C-H ACTIVATION AND CYCLIZATIONS USING STANNYLENES

by

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DEDICATION

I dedicate this work to my parents, Sefika and Abdurahman Kavara, for instilling in me the values of integrity and perseverance and for their selfless efforts to give me the best educational opportunities.

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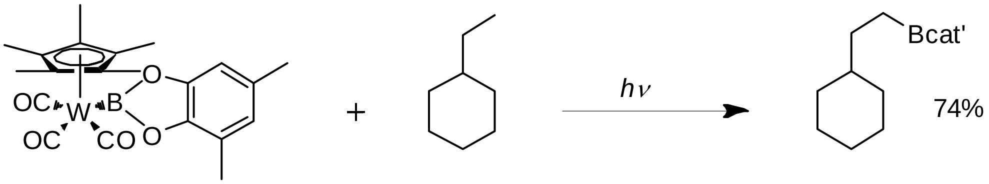
Chapter 1. Introduction

1.1 Introduction to C-H activation

C-H activation is one of the important current foci of synthetic chemistry.[1-5] Waste reduction, synthetic efficiency and utilization of cheap resources such as methane or petroleum are aspects that render C-H activation attractive to chemists. C-H activation protocols seek to sidestep the multistep introduction of leaving groups that are typically required in classical synthetic routes. In an organic molecule that incorporates a multitude of different C-H bonds the *selectivity* of activation becomes paramount. Selectivity principle is also important when we consider that the product of C-H activation needs to be less reactive with reagent/catalyst than the starting material. This is particularly true of inexpensive alkane C-H activation. In the literature of C-H activation, the distinction is often made between metal mediated reactions and methods where C-H bond is abstracted with a radical source. Metalloradical C-H activation represents a field where this distinction is blurred.[6]

1.2 Transition Metal Mediated C-H activation

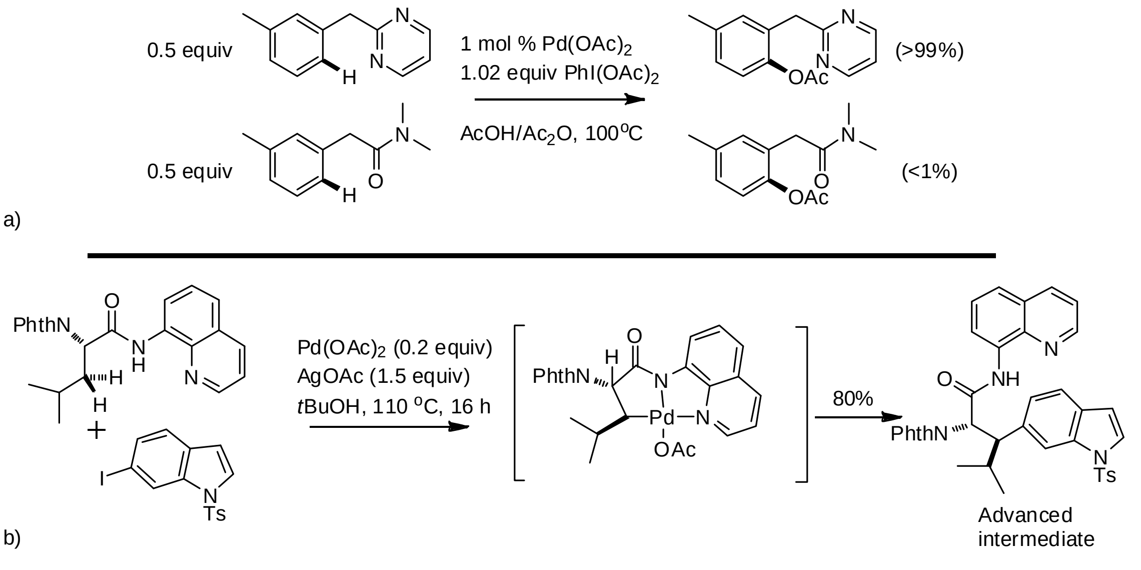
Established metal mediated C-H activation manifolds include oxidative addition by late tranisition metals, sigma bond methathesis by early transition metals, 1,2-addition to metal-nonmetal double bond and electrophilic activation of alkanes with late transition metal ions.[1] These transition metal mediated pathways generally exhibit selectivity opposite that of predicted by homolytic bond strengths. The borylation of alkanes by Waltz and Hartwig proceeds through oxidative addition pathway and exhibits 1°>2°>3° selectivity, Scheme 1.1.


OC
W
B
O
OC
CO
O
+
hν
Bcat'
74%

Scheme 1.1 Primary carbon-hydrogen bond selectivity is favored in borylation by Waltz and Hartwig.

Unique C-H activations have been achieved by complementing metals' inherent selectivity with secondary interactions such as metal ligation to a basic functional group and the use of sterically bulky ligands.

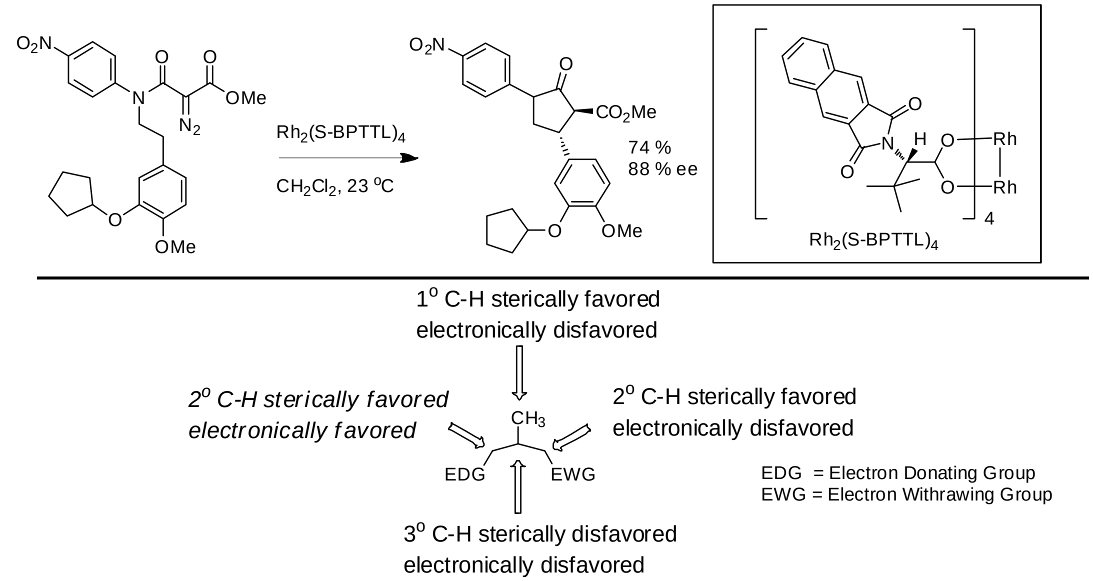
Scheme 1.2 a) Representative findings of Desai et al. b) Cyclometalation with Pd(II) is a crucial step in the synthesis of Celogentin B by Feng and Chen.


0.5 equiv
N
N
H
1 mol % Pd(OAc)2
1.02 equiv PhI(OAc)2
AcOH/Ac2O, 100°C
OAc
(>99%)
0.5 equiv
N
O
H
(<1%)
a)
PhthN
O
N
H
H
H
N
+
I
N
Ts
Pd(OAc)2 (0.2 equiv)
AgOAc (1.5 equiv)
tBuOH, 110 °C, 16 h
H
PhthN
O
N
Pd
N
OAc
80%
N
O
NH
PhthN
N
Ts
Advanced intermediate
b)

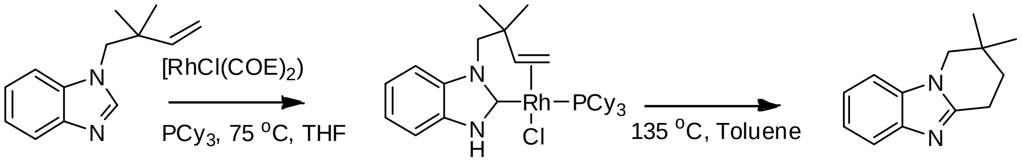
Cyclometallation by the use of a directing group has been one of the successful approaches and great advances have been made in understanding this manifold and exploiting it for natural product synthesis.[4,7] Through the series of mechanistic studies Desai et al. have determined the ordering of functionalities according to their chelating ability of Pd(II) species in cyclometallation reaction followed by acetoxylation via Pd(IV), Scheme 1.2a.[8] Stereoselective C-H activation that terminates with an arylation reaction has been used by Feng and Chen in their synthesis of Celogentin C, Scheme 1.2b.[9] These examples illustrate that C-H activation reactions are carried out for the purposes of the functionalization with a heteroatom moiety or the formation of carbon-carbon bonds.[10-11]

Steric effects of bulky chiral ligands have been harnessed via metal carbenoids by Davies et al.[12] Davies has demonstrated the direct syntheses of a variety of pharmaceutical agents including sertraline (Zoloft), threo-methylphenidate (Ritalin) and (R)-Rolipram, among others, and delineated selectivity principles of the Rhodium carbenoids toward different C-H bonds in complex organic molecules, Scheme 1.3.

Great value is posited in discovering new manifolds that have unique selectivity toward carbon-hydrogen bonds. Recently, Ellman et al. have accomplished benzimidazole functionalization via a novel manifold where a N-Heterocyclic-carbene Rhodium intermediate is obtained via intermolecular C-H activation, Scheme 1.4.[13]


O2N
O
O
N
OMe
N2
OMe
O
Rh2(S-BPTTL)4
CH2Cl2, 23 °C
O2N
O
CO2Me
74 %
88 % ee
O
OMe
O
N
H
O
Rh
Rh
O
4
Rh2(S-BPTTL)4
1° C-H sterically favored
electronically disfavored
2° C-H sterically favored
electronically favored
CH3
2° C-H sterically favored
electronically disfavored
EDG
EWG
EDG = Electron Donating Group
EWG = Electron Withrawing Group
3° C-H sterically disfavored
electronically disfavored

Scheme 1.3 a) Synthesis of an intermediate via C-H activation toward pharmaceutical agent (R)-Rolipram by Davies b) Selectivity principles delineated by Davies in Rhodium catalyized carbenoid insertion reactions with different C-H bonds.

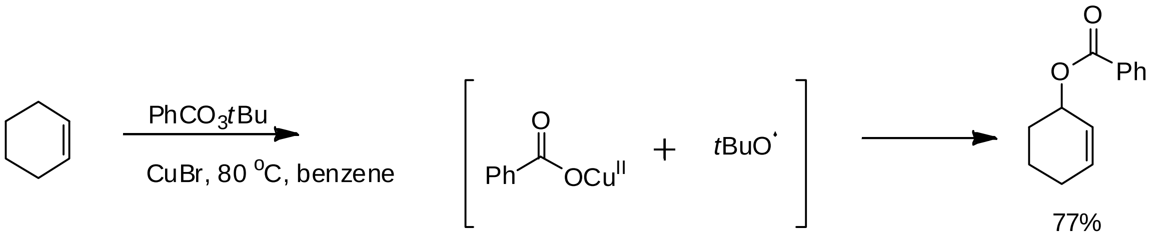

N
N
[RhCl(COE)2)
PCy3, 75 °C, THF
N
N
H
Rh
PCy3
Cl
135 °C, Toluene
N
N

Scheme 1.4. Novel Rhodium catalyzed method for C-H activation via N-Heterocyclic carbene by Bergman et al.

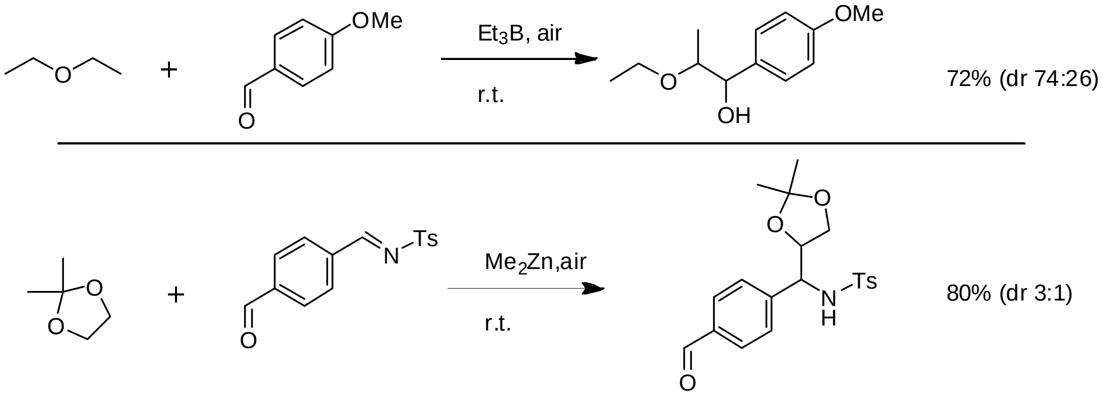
1.3 Radical Mediated C-H Activation

Despite their reputed unpredictability, radical reactions have become an irreplaceable part of organic synthesis and substantial progress has been achieved in this area, especially in enantioselective methods.[14] Perhaps the earliest example of radical mediated C-H functionalization is allylic or benzylic bromination.[15] An environmentally friendly version of this reaction that incorporates H_2O_2/HBr and sunlight was recently introduced by Podgorsek et al.[16] The Kharasch-Sosnovsky reaction represents an excellent method for selective oxidation of alkenes and alkynes using *tert*-butoxy radicals, Scheme 1.5.[17] The C2-symmetric ligands and a catalytic amount of Copper salts have been used to render this reaction enantioselective.[18]

Scheme 1.5 Kharasch-Sosnovsky functionalization using *t*-Butoxy radical as an intermediate.



Conditions using Et_3B/air or Me_2Zn/air to generate ethyl or methyl radicals, respectively, have been used to abstract the α C-H bonds of ethers, acetals, tertiary amides, ureas and amines.[19-22] In this reaction manifold, robust C-C bond formation is realized when the formed radicals are captured with aldehydes, imines or isocyanates. However, the diastereoselectivity of this reaction remains an obstacle, Scheme 1.6. Other radicals that have been extensively studied include fluoro alkyl radicals, and vinyl triflones have been used for stereospecific C-H alkenylation by Fuchs.[23-24]

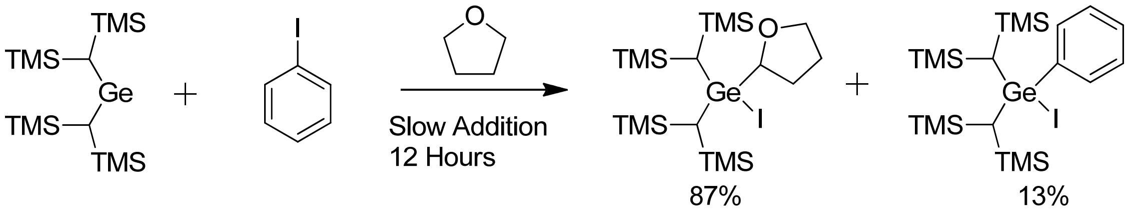


Scheme 1.6 Examples of radical abstraction of ether C-H bonds followed by capture with electrophiles.

1.4 C-H Activation with Divalent Group 14 and Aryl Halide Combination

Our lab has first reported C-H activation of alkanes and ethers utilizing stable, heavy, divalent group 14 species/aryl halide reagent combinations, Scheme 1.7.[25] Germylenes that were used in this study are stabilized by bulky ligands and exist as dimers in the solid state but dissociate into monomers in solution.[26] Involvement of a phenyl radicaloid intermediate (See Schemes 1.9 and 5.8 for details) that abstracts the homolytically weakest hydrogen from the solvent/substrate has been implicated in this manifold. Radical-like selectivity was observed thus tertiary and α to oxygen C-H bonds were preferentially activated to secondary and primary. Oxidative addition product was formed in competition and could be minimized by carrying the reaction under high dilution conditions, Scheme 1.7.

Competition studies have indicated that species involved in the C-H activation with $Ge[CH(CH_3)_2]$/aryl halide are different from free phenyl radicals generated by decomposition of phenylazotriphenylmethane (PAT).

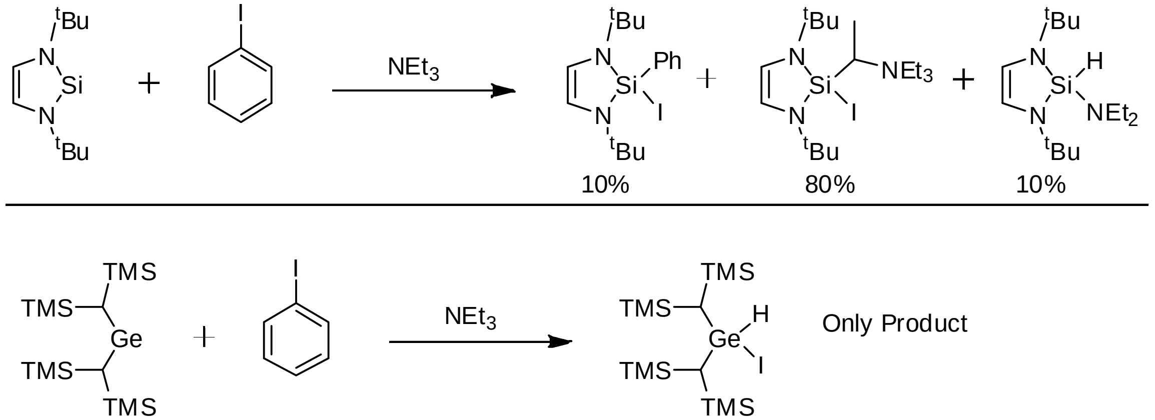


Scheme 1.7 C-H activation of THF utilizing Lappert's alkyl germylene by Miller et al.

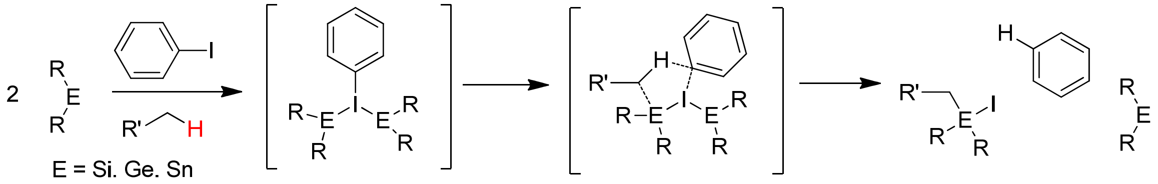
In reaction with a 50:50 mixture of cumene:THF$_{d8}$ a 4.7 ± 0.4 ratio of C-H activation products were observed with Ge[CH(CH$_3$)$_2$]/iodobenzene while PAT decomposition produced a ratio of 3.4 ± 0.4. Similarly, k$_h$/k$_d$ deuterium isotope effect measurements were found to be substantially different, 5.0 ± 0.2 for Ge[CH(CH$_3$)$_2$] and 4.2 ± 0.2 for PAT.

Walker et al. have studied C-H activation of amines with Si[N$_2$(^{t}Bu)$_2$C$_2$H$_2$] nd Ge[CH(CH$_3$)$_2$].[27] Along with the normal C-H activation manifold, the authors have observed some divergent reactivity with amines, Scheme 1.8. The reaction of Si[N$_2$(^{t}Bu)$_2$C$_2$H$_2$] and iodobenzene in the presence of triethyl amine yielded mixture of C-H activation, oxidative addition and hydrido amide products. Ge[CH(CH$_3$)$_2$] in the presence of triethylamine yielded oxidative addition product of HI across germylene.

In the same study by Walker et al., the order for Ge[CH(CH$_3$)$_2$] and iodobenzene was found to be two and one, respectively and from this data the mechanism of C-H activation was delineated, Scheme 1.9. The formation of activated complex from two equivalents of divalent species and iodoarene is proposed. The electron transfer followed by concomitant phenyl radicaloid species formation and abstraction of C-H bond/recombination generates C-H activation product.



Scheme 1.8 Walker et al. have found diveregent reactivity of the silylene and germylene and amines.



Scheme 1.9. Mechanistic hypothesis by Walker et al.

1.5 Summary

The C-H activation by group 14 divalent reagent/iodoarene represents a method for direct formation of main group organometallic compounds. Main group organometallic reagents are important species for cross-coupling applications. However, the C-H activation with $Si[N_2(^tBu)_2C_2H_2]$ and $Ge[CH(CH_3)_2]$ were narrow in their functional group scope only tolerating saturated hydrocarbons, ethers and amines.[27] The cross-coupling potential of the products was questionable since most of the coupling work with bulky substituents has been done with tin.[28-31] We were also not able to obtain any mechanistic information because the divalent reagents' reactivity. The goals of my thesis were a) to establish robust method of C-H activation of compounds that possess diverse functionality; b) to understand selectivity principles that govern C-H activation using divalent group 14 reagent/aryl halide c) to unravel mechanistic details of our C-H activation reaction d) to demonstrate utility of the products of our C-H activation reaction.

References

(1) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507.
(2) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633.
(3) Crabtree, R. H. *J. Organomet. Chem.* **2004**, *689*, 4083.
(4) Kakiuchi, F.; Kochi, T. *Synthesis* **2008**, *2008*, 3013.
(5) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879.
(6) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 5305.
(7) Newkome, G. R.; Puckett, W. E.; Gupta, V. K.; Kiefer, G. E. *Chem. Rev.* **1986**, *86*, 451.
(8) Desai, L. V.; Stowers, K. J.; Sanford, M. S. *J. Am. Chem. Soc.* **2008**, *130*, 13285.
(9) Feng, Y.; Chen, G. *Angew. Chem. Int. Ed.* **2010**, *49*, 958.
(10) Dick, A. R.; Sanford, M. S. *Tetrahedron* **2006**, *62*, 2439.
(11) Dyker, G. *Angew. Chem. Int. Ed.* **1999**, *38*, 1698.
(12) Davies, H. M. L.; Beckwith, R. E. J. *Chem. Rev.* **2003**, *103*, 2861.
(13) Tsai, A. S.; Wilson, R. M.; Harada, H.; Bergman, R. G.; Ellman, J. A. *Chem. Commun.* **2009**, 3910.
(14) Gansäuer, A. *Radicals in Synthesis I*; Springer-Verlag: Berlin/Heidelberg, 2006; Vol. 263.
(15) Djerassi, C. *Chem. Rev.* **1948**, *43*, 271.
(16) Podgorsek, A.; Stavber, S.; Zupan, M.; Iskra, J. *Tetrahedron Lett.* **2006**, *47*, 7245.
(17) Alvarez, L. X.; Christ, M. L.; Sorokin, A. B. *Applied Catalysis A: General* **2007**, *325*, 303.
(18) Eames, J.; Watkinson, M. *Angew. Chem. Int. Ed.* **2001**, *40*, 3567.
(19) Yamada, K.-i.; Yamamoto, Y.; Maekawa, M.; Tomioka, K. *J. Org. Chem.* **2004**, *69*, 1531.
(20) Yoshimitsu, T.; Arano, Y.; Nagaoka, H. *J. Org. Chem.* **2005**, *70*, 2342.
(21) Yoshimitsu, T.; Arano, Y.; Nagaoka, H. *J. Am. Chem. Soc.* **2005**, *127*, 11610.
(22) Yoshimitsu, T.; Matsuda, K.; Nagaoka, H.; Tsukamoto, K.; Tanaka, T. *Org. Lett.* **2007**, *9*, 5115.
(23) Dolbier, W. R. *Chem. Rev.* **1996**, *96*, 1557.
(24) Xiang, J.; Jiang, W.; Gong, J.; Fuchs, P. L. *J. Am. Chem. Soc.* **1997**, *119*, 4123.
(25) Miller, K. A.; Bartolin, J. M.; O'Neill, R. M.; Sweeder, R. D.; Owens, T. M.; Kampf, J. W.; Banaszak Holl, M. M.; Wells, N. J. *J. Am. Chem. Soc.* **2003**, *125*, 8986.
(26) Fjeldberg, T.; Haaland, A.; Schilling, B. E. R.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1551.
(27) Walker, R. H.; Miller, K. A.; Scott, S. L.; Cygan, Z. T.; Bartolin, J. M.; Kampf, J. W.; Banaszak Holl, M. M. *Organometallics* **2009**, *28*, 2744.
(28) Wnuk, S. F.; Garcia, P. I.; Wang, Z. Z. *Org. Lett.* **2004**, *6*, 2047.
(29) Faller, J. W.; Kultyshev, R. G. *Organometallics* **2002**, *21*, 5911.

(30) Nakamura, T.; Kinoshita, H.; Shinokubo, H.; Oshima, K. *Org. Lett.* **2002**, *4*, 3165.

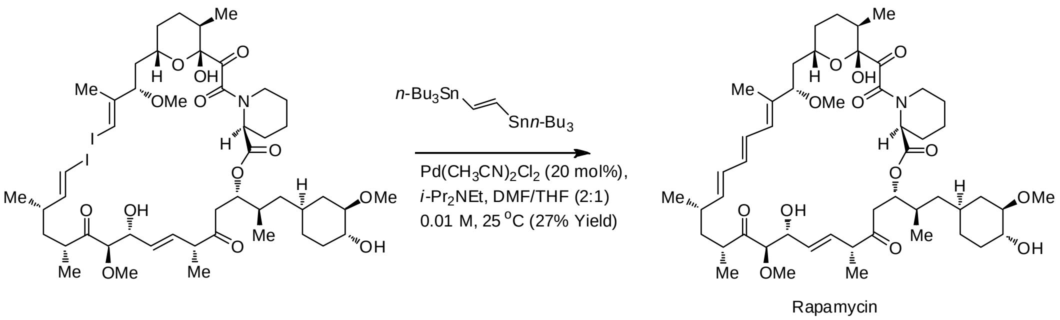
(31) Kosugi, M.; Tanji, T.; Tanaka, Y.; Yoshida, A.; Fugami, K.; Kameyama, K.; Migita, T. *J. Organomet. Chem.* **1996**, *508*, 255.

