of 2-methyl and 3-methyl C−H activation products and 5% oxidative addition product. Attempts to purify the C−H activation products via crystallization or column chromatography failed.

20 ^{1}H NMR (C_6D_6): δ 7.07 (d, $^3J_{H-H}$ = 2.0 Hz, 1H, O-C*H*), 6.02 (d, $^3J_{H-H}$ = 2.0 Hz, 1H, O-CH-C*H*), 3.05 (s with br Sn satellites, $^2J_{Sn-H}$ = 16 Hz, 2H, Sn-C*H*$_2$), 2.08−1.90 (m, 4H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$-C*H*$_2$), 0.37 (s, 18H, Si(C*H*$_3$)$_3$, 0.22 (s, 18H, Si(C*H*$_3$)$_3$). ^{13}C NMR (C_6D_6): δ 149. 3, 140.2 (O*C*═C), 116.3, 114.0 (OC═*C*), 35.01 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$-*C*H$_2$), 24.87 (Sn-*C*H$_2$), 4.50 (Si(C*H*$_3$)$_3$), 4.46 (Si(C*H*$_3$)$_3$). ^{119}Sn NMR (C_6D_6): δ 115.0. IR of the mixture (film) cm^{-1}: ν 2855, 1458, 1377, 1261, 1250, 900, 848. MS of **20** and **21** mixture (CI with methane) *m*/*z*: 671.5.

21 ^{1}H NMR (C_6D_6): δ 7.08 (d, $^3J_{H-H}$ = 2 Hz, 1H, O-C*H*), 6.63 (d, $^3J_{H-H}$ = 2 Hz, 1H, O-CH-C*H*), 2.89 (s with br Sn satellites, $^2J_{Sn-H}$ = 18 Hz, 2H, Sn-C*H*$_2$), 2.13−1.85 (m, 4H, SnC(Si(CH$_3$)$_2$C*H*$_2$-C*H*$_2$), 0.35 (s, 18H, Si(C*H*$_3$)$_3$, 0.13 (s, 18H, Si(C*H*$_3$)$_3$. ^{13}C NMR (C_6D_6): δ 148.4, 140.8 (O*C*═C), 117.1, 112.7 (OC═*C*), 33.7 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$-*C*H$_2$), 24.6 (Sn-C*H*$_2$), 4.58 (Si(C*H*$_3$)$_3$), 4.56 (Si(C*H*$_3$)$_3$). ^{119}Sn NMR (C_6D_6): 125.1.

(C_9H_{11})ISnC(SiMe$_3$)$_2$CH$_2$CH$_2$C(SiMe$_3$)$_2$ (22). A one-necked 100 mL flask fitted with a rubber septum was charged with 124 mg (0.51 mmol, 1.1 equiv) of 2,4,6-trimethyliodobenzene and 20 mL of benzene. Stannylene (**1**) (233 mg, 0.50 mmol, 1 equiv) was added in one portion, and the red solution was stirred overnight until the red color disappeared completely. Volatiles were removed *in vacuo*, and the flask was heated to 80 °C via a Kugel-Rohr apparatus to obtain a white solid. (333 mg, 93%

yield). ^{1}H NMR (C_6D_6): δ 6.67 (s, 2H, *meta*-Ph), 2.60 (s, 6H, *ortho*-CH_3), 2.21−1.99 (m, 4H, SnC(Si(CH$_3$)$_2$CH_2-CH_2), 2.07 (s, 3H, *para*-CH_3), 0.49 (s, 18H, Si(CH_3)$_3$), 0.19 (s, 18H, Si(CH_3)$_3$). ^{13}C NMR (C_6D_6): δ 149.8 (*ipso*-Ar), 142.1 (Ar), 139.7 (Ar), 128.9 (*meta*-Ar), 36.49 (SnC(Si(CH$_3$)$_2$CH_2-CH_2), 29.55 (*ortho*-CH_3), 21.27 (*para*-CH_3), 5.08 (Si(CH_3)$_3$), 4.02 (Si(CH_3)$_3$). ^{119}Sn NMR (C_6D_6): δ −3.50. MS EI *m*/*z*: 695.1 (M − CH$_3$). IR (film) cm^{-1}: ν 2918, 1458, 1377, 1251, 1071, 894, 847, 756.

(C$_7$H$_7$O)ISnC(SiMe$_3$)$_2$CH$_2$CH$_2$C(SiMe$_3$)$_2$ (23). A one-necked 50 mL flask fitted with a rubber septum was charged with 28 mg (0.12 mmol, 1.1 equiv) of 4-iodoanisole and 15 mL of benzene. Stannylene (**1**) (50 mg, 0.11 mmol, 1 equiv) was added in one portion, and the red solution was stirred overnight until the red color disappeared completely. Volatiles were evaporated, and ^{1}H and ^{13}C NMR spectra of pure oxidative product were obtained. ^{1}H NMR (C_6D_6): δ 7.87 (d with Sn satellites, $^3J_{H-H}$ = 8.5 Hz, $^2J_{Sn-H}$ = 34.0 Hz, 2H, *ortho*-Ph), 6.74 (d, $^3J_{H-H}$ = 8.5 Hz, 2H, *meta*-Ph), 3.19 (s, 3H, *para*-OCH_3), 2.19−2.16 (m, 2H, SnC(Si-(CH$_3$)$_2$CH_2-CH_2), 2.04−2.00 (m, 2H, SnC(Si(CH$_3$)$_2$CH_2-CH_2), 0.47 (s, 18H, Si(CH_3)$_3$), 0.20 (s, 18H, Si(CH_3)$_3$). ^{13}C NMR (C_6D_6): δ 161.24 (Ph), 138.11 (Ph), 137.42 (Ph), 114.99 (Ph), 54.90 (OCH_3), 35.14 (SnC(Si(CH$_3$)$_2$CH$_2$-*C*H$_2$), 4.70 (Si(CH_3)$_3$).

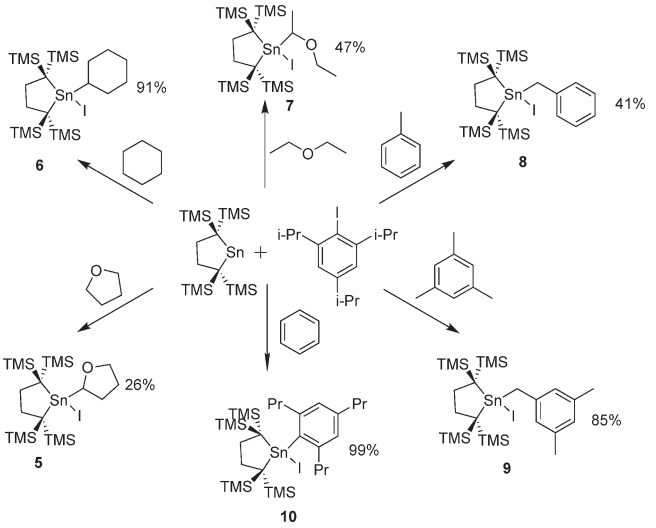
(C$_7$H$_4$N)ISnC(SiMe$_3$)$_2$CH$_2$CH$_2$C(SiMe$_3$)$_2$ (24). A one-necked 10 mL flask fitted with a rubber septum was charged with 28 mg (0.12 mmol, 1.1 equiv) of 4-iodobenzonitrile and 20 mL of benzene. Stannylene (**1**) (50 mg, 0.11 mmol, 1 equiv) was added in one portion, and the red solution was stirred overnight until the red color disappeared completely. Volatiles were evaporated and ^{1}H and ^{13}C spectra of pure oxidative product were obtained. ^{1}H NMR (C_6D_6): δ 7.68 (d with Sn satellites, $^3J_{H-H}$ = 7.5 Hz, $^2J_{Sn-H}$ = 30.5 Hz, 2H, *ortho*-Ph), 6.85 (d, $^3J_{H-H}$ = 8.0 Hz, 2H, *meta*-Ph), 2.11−2.06 (m, 2H, SnC(Si(CH$_3$)$_2$CH_2-CH_2), 1.96−1.9 (m, 2H, SnC(Si(CH$_3$)$_2$CH_2-CH_2), 0.39 (s, 18H, Si(CH_3)$_3$), 0.07 (s, 18H, Si(CH_3)$_3$). ^{13}C NMR (C_6D_6): δ 152.96 (*C*N), 136.91 (*ipso*-Ph), 131.86 (*para*-Ph), 118.52 (*ortho*-Ph), 114.09 (*meta*-Ph), 35.0 (SnC(Si(CH$_3$)$_2$CH$_2$-*C*H$_2$), 4.64 (Si(CH_3)$_3$), 4.49 (Si(CH_3)$_3$).