Chapter 2. C-H Activation with $Sn[N(SiMe_3)_2]_2$

2.1 Introduction to the Organic Chemistry of Tin

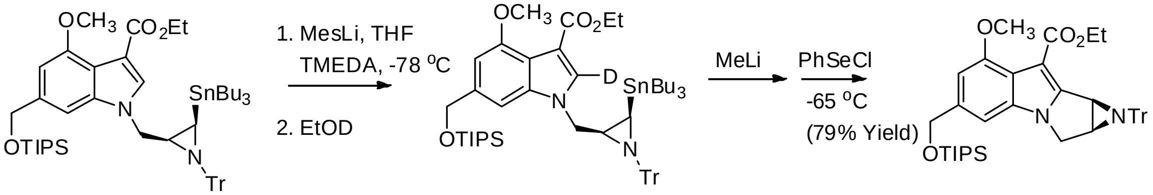
There is significant number of important uses of organotin compounds in organic synthesis today, perhaps unequal to any other metal.[1] The unique stability/reactivity profile of organotin compounds is responsible from their stability at ambient conditions and excellent functional group tolerance.[2-3] The most salient uses of organotin compounds include Stille cross-coupling, transmetallation with organolithiums, Lewis Acid mediated allylation and radical coupling.[4]

Cross-coupling of tin compounds, the Stille coupling, has been an important method for natural product synthesis.[5-7] Stille cross-coupling has been uniquely applicable for late stage transformations, Scheme 2.1. Considering the number of reactive functional groups, including alcohols, esters, amides and number of stereocenters present in the final step of Rapamycin synthesis, the success of this transformation is truly remarkable.[8]



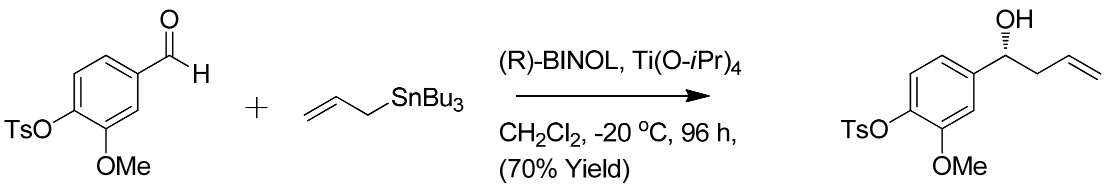
Scheme 2.1 Synthesis of Rapamycin by Nicolaou involves Stille cross-coupling at the final stage.

Lithium/Tin exchange chemistry (transmetallation) has proven to be of great preparative value in synthesis.[9] This is perhaps because it proceeds via retention of configuration.[10] Vinylic, allylic, alpha alkoxy, alpha amino, alpha sulfur and organotins connected to cyclopropane or azirinine moiety are compatible with this manifold. Vedejs et al. have reported elegant use of this chemistry in synthesis of tetracyclic aziridomitosenes, Scheme 2.2[11]


OCH3
CO2Et
SnBu3
N
N
Tr
OTIPS
1. MesLi, THF
TMEDA, -78 °C
2. EtOD
D
MeLi
PhSeCl
-65 °C
(79% Yield)
NTr

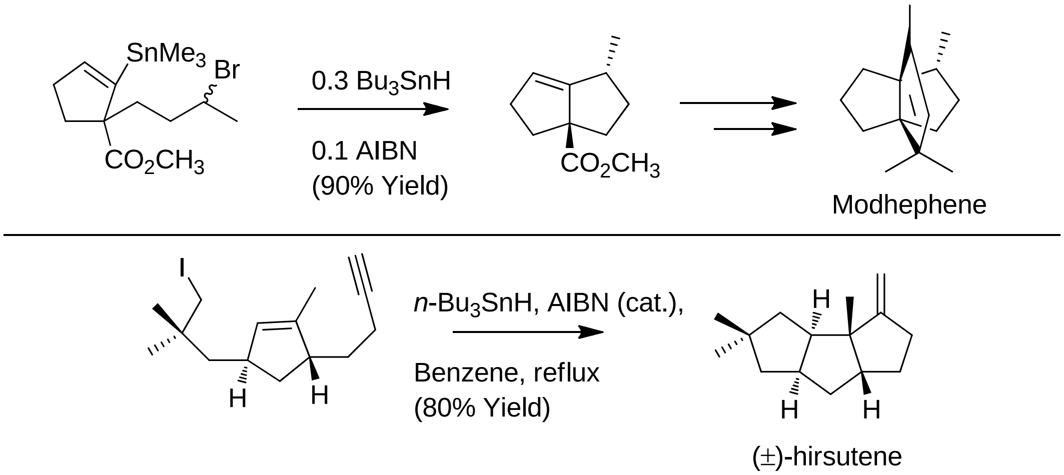
Scheme 2.2 The use of Lithium Tin exchange for synthesis of aziridomitosenes by Vedejs et al.

The inertness of the carbon-tin bond (69.2 kcal/mol for primary Sn-C) has been fruitfully exploited in numerous stereoselective allylations of aldehydes, known as Keck allylation.[12] Here, the mild nucleophilicity of organotin compounds is brought about by inclusion of a strong Lewis acid and enantioselective synthesis has been enabled via use of (R)-BINOL ligands, Scheme 2.3.[12-13] Lewis acid mediated diastereoselective addition to aldehydes via cyclic or non cyclic transition states has been subject of numerous studies.[14]


O
H
TsO
OMe
+
SnBu3
(R)-BINOL, Ti(O-iPr)4
CH2Cl2, -20 °C, 96 h,
(70% Yield)
OH
TsO
OMe

Scheme 2.3 Use of enantioselective Keck allylation towards synthesis of Rhoiptelol B by Reddy et al.

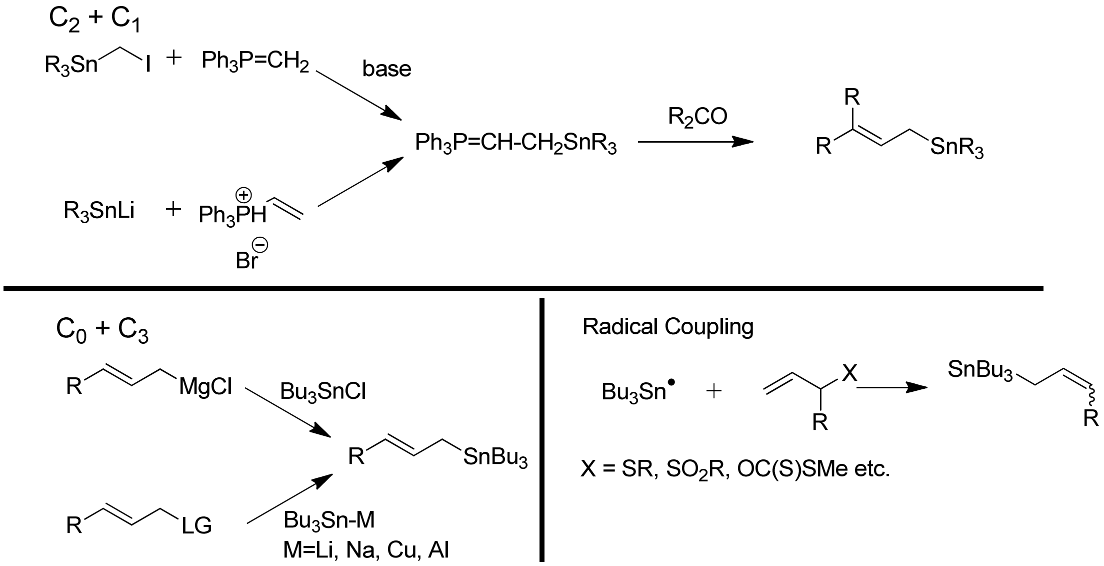
The rich radical chemistry of tin has been realized by the use of tributyltinhydride as a radical precursor or by the inclusion of a tin moiety in organic substrate.[15] Radical tin chemistry has been extensively used by Curran lab and others for numerous natural product syntheses, including synthesis of (±)-hirsutene and propellane triquinanes, Scheme 2.4. [16-17]



Scheme 2.4 Radical Tin chemistry in synthesis of natural products by Curran group.

2.2 Formation of Organotin Compounds in the Literature

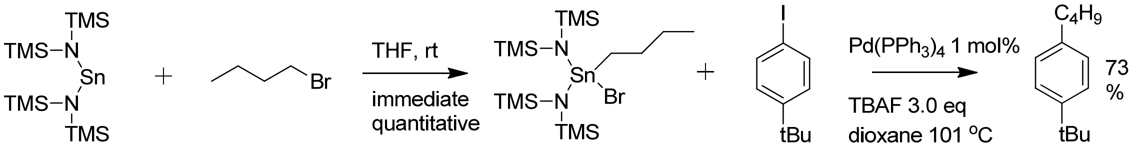
In light of the extensive applications of organotin compounds in synthesis, there is a vast literature on preparation of organotin compounds.[18] The early syntheses of allylic organotin compounds were accomplished by the use of organophosphorus compounds as electrophiles or nucleophiles, use of Grignard reagents as nucleophiles and tin halides as electrophiles, and radical methods, Scheme 2.5.[3] These methods were largely applicable towards synthesis of vinylic, primary and secondary aliphatic tin compounds.[1] Alpha-alkoxy organotin compounds were prepared with addition of tin anions to aldehydes followed by quench with electrophiles.[19] More recently, hydrostannation of alkynes via radical,[20] transition metal [21-22] and Lewis acid[23-24] mediated pathways has been a popular route for synthesis of stereodefined vinylic organotin compounds. Similar transition metal mediated carbostannylations reactions were reported in the literature.[25] However, hydrostannnations of allenes to obtain allylic tin compounds were commonly not regioselective nor stereospecific with regards to configuration of olefin.[22]



$C_2 + C_1$
R_3Sn I + $Ph_3P{=}CH_2$
base
$Ph_3P{=}CH{-}CH_2SnR_3$
R_2CO
R
R
SnR_3
R_3SnLi + Ph_3PH
Br
$C_0 + C_3$
R MgCl
Bu_3SnCl
R $SnBu_3$
R LG
$Bu_3Sn{-}M$
M=Li, Na, Cu, Al
Radical Coupling
$Bu_3Sn^\bullet$ +
X
R
$SnBu_3$
R
X = SR, SO_2R, OC(S)SMe etc.

Scheme 2.5 Literature syntheses of organotin compounds.

The Fouquet group have prepared primary organotins by oxidative addition of alkyl halides onto Lappert's amide stannylene and used these products in cross coupling reactions with aryl halides, Scheme 2.6.[26] Oxidative addition of aryl and alkyl halides onto $Sn[N(SiMe_3)_2]_2$ has been studied by Lappert's group, who has shown that this reaction proceeds via free radical pathway.[27]



TMS
TMS–N
Sn
TMS–N
TMS
Br
THF, rt
immediate
quantitative
TMS
TMS–N
Sn
Br
TMS–N
TMS
I
tBu
$Pd(PPh_3)_4$ 1 mol%
TBAF 3.0 eq
dioxane 101 °C
C_4H_9
tBu
73 %

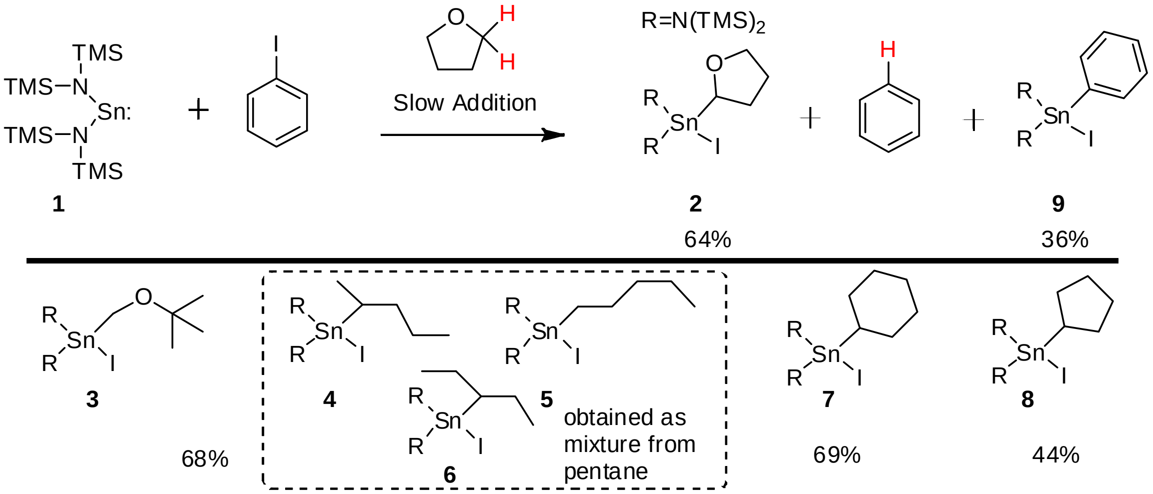
Scheme 2.6 Oxidative addition of aryl halide onto stannylene and cross coupling by Fouquet's group.

2.3 C-H Activation with $Sn[N(SiMe_3)_2]_2$

In light of the applications of organotin compounds in organic synthesis we explored the extension of the germylene C-H activation method for the direct formation of organotin compounds.[28] C-H activation was observed when equimolar amounts of **1** and phenyl iodide (0.060 mmol, 0.03 M) were mixed in hydrocarbon solvent, Scheme 2.7. Activation of C-H bonds in cyclohexane, cyclopentane, pentane, tetrahydrofuran (THF), and *tert*-butyl methyl ether were observed, Scheme 2.7. A new Sn-C bond was formed and an equivalent of benzene was formed. The cyclohexane case was also run using C_6D_{12} and *meta*-iodotoluene. Mass spectroscopy indicated the formation of monodeuteriotoluene. When the reactants are simply mixed a substantial amount of oxidative addition product **9** was also formed. Similar to the results previously observed for $[(TMS)_2CH]_2Ge/PhI$,[29] CH-activation preferentially occurs α to the oxygen in THF and the secondary sites are preferred over the primary sites for pentane (~6.2:1, secondary to primary).

The amount of CH-activation product (**2-8**) could be maximized, and the amount of oxidative-addition product (**9**) minimized by performing the reaction under highly dilute conditions. In a typical reaction, 25 mL of a 0.018 M solution of stannylene in the solvent of choice was added slowly via a syringe pump (0.07 mL/min) to a stirred 25 mL solution of 0.02 M PhI. Reactions in which the yellow color of the stannylene instantly disappeared (cyclopentane and cyclohexane) yielded no detectable **9**. However, reactions in which the yellow color of the stannylene built up (pentane, THF, *tert*-butyl methyl ether, diethyl ether) still yielded appreciable amounts of **9** (11, 36 and 32, and 63 %

respectively). The rates of addition used for this chemistry are ~4-6 times slower than were required for the analogous germylene chemistry.[29]


TMS
TMS−N
Sn:
TMS−N
TMS
1
I
O
H
H
Slow Addition
R=N(TMS)2
O
R
Sn
R
I
2
64%
H
R
Sn
R
I
9
36%
R
O
Sn
R
I
3
68%
R
Sn
R
I
4
R
Sn
R
I
5
R
Sn
R
I
6
obtained as
mixture from
pentane
R
Sn
R
I
7
69%
R
Sn
R
I
8
44%

Scheme 2.7 Activation of Alkanes and Ethers by a stable stannylene and phenyl iodide.

Slow addition techniques effectively eliminated side-product **9** and made it possible to isolate pure $[(Me_3Si)_2N]_2SnIR$ for R = cyclohexyl and cyclopentyl. The cyclopentyl product was also characterized by X-ray crystallography (Fig. 1).[30]

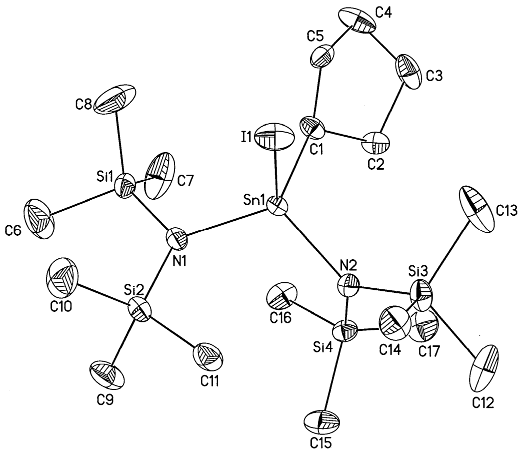

C4
C5
C3
C8
I1
C1
C2
Si1
C7
Sn1
C13
C6
N1
N2
Si3
C10
Si2
C16
Si4
C14
C17
C11
C9
C12
C15

Figure 2.1 ORTEP diagram of $[(Me_3Si)_2N]_2SnI(C_5H_9)$ (**8**). Selected bond lengths (Å) and angles (°): Sn-C1, 2.169 (2); Sn-N1, 2.049 (2); Sn-N2, 2.055 (2); Sn-I, 2.727 (5); C1-Sn-N1, 118.19 (7); C1-Sn-N2, 108.82 (7); C1-Sn-I, 103.67 (5); N2-Sn-I, 110.32 (4); N1-Sn-I, 102.23 (5); N1-Sn-N2, 112.84 (6).

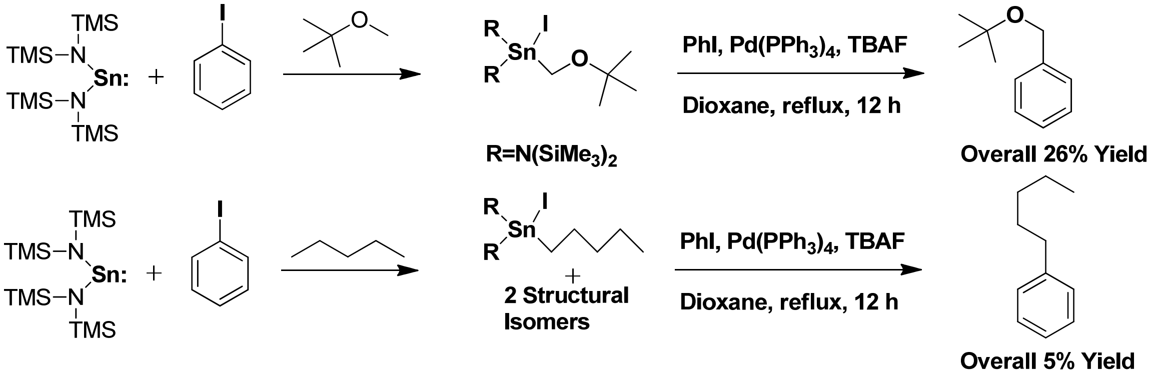
Although the mixture of primary and secondary CH-activation products and **9** that resulted from the reaction with *n*-pentane did not prove amenable to separation, pure $[(Me_3Si)_2N]_2SnI(CH_2)_4CH_3$ (**5**) was obtained by the oxidative addition of 1-iodopentane with **1**. The NMR assignments from this material were then used to positively identify the presence of the primary pentyl product in the CH-activation reaction mixture. For THF and *tert*-butyl methyl ether, neither reducing the concentration of the solutions further (as low as 0.01 M) nor further slowing the rate of addition (as low as 0.023 mL/min) were effective at lowering the amount of **9** below 36 and 32%, respectively. The solubilities of **3** and **9** are virtually identical and we were unable to separate these materials by recrystallization from hydrocarbon, aromatic, or ethereal solvents or using mixtures such as diethyl ether/acetonitrile. Attempts to separate **3** from **9** using sublimation also failed as a purification method as the materials co-sublimed. Fortunately, the presence of **9** does not prevent the cross-coupling reaction.

The use of phenyl bromide and phenyl chloride was also tested. Similar to the previously reported case for germylenes, C-H activation could be achieved using phenyl bromide but was dramatically slower. For example, refluxing **1**, phenyl bromide and cyclohexane for 24 hours resulted in 15% and 25% conversion to CH-activation and oxidative addition products, respectively. The remaining 60% of **1** did not react. Neither CH-activation nor oxidative addition was observed for reaction of phenyl chloride, even under refluxing conditions. The relative rates of PhI > PhBr >>> PhCl are consistent with the trend in both strengths with respect to homolytic C-X bond cleavage.

2.5.1 C-H activation and Cross Coupling in a Single Flask

Fouquet et al. have previously demonstrated that this class of tin reagents are excellent substrates for the Stille cross-coupling reaction.[26,31-33] Products obtained from the CH-activation reaction can be directly applied to the cross-coupling reactions. The Fouquet conditions are restricted to primary C-Sn bonds thus **3** and **5** are the only CH-activation products with the appropriate structure, Scheme 2.8. These compounds were smoothly converted into benzyl *tert*-butyl ether and amyl benzene, respectively. The reaction conditions employed differ in terms of an increase in catalyst load (3% vs. 1% for Fouquet) and a greater degree of dilution.

Ideally, the CH-activation and cross-coupling could both be performed in the same reaction flask without an isolation step. Indeed, this proved to be the best way to run these reactions. In a typical one-pot reaction, 25 mL of a 0.018 M solution of **1** in *tert*-butyl methyl ether was dripped into an equimolar 25 mL stirred 0.02 M solution of phenyl iodide over a period of 5 hours. After 12 hours of stirring to insure completion of reaction, the volatiles (excess *tert*-butyl methyl ether and benzene) were removed, leaving a yellow powder. The cross coupling reagents were then added to the same flask in order: phenyl iodide (0.440 mmol, 1 equivalent), tetrabutyl ammonium fluoride (TBAF, dissolved in THF, 1.32 mmol, 3 equivalents), tetrakis triphenyl phosphine palladium as a catalyst, (15 mg, 3% catalyst load), and 10 mL of dioxane as solvent. The solution was refluxed for 12 hours and then allowed to cool to room temperature (20 °C). The resulting dark yellow solution, also containing black sediment, was filtered through one inch of celite in a glass pipet, resulting in a light yellow solution. Milliliter aliquots were used for GC/MS experiments. A 67% yield (by GC/MS) of cross-coupled product was obtained for *tert*-butyl methyl ether (overall 26% yield from **1**), and a yield of 65% was obtained for pentane (overall 5% from **1**).

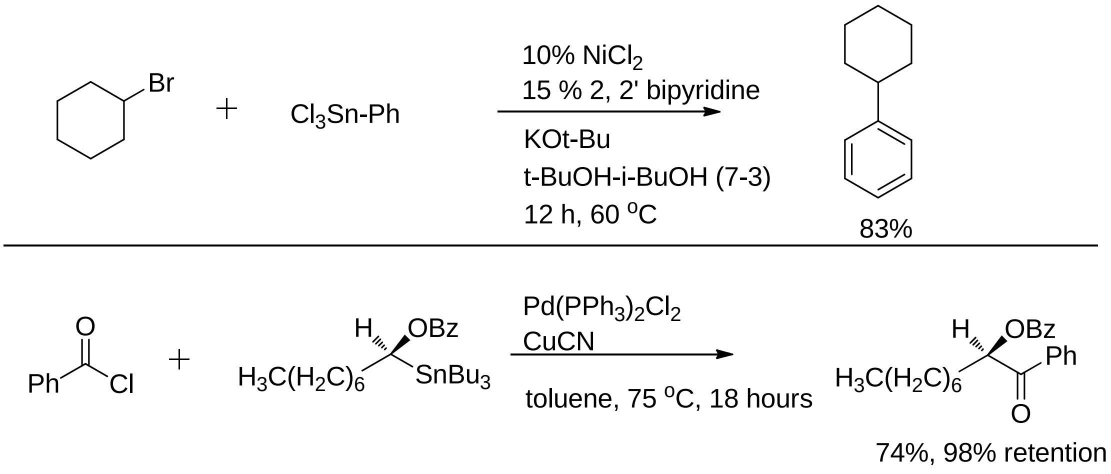


TMS
TMS–N
Sn:
TMS–N
TMS
I
R
Sn
R
O
R=N(SiMe3)2
PhI, Pd(PPh3)4, TBAF
Dioxane, reflux, 12 h
O
Overall 26% Yield
2 Structural Isomers
Overall 5% Yield

Scheme 2.8 One-pot C-H Activation and cross-coupling.

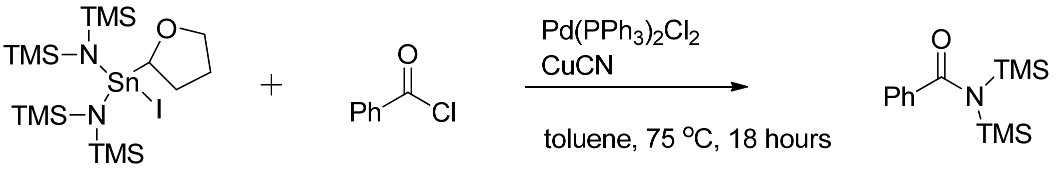
2.5.2 Cross Coupling of Substrates Containing Secondary Carbon-Tin Bonds

Our C-H activation method very reliably produces a number of compounds that contain secondary carbon-tin bonds. Products resulting from activation of THF and dioxane also contain α oxygen moiety. In the literature, a number of methods has recently been published that utilize secondary substrates as organohalides or organometalic reagent, Scheme 2.9.$^{34-35}$


Br
+
Cl3Sn-Ph
10% NiCl2
15 % 2, 2' bipyridine
KOt-Bu
t-BuOH-i-BuOH (7-3)
12 h, 60 °C
83%
O
Ph
Cl
+
H
OBz
H3C(H2C)6
SnBu3
Pd(PPh3)2Cl2
CuCN
toluene, 75 °C, 18 hours
H
OBz
Ph
H3C(H2C)6
O
74%, 98% retention

Scheme 2.9 Literature methods for cross-coupling of substrates possessing secondary carbons.

The cross-coupling of our secondary substrates with organohalides would demonstrate the wider utility of our C-H activation method. We have performed a variety of cross-coupling experiments under conditions published by Fouquet, Fu and Falck only to obtain the product derived from transmetallation of amide ligand with procedure by Falck group, Scheme 2.10. Use of other electrophiles such as iodobenzene predominantly resulted in formation of the homocoupling product, biphenyl, without any detectable formation of the desired product. Establishing useful reactivity of secondary tin products from our reactions remains a challenge.


TMS
TMS–N
Sn
O
TMS–N
I
TMS
+
O
Ph
Cl
Pd(PPh3)2Cl2
CuCN
toluene, 75 °C, 18 hours
O
Ph
N
TMS
TMS

Scheme 2.10 Cross coupling of THF product led to transmetallation of amide ligand.

2.6 Summary

In summary, a new method for CH-activation of alkanes and ethers is reported that leads directly to the formation of a Sn-C bond. The products derived from the activation of primary carbons can be carried forward directly for C-C bond formation reactions using Stille cross-coupling methodology without need of further isolation. Use of substrates containing secondary carbon-tin bonds led to undesired transamination products.

2.7 Experimental

All manipulations were performed using air-free techniques. All solvents were dried over sodium benzophenone ketyl and degassed. $Pd(PPh_3)_4$ was purchased from Strem Chemical and used as received. PhI was purchased from Aldrich Chemicals and degassed. $Sn[N(SiMe_3)_2]_2$ (**1**) was made according to literature procedures. ^{1}H and ^{13}C NMR spectra were acquired on a Varian 400 MHz instrument (400 and 100.6 MHz respectively). 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. The reactions typically yield a mixture of CH-activation product and product **3**, the oxidative-addition of PhI to **1**. The amount of **3** can be minimized by using low concentration utilizing syringe pump techniques. We were unable to separate **3** from the CH-activation products using re-crystallization or sublimation.