Results and Discussion

C−H Activation of Alkanes, Arenes, and Ethers. The reaction of **1**/2,4,6-triisopropyliodobenzene with cyclohexane, diethyl ether, tetrahydrofuran (THF), toluene, and mesitylene yielded C−H activation products as illustrated in Scheme 3. The high degree of solubility of many of the products contributed to lower isolated yields (26−99%) despite the reactions proceeding quantitatively, as indicated by ^{1}H NMR spectroscopy. The reactivity observed for cyclohexane and the regioselective activation of the weaker C−H bonds α to ether oxygen for **1** was consistent with the reactivity previously observed for Sn[N(SiMe$_3$)$_2$]$_2$ (**11**), Ge[CH(SiMe$_3$)$_2$]$_2$ (**12**), Ge[N(SiMe$_3$)$_2$]$_2$ (**13**), and SiN(^{t}Bu)CH$_2$CH$_2$N(^{t}Bu) (**14**).[14,15,18] The observation of clean C−H activation for toluene and mesitylene had not previously been observed for this chemistry. Typically, oxidative addition of the aryl halide to the germylene or silylene was the primary or only product observed for these substrates. The observation of arene C−H activation products using using **1**/2,4,6-triisopropyliodobenzene appears to result from slowing the formation of the oxidative-addition product when employing this very sterically encumbered aryl halide coupled with the differing stereoelectronic properties of **1** as compared to **11**−**14**.

The reaction of *trans*-4-methyl-2-pentene with **1**/aryl halide showed a preference for primary over tertiary C−H activation, concomitant with a decrease in oxidative addition, as a function of increased aryl halide steric bulk (Scheme 4). The statistically corrected relative rates of 3°/1° activation varied from 4.7 for iodobenzene and 4-iodoanisole, which contain H at the *ortho* position, to 1.1 when isopropyl groups were present in the *ortho* position. The C−H activation of 4-methyl-2-pentyne followed a similar trend for an increase in primary activation and a decrease in oxidative-addition product as a function of increasing aryl halide steric bulk (Scheme 5). In this case, the statistically correct relative rates for 3°/1° activation ranged from 15 to 4. In an effort to further increase the amount of primary activation, 2,6-dimesityliodobenzene was synthesized;[26] however, this aryl halide actually gave the largest amount of tertiary activation observed and little improvement in the amount of primary activation. It was effective at eliminating the formation of the oxidative-addition product. Possible reasons for this aryl halide not following the anticipated trend in steric bulk may be the ability the mesityl rings to rotate out of the way and/or the electronic effect of attaching the two mesityl rings to the parent aryl halide ring. Finally, 2,4,6-tri-*tert*-butyliodobenzene was also employed in an attempt to maximize primary activation. For this aryl halide, only C−H activation of the *ortho* ^{t}Bu groups on the aryl ring was observed regardless of substrate choice (Scheme 6).

Scheme 3. C−H Activation of Alkanes, Arenes, and Ethers Proceeds Quantitatively with 1 and 2,4,6-Triisopropylbenzene As Measured by ^{1}H NMR Spectroscopy[a]



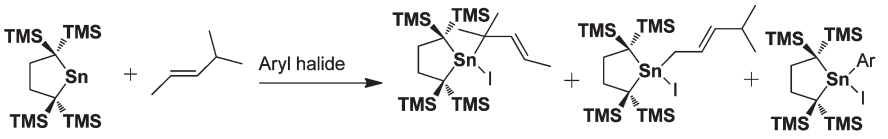
[a] When the reaction is performed in benzene, oxidative addition occurs. Isolated yields are indicated for each product.

As a more stringent test of regioselectivity, 2,3-dimethylfuran was employed as a substrate. C−H activation routes employing this substrate could offer an alternative path to natural products such as rose furan.[27] In this case, employing aryl halides of increasing bulk served to minimize formation of the oxidative-addition product and give up to a factor of 2.6 preference for the methyl group attached to the carbon α to the ether oxygen. Unfortunately, our attempts to cross-couple this tin compound to form rose furan were not successful (Scheme 7).

Effects of Aryl Halide Substitution on the Hydrogen Atom Transfer Reaction. In reactions involving hydrogen atom transfer, the factors that control tertiary/secondary/primary

(26) Schiemenz, B.; Power, P. P. *Organometallics* **1996**, *15*, 958–964.
(27) Marshall, J. A.; DuBay, W. J. *J. Org. Chem.* **1993**, *58*, 3602–3603.

Scheme 4. A Degree of Regiochemical Control Can Be Obtain for the Reaction with *trans*-4-Methyl-2-pentene When the Steric Bulk of the Aryl Halide Is Varied[a]

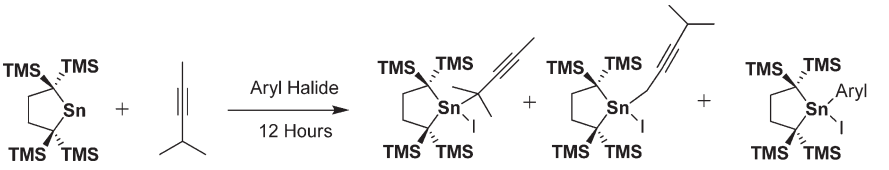


1 15 16

Aryl Halide	%	%	%	3°/1°
Iodobenzene	38	24	38	4.7
2,4,6-trimethyl iodobenzene	29	44	27	2.0
2,4,6-triisopropyl-iodobenzene	26	69	5	1.1
4-iodoanisole	39	25	36	4.7
4-iodobenzonitrile	complicated mixture			

[a] The selectivities indicated were determined by ^{1}H NMR spectroscopy.

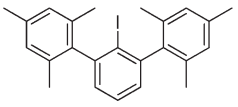
Scheme 5. A Degree of Regiochemical Control Can Be Obtain for the Reaction with 4-Methyl-2-pentyne When the Steric Bulk of the Aryl Halide Is Varied[a]



17 18

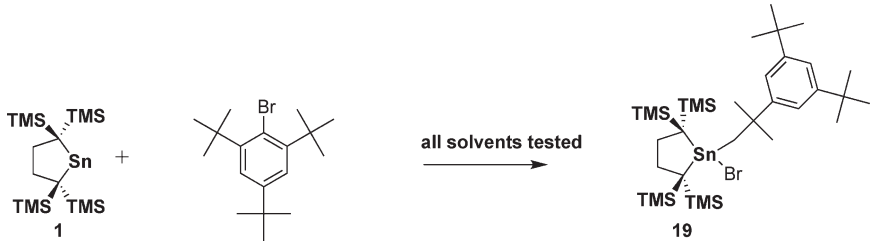
Aryl Halide	%	%	%	3°/1°
Iodobenzene	67	13	20	15
2,4,6-trimethyl-iodobenzene	58	35	7	5
2,4,6-triisopropyl-iodobenzene	39	53	8	4
2,6-mesityl-iodobenzene	83	17	0	15
4-iodoanisole	72	16	12	14
4-iodo-benzonitrile	74	15	11	15

2,6-mesityl-iodobenzene =



[a] The selectivities indicated were determined by ^{1}H NMR spectroscopy.