(**3**) **$[(Me_3Si)_2N]_2SnI[CH_2OC(CH_3)_3]$**. A 100 mL two-necked flask equipped with a septum and stir bar was charged with phenyl iodide (103 mg, 0.50 mmol) and *tert*-butyl methyl ether (25 mL, 256 mmol). An orange solution of **1** (194 mg, 0.44 mmol) in *tert*-

butyl methyl ether (25 ml, 256 mmol) was placed in a gas-tight syringe equipped with a 20-gauge needle. The stannylene solution was added to the phenyl iodide solution at a rate of approximately 6 mL/hr using a syringe pump. The solution was allowed to stir for 10 hours to insure completion of reaction, yielding a pale yellow solution, and the volatiles were removed in vacuo. ^{1}H NMR (C_6D_6) δ: 3.88 (s, 2H, Sn-C*H*$_2$), 1.00 (s, -C*Me*$_3$), 0.426 (s, 36H, Si*Me*$_3$). ^{13}C NMR (C_6D_6) δ: 76.1 (–*C*(CH_3)$_3$), 67.2 (Sn-CH_2), 26.6 (–C(*C*H_3)$_3$), 5.8 (Si*Me*$_3$). IR(film) cm^{-1} ν 2973 (C-H), 2952 (C-H), 1364 (C-O), 1262, 881 br. MS (electron impact) 567.2 (M-N($SiMe_3$)$_2$). Material synthesized in this fashion also contains **9**.

(4, 5, 6) [(Me_3Si)$_2$N]$_2$SnI(C_5H_{11}) mixture of regioisomers. A 100 mL two-necked flask equipped with a septum and stir bar was charged with phenyl iodide (101 mg, 0.50 mmol). Pentane (25 mL, 256 mmol) was added to the flask, which was then sealed with a needle valve with stopcock under an atmosphere of nitrogen. An orange solution of **1** (196 mg, 0.44 mmol) in pentane (25 ml, 256 mmol) was placed in a gas-tight syringe equipped with a 20-gauge needle. The stannylene solution was added to the phenyl iodide solution at a rate of approximately 5 mL/hr using a syringe pump. The solution was allowed to stir for 14 hours to insure completion of reaction, yielding a cloudy, white solution. The volatiles were removed in vacuo ^{1}H NMR (C_6D_6) δ: 3.88 (s, 2H, Sn-C*H*$_2$), 1.00 (s, -C*Me*$_3$), 0.426 (s, 36H, Si*Me*$_3$) . ^{13}C NMR (C_6D_6) δ: 76.1 (–*C*(CH_3)$_3$), 67.2 (Sn-CH_2), 26.6 (–C(*C*H_3)$_3$), 5.8 (Si*Me*$_3$). IR(film) cm^{-1} ν 2973 (C-H), 2952 (C-H), 1364 (C-O), 1262, 881 br. Material synthesized in this fashion also contains **9**.

(5) **[(Me$_3$Si)$_2$N]$_2$SnI(C$_5$H$_{11}$)**. A 100 mL flask was charged with 200 mg of **1** (0.455 mmol), 98 mg of 1-iodopentane (0.49 mmol, 1.1 equivalents), and 13 mL of pentane and allowed to stir 6 hours. The volatiles were removed in vacuo and the resulting solid was recrystallized at -78 °C from cold pentane giving 199 mg of a fine white powder (69% yield). ^{1}H NMR (C$_6$D$_6$) δ: 1.67 (m, 4H, C*H*$_2$), 1.24 (m, 4H, C*H*$_2$), 0.48 (t, 3H, C*H*$_3$), 0.37 (s, 36H, Si*Me*$_3$) . ^{13}C NMR (C$_6$D$_6$) δ: 35.3 (Sn−*C*H$_2$), 31.8 (*C*H$_2$), 26.6 (*C*H$_2$), 22.2 (*C*H$_2$), 14.1 (*C*H$_3$), 6.1 (Si(*C*H$_3$)$_3$). E.A. Calc'd for C$_{17}$H$_{47}$IN$_2$Si$_4$Sn: C: 32.03; H: 7.43; N: 4.39; found C: 32.45; H: 7.23; N: 4.15.

(2) **[(Me$_3$Si)$_2$N]$_2$SnI(C$_4$H$_7$O).** A 100 mL two-necked flask equipped with a septum and stir bar was charged with phenyl iodide (122 mg, 0.60 mmol). THF (25 mL, 308 mmol) was added to the flask, which was then sealed with a needle valve with stopcock under an atmosphere of nitrogen. An orange solution of **1** (190 mg, 0.432 mmol) in THF (25 ml, 308 mmol) was placed in a gas-tight syringe equipped with a 20-gauge needle. The stannylene solution was added to the phenyl iodide solution at a rate of approximately 6 mL/hr using a syringe pump. The solution was allowed to stir for 11 hours to insure completion of reaction, yielding a pale yellow solution. The volatiles were removed in vacuo ^{1}H NMR (C$_6$D$_6$) δ: 4.29 (m, 1, SnC*H*), 3.45 (m, 2H, OCH$_2$), 2.20 (m, 1H, CHC*H*$_2$), 1.96 (m, 1H, CHC*H*$_2$), 1.52 (m, 2H, OCH$_2$C*H*$_2$), 0.44 (s, 18H, Si*Me*$_3$), 0.39 (s, 18H, Si*Me*$_3$). ^{13}C NMR (C$_6$D$_6$) δ: 83.4 (Sn-*C*H), 69.7 (O-*C*H$_2$), 31.2 (Sn-CH-*C*H$_2$), 25.7 (O-CH$_2$-*C*H$_2$), 6.3 (Sn(*C*H$_3$)$_3$), 6.0 (Sn(*C*H$_3$)$_3$). Material synthesized in this fashion also contains **9**.

(**7**) **$[(Me_3Si)_2N]_2SnI(C_6H_{11})$**. A 100 mL two-necked flask equipped with a septum and stir bar was charged with phenyl iodide (102 mg, 0.50 mmol). Cyclohexane (25 mL, 231 mmol) was added to the flask, which was then sealed with a needle valve with stopcock under an atmosphere of nitrogen. An orange solution of **1** (193 mg, 0.44 mmol) in cyclohexane (25 ml, 231 mmol) was placed in a gas-tight syringe equipped with a 20-gauge needle. The stannylene solution was added to the phenyl iodide solution at a rate of approximately 6 mL/hr using a syringe pump. This rate was chosen so that the orange color of the Sn solution disappeared before the next drop was added. The solution was allowed to stir for 14 hours to insure completion of reaction, yielding a clear, colorless solution. The volatiles were removed in vacuo, yielding a fine white powder, which was analytically pure by ^{1}H NMR and elemental analysis, and also showed >99% conversion to C-H activation product by ^{1}H NMR. The powder was recrystallized from pentane and filtered through a sintered glass frit, yielding 125 mg (44%) of a fine, white powder. ^{1}H NMR (C_6D_6) δ: 2.12, 1.60, 1.39, 1.12 (multiplets, 11H, cy) 0.394 (s, 36H, Si*Me*$_3$). ^{13}C NMR (C_6D_6) δ: 42.4 (*C*H) 32.3 (*C*H$_2$), 29.3 (*C*H$_2$), 26.4 (*C*H$_2$), 6.3 (Si(*C*H$_3$)$_3$). E.A. Calc'd for $C_{18}H_{47}IN_2Si_4Sn$: C: 33.28; H: 7.29; N: 4.31; found C: 32.98; H: 7.14; N: 4.14. IR(film) cm^{-1} ν 2928 (C-H), 1249, 872. Mass Spectrum (chemical ionization, methane) 635.2 (M-CH_3).

(**8**) **$[(Me_3Si)_2N]_2SnI(C_5H_9)$**. A 100 mL two-necked flask equipped with a septum and stir bar was charged with phenyl iodide (106 mg, 0.52 mmol). Cyclopentane (25 mL, 267 mmol) was added to the flask, which was then sealed with a needle valve with stopcock under an atmosphere of nitrogen. An orange solution of **1** (198 mg, 0.45 mmol) in cyclopentane (25 ml, 267 mmol) was placed in a gas-tight syringe equipped with a 20-gauge needle. The stannylene solution was added to the phenyl iodide solution at a rate of approximately 6 mL/hr using a syringe pump. This rate was chosen so that the orange color of the Sn solution disappeared before the next drop was added. The solution was allowed to stir for 12 hours to insure completion of reaction, yielding a clear, colorless solution. The volatiles were removed in vacuo, yielding white powder in which 2g was the only product detectable by ^{1}H NMR. However, using this synthetic method, we are unable to produce analytically pure material. An alternative synthesis for this product involved the direct reaction of **1** with 1-iodopentane. A 100 mL flask was charged with 200 mg of **1** (0.455 mmol) and 98 mg (0.49 mmol, 1.1 equiv) of 1-iodopentane. 8 g of pentane was added and the reaction was stirred. After 10 minutes, the yellow color had faded leaving a pale yellow solution. After 6 hours the volatiles were removed in vacuo, leaving a fine, white powder that was analytically pure. ^{1}H NMR spectroscopy showed quantitative conversion of the starting materials to the desired product. The powder was recrystallized out of cold pentane, leaving 199 mg (69% yield) of a fine white powder. ^{1}H NMR (C_6D_6) δ: 1.98 (1 H, m), 1.90 (2H, m), 1.79 (2H, m), 1.54 (2H, m), 1.32 (2H, m), 0.39 (36H, s). ^{13}C NMR (C_6D_6) δ: 40.33 (CH), 31.03 (CH$_2$), 26.02 (CH$_2$), 6.29 (Si(CH$_3$)$_3$). E.A. Calc'd for $C_{17}H_{47}IN_2Si_4Sn$: C: 32.03; H: 7.43; N: 4.39; found C: 32.45; H: 7.23; N: 4.15.

(**9**) **$[(Me_3Si)_2N]_2SnI(C_6H_5)$**. A 100 mL flask was charged with 500 mg of **1**, 255 mg of phenyl iodide (1.25 mmol, 1.1 equivalents), and 45 mL of acetonitrile. The initial color of the reaction solution was light yellow, and it did not fade or change over the next 40 hours as it stirred. After 40 hours, the volatiles were removed in vacuo, leaving a yellow-orange solid. The reaction had gone to completion as monitored by ^{1}H NMR spectroscopy. A 550 mg sample was then filtered through a sintered glass frit in cold (-78 C) pentane. Yellow-orange by products were largely insoluble in cold pentane while the white oxidative addition product was soluble and passed through the frit. Evaporation of the solvent left 350 mg (64% yield) of a white powder. Analytically pure material was obtained by sublimation of a sample (100 mg) of the crude product for 12 hours at 75 °C, yielding 63 mg of white solid. ^{1}H NMR (C_6D_6) δ: 7.91 (d, 2H, o-Ph), 7.13 (t, 2H, m-Ph), 7.01 (t, 1H, p-Ph) 0.362 (s, 36H, -C*Me*$_3$) ^{13}C NMR (C_6D_6) δ: 135.6 (Ar), 131.0 (Ar), 129.5 (Ar), 127.9 (Ar), 6.0 (Si(*C*H$_3$)$_3$). E.A. Calc'd for $C_{18}H_{41}IN_2Si_4Sn$: C: 33.60; H: 6.43; N: 4.36; found C: 33.23 ; H: 6.33 ; N: 4.14.

Protocol for sequential CH-activation and cross-coupling:

A 100 mL two-necked flask equipped with a septum and stir bar was charged with phenyl iodide (106 mg, 0.50 mmol) and 25 mL *tert*-butyl methyl ether. An orange solution of **1** (194 mg, 0.44 mmol) in 25 mL *tert*-butly methyl ether was placed in a gas-tight syringe equipped with a 20-gauge needle. The stannylene solution was added to the phenyl iodide solution at a rate of approximately 6 mL/hr using a syringe pump. The solution was allowed to stir for 12 hours to insure completion of reaction, yielding a pale yellow solution. The volatiles were removed in vacuo. A small sample of material was removed from the flask to determine the ratio of oxidative addition to C-H activation. This ratio was determined by ^{1}H NMR spectroscopy, and was 1.5:1. At this point 105 mg (0.50

mmol) PhI, 15 mg of $Pd(PPh_3)_4$ and 18 mL of 1,4-dioxane were added and the flask fitted with a reflux condenser. After the addition of 1.32 mL of a 1.0 *M* solution of tetrabutyl ammonium fluoride (TBAF, 3 eq.) and 51μL of hexadecane (GC/MS standard) the mixture was heated to reflux (101 °C) for 14 hours. After 14 hours, the mixture was filtered through 1" of Celite in a Pasteur pipette. 1 mL of the filtrate was removed for GC/MS analysis which revealed a 67% yield of benzyl tert-butyl ether based upon C-H activation product. That corresponds to a 26% overall yield from starting stannylene.

Protocol for deuterium labeling experiment:

An NMR tube was charged with 0.5 ml of deuterated cyclohexane, 50 mg of **1**, and 15 μL of 3-iodotoluene. After 24 hours, an NMR spectrum was acquired to confirm that the CH-activation reaction had occurred. An aliquot of the reaction was injected into the GC/MS system.

References

(1) Smith, P. *Chemistry of Tin*; Chapman & Hill, 1998.
(2) Sato, T. *Synthesis-Stuttgart* **1990**, 259.
(3) Jarosz, S.; Gawel, A. *Eur. J. Org. Chem.* **2005**, 3415.
(4) Espinet, P.; Echavarren, A. M. *Angew. Chem. Int. Ed.* **2004**, *43*, 4704.
(5) Mitchell, T. N. *Synthesis* **1992**, *1992*, 803.
(6) De Souza, M. V. N. *Curr Org Synth* **2006**, *3*, 313.
(7) Stille, J. K. *Angew. Chem. Int. Ed.* **1986**, *25*, 508.
(8) Nicolaou, K. C.; Chakraborty, T. K.; Piscopio, A. D.; Minowa, N.; Bertinato, P. *J. Am. Chem. Soc.* **1993**, *115*, 4419.
(9) Gawley, R. E.; Zhang, Q.; Campagna, S. *J. Am.Chem. Soc.* **1995**, *117*, 11817.
(10) Reich, H. J.; Borst, J. P.; Coplien, M. B.; Phillips, N. H. *J. Am. Chem. Soc.* **1992**, *114*, 6577.
(11) Kim, M.; Vedejs, E. *J. Org. Chem.* **2004**, *69*, 7262.
(12) Keck, G. E.; Tarbet, K. H.; Geraci, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 8467.
(13) Keck, G. E.; Geraci, L. S.; Krishnamurthy, D.; Grier, M. C. *Abstr Pap Am Chem S* **1994**, *207*, 399.
(14) Marshall, J. A. *J. Org. Chem.* **2007**, *72*, 8153.
(15) Jasperse, C. P.; Curran, D. P.; Fevig, T. L. *Chem. Rev.* **1991**, *91*, 1237.
(16) Curran, D. P.; Rakiewicz, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 1448.
(17) Jasperse, C. P.; Curran, D. P. *J. Am. Chem. Soc.* **1990**, *112*, 5601.
(18) Ingham, R. K.; Rosenberg, S. D.; Gilman, H. *Chem. Rev.* **1960**, *60*, 459.
(19) Sato, T. *Synthesis* **1990**, *1990*, 259.
(20) Thiele, Christina M.; Mitchell, Terence N.*: Eur. J. Org. Chem.* ***2004**, 337.*
(21) Zhang, H. X.; Guibe, F.; Balavoine, G. *J. Org. Chem.* **1990**, *55*, 1857.
(22) Smith, N. D.; Mancuso, J.; Lautens, M. *Chem. Rev.* **2000**, *100*, 3257.
(23) Asao, N.; Liu, J. X.; Sudoh, T.; Yamamoto, Y. *J. Chem. Soc. Chem. Comm.* **1995**, 2405.
(24) Asao, N.; Yamamoto, Y. *Bull. Chem. Soc. Jap.* **2000**, *73*, 1071.
(25) Shirakawa, E.; Hiyama, T. *Bull. Chem. Soc. Jap.* **2002**, *75*, 1435.
(26) Herve, A.; Rodriguez, A. L.; Fouquet, E. *J. Org. Chem.* **2005**, *70*, 1953.
(27) Gynane, M. J. S.; Lappert, M. F.; Miles, S. J.; Power, P. P. *J. Chem. Soc. Chem. Comm.* **1976**, 256.
(28) Bartolin, J. M.; Kavara, A.; Kampf, J.; Banaszak Holl, M. M. *Organometallics* **2006**, *25*, 4738.
(29) Miller, K. A.; Bartolin, J. M.; O'Neill, R. M.; Sweeder, R. D.; Owens, T. M.; Kampf, J. W.; Banaszak Holl, M. M.; Wells, N. J. *J. Am. Chem. Soc.* **2003**, *125*, 8986.
(30) Crystal Data for (2g):$C_{17}H_{45}N_2Si_4ISn$, g. m., orthorhombic Pbca, colorless block, a = 13.481(2) A, b = 17.536(3) A, c = 23.734(4) A, V = 5610.8(2)

A3, T = 123(2) K, Z = 8, R(F, observed data) = 0.0202, GOF = 1.104. Data was collected on a Bruker SMART CCD-based X-ray diffractomer. The structure was solved and refined using Bruker SHELXTL software. Hydrogen atoms were placed in idealized positions and refined istropically; non-hydrogen atoms were refined anisotropically.

(31) Rodriguez, A. L.; Peron, G.; Duprat, C.; Vallier, M.; Fouquet, E.; Fages, F. *Tetrahedron. Lett.* **1998**, *39*, 1179.

(32) Fouquet, E.; Pereyre, M.; Rodriguez, A. L. *J. Org. Chem.* **1997**, *62*, 5242.

(33) Fouquet, E.; Pereyre, M.; Roulet, T. *J. Chem. Soc. Chem. Comm.* **1995**, 2387.

(34) Han, C.; Buchwald, S. L. *J. Am. Chem. Soc.* **2009**, *131*, 7532.

(35) Ye, J.; Bhatt, R. K.; Falck, J. R. *J. Am. Chem. Soc.* **1994**, *116*, 1.

Chapter 3. $\overline{\mathrm{SnC(SiMe_3)_2CH_2CH_2C}}\mathrm{(SiMe_3)_2}$: C-H Activation of Alkenes, Arenes and Ethers

3.1 Challenges of C-H Activation with Group 14 Divalent/Aryl Halide

We have encountered a number of challenges while performing the C-H activation chemistry with group 14 divalent reagents.[1-2] The oxidative addition product formation of aryl halide onto divalent reagent was limiting the yield, and it was often not suppressed even under slow addition conditions. Separation via column chromatography of the desired, water sensitive C-H activation products from the oxidative addition product was not practical. The group 14 divalent compounds were reactive with compounds containing any degree of nonaromatic unsaturation, limiting the functional group tolerance in the substrates for C-H activation.[3-4] This was particularly restrictive in light of the number of applications of allylic organo-tin compounds.[5-6] The coupling conditions developed up to date only tolerate primary organo-tin compounds and attempted other types of coupling reactions have often failed in our hands because the -$\mathrm{N(SiMe_3)_2}$ substituent on tin transfers instead of the desired –R group.[7-8]

3.2 Properties and Preparation of $\overline{\mathrm{SnC(SiMe_3)_2CH_2CH_2C}}\mathrm{(SiMe_3)_2}$

We thought that the stannylene synthesized in 1991 by Kira et al., $\overline{\mathrm{SnC(SiMe_3)_2CH_2CH_2C}}\mathrm{(SiMe_3)_2}$ (**10**)[9-10] would provide a solution to the limitations mentioned above. **10** has been shown not to react with alkenes, including ethylene, although it does readily undergo 4+2 cycloaddition with 1,3-butadiene.[11] Stannylene **10** was shown to be monomeric in liquid and solid state, which seemed to indicate a larger steric encumbrance around tin atom relative to the carbene analogs we used to date, Figure 3.1.

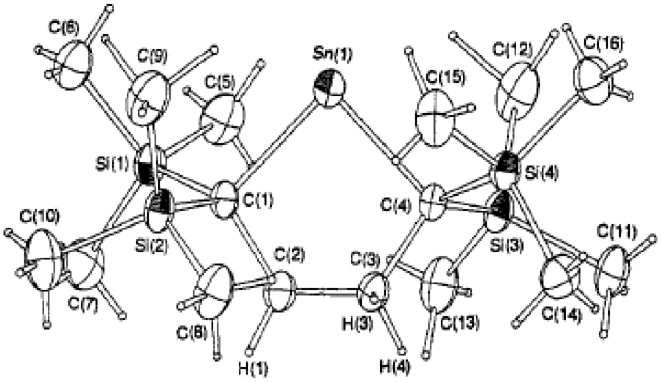


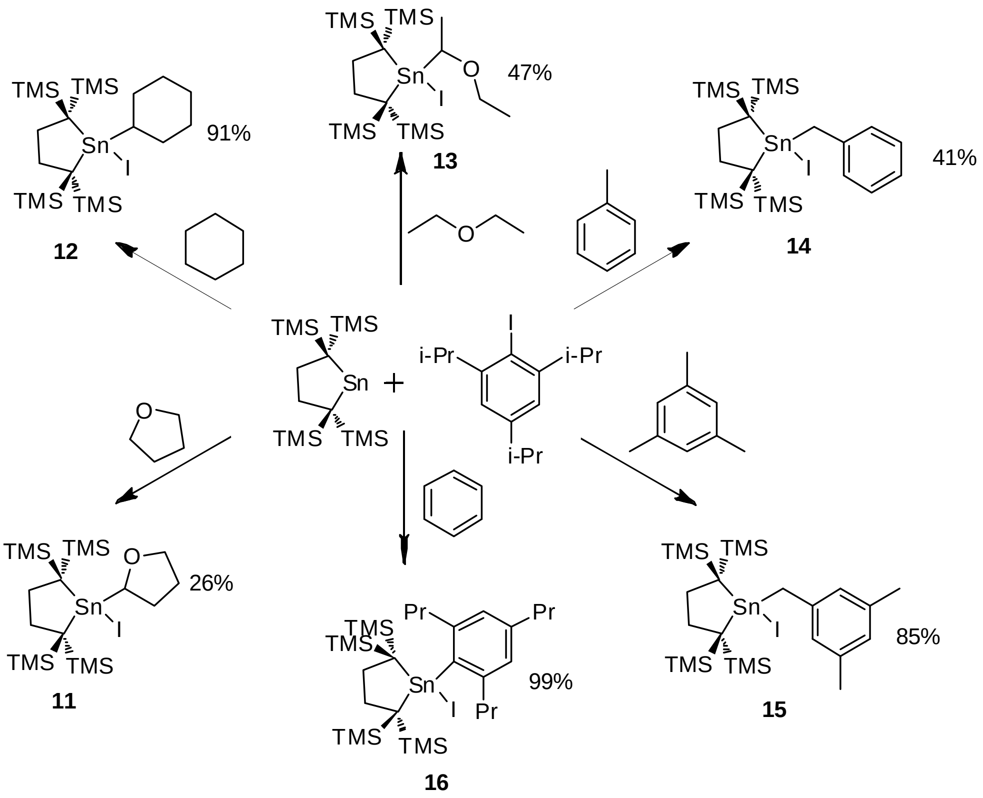
Figure 3.1 The crystal structure shows that Kira stannylene is monomeric in solid state.

In our hands, **1** can most conveniently be prepared by potassium/graphite reduction of the corresponding dichloro compound.[12] The dichloro compound can be prepared by lithium reduction of 1,1-di(trimethylsilyl)ethylene (synthesized from commercially available tri(trimethylsilyl)methane and formaldehyde)[13] followed by quenching with $SnCl_4$ mediated by CuCN. We have used this route to routinely prepare 10 g of air sensitive **1** in 10-30% overall yield in 4 steps. Admittedly, the laborious starting material preparation limits the practicality of these C-H activation and cyclization methods.

3.3 C-H Activation of Alkanes, Arenes, and Ethers

The reaction of **10**/2,4,6-triisopropyl iodobenzene with cyclohexane, diethyl ether, tetrahydrofuran (THF), toluene, and mesitylene yielded C-H activation products as illustrated in Scheme 3.1. The high degree of solubility of many of products contributed to modest to excellent (26 – 99%) isolated yields 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 **10** and $Sn[N(SiMe_3)_2]_2$ (**1**) was consistent with the reactivity previously observed for $Ge[CH(SiMe_3)_2]_2$ (**17**), $Ge[N(SiMe_3)_2]_2$ (**18**), and $Si[N_2(^tBu)_2C_2H_2]$ (**19**).[1-2,14] Clean C-H activations of toluene and mesitylene was not previously observed for this chemistry. Typically, oxidative-addition of the aryl halide to the germylene or silylene was the primary or only product for these substrates. Successful arene C-H activation using **10**/2,4,6-triisopropyl iodobenzene appears to result from slowing the formation of oxidative-addition product by employing **10**, which is more sterically constrained than $Sn[N(SiMe_3)_2]_2$ (**1**), $Ge[CH(SiMe_3)_2]_2$ (**17**), $Ge[N(SiMe_3)_2]_2$ (**18**), and $Si[N_2(^tBu)_2C_2H_2]$ (**19**) as well as a very sterically encumbered aryl halide. The primary isotope effect for the reaction of **1** and 2,4,6-triisopropyl iodobenzene in toluene/toluene-*d7* was found to be 4.9 ± 0.5. This is in good agreement with the values previously measured for $Ge[CH(SiMe_3)_2]_2$ (**17**), $Ge[N(SiMe_3)_2]_2$ (**18**), and $Si[N_2(^tBu)_2C_2H_2]$ (**19**) which were determined to be 5.0 ± 0.2 (THF/THF-*d8*), 4.1 ± 0.2 (THF/THF-*d8*) and 5.7 ± 0.1 (Et_2O/Et_2O-*d10*), respectively.[1]

Scheme 3.1 C-H activation of alkanes, arenes, and ethers proceeds quantitatively with 1 and 2,4,6-triisopropyliodobenzene. When the reaction is performed in benzene, oxidative addition occurs. Yields for all products are provided.



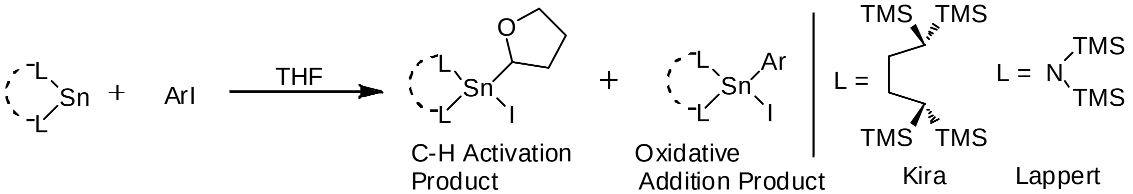
In contrast to the Sn[N(SiMe$_3$)$_2$]$_2$ (**1**), **10** successfully C-H activates aromatic hydrocarbons. This has been a vexing aspect of our chemistry since radical reagents are known to exhibit excellent reactivity with benzylic sites. **1**, **18** and **19** do not successfully C-H activate toluene. Only oxidative addition product is observed when **18** is used but **1** and **19** show no reactivity whatsoever when substrates with benzylic protons is present. **10** and **17** C-H activate toluene in excellent yields under slow addition conditions.