Scheme 6. 2,4,6-*tert*-Butylbromobenzene Undergoes Intermolecular C−H Activation Regardless of the Choice of Solvent



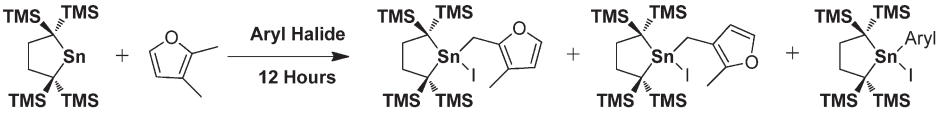
1 19

C−H bond selectivity are the amount of hydrogen atom transfer in the transition state, charge separation in the transition state, and co-linearity of the incipient radical with the π system.[28] The first two of these effects work to increase the selectivity toward the tertiary C−H bond. When a significant amount of hydrogen atom transfer is involved in the transition state, the bond dissociation energies of C−H bonds become important. If some charge separation occurs in the transition state, the polar effects favor the partial formation of a tertiary carbocation over a secondary or primary carbocation. Previous studies have determined that the co-linearity condition becomes difficult to satisfy when the steric bulk of the aryl halide is increased. In this case the steric effects influence tertiary/secondary/primary selectivity in a direction opposite that predicted by thermodynamic and polar effects.[28]

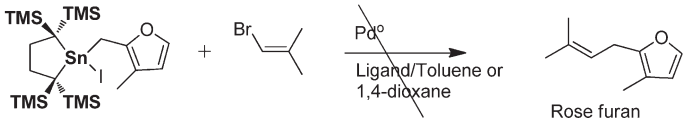
The statistically averaged tertiary versus primary selectivity observed in reactions of the phenyl radical precursor phenylazotriphenylmethane (PAT) with toluene/triisopropylbenzene was determined to be 9.7.[28] Our results in the reaction with *trans*-4-methyl-2-pentene and 4-methyl-2-pentyne and iodobenzene/**I**, Schemes 4 and 5, do not grossly vary

(28) Baciocchi, E.; D'Acunzo, F.; Galli, C.; Lanzalunga, O. *J. Chem. Soc., Perkin Trans. 2* **1996**, 133–140.

Scheme 7. Regiochemistry of C−H Activation of 2,3-Dimethyl Furan Can Be Controlled by Varying the Bulk of the Aryl Halide[a]



Aryl Halide	%	%	%
Iodobenzene	40	20	40
2,4,6-trimethyl-iodobenzene	61	26	13
2,4,6-triisopropyl-iodobenzene	67	26	8



[a] Utilization of this C−H activation product in cross-coupling reactions was not successful. The selectivities indicated were determined by ^{1}H NMR spectroscopy.

from the PAT values. The *trans*-4-methyl-2-pentene tertiary/primary selectivity (4.7) with iodobenzene/**I** is lower than the PAT value, while the value for 4-methyl-2-pentyne (15) selectivity with iodobenzene/**I** is higher.

The energy of formation for the tertiary versus primary radicals for *trans*-4-methyl-2-pentene and 4-methyl-2-pentyne was calculated using density functional theory (B3LYP, 6-31G*). The difference in bond dissociation energies was calculated to be 6.7 kcal/mol for 4-methyl-2-pentyne. The value for *trans*-4-methyl-2-pentene with the same method was calculated to be 6.0 kcal/mol. This translates into a roughly 3-fold increase for tertiary/primary selectivity with 4-methyl-2-penyne as compared to *trans*-4-methyl-2-pentene, as calculated using the Arrhenius equation. This agrees with our experimental results discussed above, 15 for 4-methyl-2-pentyne versus 4.7 for *trans*-4-methyl-2-pentene.