It is known that amide substituents perturb the frontier orbitals on silylenes. These species are different from true analogs of a singlet carbene.[15] Why this difference, if responsible at all, manifests itself only in the case of benzylic C-H activation at present defies our understanding. Our speculation based on our current mechanistic understanding of our C-H activation reaction is that toluene interferes with the activated complex formation of a divalent species with the aryl halide or with the kinetics of electron transfer from divalent species to the aryl halide.[1] First ionization potentials of Lappert's alkyl (**11**) and amide germylenes (**12**) are identical (7.75 and 7.72 eV respectivaly) and values for stannylenes **1** and **10** are comparable (7.42 and 7.75 eV).[16] Thus, there should not be significant difference in propensities of divalent, alkyl and amide germanium and tin species to transfer electrons. The formation of the activated complex between the aryl halide and two amide species in solvents with benzylic functional groups might not be a favored equilibrium. This is supported by the fact that donation from amide ligands into empty *p* orbital of the metal makes these species more stable and relatively unreactive as observed in the oxidative addition reactions described above.

3.4 Dependence of Oxidative Addition on Sterics and Electronics of Aryl Halide

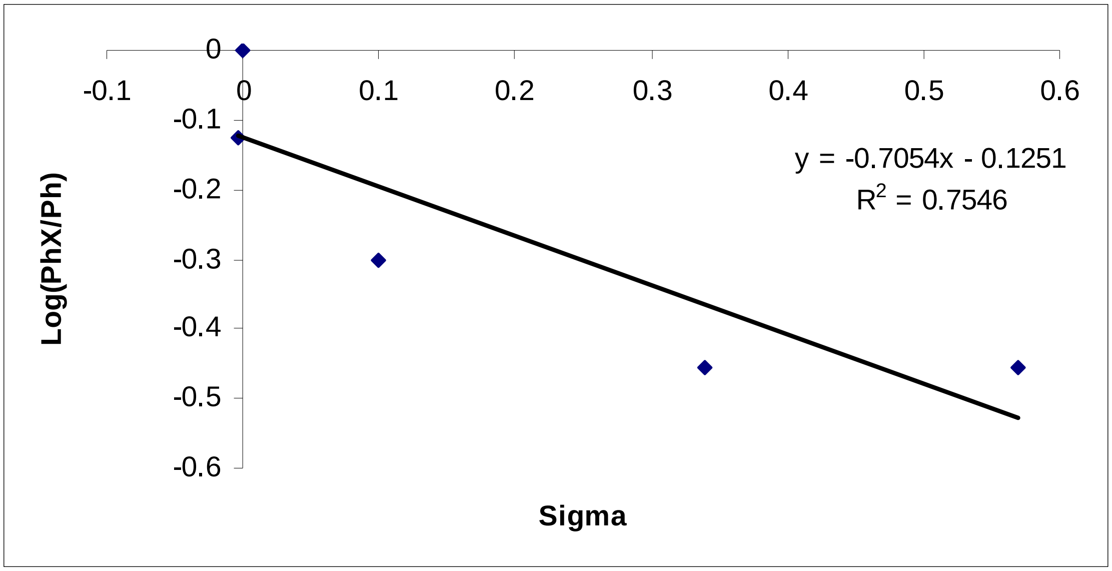
We have found that C-H activations for both **1** and **10** are sensitive to σ inductive parameters, Table 1. According to our results, **1** is less reactive toward THF as a substrate and more sensitive to inductive effects than **10**. The *t*-butyl substitution in the *para* position did not increase the amount of oxidative addition relative to simple iodobenzene in the case of **10**. There was no discrimination between *para* methoxy and *para* cyano with **10**, while slower reacting **1** did discriminate between them and gave fairly linear plot (% oxidative addition vs. σ_I) with R^2 value of 0.91 (0.75 value was found for **10**). Electron withdrawing groups stabilize incipient aryl radical that consequently has more time to abstract the substrate hydrogen atom. Our general conclusion about the steric bulk and electronics of the aryl halide is that bulky electron donating groups in the *ortho* position electronically influence the system in direction of more oxidative addition product while their steric bulk tends to thwart the formation of oxidative addition product. One variable that is overlooked in this analysis is the electronics on the stannylenes **1** and **11**. We have also synthesized $Sn[CH(CH_3)_2]_2$ but found it to be thermally unstable for further experimentation.[16-17]

Table 3.1 Percent oxidative addition product obtained as function of substitution on aryl halide in THF. Experiments were performed with Kira's alkyl stannylene and Lappert's amide stannylene.

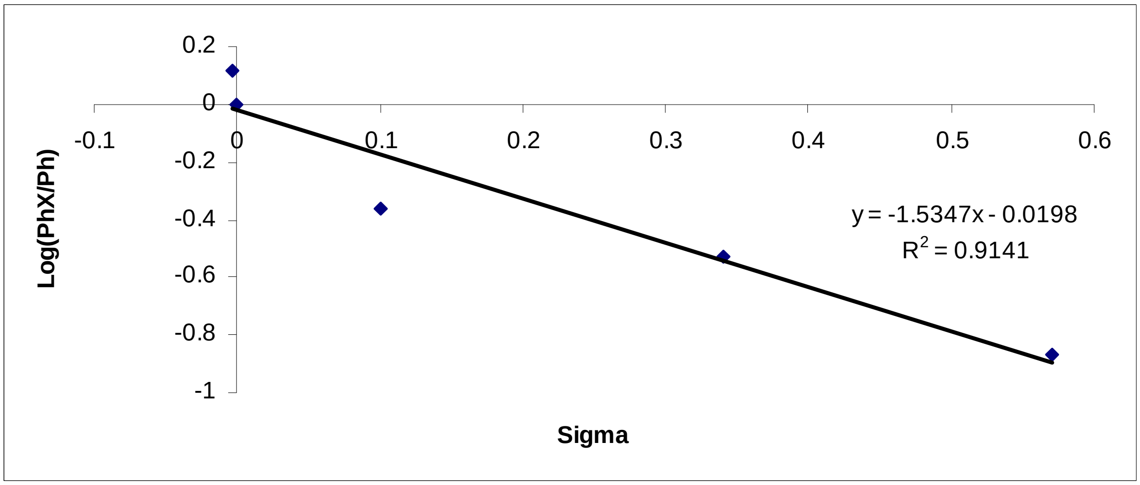


	Aryl Halide (Product Number)						
	PhI	2,4,6-trimethyl	2,4,6-triisopropyl	p-OMe	p-CN	p-Ph	p-*t*-Bu
σ_I	0			0.34	0.57	0.10	-0.03
10	20(**17**)	8(**18**)	12(**16**)	7 (**19**)	7 (**20**)	10 (**21**)	15 (**22**)
1	37(**9**)	10(**23**)	Trace(**24**)	11(**25**)	5(**26**)	16(**27**)	38(**28**)
Log(PhX/Ph) 10	0			-0.46	-0.46	-0.30	-0.13
Log(PhX/Ph) 1	0			-0.53	-0.87	-0.36	-0.011

σ_I values were taken from Anselyn, E. V.; Dougherty, D. A. Modern Physical Organic Chemistry, University Science Books: Sausalito CA, 2004.



Plot 3.1 Hammet plot of **10** for the oxidative addition amount vs. the inductive σ parameter.

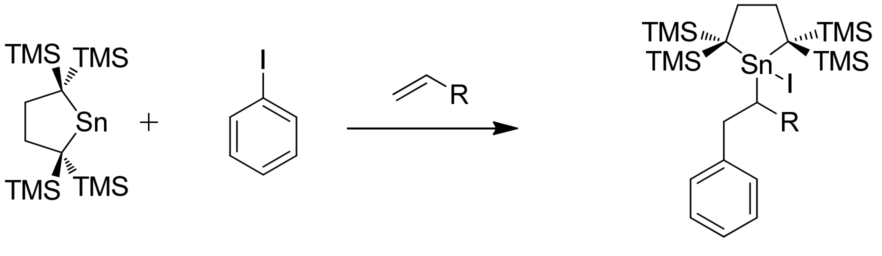


Plot 3.2 Hammet plot of **1** for oxidative addition amount vs. σ parameter.

3.5 C-H Activation of Alkenes

Employing stannylene **10**, allylic CH-activation chemistry has been successfully achieved. Surprisingly, the **10**/PhI reagent is also observed to add across C=C double bonds. The regiochemistry of the reaction is anti-Markovnikov consistent with an initial attack by a phenyl radical and subsequent trapping by the iodostannyl radical. Replacing

PhI with the more bulky mesityl iodide (MesI) reagent has a dramatic impact on the distribution of products formed, Eq 3.1. The amount of oxidative addition product $ArISn[C_2(SiMe_3)_4C_2H_4]$ and double bond addition products formed is dramatically reduced.



(3.1)

Activation of the allylic CH-bond was achieved when a 1:1 mixture of **10**/PhI was added to tetramethylethylene, cyclohexene, cyclopentene, 1-pentene, 1-hexene, or 3,4-dihydro-2H-pyran (Scheme 3.2, Table 3.2). Formation of the CH-activation products ranged from 5 – 80% when employing ~ 0.05 M solutions and slow addition of reagents using a syringe pump. The other major species produced in the reaction were those of the oxidative-addition of PhI to **10** to form $\mathrm{PhI\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2}$ $[C_2(SiMe_3)_4C_2H_4]$ (**29**) and of the unexpected addition of **1**/PhI across the double bond (*vida infra*) to form **33**, **35,** **37** and **39**. Separation of the CH-activation, double bond addition, and oxidative addition products could be achieved by fractional crystallization or column chromatography. Column chromatography on silica gel was typically the most convenient and gave the highest yields. The structures of all compounds were assigned via a combination of ^1H, ^{13}C, and ^{119}Sn NMR spectroscopy, elemental analysis, infrared spectroscopy, and in the case of **30**, **33**, **37**, and **38,** single crystal X-ray diffraction (Fig. 3.2). In addition, the bromine-derivative of cyclohexene product **31**, $\mathrm{(C_6H_9)Br\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2}$ (**31'**), was synthesized independently by the reaction of **10** with 3-bromocyclohexene and fully characterized.

In previous studies employing Ge[CH(SiMe$_3$)$_2$]$_2$ (**17**), varying the steric bulk of the aryl iodide did not have a large impact on the ratio of CH-activation/oxidative addition product formed.[18] However, for the chemistry employing stannylene **10**, increasing the steric bulk of the aryl halide had a major impact on the product distributions. Employing mesityliodide (MesI) in reactions with tetramethylethylene, cyclohexene, and cyclopentene resulted in a dramatic reduction in the formation of oxidative-addition product. Furthermore, the use of MesI also reduced the amount of double bond addition product observed with cyclopentene and 1-hexene. The use of PhBr dramatically reduced the rate of both the CH-activation and double bond addition reactions.

Tin compounds derived from stannylenes containing primary and aromatic Sn-C bonds have previously been employed for Stille-type cross-coupling reactions using chemistry developed by Fouquet et al.[7,14,19] In order to assess the utility of secondary allylic Sn-C bonds derived from the CH-activation chemistry for Stille-type cross-coupling, compound **4** was mixed with 1.5 equiv of PhI, 3 equiv of Me$_4$NF, and 10 mol% Pd(PPh$_3$)$_4$ in 10 mL of dioxane with a 1,3,5-trimethoxybenzene integration standard. After heating at 77 ºC for 16 hours, 3-phenylcyclohexene was obtained in 70% yield.

Scheme 3.2 a) C-H activation and addition across double bond of alkenes. b) Terminal alkenes and cyclopentene exhibit addition across double bond of aryl halide and **10**.

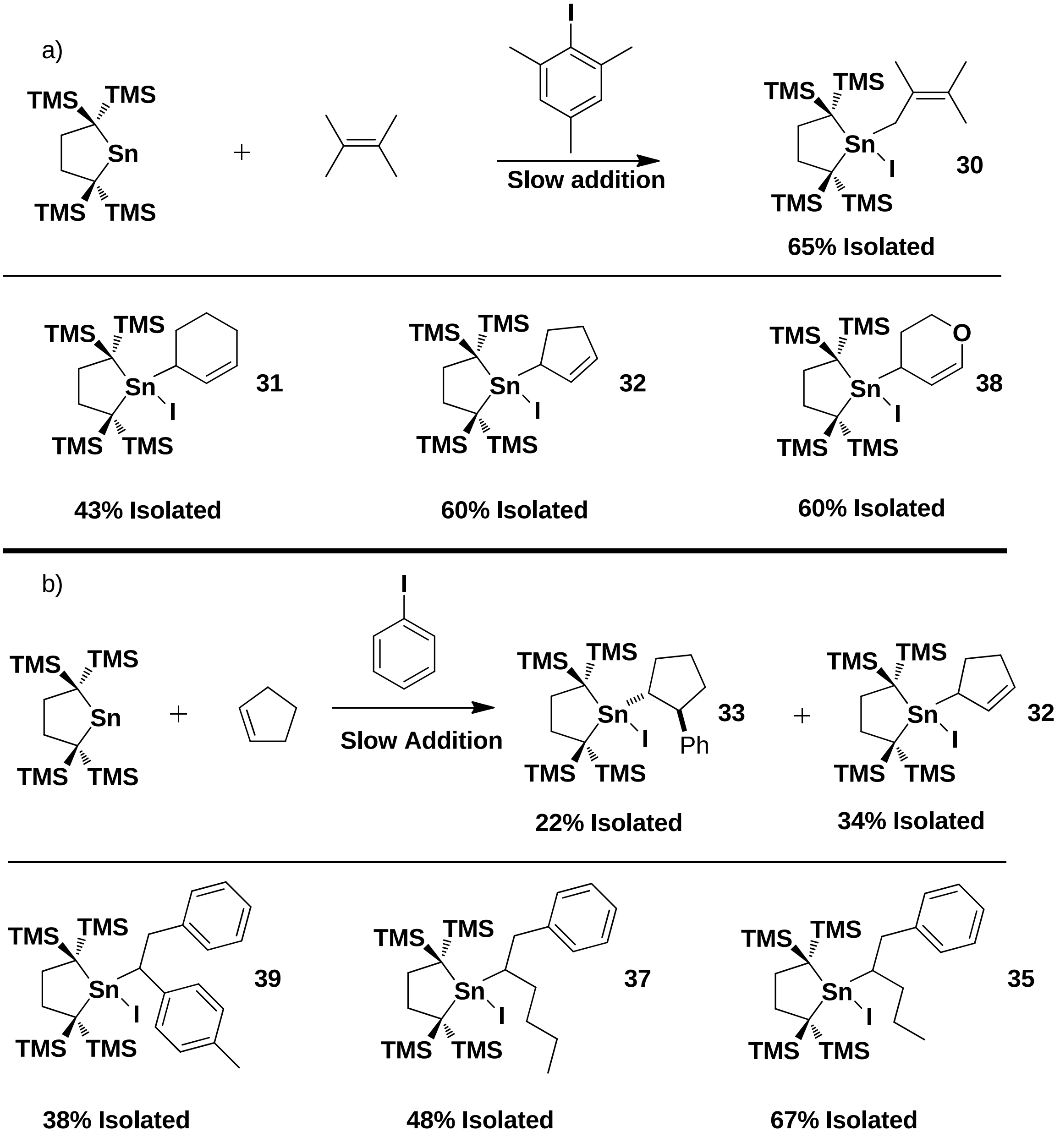

a)
TMS
Sn
I
Slow addition
30
65% Isolated
31
43% Isolated
32
60% Isolated
O
38
60% Isolated
b)
Slow Addition
33
Ph
22% Isolated
32
34% Isolated
39
38% Isolated
37
48% Isolated
35
67% Isolated

Table 3.2 Product distributions as measured by ^{1}H NMR spectroscopy. All reactions were performed using syringe pump techniques. Other unidentified products were also present for cases where the total sums to less than 100%.

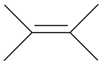
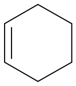
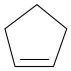
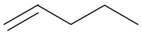
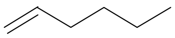
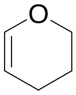
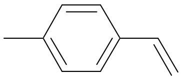
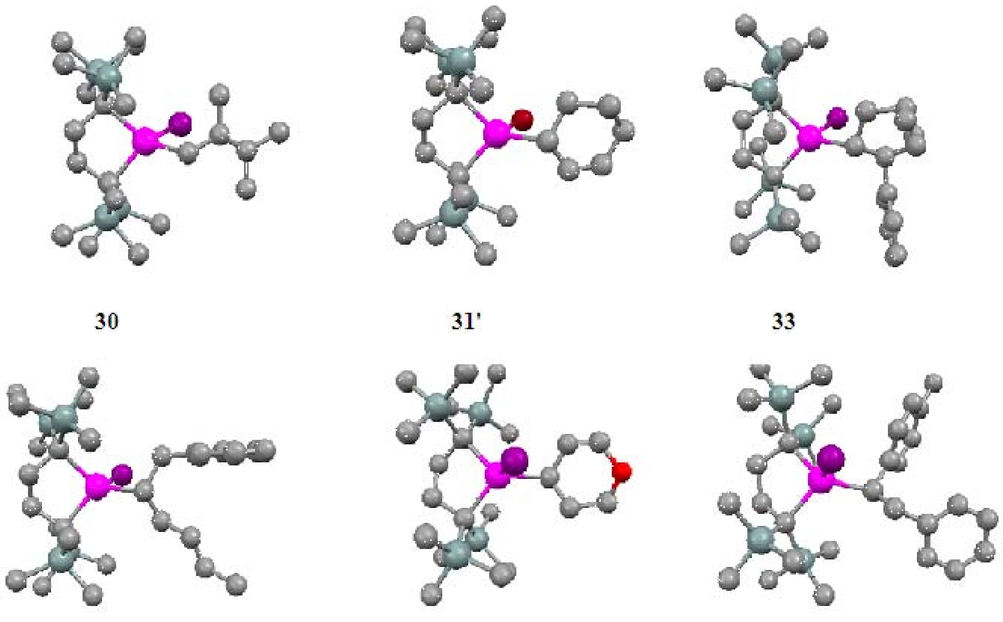
Alkene Substrate	% CH-Activation		% Oxidative-addition		% Double-Bond Addition	
	PhI	MesI	PhI	MesI	PhI	MesI
	67	100	33	0	0	0
	74	100	20	0	6	0
	67	100	1	0	32	0
	20	40	7	15	67	40
	5	30	0	15	60	50
	80	90	0	1	0	0
	0	0	0	5	90	50

Figure 3.2. Ball and Stick plots of $(C_6H_{11})I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$ (**30**), $(C_6H_9)Br\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$ (**31'**), $(C_{11}H_{13})I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$ (**33**), $(C_{12}H_{17})I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$ (**37**), $(C_5OH_7)I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$ (**38**), $(C_{14}H_{15})I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$ (**12**). Full experimental details and ORTEPs are provided in the supplementary material.



30 **31'** **33**

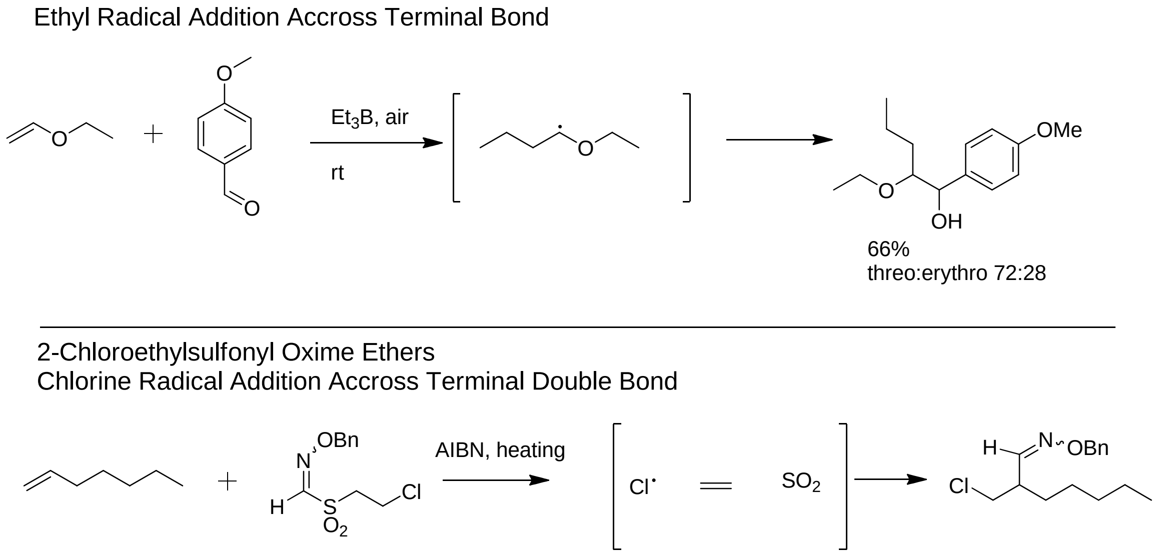
37 **38** **12**

3.6 Addition to Double Bonds

In addition to the anticipated allylic CH-activation and oxidative addition products, a third species was also present in the reactions with tetramethylethylene, cyclohexene, cyclopentene, 1-pentene, and 1-hexene. ^1H NMR spectroscopy indicated that the phenyl group was present but not attached to the tin atom as could be ascertained by the absence of the characteristic ortho protons at δ 7.92 with $^3J_{119Sn\text{-}H} = 16.5$ Hz. In addition, vinylic protons in the region δ 6.0-5.8 indicative of double bonds were absent. The implication of phenyl and tin addition across the double bond, as well as the anti-

Markovnikov regiochemistry of this addition, were confirmed by a single crystal X-ray diffraction study of products **33** and **37**. In the case of 4-methylstyrene, no CH-activation was observed at the methyl group and only double bond addition to give **39** was observed. The reaction is sensitive to the steric constraints of the substrates as indicated by the formation of both CH-activation and double bond addition products for cyclopentene, in 67% and 32% conversion, respectively, as indicated by ^{1}H NMR spectroscopy, whereas little to no double bond addition was observed in the reaction with cyclohexene (6%) or 3,4-dihydro-2H-pyran (0%). The C=C-C angle in cyclopentene is 112° as opposed to 123° in cyclohexene and 122° and 124° in 3,4-dihydro-2H-pyran thus substantially reducing the steric restriction around the cyclopentene double bond. 1-Pentene, 1-hexene, and 4-methylstyrene, which contain only one R substituent on the double bond, are substantially less sterically constrained and give double-bond addition in yields of 67, 60, and 90%, respectively (Table 3.2). The double bond addition chemistry follows the behavior expected for a radical process in terms of the anti-Markovnikov regiochemistry of addition to the terminal olefins and the anti-addition to the cyclopentene.[20] Addition across terminal double bond has been observed in the study of C-H abstraction with ethyl radicals and chlorine radicals, Scheme 3.2b.[21] [22]

Scheme 3.2b. Literature examples of radical addition across terminal double bonds


Ethyl Radical Addition Accross Terminal Bond
O
O
O
Et3B, air
rt
O
OMe
O
OH
66%
threo:erythro 72:28
2-Chloroethylsulfonyl Oxime Ethers
Chlorine Radical Addition Accross Terminal Double Bond
OBn
N
H
S
O2
Cl
AIBN, heating
Cl•
SO2
H
N
OBn
Cl

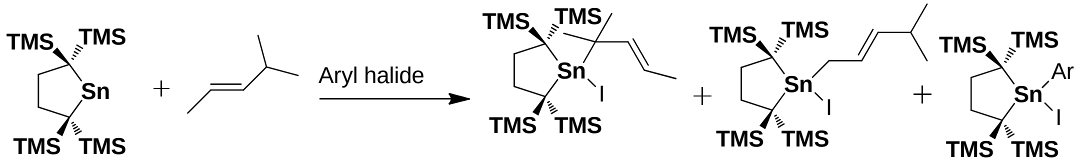
3.7 Regiochemistry of C-H Activation

Regioselective C-H activation of alkanes has been a longstanding goal.[23] In terms of regiochemical preference, transition metal mediated pathways generally give products of less hindered functionalization, i.e. primary > secondary > tertiary.[24] 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.[1-2,25] We have investigated 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.

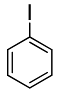
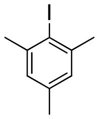
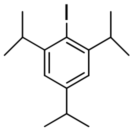
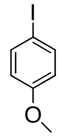
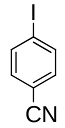
The reaction of trans-4-methyl-2-pentene with **10**/aryl halide showed a preference for primary over tertiary C-H activation, concomitant with a decrease in oxidative-addition, as a function of increased aryl halide steric bulk (Scheme 3.3).

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 increase aryl halide steric bulk (Scheme 3.4).

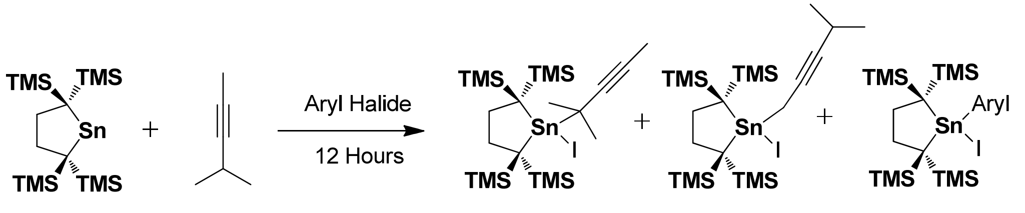
Scheme 3.3 A degree of regiochemical control can be obtained for the reaction with *trans*-4-methyl-2-pentene when the steric bulk of the aryl halide is varied.


TMS
TMS
Sn
TMS
TMS
+
Aryl halide
Sn
I
+
Sn
I
+
Sn
Ar
I

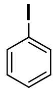
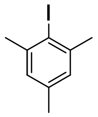
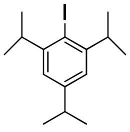
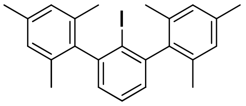
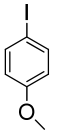
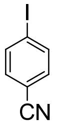
10 40 41

Aryl Halide	%	%	%	$3^{\circ}/1^{\circ}$
	38	24	38	4.7
	29	44	27	2.0
	26	69	5	1.1
	39	25	36	4.7
	complicated mixture			

Scheme 3.4 A degree of regiochemical control can be obtained for the reaction with 4-methyl-2-pentyne when the steric bulk of the aryl halide is varied.



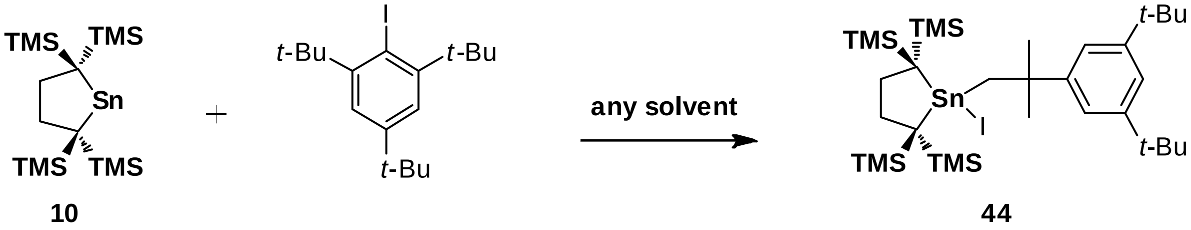
10 42 43

Aryl Halide	%	%	%	3°/1°
	67	13	20	15
	58	35	7	5
	39	53	8	4
	83	17	0	15
	72	16	12	14
	74	15	11	15

In this case, the statistically-correct relative rates of 3°/1° activation ranged from 15 to 4. In an effort to further increase the amount of primary activation, 2,6-dimesityl-iodobenzene 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.

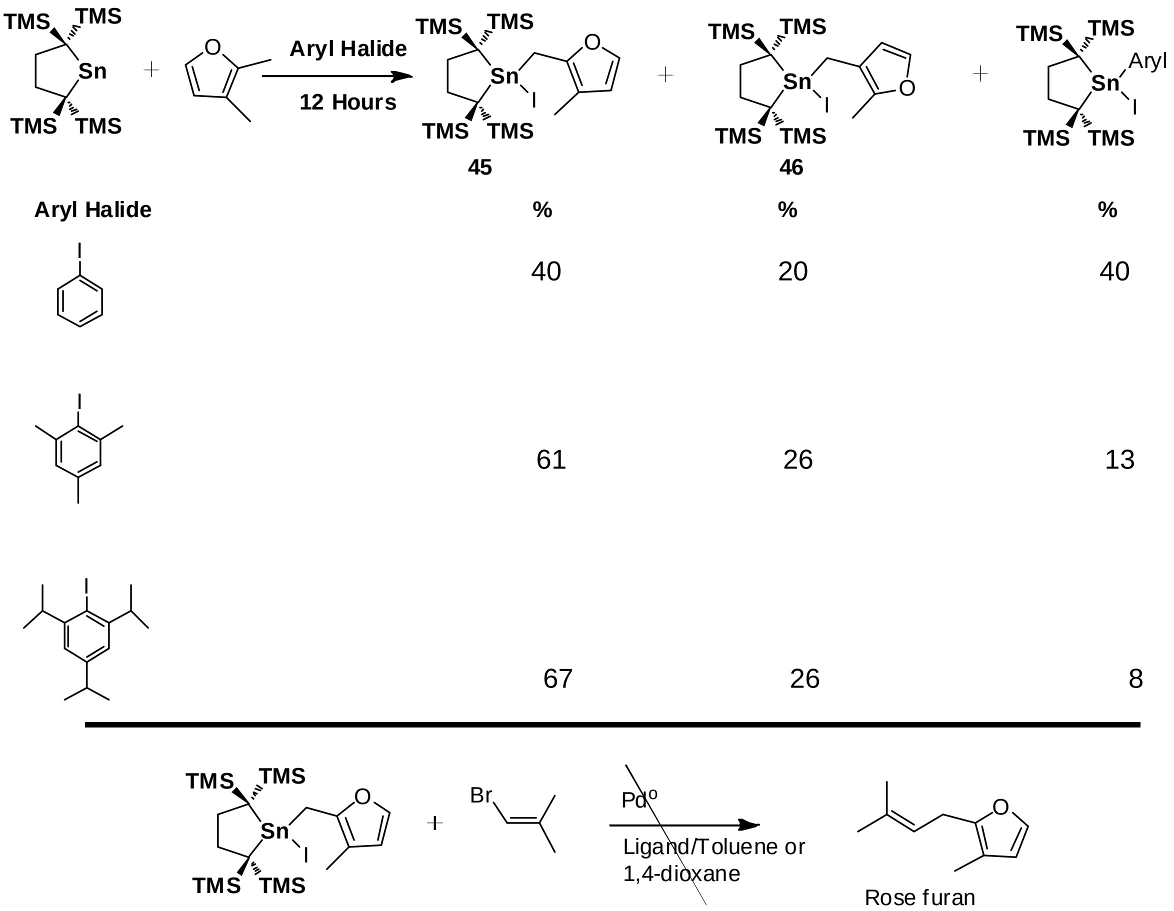
Finally, 2,4,6-tri-*t*-butyl iodobenzene was also employed in an attempt to maximize primary activation. For this aryl halide, only intermolecular C-H activation product **44** was observed regardless of substrate choice (Scheme 3.5).

Scheme 3.5 2,4,6-tbutyl-iodobenzene is intermolecularly C-H activated regardless of the choice of solvent.



As a more stringent test of regioselectivity, 2,3-dimethyl furan 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 3.6).

Scheme 3.6 Regiochemistry of C-H activation of 2,3-dimethyl furan can be controlled by varying the bulk of the aryl halide. Utilization of this C-H activation product in cross coupling reactions was not successful.


TMS TMS Sn TMS TMS
Aryl Halide
12 Hours
45
46
Aryl
Aryl Halide
%
%
%
40 20 40
61 26 13
67 26 8
Br
Pd⁰
Ligand/Toluene or
1,4-dioxane
Rose furan

3.8 Discussion of Hydrogen Atom Transfer Reactions

In reactions involving hydrogen atom transfer the factors that control tertiary/secondary/primary C-H bond selectivity are the amount of hydrogen atom breakage 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 synergistically to increase the selectivity toward the tertiary C-H bond. When significant amount of hydrogen atom breakage is involved in the transition state the bond dissociation energies of C-H bonds becomes 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 aryl halide is increased. In this case the stereolectronic effects influenced tertiary/secondary/primary selectivity in direction opposite to that predicted by thermodynamic and polar effects.[28]

The statistically averaged tertiary vs. primary selectivity observed in reactions of 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/**10**, Schemes 2 and 3, do not grossly vary from the PAT values. The *trans*-4-methyl-2-pentene tertiary/primary selectivity (4.7) with iodobenzene/**10** is lower than the PAT value, while the value for 4-methyl-2-pentyne (15) selectivity with iodobenzene/**10** is higher.

The energy of formation for the tertiary vs. primary radical for *trans*-4-methyl-2-pentene and 4-methyl-2-pentyne were 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-penyne. The value for *trans*-4-methyl-2-pentene with the same method was calculated to be 6.0 kcal/mol. This translates into roughly three fold increase for tertiary/primary selectivity with 4-methyl-2-penyne as compared to *trans*-4-methyl-2-pentene, as calculated using the Arhenius Equation. This exactly agrees with our experimental results discussed above, 15 for 4-methyl-2-pentyne vs. 4.7 *trans*-4-methyl-2-pentene.

Our general conclusion is that that the ER_2/PhX radical species involved here are not very sensitive to the bond dissociation energies. There is relatively little C-H bond breakage in the transition state in C-H activation with iodoarene/**10**, as 6.7 kcal/mol would translate into $8.1*10^4$ rate difference for tertiary/primary C-H site. The tertiary/primary selectivity with NBS and Br_2 /hυ being 58 and 37, respectively, indicates that the ER_2/PhX radical species involved in our C-H activation reaction are highly reactive and comparable to *t*BuO radical or O_2 that have tertiary/primary selectivity of 6.8 and 13, respectively.

Previously, we measured the primary isotope effects of C-H activation reaction with different divalent group 14/iodoarene species. The primary kinetic isotope effect (KIE) for the reaction of West's silylene (**19**) with Et_2O/Et_2O-*d10* was found to be 5.7 ± 0.1.[1] 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-*d8* was found to be 5.0 ± 0.2 and 4.1 ± 0.2, respectively.[2] Based on the value found for phenyl radical generated by PAT (4.2 ± 0.2) we have argued against formation of a common intermediate in these reactions, including the phenyl radical. The primary isotope effect (KIE) reported herein in the reaction of *tri*-isopropyl-iodobenzene and **1** in toluene/toluene-*d7* was found to be 4.9 ± 0.5 as measured by ^1H NMR spectroscopy. This is consistent with the previously reported values. The range of KIE values indicates that the ER_2/PhX radical intermediate involved is dependent on the exact nature of group 14 reagent, 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 a switch in the regiochemistry when steric bulk of the aryl halide *ortho* substituents are increased.

When the *ortho* substituents are increased in size from hydrogen to methyl there is a fall of tertiary/primary selectivity by 2.3 for *trans*-4-methyl-2-pentene and 3 fold for 4-methyl-2-pentyne, Scheme 2 and 3 respectively. With isopropyl substitution there is 4.2 fold drop in tertiary/primary selectivity with the alkene and 3.7 fold drop for the alkyne. Thus the intrinsic propensity to abstract the tertiary C-H bond is overcome only when the statistical ratio of three hydrogens on primary site to one on tertiary site is taken into account. 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 decline of tertiary/primary selectivity. We have further investigated the effects of electronics on the aryl halide ring on the amount of oxidative addition product.

3.9 Summary

We have demonstrated C-H activation of simple alkanes, ethers and aromatics with **1** and aryl halides in excellent yield. The direct formation of Sn-C bonds from allylic CH-bonds has been demonstrated by employing the mixed reagent $Sn[C_2(SiMe_3)_4C_2H_4]$ / PhI. The products of these reactions are viable for C-C bond forming reactions under Stille-type cross-coupling conditions. The unexpected addition of phenyl and the tin complex across double bonds was also discovered. The product distribution and regiochemistry of C-H activation can be controlled to an extent with *ortho* substitution on aryl halide. Oxidative addition product can be decreased by using more sterically bulky/electron donating substituents. In substrates with alkenes and alkyne functionality possessing primary and tertiary C-H bond, the yield of primary C-H activation can be increased by increasing steric bulk on the aryl halide. C-H activation using 2,4,6-tri-t-butyl-iodobenzene yields intermolecular C-H activation product.

Experimental

Manipulations involving $\overline{\mathrm{SnC(SiMe_3)_2CH_2CH_2C}}\mathrm{(SiMe_3)_2}$ (**10**) 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-Triisopropyl iodobenzene was synthesized according to literature procedures.[29] 2,4,6-Tri-*t*-butyl-bromobenzene was borrowed from Arthur Ashe III lab, who prepared it by bromination of 2,4,6-tri-*t*-butylbenzene.[30] (**10)** and $\mathrm{Sn[N(SiMe_3)_2]_2}$ (**1**) were synthesized according to literature procedures.[10,31] Pd(PPh3)4 was purchased from Strem Chemical and used as received. Tetramethylammonium fluoride was used as received. ^{1}H and ^{13}C NMR spectra were acquired on a Varian 500 MHz instruments (499.904 and 125.714 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 $\mathrm{Me_4Sn}$.[32] 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.

(11) $(C_4H_7O)ISnC(SiMe_3)_2CH_2CH_2C(SiMe_3)_2$ A 1-necked 100 mL flask fitted with a rubber septum was charged with 165 mg of 2,4,6-tri-methyl iodobenzene (0.67 mmol, 1.1 eq.), and 5 mL of THF. A solution containing 300 mg of **10** (0.65 mmol, 1 eq) and 10 mL of THF was placed in a gas tight syringe equipped with a 20-gauge needle. 15 mL of the red stannylene solution was added to the iodomesitylene/THF 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 sublimed to give elementally pure material. (110 mg, 25.7 % yield). ^{1}H NMR (C_6D_6) δ: 4.23 (dd, $^3J_{H\text{-}H}$= 2.00 Hz, $^3J_{H\text{-}H}$ = 7.21 Hz, 1H, Sn-C*H*), 3.74 (pseudo-quartet, $J_{H\text{-}H}$ = 7.21 Hz, 1H, O-CH_2), 3.46 (dt, $^3J_{H\text{-}H}$= 8.0 Hz, $^2J_{H\text{-}H}$ = 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 (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$(CH_3)_3$), 4.61 (Si$(CH_3)_3$), 4.52 (Si$(CH_3)_3$), 4.37 (Si$(CH_3)_3$). ^{119}Sn (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

(12) $(C_6H_{11})ISnC(SiMe_3)_2CH_2CH_2C(SiMe_3)_2$ A 1-necked 100 mL flask fitted with a rubber septum was charged with 236 mg of 2,4,6-triisopropyliodobenzene (0.71 mmol, 1 eq.), and 5 mL of cyclohexane. A solution containing 300 mg of **10** (0.65 mmol, 1 eq.) and 15 mL of cyclohexane was placed in a gas tight syringe equipped with a 20-gauge needle. 10 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 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-$C(SiMe_3)_2$-C*H*$_2$-C*H*$_2$ and SnCHC*H*$_2$), 1.77 (tt, $^3J_{H\text{-}H}$= 12.5 Hz, $^3J_{H\text{-}H}$ = 3.5 Hz, 1H, Sn-C*H*), 1.68 (m, 2H, SnCHCH_2C*H*$_2$), 1.52 (m, 1H, SnCHCH_2CH_2C*H*$_2$), 1.27 (m, 3H, SnCHCH_2C*H*$_2$ and SnCHCH_2CH_2C*H*$_2$), 0.39 (s, 18H, Si(C*H*$_3$)$_3$), 0.18 (s, 18H, Si(C*H*$_3$)$_3$). ^{13}C (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_2CH_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 E.A. Calc'd for $C_{22}H_{51}ISi_4Sn$ C: 39.23; H: 7.63; found C: 39.53; H: 7.84.

(13) $(C_4H_9O)ISnC(SiMe_3)_2CH_2CH_2C(SiMe_3)_2$ A 1-necked 100 mL flask fitted with a rubber septum was charged with 175.2 mg of 2,4,6-tri-methyl iodobenzene (0.71 mmol, 1.1 eq.), and 5 mL of diethyl ether. A solution containing 300 mg of **10** (0.65 mmol, 1 eq) and 10 mL of diethyl ether was placed in a gas tight syringe equipped with a 20-gauge needle. 15 mL 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 (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 (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 E.A. Calc'd for $C_{20}H_{49}IOSi_4Sn$ C: 37.22; H: 7.59; found C: 37.17; H: 7.65.

(14) $(C_7H_7)I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$ A 1-necked 100 mL flask fitted with a rubber septum was charged with 157 mg of 2,4,6-triisopropyliodobenzene (0.48 mmol, 1.1 eq.), and 5 mL of toluene. A solution containing 200 mg of **10** (0.43 mmol, 1 eq.) and 10 mL of toluene was placed in a gas tight syringe equipped with a 20-gauge needle. 15 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$_3$)$_2$C*H*$_2$), 0.32 (s, 18H, Si(C*H*$_3$)$_3$), 0.13 (s, 18H, Si(C*H*$_3$)$_3$). ^{13}C (C$_6$D$_6$) 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 (C$_6$D$_6$) 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 E.A. Calc'd for $C_{23}H_{47}ISi_4Sn$ C: 40.53; H: 6.95; found C: 40.84; H: 7.22.

(15) $\mathbf{(C_7H_7)I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2}$ A 1-necked 100 mL flask fitted with a rubber septum was charged with 157 mg of 2,4,6-triisopropyliodobenzene (0.48 mmol, 1.1 eq.), and 5 mL of mesitylene. A solution containing 200 mg of **10** (0.43 mmol, 1 eq.) and 15 mL of toluene was placed in a gas tight syringe equipped with a 20-gauge needle. 15 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$_6$D$_6$) δ: 7.14 (s, 2H, *ortho*-Ph), 6.69 (s, 1H, *para*-Ph), 3.33 (s with Sn satellites, $^2J_{Sn\text{-}H}$ = 30.0 Hz, 2H, Sn-C*H*$_2$), 2.21 (s, 6H, ArC*H*$_3$), 2.07 (m, 2H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$), 1.90 (m, 2H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$), 0.33 (s, 18H, Si(C*H*$_3$)$_3$), 0.14 (s, 18H, Si(C*H*$_3$)$_3$). ^{13}C (C$_6$D$_6$) 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 (C$_6$D$_6$)

δ 96.59. MS EI *m/z*: 695.5 (M-CH_3). IR(film) cm^{-1} ν 2925, 1598, 1463, 1377, 1245, 902, 844 E.A. Calc'd for $C_{25}H_{51}ISi_4Sn$ C: 42.31; H: 7.24; found C: 42.31; H: 7.17.

(16) $\mathbf{(C_{15}H_{23})I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2}$ A 1 necked 100 ml flask fitted with a rubber septum was charged with 156.7 mg (0.47 mmol, 1.1 eq) of 2,4,6-tri-isopropyl-iodobenzene and 10 ml of benzene. Stannylene (**10**) 200 mg (0.43 mmol, 1eq) was added in one portion and 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 Kugel-Rohr apparatus to obtain a white solid. (340 mg, 99.3 % yield). ^1H NMR (C_6D_6) δ: 7.17 (s, 2H, *meta*-Ph), 3.05 (m, 2H, *ortho*-C*H*(CH_3)$_2$, 2.73 (septet, $^3J_{H\text{-}H} = 7.0$ Hz, *para*-C*H*(CH_3)$_2$), 2.23-2.00 (m, 4H, SnC(Si(CH_3)$_2$C*H*$_2$-C*H*$_2$), 1.42 (d, $^3J_{H\text{-}H} = 6.5$ Hz, 6H, *para*-CH(C*H*$_3$)$_2$), 1.15 (d, $^3J_{H\text{-}H} = 7.0$ Hz, 12H, *ortho*-CH(C*H*$_3$)$_2$, 0.50 (s, 18H, Si(C*H*$_3$)$_3$), 0.20 (s, 18H, Si(C*H*$_3$)$_3$). ^{13}C (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)$_2$*C*H$_2$-*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 (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 E.A. Calc'd for $C_{31}H_{63}ISi_4Sn$ C: 46.91; H: 8.00; found C: 46.88; H: 8.01.

(18) $\mathbf{(C_9H_{11})I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2}$ A 1 necked 100 ml flask fitted with a rubber septum was charged with 124 mg (0.51 mmol, 1.1 eq) of 2,4,6-tri-methyl-iodobenzene and 20 ml of benzene. Stannylene (**10**) 233 mg (0.50 mmol, 1eq) was added in one portion and 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 Kugel-Rohr apparatus to obtain a white solid. (333 mg, 93 % yield). ^1H NMR (C_6D_6) δ: 6.67 (s, 2H, *meta*-Ph), 2.60 (s, 6H, *ortho*-CH_3), 2.21-1.99 (m, 4H, $SnC(Si(CH_3)_2CH_2$-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 (C_6D_6) δ 149.8 (*ipso*-Ar), 142.1 (Ar), 139.7 (Ar), 128.9 (*meta*- Ar), 36.49 ($SnC(Si(CH_3)_2CH_2$-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 (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.

(19) $(C_7H_7O)I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$ A 1 necked 50 ml flask fitted with a rubber septum was charged with 28 mg (0.12 mmol, 1.1 eq) of 4-iodoanisole and 15 ml of benzene. Stannylene (**10**) 50 mg (0.11 mmol, 1eq) was added in one portion and red solution was stirred overnight until the red color disappeared completely. Volatiles were evaporated and ^1H and ^{13}C NMR spectra of pure oxidative product were obtained. ^1H NMR (C_6D_6) δ: 7.87 (d with Sn satellites, $^3J_{H\text{-}H} = 8.5$ Hz, $^2J_{Sn\text{-}H} = 34.0$ Hz, 2H, *ortho*-Ph), 6.74 (d, $^3J_{H\text{-}H} = 8.5$ Hz, 2H, *meta*-Ph), 3.19 (s, 3H, *para*-OCH_3), 2.19-2.16 (m, 2H, $SnC(Si(CH_3)_2CH_2$-CH_2), 2.04-2.00 (m, 2H, $SnC(Si(CH_3)_2CH_2$-CH_2), 0.47 (s, 18H, $Si(CH_3)_3$), 0.20 (s, 18H, $Si(CH_3)_3$). ^{13}C (C_6D_6) δ 161.24 (Ph), 138.11 (Ph), 137.42 (Ph), 114.99 (Ph), 54.90 (OCH_3), 35.14 ($SnC(Si(CH_3)_2CH_2$-CH_2), 4.70 ($Si(CH_3)_3$).

(20) $(C_7H_4N)I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$ A 1 necked 10 ml flask fitted with a rubber septum was charged with 28 mg (0.12 mmol, 1.1 eq) of 4-iodobenzonitrile and 20 ml of benzene. Stannylene (**10**) 50 mg (0.11 mmol, 1eq) was added in one portion and 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, $SnC(Si(CH_3)_2CH_2-CH_2)$), 1.96-1.9 (m, 2H, $SnC(Si(CH_3)_2CH_2-CH_2)$), 0.39 (s, 18H, $Si(CH_3)_3$), 0.07 (s, 18H, $Si(CH_3)_3$). ^{13}C (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 ($SnC(Si(CH_3)_2CH_2-CH_2)$), 4.64 ($Si(CH_3)_3$), 4.49 ($Si(CH_3)_3$).

(21) $(C_{12}H_9)I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$ A 1 necked 10 ml flask fitted with a rubber septum was charged with 33 mg (0.12 mmol, 1.1 eq) of 4-phenyl-iodobenzene and 10 ml of benzene. Stannylene (**10**) 50 mg (0.11 mmol, 1eq) was added in one portion and 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: 8.00 (d with br Sn satellites, $^3J_{H-H}$ = 8.0 Hz, $^2J_{Sn-H}$ = 24.4 Hz, 2H, *ortho*-Ar), 7.39 (d, $^3J_{H-H}$ = 8.0 Hz, *meta*-Ar) 7.32 (d, $^3J_{H-H}$ = 7.50 Hz, 2H, Ar), 7.24-7.08 (m, 3H, Ar), 2.16 (m, 2H, $SnC(Si(CH_3)_2CH_2-CH_2)$), 2.07 (m, 2H, $SnC(Si(CH_3)_2CH_2-CH_2)$), 0.48 (s, 18H, $Si(CH_3)_3$), 0.22 (s, 18H, $Si(CH_3)_3$). ^{13}C (C_6D_6) δ 145.94 (Ar), 142.77 (Ar), 140.85 (Ar), 138.47 (Ar), 137.24 (Ar), 129.32 (Ar), 127.82 (Ar), 127.73 (Ar), 35.18 ($SnC(Si(CH_3)_2CH_2-CH_2)$), 4.76 ($Si(CH_3)_3$), 4.70 ($Si(CH_3)_3$).

(22) $(C_{12}H_9)I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$ A 1 necked 10 ml flask fitted with a rubber septum was charged with 21.4 µl (0.12 mmol, 1.1 eq) of 4-*t*-butyl-iodobenzene and 10 ml of benzene. Stannylene (**10**) 50 mg (0.11 mmol, 1eq) was added in one portion and 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: 7.94 (d with br Sn satellites, $^3J_{H-H} = 8.0$ Hz, $^2J_{Sn-H} = 25.6$ Hz, 2H, *ortho*-Ar), 7.28 (d, $^3J_{H-H} = 8.0$ Hz, 2H, *meta*- Ar), 2.18 (m, 2H, $SnC(Si(CH_3)_2CH_2$-$CH_2)$, 2.04 (m, 2H, $SnC(Si(CH_3)_2CH_2$-$CH_2)$, 1.11 (s, 9H, *t*-Bu), 0.47 (s, 18H, $Si(CH_3)_3$), 0.19 (s, 18H, $Si(CH_3)_3$). ^{13}C (C_6D_6) δ 152.99, 143.71, 136.71, 126.20 (Ar), 36.16 ($SnC(Si(CH_3)_2CH_2$-CH_2), 31.55 (*t*-Bu), 4.71 ($Si(CH_3)_3$).

(23) $(C_9H_{11})ISn[N(SiMe_3)]_2$ A 1 necked 10 ml flask fitted with a rubber septum was charged with 30 mg (0.12 mmol, 1.1 eq) of 2,4,6-trimethyl-iodobenzene and 5 ml of benzene. Amide stannylene (**1**) 50 mg (0.11 mmol, 1eq) was added in one portion and 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: 6.63 (s, 2H, *meta*-Ar), 2.74 (s, 6H, *ortho*-CH_3), 2.00 (s, 3H, *para*-CH_3), 0.42 (s, 36H, $Si(CH_3)_3$). ^{13}C (C_6D_6) δ 144.4, 143.6, 140.7, 130.5 (Ar), 27.02 (*ortho*-CH_3), 21.25 (para-CH_3), 7.53 ($Si(CH_3)_3$).

(24) $(C_{15}H_{23})ISn[N(SiMe_3)]_2$ A 1 necked 10 ml flask fitted with a rubber septum was charged with 29 mg (0.12 mmol, 1.1 eq) of 2,4,6-triisopropyl-iodobenzene and 5 ml of benzene. Amide stannylene (**1**) 48 mg (0.11 mmol, 1eq) was added in one portion and 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: 7.10 (s, 2H, *meta*-Ar), 3.90 (m, 2H, *ortho*-$CH(CH_3)$), 2.67 (m, 1H, *para*-

C*H*(CH$_3$)$_2$), 1.41 (d, $^3J_{H\text{-}H}$ = 6.40 Hz, 12H, *ortho*-CH(C*H*$_3$)$_2$), 1.07 (d, $^3J_{H\text{-}H}$ = 6.80 Hz, 6H, *p*-CH(C*H*$_3$)$_2$), 0.46 (s, 36H, Si(C*H*$_3$)$_3$). ^{13}C (C_6D_6) δ 155.0, 152.2, 124.78, 122.78 (Ar), 35.56 (*ortho*-*C*H(CH$_3$)$_2$), 34.58 (*para*-*C*H(CH$_3$)$_2$), 26.85 (*ortho*-CH(*C*H$_3$)$_2$), 24.13 (*para*-CH(*C*H$_3$)$_2$), 8.15 (Si(C*H*$_3$)$_3$).

(25) $(C_7H_7O)ISn[N(SiMe_3)]_2$ A 1 necked 10 ml flask fitted with a rubber septum was charged with 31 mg (0.12 mmol, 1.1 eq) of 4-iodoanisole and 5 ml of benzene. Amide stannylene (**1**) 48 mg (0.11 mmol, 1eq) was added in one portion and 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: 7.83 (d with br Sn satellites, $^3J_{H\text{-}H}$ = 8.8 Hz, $^2J_{Sn\text{-}H}$ = 38.0 Hz, 2H, *ortho*-Ar), 6.75 (d, $^3J_{H\text{-}H}$ = 8.8 Hz, 2H, *meta*-Ar), 3.18 (s, 3H, OC*H*$_3$), 0.39 (s, 36H, Si(C*H*$_3$)$_3$). ^{13}C (C_6D_6) δ 162.14, 136.95, 135.15, 115.25 (Ar), 54.95 (O-*C*H$_3$), 6.45 (Si(C*H*$_3$)$_3$).

(26) $(C_7H_4N)ISn[N(SiMe_3)]_2$ A 1 necked 10 ml flask fitted with a rubber septum was charged with 31 (0.12 mmol, 1.1 eq) of 4-iodobenzonitrile and 5 ml of benzene. Amide stannylene (**1**) 48 mg (0.11 mmol, 1eq) was added in one portion and 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: 7.65 (d with br Sn satellites, $^3J_{H\text{-}H}$ = 8.0 Hz, $^2J_{Sn\text{-}H}$ = 35.2 Hz, 2H, *ortho*-Ar), 6.88 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H, *meta*-Ar), 0.28 (s, 36H, Si(C*H*$_3$)$_3$). ^{13}C (C_6D_6) δ 150.4 (CN), 135.79, 133.21, 128.92, 115.12 (Ar), 6.30 (Si(*C*H$_3$)$_3$).