Despite this good agreement with experimental ratios when considering the delta in bond dissociation energy values between 4-methyl-2-pentyne and *trans*-4-methyl-2-pentene, when considering the relative selectivity between competing sites within a molecule good agreement with calculated values is not obtained. The 6.7 kcal/mol difference should translate into a $\sim 8 \times 10^4$ rate difference for the tertiary versus primary C−H site. By way of comparison with other systems, the tertiary/primary selectivities for NBS and $Br_2/h\nu$ are 58 and 37, respectively. The EL_2/PhX radical species involved in the C−H activation reaction are highly reactive and more comparable to ^{t}BuO radical or autoxidation by O_2, which have tertiary/primary selectivities of 6.8 and 13, respectively.[28] This suggests that there is relatively little C−H bond breakage in the transition state in C−H activation with iodoarene/**1**. Our general conclusion is that the EL_2/PhX radical species involved here are not very sensitive to bond dissociation energies, although the differential reactivity between different molecules does track well with the bond dissociation energy differences.

Previously, we measured the primary isotope effects of the C−H activation reaction with different divalent group 14/iodoarene species. The primary kinetic isotope effect (KIE) for the reaction of $\overline{SiN(^tBu)CH_2CH_2N(^tBu)}$ (**14**) with Et_2O/Et_2O-d_{10} was found to be 5.7 ± 0.1.[18] The primary KIE for the reaction of $Ge[CH(SiMe_3)_2]_2$ (**12**) and $Ge[N(SiMe_3)_2]_2$ (**13**) with THF/THF-d_8 was found to be 5.0 ± 0.2 and 4.1 ± 0.2, respectively.[14] On the basis of the value found for phenyl radical generated by PAT THF/THF-d_8 (4.2 ± 0.2), we have argued against formation of a common intermediate in these reactions, including the phenyl radical. The primary KIE reported herein for the reaction of tri-isopropyliodobenzene and **1** in toluene/toluene-d_7 was found to be 4.9 ± 0.5, as measured by ^{1}H NMR spectroscopy. This is consistent with the previously reported values. The range of KIE values indicates that the EL_2/PhX radical intermediate involved is dependent on the exact nature of the group 14 reagent, the aryl halide, and the solvent. This is logical since polar effects and co-linearity conditions work in the opposite direction to increase or decrease tertiary/primary selectivity, respectively. With *trans*-4-methyl-2-pentene and 4-methyl-2-pentyne, co-linearity with the π system becomes important, as evidenced by switch in the regiochemistry when the steric bulk of the aryl halide *ortho* substituents is increased.

When the *ortho* substituents are increased from hydrogen to methyl, there is a decrease in tertiary/primary selectivity by a factor of 2.3 for *trans*-4-methyl-2-pentene and 3-fold for 4-methyl-2-pentyne, Schemes 4 and 5, respectively. With isopropyl substitution there is 4.2-fold decrease in tertiary/primary selectivity with the alkene and a 3.7-fold decrease for the alkyne. It should be noted that with the increase of steric bulk in *ortho* positions there is a drop in the amount of oxidative addition product concomitant with the increase of primary/tertiary selectivity.

Conclusion

We have demonstrated C−H activation of simple alkanes, ethers, and aromatics with **1** and aryl halides in excellent yield. The product distribution and regiochemistry of C−H activation can be controlled to an extent with *ortho* substitution on the aryl halide. Oxidative addition product can be decreased by using more sterically bulky/electron-donating substituents. In substrates with alkenes and alkyne functionalities possessing primary and tertiary C−H bonds, the yield of primary C−H activation can be increased by increasing the steric bulk on the aryl halide. Reactions employing 2,4,6-tri-*tert*-butyliodobenzene result only in the CH activation of the *ortho tert*-butyl groups.