(27) $(C_{12}H_9)ISn[N(SiMe_3)]_2$ A 1 necked 10 ml flask fitted with a rubber septum was charged with 33.8 mg (0.12 mmol, 1.1 eq) of 4-phenyl-iodobenzene and 5 ml of benzene. Amide stannylene (**1**) 48 mg (0.11 mmol, 1eq) was added in one portion and red solution was stirred overnight until the red color disappeared completely. Volatiles were evaporated and ^1H and ^{13}C spectra of pure oxidative product were obtained. ^1H NMR (C_6D_6) δ: 7.97 (d with br Sn satellites, $^3J_{H\text{-}H} = 8.5$ Hz, $^2J_{Sn\text{-}H} = 37.5$ Hz, 2H, *ortho*-Ar), 7.43 (d, $^3J_{H\text{-}H} = 8.5$ Hz, *meta*-Ar), 7.34 (d, $^3J_{H\text{-}H} = 7.0$ Hz, Ar), 7.24-7.12 (m, Ar), 0.40 (s, 36H, $Si(CH_3)_3$). ^{13}C (C_6D_6) δ 143.8, 143.5, 140.6, 136.07, 129.37, 128.92, 128.06, 127.82 (Ar), 6.47 ($Si(CH_3)_3$).

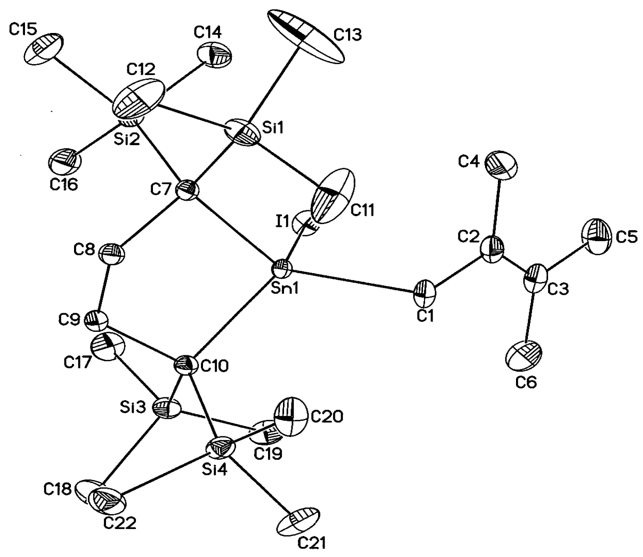
(28) $(C_{10}H_{13})ISn[N(SiMe_3)]_2$ A 1 necked 10 ml flask fitted with a rubber septum was charged with 21.4 µl (0.12 mmol, 1.1 eq) of 4-*t*-butyl-iodobenzene and 5 ml of benzene. Amide stannylene (**1**) 48 mg (0.11 mmol, 1eq) was added in one portion and red solution was stirred overnight until the red color disappeared completely. Volatiles were evaporated and ^1H and ^{13}C spectra of pure oxidative product were obtained. ^1H NMR (C_6D_6) δ: 7.90 (d with br Sn satellites, $^3J_{H\text{-}H} = 8.50$ Hz, $^2J_{Sn\text{-}H} = 38.2$ Hz, 2H, *ortho*-Ar), 7.28 (d, $^3J_{H\text{-}H} = 8.50$ Hz, 2H, *meta*-Ar), 1.11 (s, 9H, *t*-Bu), 0.39 (s, 36H, $Si(CH_3)_3$). ^{13}C (C_6D_6) δ 154.27, 141.45, 135.54, 126.55 (Ar), 31.51 (*t*-Bu), 6.46 ($Si(CH_3)_3$).

(29) **$(C_6H_5)I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$**

A 50 mL flask was charged with 106 µL of phenyl iodide (0.95 mmol, 1 eq.),10 mL of benzene, and 400 mg (0.86 mmol, 0.9 eq.) of **10.** The reaction mixture was stirred at room temperature for 16 hours. All volatiles were removed *in vacuo* and the resulting solid recrystallized from pentane at -78 ^{o}C to give a white powder (170 mg, 30% yield). ^{1}H NMR (C_6D_6) δ 7.94 (d with Sn satellites, $^3J_{H\text{-}H}$ = 7.5 Hz, $^3J_{119Sn\text{-}H}$ = 65.5 Hz 2H, *o*-Ph), 7.12 (pseudo-t, J = 7.5Hz, 2H, *m*-Ph), 6.97 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 1H, *p*-Ph), 2.15 (m, 2H, Sn-C$(SiMe_3)_2$-C*H*$_2$), 2.00 (m, 2H, Sn-C$(SiMe_3)_2$-C*H*$_2$), 0.45 (s, 18H, Si(C*H*$_3$)$_3$), 0.17 (s, 18H, Si(C*H*$_3$)$_3$). ^{13}C (C_6D_6) δ 147.27 (*i*-Ph), 136.80 (*o*-Ph), 130.00 (*m*-Ph), 129.17 (*p*-Ph), 67.55 (Sn-*C*$(SiMe_3)_2$), 35.12 (Sn-C$(SiMe_3)_2$-*C*H$_2$), 4.66 (Si(*C*H$_3$)$_3$), 4.63 (Si(*C*H$_3$)$_3$). MS EI *m/z*: 653.1 (M-CH$_3$), 541.2 (M-I). IR(film) cm^{-1} ν 2922, 1626, 1249, 847. E.A. Calc'd for $C_{22}H_{45}ISi_4Sn$ C: 39.58; H: 6.79; found C: 38.92; H: 6.79.

(30) $(C_6H_{11})I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$. A 1-necked 100 mL flask fitted with a rubber septum was charged with 178 μL of iodomesitylene (0.95 mmol, 1 eq.), and 15 mL of 2,3-dimethyl-2-butene. A solution containing 400 mg **10** (0.86 mmol, 0.9 eq.) and 25 mL of 2,3-dimethyl-2-butene was placed in a gas tight syringe equipped with a 20-gauge needle. 20 mL of the red stannylene solution was added to the iodomesitylene solution at a rate of 8 mL/hr using a syringe pump. The last 5 mL of 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 resulting solid was recrystallized from pentane at -78 ^{o}C to give a white powder (341 mg, 60 % yield). ^{1}H NMR (C_6D_6) δ: 2.61 (s with br Sn satellites, $^2J_{Sn\text{-}H}$ = 43.0 Hz, 2H, Sn-C*H*$_2$), 1.81 (s, 3H, Sn-CH$_2$-C-C*H*$_3$), 2.11 (m, 2H, Sn-C$(SiMe_3)_2$-C*H*$_2$), 1.93 (m, 2H, Sn-C$(SiMe_3)_2$-C*H*$_2$), 1.75 (s, 3H, C=C-C*H*$_3$), 1.73 (s, 3H, C=C-C*H*$_3$), 0.40 (s, 18H, Si(C*H*$_3$)$_3$), 0.19 (s, 18H, Si(C*H*$_3$)$_3$) ^{13}C (C_6D_6) δ 127.25 (Sn-CH$_2$-*C*=C), 126.31 (Sn-CH$_2$-C=*C*), 35.59 (Sn-C-*C*H$_2$), 35.11 (Sn-C-*C*H$_2$), 22.76 (Sn-*C*H$_2$), 22.32 (Sn-C-*C*H$_3$), 21.83 (Sn-C=C-C*H*$_3$), 21.23 (Sn-C=C-*C*H$_3$), 4.66 (Si(*C*H$_3$)$_3$), 4.64 (Si(CH_3)$_3$), tertiary carbon not observed in this case.. ^{119}Sn (C_6D_6) δ 163.9. MS *m/z* (relative intensity): EI: 659.3 M-CH_3 (3.0), 591.2 (38.4), 419.0 (7.1), 229.1 (8.9), 246.9 (32.7), 157.1 (21.0), 73.1 (100.0) IR(film) cm^{-1} ν 2923, 2853, 1247. E.A. Calc'd for $C_{22}H_{51}ISi_4Sn$ C: 39.23; H: 7.63; found C: 39.20; H: 7.70.

Structure Determination of **30**. Colorless blocks were grown from a pentane solution at 23 °C. A crystal of dimensions 0.33 x 0.29 x 0.25 mm was 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 5.055 cm from the crystal. A total of 4095 frames were collected with a scan width of 0.5 in ω and φ with an exposure time of 10 s/frame. The integration of the data yielded a total of 115591 reflections to a maximum 2θ value of 58.84° of which 8440 were independent and 8142 were greater than 2σ(I). The final cell constants (Table 1) were based on the xyz centroids of 9333 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 $P2_1/n$ with Z = 4 for the formula $C_{22}H_{51}Si_4SnI$. 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 = 0.0196 and wR2 = 0.0504 [based on I > 2σ(I)], R1 = 0.0205 and wR2 = 0.0510 for all data. CCDC 663917.



ORTEP of **30** (50% thermal elliposoids).

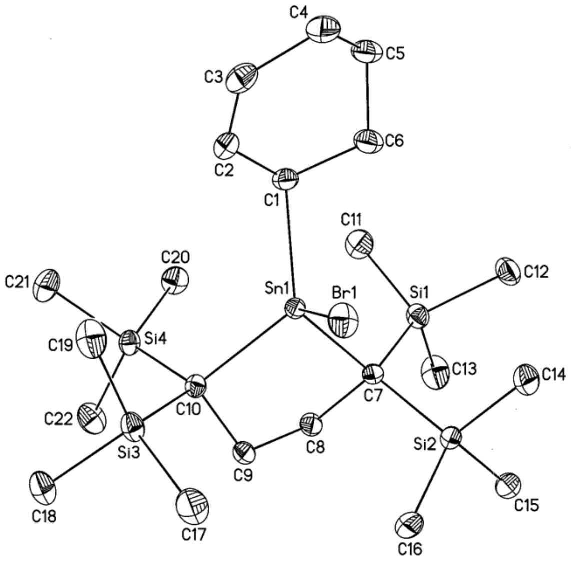
(**31**) **$(C_6H_9)I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$**. A 1-necked 100 mL flask fitted with a rubber septum was charged with 178 μL of iodomesitylene (0.95 mmol, 1 eq). Cyclohexene was added to the flask (15 mL) which was then capped with a rubber septum. Red solution containing **10** (400 mg, 0.863 mmol) and 25 mL of cyclohexene was placed in a gas tight syringe equipped with a 20-gauge needle. The stannylene solution was added to the phenyl iodide solution at a rate of approximately 6 mL/hr using a syringe pump. Last 5 mL of solution were added at rate of 1 mL/hr. The solution was stirred for 8 h to insure completion of reaction, yielding a cloudy, white solution. The volatiles were removed in vacuo and resulting solid was recrystallized twice from pentane at -78 ^{o}C yielding 250 mg of white powder (43 % yield). ^{1}H NMR (C_6D_6) δ: 5.91 (s, 2H, Sn-CH-C*H*=C*H*), 2.89 (m, 1H, Sn-C*H*), 2.10 (m, 2H, Sn-C(SiMe$_3$)$_2$-CH_2) 1.94 (m, 2H, Sn-C(SiMe$_3$)$_2$-CH_2), 2.31 (m, 1H, Sn-CH-CH=CH-CH_2), 2.10 (m, 1H, Sn-CH-CH=CH-CH_2), 2.10 (m, 1H, Sn-CH-CH_2), 1.82 (m, 1H, Sn-CH-CH_2), 1.82 (m, 1H, Sn-

CH-CH$_2$-C*H*$_2$), 1.46 (m, 1H, Sn-CH-CH$_2$-C*H*$_2$). 0.40 (s, 18H, Si(C*H*$_3$)$_3$), 0.19 (s, 9H, Si(C*H*$_3$)$_3$), 0.16 (s, 9H, Si(C*H*$_3$)$_3$). ^{13}C (C_6D_6) δ 130.59 (Sn-CH-*C*=C), 128.21 (Sn-CH-C=*C*), 67.52 (Sn-*C*(Si(CH$_3$)$_2$), 40.91 (Sn-CH), 35.50 (Sn-C-*C*H$_2$), 35.44, (Sn-C-*C*H$_2$), 27.99 (Sn-CH-CH=CH-*C*H$_2$), 25.29 (Sn-CH-*C*H$_2$), 23.45 (Sn-CH-CH$_2$-*C*H$_2$), 4.59 (Si(*C*H$_3$)$_3$), 4.56 (Si(*C*H$_3$)$_3$), 4.51 (Si(*C*H$_3$)$_3$), 4.47 (Si(*C*H$_3$)$_3$). ^{119}Sn (C_6D_6) δ 160.8. MS EI *m/z*: 657.1 (M-CH$_3$). IR(film) cm^{-1} ν 2923, 2853, 1251. E.A. Calc'd for $C_{22}H_{49}ISi_4Sn$ C: 39.35; H: 7.35; found C: 39.27; H: 7.48.

(**31'**) **$(C_6H_9)Br\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$**. A 2-necked 25 mL flask was charged with 55 mg of **1** (0.13 mmol) and 10 mL benzene. 21 μL of 3-bromocyclohexene (0.20 mmols) was added to the red solution resulting in a clear, colorless solution. Removing volatiles resulted in a white solid consisting of **31'** and $[C_2H_4(SiMe_3)_4C_2]SnBr_2$. **31'** was purified using a silica gel column eluting with hexane. Removal of the hexane gave 33 mg (41% yield) of a white solid. ^{1}H NMR of **31'** (C_6D_6) δ: 5.980 (pseudo-d, 1H, Sn-CH-C*H*=CH), 5.857 (m, 1H, Sn-CH-CH=C*H*), 2.873 (m, 1H, Sn-C*H*), 2.343 (m, 1H, Sn-CH-C*H*$_2$), 2.099 (m, 1H, Sn-CH-C*H*$_2$), 2.099 (m, 1H, Sn-CH-CH=CH-C*H*$_2$), 1.951 (m, 1H, Sn-CH-CH=CH-C*H*$_2$), 1.813 (2H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$), 1.281 (2H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$), 1.451 (2H, m, Sn-CH-CH$_2$-C*H*$_2$),), 0.373 (18H, Si(C*H*$_3$)$_3$), 0.175 (9H, Si(C*H*$_3$)$_3$), 0.153 (9H, Si(C*H*$_3$)$_3$). ^{13}C NMR (C_6D_6) δ: 129.35 (Sn-CH-CH=*C*H), 126.71 (Sn-CH-*C*H=CH), 66.13 (Sn-*C*(Si(CH$_3$)$_2$), 41.27 (Sn-*C*H), 34.28 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 34.16 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 26.50 (Sn-CH-*C*H$_2$), 24.53 (Sn-CH-CH=CH-*C*H$_2$), 22.66 (Sn-CH-CH$_2$-*C*H$_2$), 3.55 (Si(*C*H$_3$)$_3$), 3.53 (Si(*C*H$_3$)$_3$), 3.31 (Si(*C*H$_3$)$_3$). ^{1}H NMR of

$[C_2H_4(SiMe_3)_4C_2]SnBr_2$ (C_6D_6) δ: 1.893 (4H, Sn-C(Si(CH_3)$_3$-CH_2), 0.273 (36H, Si(CH_3)$_3$).

Structure Determination of **31'**. Colorless needles were grown from a benzene solution at 23 °C. A crystal of dimensions 0.25 x 0.21 x 0.11 mm was 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 ($\lambda = 0.71073$ 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 5.055 cm from the crystal. A total of 4095 frames were collected with a scan width of 0.5 in ω and φ with an exposure time of 15 s/frame. The integration of the data yielded a total of 104081 reflections to a maximum 2θ value of 56.70° of which 7416 were independent and 7272 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 9090 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 6.12) software package, using the space group $P2_1/c$ with Z = 4 for the formula $C_{22}H_{49}Si_4SnBr$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. The cyclohex-2-enyl ligand is rotationally disordered. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0259 and wR2 = 0.0619 [based on $I > 2\sigma(I)$], R1 = 0.0267 and wR2 = 0.0644 for all data. CCDC 663922.

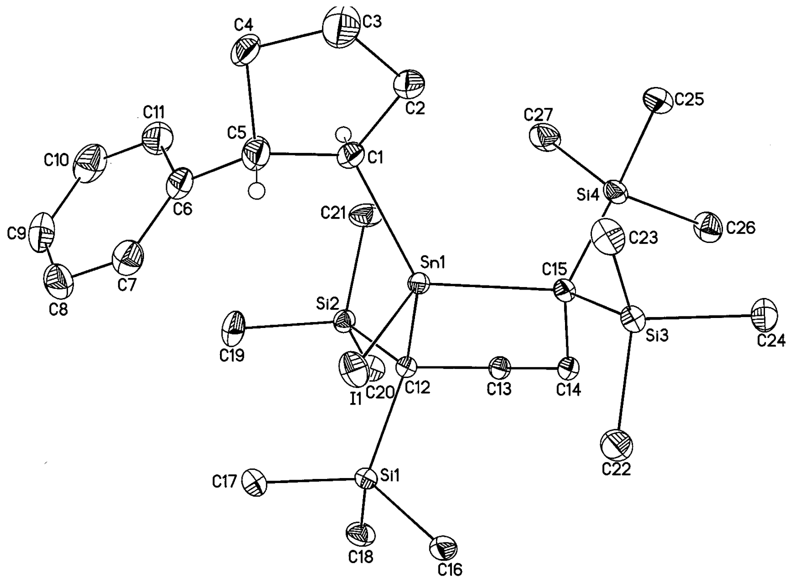


ORTEP of **31’** (50% thermal ellipsoids)

(**32**) $\mathbf{(C_5H_8)I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2}$ A 1-necked 100 mL flask capped with a rubber septum was charged with 178 μL of iodomesitylene (0.95 mmol, 1 eq) and 15 mL of cyclopentene. A solution containing 400. Mg of **10** (0.86 mmol, 0.9 eq)) and 25 mL of cyclopentene was placed in a gas tight syringe equipped with a 20-gauge needle. 20 mL of the red stannylene solution was added to the iodomesitylene solution at a rate 3 mL/hr using a syringe pump. The last 5 mL of stannylene solution were added at 1 mL/hr. The solution was stirred for 8 h yielding a cloudy, white solution. The volatiles were removed *in vacuo* and the resulting solid was recrystallized from pentane at -78 ^{o}C giving a white powder (340 mg, 60 % yield). ^{1}H NMR (C_6D_6) δ: 5.90 (m, 1H, Sn-CH-C*H*=CH), 5.83 (m, 1H, Sn-CH_2-CH=C*H*), 3.08 (m, 1H, Sn-C*H*), 2.65 (m, 1H, CH=CH-CH_2), 2.45 (m, 1H, Sn-CH-CH_2), 2.28 (m, 1H, CH=CH-CH_2), 2.19 (m, 1H, Sn-CH-CH_2), 2.18 (m, 1H, Sn-C($SiMe_3$)$_2$-CH_2), 2.05 (m, 1H, Sn-C($SiMe_3$)$_2$-CH_2-CH_2), 1.96 (m, 1H, Sn-C($SiMe_3$)$_2$-CH_2), 1.88 (m, 1H, Sn-C($SiMe_3$)$_2$-CH_2), 0.39 (s, 9H, Si(CH_3)$_3$) 0.37 (s, 9H, Si(CH_3)$_3$), 0.17 (s, 9H, $\mathrm{Si(C}H_3)_3$), 0.16 (s, 9H, $\mathrm{Si(C}H_3)_3$). ^{13}C ($\mathrm{C_6D_6}$) δ 132.31 (Sn-CH-*C*=C), 132.30 (Sn-CH-C=*C*), 67.52 (Sn-*C*$\mathrm{(SiMe_3)_2}$, 47.68 (Sn-CH), 35.39 (Sn-C-*C*$\mathrm{H_2}$), 35. 29 (Sn-C-*C*$\mathrm{H_2}$), 34.18 (Sn-CH-C=C-*C*$\mathrm{H_2}$), 29.37 (Sn-CH-*C*$\mathrm{H_2}$), 4.65 (Si(*C*$\mathrm{H_3)_3}$), 4.61(Si(*C*$\mathrm{H_3)_3}$), 4.53(Si(*C*$\mathrm{H_3)_3}$), 4.48(Si(*C*$\mathrm{H_3)_3}$). ^{119}Sn ($\mathrm{C_6D_6}$) δ 150.67. MS *m/z* (relative intensity): EI: 643.1 M-$\mathrm{CH_3}$ (1.3), 591.1 (25.5). 419.0 (2.5), 292.1 (7.5), 246.8 (27.2), 157.1 (22.1), 73.1 (100.0). IR(film) cm^{-1} ν 2923, 1462, 1377, 1251. E.A. Calc'd for $\mathrm{C_{21}H_{47}ISi_4Sn}$ C: 38.36; H: 7.20; found C: 38.55; H: 7.47.

(32) $\mathbf{(C_5H_8)I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2}$ and (33) $\mathbf{(C_{11}H_{13})I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2}$. A 1-necked 100 mL flask with a rubber septum was charged with 106 μL of phenyl iodide (0.95 mmol, 1 eq.) and 15 mL of cyclopentene. A solution containing 400. mg of **10** (0.86 mmol, 0.9 eq.) and 20 mL of cyclopentene was placed in a gas tight syringe equipped with a 20-gauge needle. The red stannylene solution was added to the phenyl iodide solution at a rate of 5 mL/hr using a syringe pump. The mixture was stirred for 8 h yielding a cloudy, white solution. After removal of all volatiles *in vacuo*, column chromatography on silica gel was performed using 50:1 mixture of hexane and ethyl acetate and 1% triethyl amine. Compound **32** eluted first and was obtained as a white solid upon removal of solvent (0.192 g, 34% yield). Compound **33** eluted second and was isolated as a white powder upon removal of solvent (0.137g , 22% yield). Characterization for **6** is provided below. ^{1}H NMR ($\mathrm{C_6D_6}$) δ: 7.21 (m, 2H, *o*-Ph), 7.12 (m, 2H, *m*-Ph), 7.03 (m, 1H, *p*-Ph), 3.80 (m with Sn satellites, $^2J_{\mathrm{Sn\text{-}H}}$ = 105 Hz, 1H, Sn-CH), 2.28 (m, 1H, Ph-CH), 2.28 (m, 1H, Ph-CH-CH_2), 2.12 (m, 1H, Ph-CH-CH_2), 2.10 (m, 2H, Sn-$\mathrm{C(SiMe_3)_2}$-CH_2), 1.90 (m, 2H, Sn-$\mathrm{C(SiMe_3)_2}$-CH_2), 2.10 (m, 1H, Sn-CH-C*H*$_2$), 1.50 (m, 1H, Sn-CH-C*H*$_2$), 1.86-1.92 (m, 2H, Sn-CH-CH$_2$-C*H*$_2$), 0.43 (s, 9H, Si(C*H*$_3$)$_3$), 0.37 (s, 9H, Si(C*H*$_3$)$_3$), 0.24 (s, 9H, Si(C*H*$_3$)$_3$), -0.20 (s, 9H, Si(C*H*$_3$)$_3$). ^{13}C (C_6D_6) δ 146.39 (*i*-Ph), 129.35 (Ph), 128.85 (Ph), 127.26 (*p*-Ph), 67.25 (Sn-*C*(Si(CH$_3$)$_2$), 51.31 (Sn-*C*H-CH$_2$), 45.90 (Ph-*C*H-CH$_2$), 35.94 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 35.51 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 39.47 (Sn-CH-*C*H$_2$), 34.00 (Ph-CH-*C*H$_2$), 26.98 (Sn-CH-CH$_2$-*C*H$_2$), 0.43 (Si(*C*H$_3$)$_3$), 0.37(Si(*C*H$_3$)$_3$), 0.24(Si(*C*H$_3$)$_3$), -0.20(Si(*C*H$_3$)$_3$). ^{119}Sn (C_6D_6) δ 180.27. MS EI *m/z*: 721.1 (M-CH$_3$). IR(film) cm^{-1} ν 2922, 1248. E.A. Calc'd for $C_{26}H_{51}ISi_4Sn$ C: 44.08; H: 7.26; found C: 44.13; H: 7.31.

Structure Determination of **33**. Colorless plates were grown from a hexane solution at 23 °C. A crystal of dimensions 0.29 x 0.16 x 0.06 mm was 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 5.055 cm from the crystal. A total of 4460 frames were collected with a scan width of 0.5 in ω and φ with an exposure time of 15 s/frame. The integration of the data yielded a total of 64833 reflections to a maximum 2θ value of 56.72° of which 8183 were independent and 7887 were greater than 2σ(I). The final cell constants (Table 1) were based on the xyz centroids of 9897 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 $C_{27}H_{53}Si_4SnI$. Two carbon atoms of the five-member ring of the cyclopentyl-phenyl ligand were disordered and were modeled with partial occupancy atoms. 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 = 0.0235 and wR2 = 0.0541[based on I > 2σ(I)], R1 = 0.0248 and wR2 = 0.0549 for all data. CCDC 663919.



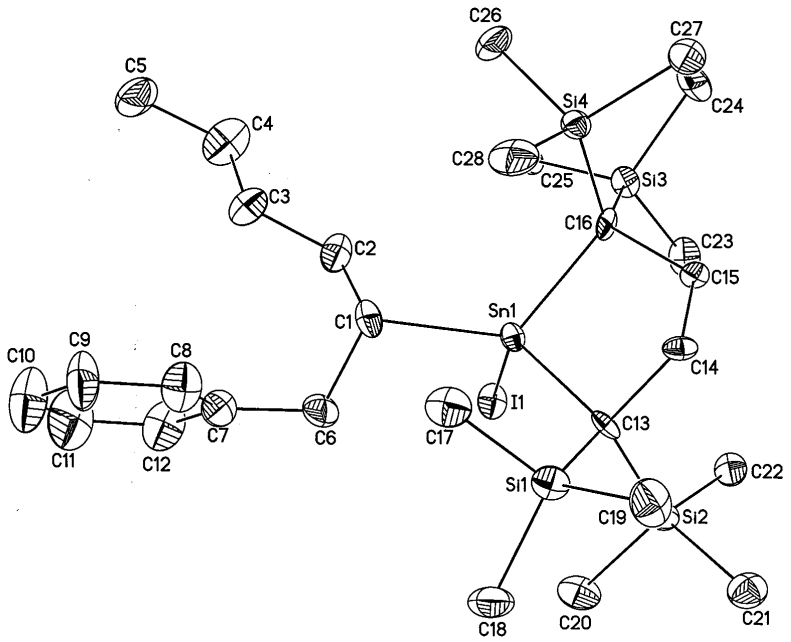
ORTEP of **33** (50% thermal elliposoids)

(**35**) **$(C_{11}H_{15})I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$** A 1-necked 100 mL flask fitted with a rubber septum was charged with 106 μL of phenyl iodide (0.95 mmol, 1 eq.) and 15 mL of 1-pentene. A solution containing 400. Mg of **10** (0.863 mmol, 0.9 eq.) and 20 mL of 1-hexene was placed in a gas tight syringe equipped with a 20-gauge needle. Due to volatility of the 1-pentene, precise control of the addition rate was not possible. However, the red stannylene solution was added batch wise over 6 hours allowing the color of the mixture to fade from red to colorless before each addition. The solution was stirred for an additional 8 h to insure completion of reaction, giving a cloudy, white solution. The volatiles were removed in vacuo. Column chromatography of the crude mixture with hexane as a solvent gave **8** as a white powder. (137 mg, 21 % yield.). ^{1}H NMR (C_6D_6) δ 7.20 (d, $^3J_{H\text{-}H}$ = 7.5Hz, 2H, *o*-Ph), 7.12 (pseudo-t, J = 7.5 Hz, 2H, *m*-Ph), 7.04 (t, $^3J_{H\text{-}H}$ = 7.5Hz, 1H, *p*-Ph), 3.44 (dd, $^2J_{H\text{-}H}$ = 3.0 Hz,$^3J_{H\text{-}H}$ =13.5 Hz, 1H, Ar-C*H*$_2$), 3.21 (pseudo-t, J = 12.5 Hz, 1H, Ar-C*H*$_2$), 2.29 (m, 1H, Sn-C*H*), 2.18 (m, 1H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$), 2.00 (m, 1H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$), 1.93 (m, 2H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$, 2.09 (m, 1H, Sn-CH-C*H*$_2$), 1.93 (m, 1H, Sn-CH-C*H*$_2$), 1.24 (m, 1H, Sn-CH-CH$_2$-C*H*$_2$), 1.06 (m, 1H, Sn-CH-CH$_2$-C*H*$_2$), 0.75 (t, $^3J_{H\text{-}H}$ = 7.0 Hz, 3H, Sn-CH-CH$_2$-CH$_2$-C*H*$_3$), 0.42 (s, 18H, Si(C*H*$_3$)$_3$), 0.23 (s, 9H, Si(C*H*$_3$)$_3$), 0.22 (s, 9H, Si(C*H*$_3$)$_3$). ^{13}C (C_6D_6) δ 142.56 (*i*-Ph), 129.60 (*o*-Ph), 129.32 (*m*-Ph), 127.10 (*p*-Ph), 67.51 (Sn-*C*(SiMe$_3$)$_2$), 44.26 (Sn-CH), 41.28 (Ph-CH$_2$), 36.67 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 36.23 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 35.40 (Sn-CH-*C*H$_2$), 25.75 (Sn-CH-CH$_2$-*C*H$_2$), 14.69 (Sn-CH-CH$_2$-CH$_2$-*C*H$_3$), 4.77 (Si(*C*H$_3$)$_3$), 4.63 (Si(*C*H$_3$)$_3$), 4.45 (Si(*C*H$_3$)$_3$), 4.39 (Si(*C*H$_3$)$_3$). ^{119}Sn (C_6D_6) δ 171.0. MS EI *m/z*: 722.9 (M-CH$_3$). IR(film) cm^{-1} ν 2922, 2853, 1250, 896, 848. E.A. Calc'd for $C_{27}H_{55}ISi_4Sn$ C: 43.96; H: 7.51; found C: 44.63; H: 7.69.

(37) $\mathbf{(C_{12}H_{17})I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2}$. A 1-necked 100 mL flask fitted with a rubber septum was charged with 106 μL of phenyl iodide (0.95 mmol, 1 eq.) and 15 mL of 1-hexene. A solution containing 400 mg of **10** (0.863 mmol, 0.9 eq.) and 20 mL of 1-hexene was placed in a gas tight syringe equipped with a 20-gauge needle. The red stannylene solution was added in fractions of 2.5 mL over 8 hours. The solution was stirred for 16 h to insure completion of reaction, yielding a cloudy, white solution. The volatiles were removed *in vacuo*. Column chromatography of the crude mixture with hexane as a solvent and removal of volatiles gave a white powder (312 mg, 48% yield.). ^{1}H NMR (C_6D_6) δ 7.19 (d, $^3J_{H\text{-}H}$ = 7.5Hz, 2H, *o*-Ph), 7.13 (pseudo-t, J = 7.5 Hz, 2H, *m*-Ph), 7.04 (t, $^3J_{H\text{-}H}$ = 7.5Hz, 1H, *p*-Ph), 3.43 (dd, $^2J_{H\text{-}H}$ = 2.5 Hz,$^3J_{H\text{-}H}$ =13.7 Hz, Ph-C*H*$_2$), 3.20 (pseudo-t, J = 12.5 Hz, Ph-C*H*$_2$), 2.24 (m, 1H, Sn-C*H*), 2.21 (m, 1H, Sn-CH-C*H*$_2$), 1.85 (m, 1H, Sn-CH-C*H*$_2$), 2.02 (m, 2H, Sn-CH-CH$_2$-C*H*$_2$), 2.02 (m, 1H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$), 1.86 (m, 1H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$), 1.22 (m, 1H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$), 1.01 (m, 1H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$), 1.22 (m, 1H, Sn-CH-CH$_2$-CH$_2$-C*H*$_2$), 1.06 (m, 1H, Sn-CH-CH$_2$-CH$_2$-C*H*$_2$), 0.78 (t, $^3J_{H\text{-}H}$ = 7.0 Hz, 3H), Sn-CH-CH$_2$-CH$_2$-CH$_2$-C*H*$_3$) 0.43 (s, 18H, SiMe$_3$), 0.24 (s, 18H, SiMe$_3$). ^{13}C (C_6D_6) δ 142.05 (*i*-Ph), 129.56 (*o*-Ph), 129.24 (*m*-Ph), 127.02 (*p*-Ph), 67.12 (Sn-*C*(SiMe$_3$)$_2$), 44.15 (Sn-*C*H), 41.26 (Ar-*C*H$_2$), 36.29 (Sn-CH-*C*H$_2$), 35.28 (Sn-CH-CH$_2$-*C*H$_2$), 34.26 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 34.24 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 23.78 (Sn-CH-CH$_2$-CH$_2$-*C*H$_2$), 14.45 (Sn-CH-CH$_2$-CH$_2$-CH$_2$-*C*H$_3$), 4.75 (Si(*C*H$_3$)$_3$), 4.60 (Si(*C*H$_3$)$_3$), 4.46 (Si(*C*H$_3$)$_3$), 4.28 (Si(*C*H$_3$)$_3$). ^{119}Sn (C_6D_6) δ 172.3. MS EI *m/z*: 737.1 (M-CH$_3$). IR(film) cm^{-1} ν 2924, 2854, 1250, 895, 847. E.A. Calc'd for $C_{28}H_{57}ISi_4Sn$ C: 44.74; H: 7.64; found C: 44.34; H: 7.94.

Structure Determination of **37**. Colorless needles were grown from pentane solution at 23 °C. A crystal of dimensions 0.23 x 0.03 x 0.01 mm was 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 5.055 cm from the crystal. A total of 2700 frames were collected with a scan width of 0.5 in ω and φ with an exposure time of 60 s/frame. The integration of the data yielded a total of 54809 reflections to a maximum 2θ value of 46.80° of which

5130 were independent and 4066 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 6175 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 6.12) software package, using the space group $P2_1/n$ with Z = 4 for the formula $C_{28}H_{57}Si_4SnI$. 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 = 0.0547 and wR2 = 0.1282 [based on $I > 2\sigma(I)$], R1 = 0.0768 and wR2 = 0.1417 for all data. CCDC 663920.

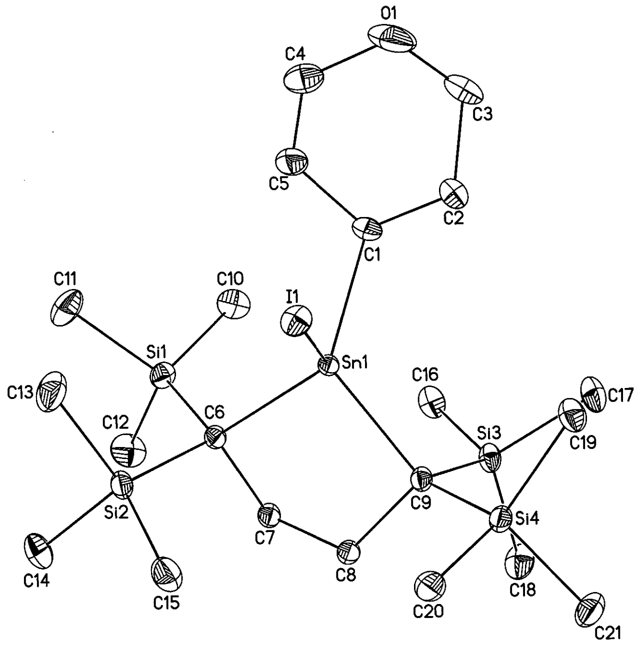

C26
C27
C5
C4
Si4
C24
C28
C25
Si3
C3
C16
C23
C2
C15
Sn1
C1
C9
C10
C8
C14
I1
C17
C13
C7
C6
C11
C12
Si1
C22
C19
Si2
C18
C20
C21

ORTEP of **37** (50% thermal ellipsoids)

(38) $(C_5OH_7)\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$. A 1-necked 100 mL flask fitted with a rubber septum was charged with 106 μL of phenyl iodide (0.95 mmol, 1 eq.) and 15 mL of 3,4-dihydro-2H-pyran. A solution containing 400. Mg of **10** (0.863 mmol, 0.9 eq.) and

20 mL of 3,4-dihydro-2H-pyran was placed in a gas tight syringe equipped with a 20-gauge needle. The red stannylene solution was added to the phenyl iodide solution at a rate of approximately 5 mL/hr using a syringe pump. The solution was allowed to stir for 8 hours to insure completion of reaction, yielding a cloudy, white solution. The volatiles were removed *in vacuo*. Column chromatography on silica gel was performed using 10:1 mixture of hexane/ethyl acetate and 1% triethyl amine. A white powder was obtained upon removal of solvent. (341 mg, 60% yield). ^{1}H NMR (C_6D_6) δ: 4.81 (d with Sn satellites, $^3J_{H-H}$ = 6.50 Hz, $^3J_{Sn-H}$ = 50 Hz, 1H, Sn-CH-C*H*=CH), 6.61 (d, $^3J_{H-H}$ = 6.50 Hz, 1H, Sn-CH-CH=C*H*), 4.04 (m, 1H, O-C*H*$_2$), 3.53 (pseudo-t, J = 8.5 Hz, 1H, O-C*H*$_2$), 2.67 (m, 1H, Sn-CH), 2.47 (m, 1H, Sn-CH-C*H*$_2$), 1.94 (m, 1H, Sn-CH-C*H*$_2$), 2.09 (m, 2H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$), 1.93 (m, 2H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$), 0.38 (s, 9H, SiMe$_3$), 0.37 (s, 9H, SiMe$_3$), 0.19 (s, 9H, SiMe$_3$), 0.11 (s, 9H, SiMe$_3$). ^{13}C (C_6D_6) δ 147.36 (Sn-CH-CH=*C*H) 102.62 (Sn-CH-*C*H=CH), 67.27 (Sn-*C*(SiMe$_3$)$_2$), 66.05 (O-CH$_2$), 35.42 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 33.98 (Sn-*C*H), 28.60 (Sn-CH-*C*H$_2$), 4.60 (Si(*C*H$_3$)$_3$), 4.52 (2 x Si(*C*H$_3$)$_3$), 4.50 (Si(*C*H$_3$)$_3$). ^{119}Sn (C_6D_6) δ 159.79. MS EI *m/z*: 659.1 (M-CH$_3$). IR(film) cm^{-1} ν 2924, 1253, 847. E.A. Calc'd for $C_{21}H_{47}ISi_4Sn$ C: 37.45; H: 7.03; found C: 37.78; H: 7.07.

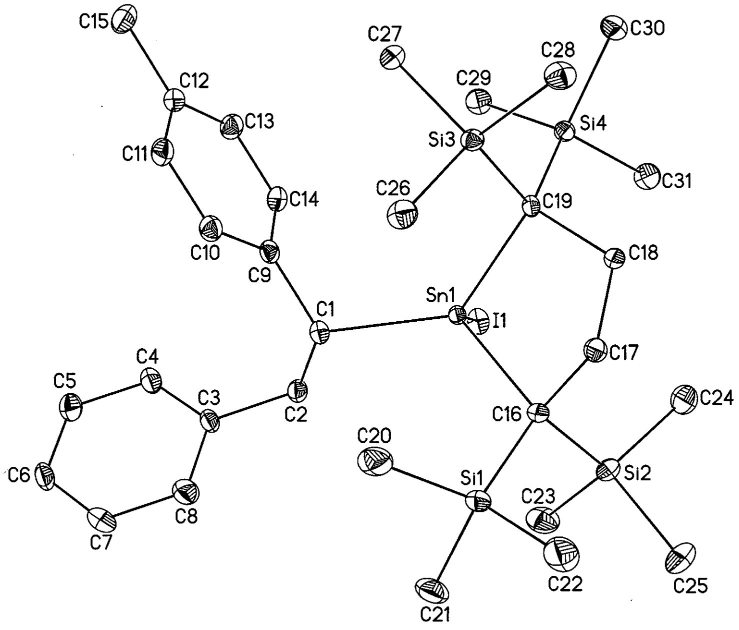
Structure Determination of **38**. Colorless blocks were grown from a pentane solution at 23 °C. A crystal of dimensions 0.48 x 0.38 x 0.25 mm was mounted on a Bruker SMART APEX CCD-based X-ray diffractometer equipped with a low temperature device and fine focus Mo-target X-ray tube (λ = 0.71073 A) operated 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 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 112982 reflections to a maximum 2θ value of 59.26° of which 8277 were independent and 8164 were greater than 2σ(I). The final cell constants (Table 1) were based on the xyz centroids of 9813 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 $P2_1/n$ with Z = 4 for the formula $C_{21}H_{47}OSi_4SnI$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. The pyranyl ligand is disordered. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0166 and wR2 = 0.0425[based on I > 2σ(I)], R1 = 0.0170 and wR2 = 0.0427 for all data. CCDC 663918.



ORTEP of **38** (50% thermal ellipsoids)

(39) $(C_{15}H_{15})SnC(SiMe_3)_2CH_2CH_2C(SiMe_3)_2$. A 1-necked 100 mL flask fitted with a rubber septum was charged with 106 μL of phenyl iodide (0.95 mmol, 1 eq) and 10 mL of 4-methyl styrene. A solution containing 400 mg of **10** (0.863 mmol, 0.9 eq.) and 10 mL of 4-methyl styrene was placed in a gas tight syringe equipped with a 20-gauge needle. 5 mL of the red stannylene solution was added to the phenyl iodide solution at a rate of approximately 3 mL/hr using a syringe pump. The last 5 mL of solution were added at rate of 1 mL/hr. The solution was stirred for 8 h to insure completion of reaction, yielding a cloudy, white solution. The volatiles were removed in vacuo and the resulting solid was recrystallized three times from pentane at -78 °C give a white powder (259 mg, 38 % yield). ^{1}H NMR (C_6D_6) δ 7.40 (pseudo-d, J = 8 Hz, 2H, o-Ar), 7.01 (m, 4H, *o,m*-Ph), 6.92 (m, 1H, *p*-Ph), 6.84 (pseudo-d, J = 8 Hz, 2H, m-Ar), 3.89 (pseudo-t, J = 23.0 Hz, 1H, Ph-C*H*$_2$), 3.48 (m, 2H, Sn-C*H* and Ph-C*H*$_2$), 2.25 (m, 1H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$), 2.10 (m, 1H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$), 2.03 (m, 1H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$), 1.82 (m, 1H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$), 1.99 (s, 3H, Ar-CH3), 0.46 (s, 9H, SiMe$_3$), 0.34 (s, 9H, SiMe$_3$), 0.27 (s, 9H, SiMe$_3$), -0.08 (s, 9H, SiMe$_3$). ^{13}C (C_6D_6) δ 141.18, 138.60, 136.53 (quaternary aromatic), 129.97 (*o*-Ph), 129.64, 129.60 (*C*H, *o,m*-Ar), 128.83 (*m*-Ph), 126.77 (*p*-Ph), 66.39 (Sn-*C*(SiMe$_3$)$_2$), 47.09 (Sn-*C*H), 44.16 (Ph-*C*H$_2$), 35.67 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$) , 34.94 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 5.20 (Si(*C*H$_3$)$_3$), 4.84 (Si(*C*H$_3$)$_3$), 4.40 (Si(*C*H$_3$)$_3$), 4.07 (Si(*C*H$_3$)$_3$). MS EI *m/z*: 721.1 (M-CH$_3$). IR(film) cm^{-1} ν 2925, 2854, 1249, 893, 950. E.A. Calc'd for $C_{26}H_{55}ISi_4Sn$: 47.39; H: 7.0; found C: 47.03; H: 7.11.

Structure Determination of **39**. Colorless needles were grown from a pentane solution at 23 °C. A crystal of dimensions 0.42 x 0.12 x 0.09 mm was 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 ($\lambda = 0.71073$ 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 5.055 cm from the crystal. A total of 3880 frames were collected with a scan width of 0.5 in ω and 0.45 in φ with an exposure time of 15 s/frame. The integration of the data yielded a total of 119042 reflections to a maximum 2θ value of 57.40° of which 9046 were independent and 8867 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 9331 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 6.12) software package, using the space group P2(1)/c with Z = 4 for the formula $C_{31}H_{55}Si_4SnI$. 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 = 0.0276 and wR2 = 0.0284 [based on $I > 2\sigma(I)$], R1 = 0.0703 and wR2 = 0.0710 for all data. CCDC 663921.



ORTEP of **39** (50% thermal ellipsoids)

Cross-Coupling conditions: A 20 mL scintillation vial was charged with 20 mg of **31** (0.30 mmol, 1 eq), 5.0 µL of PhI (0.45 mmol, 1.5 eq), 8 mg of Me_4NF (0.9 mmol, 3 eq), 3 mg of $Pd(PPh_3)_4$ (0.03 mmol, 10 mol%) and 10 mL of dioxane containing 0.0268 mmol 1,3,5-trimethoxybenzene as an integration standard. The solution was stirred at 77 ºC for 16 hours and then filtered through a plug of celite. The yield, as determined by ^1H NMR spectroscopy, was 70%.

(40) and (41) $(C_6H_9)I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$ A 1-necked 100 mL flask fitted with a rubber septum was charged with 157 mg of 2,4,6-triisopropyliodobenzene (0.48 mmol, 1.1 eq.), and 5 mL of *trans*-4-methyl-2-pentene. A solution containing 200 mg of **10** (0.43 mmol, 1 eq.) and 10 mL of *trans*-4-methyl-2-pentene was placed in a gas tight syringe equipped with a 20-gauge needle. 10 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 of 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 ^1H 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). **40** ^1H NMR (C_6D_6) δ: 5.82 (pseudo-dt, 2H, $J_{H\text{-}H}$ = 11.5 Hz, $J_{H\text{-}H}$ = 1.6 Hz, *H*C=C*H*), 2.81 (m, 3H, CH_3CH=CH), 2.19 (m, 2H, SnC(Si$(CH_3)_2$CH_2), 1.82 (m, 2H, SnC(Si$(CH_3)_2$CH_2), 1.65 (s with br Sn satellites, $^3J_{Sn\text{-}H}$ = 9.19 Hz, 6H, Sn-C(C$H_3$$)_2$), 0.40

(9H, $Si(C\mathit{H}_3)_3$), 0.39 (9H, $Si(C\mathit{H}_3)_3$), 0.21 (9H, $Si(C\mathit{H}_3)_3$), 0.13 (9H, $Si(C\mathit{H}_3)_3$) ^{13}C (C_6D_6) δ 128.94 ($H\mathit{C}{=}\mathit{C}H$), 35.78 ($Sn\text{-}C(SiMe_3)_2\text{-}\mathit{C}H_2$), 35.74 ($\mathit{C}H_3\text{-}HC{=}C$), 34.8 (($Sn\text{-}\mathit{C}(CH_3)_2$), 26.2 ($Sn\text{-}C(\mathit{C}H_3)_2$) 4.78 ($Si(\mathit{C}H_3)_3$), 4.37 ($Si(\mathit{C}H_3)_3$), 4.28 ($Si(\mathit{C}H_3)_3$), 4.25 ($Si(\mathit{C}H_3)_3$). ^{119}Sn (C_6D_6) δ 169.2. MS EI *m/z*: 659.1 ($M\text{-}CH_3$). **41** ^1H NMR (C_6D_6) δ: 5.77 (m, 1H, $\mathit{H}C{=}C$), 5.56 (m, 1H, $C{=}C\mathit{H}$), 2.58 (d with Sn satellites, $^3J_{H\text{-}H} = 8.4$Hz, $^2J_{Sn\text{-}H} = 23.6$ Hz, 2H, $Sn\text{-}C\mathit{H}_2$), 2.32 (septet, $^3J_{H\text{-}H} = 6.8$ Hz, $(CH_3)_2\text{-}C\mathit{H}$), 2.10 (m, 2H, $SnC(Si(CH_3)_2C\mathit{H}_2$), 1.86 (m, 2H, $SnC(Si(CH_3)_2C\mathit{H}_2$) 1.1 (d, $^3J_{H\text{-}H} = 6.8$ Hz, 6H, $(C\mathit{H}_3)_2\text{-}CH$), 0.37 (s, 18H, $Si(C\mathit{H}_3)_3$), 0.15 (s, 18H, $Si(C\mathit{H}_3)_3$). ^{13}C (C_6D_6) δ 139.6, 123.5 ($H\mathit{C}{=}CH$), 35.0 ($Sn\text{-}C(SiMe_3)_2\text{-}\mathit{C}H_2\text{-}\mathit{C}H_2$), 32.1 ($Sn\text{-}\mathit{C}H_2$), 23.9 ($(CH_3)\mathit{C}H$), 23.2 ($(\mathit{C}H_3)CH$), 4.51 ($Si(\mathit{C}H_3)_3$), 4.49 ($Si(\mathit{C}H_3)_3$) ^{119}Sn (C_6D_6) δ 132.0. MS EI *m/z of mixture*: 659.1 ($M\text{-}CH_3$). IR(film) of mixture cm^{-1} ν 2954, 2866, 1464, 1406, 1251, 901, 843 E.A. for the mixture Calc'd for $C_{22}H_{51}ISi_4Sn$ C: 39.23; H: 7.63; found C: 38.97; H: 7.74.

(42) and (43) $(C_6H_9)I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$

A 1-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 eq.), and 2 mL of 4-methyl-2-butyne. A solution containing 300 mg of **10** (0.43 mmol, 1 eq.) and 10 mL of 4-methyl-2-butyne was placed in a gas tight syringe equipped with a 20-gauge needle. 15 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. **(42)** ^{1}H NMR (C_6D_6) δ: 2.20 (s with br Sn satellites, $^2J_{Sn\text{-}H}$ = 29.6 Hz, 3H, $C\equiv C\text{-}C\mathit{H}_3$), 2.11 (m, 2H, $SnC(Si(CH_3)_2C\mathit{H}_2)$, 1.97 (m, 2H, $SnC(Si(CH_3)_2C\mathit{H}_2)$, 1.59 (s with br Sn satellites, $^3J_{Sn\text{-}H}$ = 17.6 Hz, 6H, $Sn\text{-}C\text{-}(C\mathit{H}_3)_2$), 0.42 (s, 18H, $Si(C\mathit{H}_3)_3$), 0.22 (s, 18H, $Si(C\mathit{H}_3)_3$). ^{13}C (C_6D_6) δ 98.1 ($Sn\text{-}C(CH_3)_2\text{-}\mathit{C}\equiv C$), 91.7 ($Sn\text{-}C\text{-}C\equiv\mathit{C}$), 35.0 ($Sn\text{-}C(SiMe_3)_2\text{-}\mathit{C}H_2\text{-}\mathit{C}H_2$), 22.2 ($Sn\text{-}\mathit{C}(CH_3)_2$), 21.6 ($C\equiv CCH_3$), 21.1 ($(\mathit{C}H_3)_2\mathit{C}\text{-}C\equiv C$), 4.49 ($Si(C\mathit{H}_3)_3$), 4.28 ($Si(C\mathit{H}_3)_3$). ^{119}Sn ($C_6D_6$) δ 57.9 MS EI *m/z*: 658.0 (M-CH_3). E.A. Calc'd for $C_{25}H_{51}ISi_4Sn$ C: 39.35 ; H: 7.35; found C: 39.32; H: 7.44.

(43) ^{1}H NMR (C_6D_6) δ: 2.56 (m, 1H, $(CH_3)_2\text{-}C\mathit{H}\text{-}C\equiv C$), 2.44 (d with br Sn satellites, $^2J_{H\text{-}H}$ = 2.0 Hz, $^2J_{Sn\text{-}H}$ = 23.2 Hz, 2H, $C\mathit{H}_2$), 2.13-1.85 (m, 4H, $SnC(Si(CH_3)_2C\mathit{H}_2\text{-}C\mathit{H}_2$), 1.18 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 6H, $CH(C\mathit{H}_3)_2$), 0.39 (s, 18H, $Si(C\mathit{H}_3)_3$), 0.20 (s, 18H, $Si(C\mathit{H}_3)_3$) ^{13}C (C_6D_6) δ: 88.8 ($Sn\text{-}CH_2\text{-}\mathit{C}\equiv C$), 77.9 ($Sn\text{-}CH_2\text{-}C\equiv\mathit{C}$), 34.8 ($Sn\text{-}C(SiMe_3)_2\text{-}\mathit{C}H_2\text{-}\mathit{C}H_2$), 23.9 ($Sn\text{-}CH_2$), 21.9 ($\mathit{C}H(CH_3)_2$), 21.6 ($CH(\mathit{C}H_3)_2$), 4.50 ($Si(C\mathit{H}_3)_3$), 4.33 ($Si(C\mathit{H}_3)_3$). ^{119}Sn ($C_6D_6$) δ 104.0. IR of the mixture (film) cm^{-1} ν 2951, 1941, 1445, 1360, 1320, 1248, 958, 857, 756, 680, 654. E.A. mixture of primary and tertiary product Calc'd for $C_{25}H_{51}ISi_4Sn$ C: 39.35 ; H: 7.35; found C: 39.53; H: 7.52. MS of **29** and **30** mixture CI with methane *m/z*: 658 (M-CH_3)

(44) $\mathbf{(C_{18}H_{29})ISnC(SiMe_3)_2CH_2CH_2C(SiMe_3)_2}$ A 1 necked 100 ml flask fitted with a rubber septum was charged with 154.4 mg (0.47 mmol, 1.1 eq) of 2,4,6-tri-*t*-butyl-bromobenzene and 40 ml of pentane. Stannylene (**10**) 200 mg (0.43 mmol, 1eq) was added in one portion and red solution was stirred for three days until the red color disappeared completely. Volatiles were removed and 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, $^{3}J_{\text{Sn-H}}$ = 15.6 Hz, 2H, Sn-CH_2), 2.12 (m, 2H, SnC(Si(CH$_3$)$_2$CH_2), 1.92 (m, 2H, SnC(Si(CH$_3$)$_2$CH_2), 1.02 (s, 6H, Sn-CH$_2$-C-(CH_3)$_2$), 1.36 (s, 18H, Ar-(C(CH_3)$_3$)$_2$, 0.36 (s, 18H, Si(CH_3)$_3$), 0.18 (s, 18H, Si(CH_3)$_3$). ^{13}C (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 (C_6D_6) δ 175.7. MS CI with methane *m/z*: 775.5 (M-CH$_3$).

(45) and (46) $(C_6H_7O)I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$

A 1 necked 100 ml flask fitted with a rubber septum was charged with 79 mg (0.24 mmol, 1.1 eq) of 2,4,6-tri-isopropyl-iodobenzene and 3 ml of 2,3-dimethyl furan. Stannylene (**10**) 100 mg (0.22 mmol, 1eq) dissolved in 2 ml of 2,3-dimethyl furan was added slowly with syringe and 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 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.

(45) ^{1}H NMR (C_6D_6) δ: 7.07 (d, $^{3}J_{H\text{-}H}$ = 2.0 Hz, 1H, O-C*H*), 6.02 (d, $^{3}J_{H\text{-}H}$ = 2.0 Hz, 1H, O-CH-C*H*), 3.05 (s with br Sn satellites, $^{2}J_{Sn\text{-}H}$ = 16 Hz, 2H, Sn-CH_2), 2.08-1.90 (m, 4H, Sn-C($SiMe_3)_2$-CH_2-CH_2), 0.37 (s, 18H, Si(C$H_3)_3$, 0.22 (s, 18H, Si(C$H_3)_3$). ^{13}C (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 (C_6D_6) 115.0 IR of the mixture (film) cm^{-1} ν 2855, 1458, 1377, 1261, 1250, 900, 848 MS of **45** and **46** C-H activated mixture CI with methane *m/z*: 671.5

(46) ^{1}H NMR (C_6D_6) δ: 7.08 (d, $^{3}J_{H\text{-}H}$ = 2 Hz, 1H, O-C*H*), 6.63 (d, $^{3}J_{H\text{-}H}$ = 2 Hz, 1H, O-CH-C*H*), 2.89 (s with br Sn satellites, $^{2}J_{Sn\text{-}H}$ = 18 Hz, 2H, Sn-CH_2), 2.13-1.85 (m, 4H, SnC(Si(C$H_3)_2$CH_2-CH_2), 0.35 (s, 18H, Si(C$H_3)_3$, 0.13 (s, 18H, Si(C$H_3)_3$. ^{13}C (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-CH_2), 4.58 (Si(C$H_3)_3$), 4.56 (Si(C$H_3)_3$). ^{119}Sn (C_6D_6) 125.1

References

(1) Walker, R. H.; Miller, K. A.; Scott, S. L.; Cygan, Z. T.; Bartolin, J. M.; Kampf, J. W.; Banaszak Holl, M. M. *Organometallics* **2009**, *28*, 2744.

(2) Miller, K. A.; Bartolin, J. M.; O'Neill, R. M.; Sweeder, R. D.; Owens, T. M.; Kampf, J. W.; Banaszak Holl, M. M.; Wells, N. J. *J. Am. Chem. Soc.* **2003**, *125*, 8986.

(3) Tokitoh, N.; Okazaki, R. *Coordin. Chem. Rev.* **2000**, *210*, 251.

(4) Sweeder, R. D.; Miller, K. A.; Edwards, F. A.; Wang, J.; Banaszak Holl, M. M.; Kampf, J. W. *Organometallics* **2003**, *22*, 5054.

(5) Keck, G. E.; Geraci, L. S. *Tet. Lett.* **1993**, *34*, 7827.

(6) Marshall, J. A. *J. Org. Chem.* **2007**, *72*, 8153.

(7) Herve, A.; Rodriguez, A. L.; Fouquet, E. *J. Org. Chem.* **2005**, *70*, 1953.

(8) Ye, J.; Bhatt, R. K.; Falck, J. R. *J. Am. Chem. Soc.* **1994**, *116*, 1.

(9) Kira, M.; Yauchibara, R.; Hirano, R.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 7785.

(10) Kira, M.; Ishida, S.; Iwamoto, T.; Yauchibara, R.; Sakurai, H. *J. Organomet. Chem.* **2001**, *636*, 144.

(11) Kira, M.; Ishida, S.; Iwamoto, T. *The Chemical Record* **2004**, *4*, 243.

(12) Iwamoto, T.; Masuda, H.; Ishida, S.; Kabuto, C.; Kira, M. *J. Organomet. Chem.* **2004**, *689*, 1337.

(13) Sakurai, H. In *e-EROS Encyclopedia of Reagents for Organic Synthesis* John Wiley & Sons: 2001.

(14) Bartolin, J. M.; Kavara, A.; Kampf, J.; Banaszak Holl, M. M. *Organometallics* **2006**, *25*, 4738.

(15) Tokitoh, N.; Ando, W. In *Reactive Intermediate Chemistry*; Moss, R. A., Platz, M. S., Jones, M. J., Eds.; John Wiley & Sons: New Jersey, 2004, p 651.

(16) Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Chem. Comm.* **1974**, 895.

(17) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268.

(18) Bartolin, J. M. B. H., M. M. ; University of Michigan: Ann Arbor.

(19) Fouquet, E.; Pereyre, M.; Rodriguez, A. L. *J. Org. Chem.* **1997**, *62*, 5242.

(20) Smith, M. B. M., J. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*; John Wiley and Sons: New York, 2001.

(21) Yoshimitsu, T.; Arano, Y.; Nagaoka, H. *J. Org. Chem.* **2005**, *70*, 2342.

(22) Kim, S.; Kim, N.; Chung, W.-j.; Cho, C. H. *Synlett* **2001**, *2001*, 0937.

(23) Hartwig, J. F. In *Activation and Functionalization of C-H Bonds*; Goldberg, K. I., Goldman, A. S., Eds.; American Chemical Society: Washington, DC, 2004; Vol. 885.

(24) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem. Int. Ed.* **1998**, *37*, 2180.

(25) Kavara, A.; Cousineau, K. D.; Rohr, A. D.; Kampf, J. W.; Banaszak Holl, M. M. *Organometallics* **2008**, *27*, 1041.

(26) Schiemenz, B.; Power, P. P. *Organometallics* **1996**, *15*, 958.

(27) Marshall, J. A.; DuBay, W. J. *J. Org.Chem.* **1993**, *58*, 3602.

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

(29) Togo, H.; Nabana, T.; Yamaguchi, K. *J. Org. Chem.* **2000**, *65*, 8391.

(30) Knorr, R.; Pires, C.; Behringer, C.; Menke, T.; Freudenreich, J.; Rossmann, E. C.; Böhrer, P. *J. Am. Chem. Soc.* **2006**, *128*, 14845.

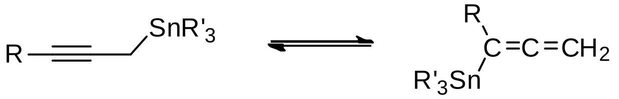
(31) Lappert, M. F.; Misra, M. C.; Onyszchuk, M.; Rowe, R. S.; Power, P. P.; Slade, M. J. *J. Organomet. Chem.* **1987**, *330*, 31.

(32) Harris, R. K.; Becker, E. D.; De Menezes, S. M. C.; Goodfellow, R.; Granger, P. *Pure Appl. Chem.* **2001**, *73*, 1795.

Chapter 4. Direct Formation of Propargyltin Compounds via CH-Activation

4.1 Background on the Formation of Propargyl Tin Compounds

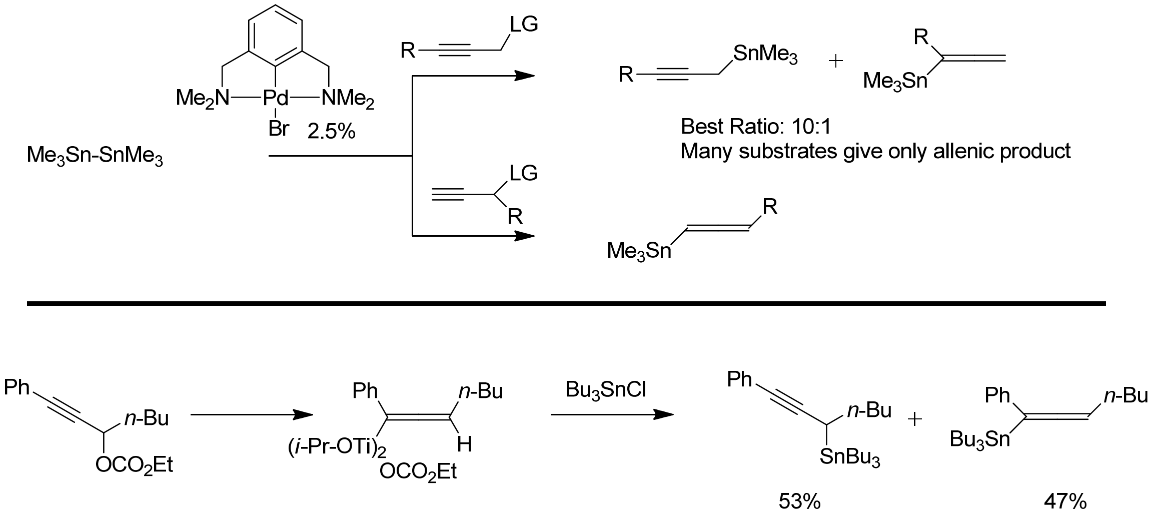
A variety of synthetic methods have been developed for the synthesis of propargylmetal compounds.[1] Such compounds are useful as coupling reagents for the formation of C-C bonds.[2-4] Propargyltin compounds are especially useful due to their functional group tolerance and air stability.[5-6] One of the main challenges in their synthesis is avoiding the formation of allenyl isomers. This difficulty arises because both electron donor solvents and Lewis acids catalyze the interconversion of propargyl- and allenyltin isomers (eq 4.1).[7]



(4.1)

Propargyl chlorides react with hexamethylditin in the presence of a Pd(II) catalyst that contains a pincer ligand, Scheme 4.1. In optimal cases, 7:1 to 10:1 ratios of propargyl-/allenyltin isomers are obtained. However, many propargylic chlorides react to give less than 50% of the propargyl isomer and others give only the allenyl isomer, Scheme 4.1.[8-9] Propargyl acetates, carbonates, and phosphates can be stoichiometrically converted to propargyltin complexes upon reaction with tributyltin chloride after activation with a $Ti(O^iPr)_4/2\ ^iPrMgCl$ reagent, Scheme 5.1. This method frequently gives excellent propargyl/allenyl ratios of > 40:1 with both primary and secondary propargyl carbonates.[6] In addition, this method has been extended to the formation of chiral propargyltin compounds by starting with chiral, secondary propargyl phosphates.[5]

Scheme 4.1 Literature methods for synthesis of propargyl tin compounds.



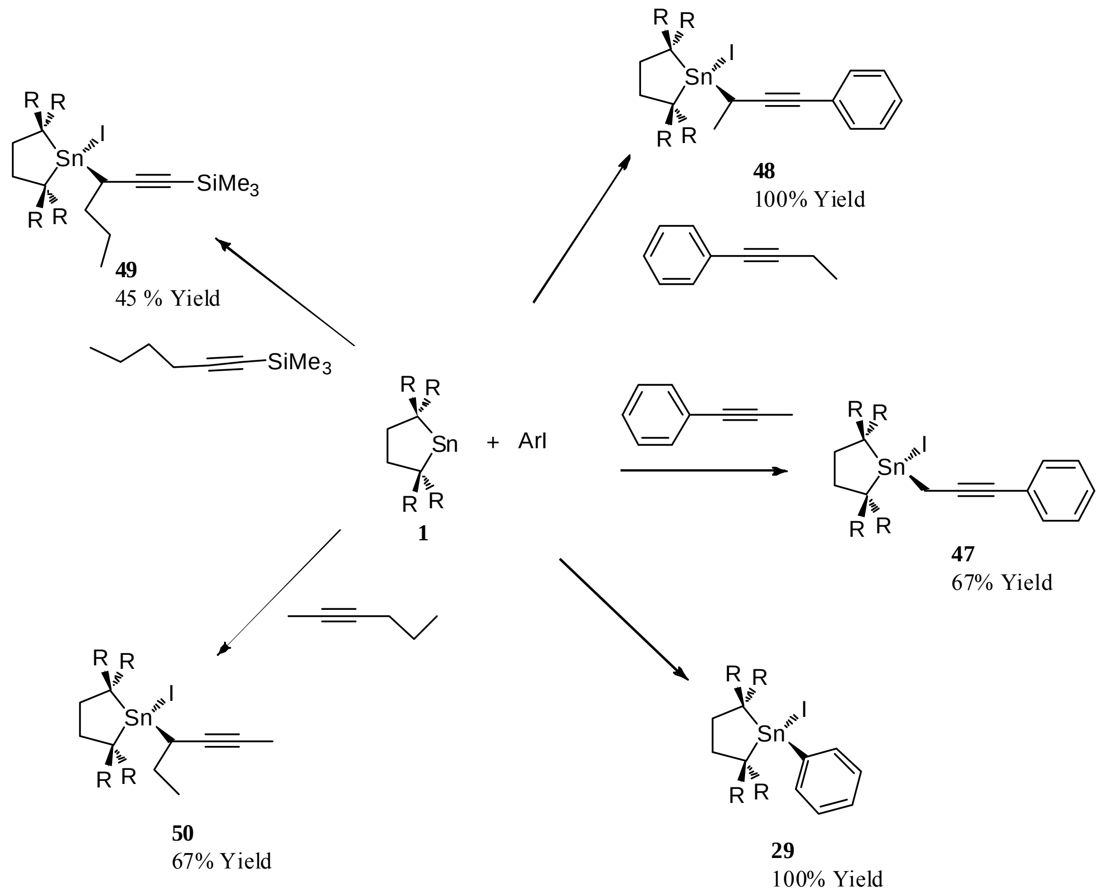
Me2N—Pd—NMe2
Br 2.5%
Me3Sn-SnMe3
R
LG
R
SnMe3
+
R
Me3Sn
Best Ratio: 10:1
Many substrates give only allenic product
LG
R
R
Me3Sn
Ph
n-Bu
OCO2Et
Ph
n-Bu
(i-Pr-OTi)2
H
OCO2Et
Bu3SnCl
Ph
n-Bu
+
SnBu3
Ph
n-Bu
Bu3Sn
53%
47%

All of these methods for the synthesis of propargyl tin compounds require the propargyl acetate, carbonate, halide, or phosphate species. Many of these species are not commercially available and examination of alternative routes to propargyl compounds that do not involve such starting materials was of interest. Direct CH-activation at the carbon atom alpha to the triple bond, concomitant with tin-carbon bond formation could, in principle, provide a direct route to propargyltin compounds. However, CH-activations involving alkynes are rare and have not been used to yield a tin-carbon bond

4.2 Propargylic C-H Activation

We discovered that **10** did not react with any of the alkynes used in this study and that the **10**/PhI combination was effective in activating both primary and secondary propargyl CH-bonds. These reactions could be carried out at ambient temperature and did not require electron donor solvents or Lewis acid additives. Thus, no problems with isomerization to allenyl isomers were encountered.

Activation of the propargylic CH-bond was achieved when 1 equivalent of **10** dissolved in 10 mL benzene and 15 mL alkyne was added to 1.1 equivalents of aryl iodide dissolved in 5 mL of 1-phenylpropyne, 1-phenylbutyne, or 2-hexyne.[10] When employing phenyl iodide, simple mixing of the reagents also gave oxidative-addition product $\mathrm{PhI\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2}$ (**29**).[11] The amount of **29** formed could be minimized and/or eliminated by employing syringe pump addition of PhI and/or the use of bulkier aryl iodides such as 2,4,6-trimethyliodobenzene or 2,4,6-triisopropyliodobenzene. Addition rates were chosen such that a substantial degree of red color did not build up during the addition of the intensely red stannylene solution to the aryl iodide solution. For the cases of 1-phenylpropyne, 1-phenylbutyne, and 2-hexyne, employing the syringe pump techniques and using 2,4,6-triisopropyliodobenzene resulted in quantitative formation of propargylic CH-activation products **47**, **48**, and **50**, respectively. For the case of 1-trimethylsily1hexyne, 1 equivalent of **10** dissolved in 15 mL of alkyne was added to 1.1 equivalents of iodobenzene dissolved in 5 mL of alkyne. ^{1}H NMR spectroscopy of the reaction mixture indicated a 95% conversion to propargylic CH-activation product **49** along with 5% conversion to oxidative-addition product **29**. The use of alkyne as solvent dramatically reduces the amount of **29** formed. When stoichiometric amounts of alkyne are employed **29** is the predominant product. Even when employing alkyne as solvent it is necessary to employ high-dilution techniques to minimize formation of **29** and give high yields of the desired CH-activation product. All compounds were characterized by a combination of ^{1}H, ^{13}C, ^{119}Sn NMR spectroscopy, infrared spectroscopy, mass spectrometry, and elemental analysis. Compound **47**, the result of the CH-activation of a primary CH-bond, exhibits two –SiMe$_3$ resonances in the ^{1}H NMR spectrum. Compounds **48**, **49**, and **50**, the result of the CH-activation of a secondary CH-bond, all exhibit four –SiMe$_3$ resonances. In the case of compound **5**, an additional –SiMe$_3$ resonance is present from the 1-trimethylsily1hexyne substrate. The ^{119}Sn NMR spectrum also provided a means of differentiating the primary vs secondary CH-activation products as the resonance of **47** occurred at 96.59 ppm whereas the resonances of **48**, **49**, and **50** were observed at 142.76, 130.55, and 132.72 ppm, respectively. The assignment of a $^5J_{Sn\text{-}H}$ coupling constant of 36.49 Hz for compound **50** was surprising. To confirm this spectroscopic assignment, an X-ray crystallographic study of **50** was undertaken using colorless a crystal grown from pentane at 25 °C (Fig. 3.1). The bond connectivity assigned spectroscopically was confirmed including the propargylic CH-activation and the presence of the triple bond.

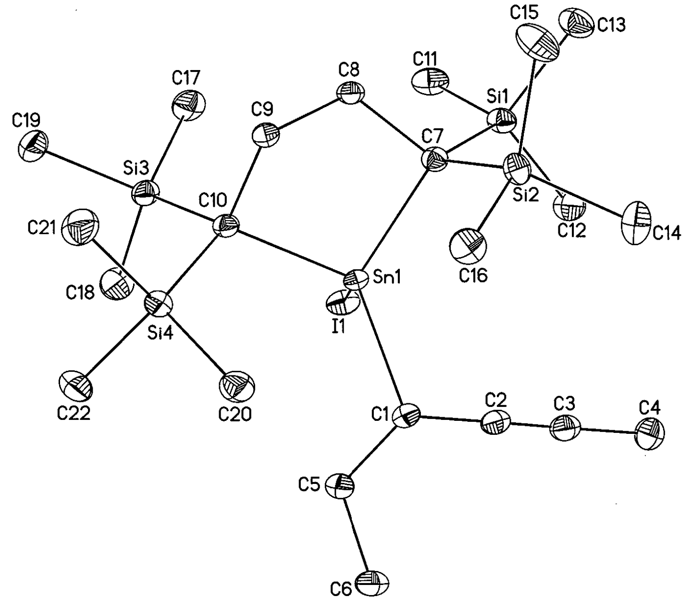

48
100% Yield
49
45 % Yield
SiMe3
1
+ ArI
47
67% Yield
50
67% Yield
29
100% Yield
R
Sn
I

(R = SiMe$_3$)

(Ar = Ph, 2,4,6-(^{i}Pr)$_3$C$_6$H$_2$

Scheme 4.2 Reactions of $\overline{\mathrm{SnC(SiMe_3)_2CH_2CH_2C}}\mathrm{(SiMe_3)_2}$ / ArI with alkynes. Isolated yields indicated.

Figure 4.1 ORTEP diagram of $(C_6H_9)I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$ (**50**) (50% thermal ellipsoids). Selected bond lengths (Å) and angles(°): Sn-C1, 2.1841(14); Sn-I, 2.73712(19); C1-C2, 1.455(2); C2-C3, 1.193(2); C3-C4, 1.460(2); C1-C5, 1.533(2); C5-C6, 1.525(2); Sn-C10, 2.1841(14); Sn-C7, 2.1832(14); Sn-C1-C2, 107.86(10); Sn-C1-C5, 111.73(9); C2-C1-C5, 112.97(12);C1-C2-C3, 178.89(17); C2-C3-C4, 178.18(18); C7-Sn-C1, 121.32(5); C10-Sn-C1,122.18(5); C7-Sn-I, 113.24(4); C10-Sn-I, 111.63(4); I-Sn-C1, 96.61(4)



Comparing this approach to the previously published methods of Szabó,[8-9] the use of hexamethylditin/Pd(II) pincer catalyst/(3-chloroprop-1-ynl)benzene resulted in an 87% isolated yield of trimethyl(3-phenylprop-2-ynyl)tin with an 8:1 propargylic/allenyl product ratio. The reaction of **10**/2,4,6-triisopropyliodobenzene with 1-phenylpropyne proceeded quantitatively (67% isolated yield) with no formation of the allenyl isomers. Attempts to use hexamethylditin and the Pd(II) pincer catalyst to give secondary propargylic products resulted in purely allenyl products. No propargylic isomer could be detected by ^{1}H NMR spectroscopy for other substrates such as (1-chloroprop-2-ynyl)benzene, (2-chlorobut-3-ynyl)benzene, and (3-chloroprop-1-yne-1,3-diyl)dibenzene. In contrast, secondary CH-activations proceeded quantitatively employing the **1**/2,4,6-triisopropyliodobenzene combination to give compounds **48** and **50**. Using the **1**/PhI reagent, **49** was obtained with 95% conversion as indicated by ^{1}H NMR spectroscopy (45% isolated yield). Sato et al. previously have reported effective methods for the synthesis of secondary propargylic tin compounds. For example, ethyl non-2-yn-4-yl carbonate was converted to tributyl(non-2-yn-4-yl)tin in 72% yield with a 31:1 propargylic/allenyl product ratio using the mixed $Ti(O^iPr)_4/2^iPrMgCl$ reagent.[6]

4.3 Comparison with Literature Methods

All three of the synthetic methods published to date have their advantages and drawbacks, Table 4.1. Our approach requires the synthesis and use of air-sensitive stannylene **10**, the use of a syringe pump and/or a bulky aryl iodide, and the use of alkyne as solvent. The primary advantages are that it does not require the preparation of alkynes with leaving groups and leads to no detectable amount of isomerization to allenyl products. The method of Szabo et al. requires the synthesis of the palladium pincer catalysts, the use of hexamethylditin, and alkynes with a leaving group (typically Cl) at the appropriate position but can be employed with functional groups (COOEt, OH, NAc) not tolerated by the stannylene. The method of Sato et al. requires preparation of carbonate functionalized alkynes but can be employed to make stereospecific propargyltin compounds.

Table 4.1 Comparison of the C-H activation of alkynes using stannylene/aryl halide with literature methods.

Method	Stannylene/Aryl halide	Palladium Pincer Szabo et al.	Ti(OiPr)4/iPrMgCl Sato et al.
Advantages	-No leaving groups -No isomerization to allene -Phenyl substituted alkynes compatible -Both secondary and primary propargyl substrates compatible	-Functional groups such as esters, alcohol and amine tolerated -Catalytic	-Chiral propargyl tins -Both secondary and primary propargyl substrates compatible
Disadvantages	-Solvent is substrate -Atom economy -Stannylene reagent preparation -Use of bulky aryl halide -Stannylene air sensitive	-Synthesis of Palladium pincer catalyst -Functionalization of alkyne with leaving group required -Use of Hexamethylditin	-Phenyl substituted alkynes readily isomerizes to allene -Functionalization of alkyne with leaving group required -Air sensitive and unstable reagent

Experimental

(**47**) **$(C_9H_7)I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$**. A 1-necked 100 mL flask fitted with a rubber septum was charged with 315 mg of 2,4,6-triisopropyliodobenzene (0.95 mmol, 1 eq.), and 5 mL of 1-phenylpropyne. A solution containing 400 mg of **10** (0.86 mmol, 0.9 eq.) and 15 mL of 1-phenylpropyne and 10 mL of benzene was placed in a gas tight syringe equipped with a 20-gauge needle. 25 mL of the red stannylene solution was added to the iodomesitylene/alkyne solution at a rate of 8 mL/h using a syringe pump. The last 5 mL of 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 as indicated 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 (402 mg, 67 % yield). ^{1}H NMR (C_6D_6) δ: 7.64 (d, $^3J_{H\text{-}H}$ = 7.0 Hz, 2H, *o*-Ph), 7.04 (pseudo-t, J = 7.5 Hz, 2H, *m*-Ph), 6.98 (t, J = 7.0 Hz, 1H, *p*-Ph), 2.68 (s with br Sn satellites, $^2J_{Sn\text{-}H}$ = 45.0 Hz, 2H, Sn-C*H*$_2$), 2.00 (m, 2H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$), 1.87 (m, 2H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$), 0.39 (s, 18H, Si(C*H*$_3$)$_3$), 0.15 (s, 18H, Si(C*H*$_3$)$_3$) ^{13}C (C_6D_6) δ 132.32 (*i*-Ph), 128.93 (*o*-Ph), 128.06 (*m*-Ph), 125.39 (*p*-Ph), 89.59 (Sn-CH$_2$-*C*C), 83.96 (Sn-CH$_2$-C*C*), 34.75 (Sn-*C*H$_2$), 21.79 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 17.02 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 4.37 (Si(*C*H$_3$)$_3$), 4.34 (Si(*C*H$_3$)$_3$). ^{19}Sn (C_6D_6) δ 96.59. MS EI *m/z*: 691.2 (M-CH$_3$). IR(film) cm^{-1} ν 2922, 2361, 1251, 898, 848, 753. E.A. Calc'd for $C_{25}H_{47}ISi_4Sn$ C: 42.56; H: 6.71; found C: 42.20; H: 6.79. The quaternary center (Sn-*C*(SiMe$_3$)$_2$) was not observed by ^{13}C NMR.

(48) $(C_{10}H_9)$ $ISnC(SiMe_3)_2CH_2CH_2C(SiMe_3)_2$. A 1-necked 100 mL flask fitted with a rubber septum was charged with 315 mg of 2,4,6-triisopropyliodobenzene (0.95 mmol, 1 eq.), and 5 mL of 1-phenylbutyne. A solution containing 400 mg of **10** (0.86 mmol, 0.9 eq.) and 15 mL of 1-phenylbutyne and 10 mL of benzene was placed in a gas tight syringe equipped with a 20-gauge needle. 25 mL of the red stannylene solution was added to the 2,4,6-triisopropyliodobenzene/alkyne 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* yielding 632 mg of white powder (100 % yield). Analytically pure material was obtained by two recrystallizations from pentane at -78 °C. ^{1}H NMR (C_6D_6) δ: 7.61 (d, $^3J_{H\text{-}H}$ = 5.9 Hz, 2H, *o*-Ph), 7.03 (pseudo-t, J = 7.2 Hz, 2H, *m*-Ph), 6.96 (t, J = 7.2 Hz, 1H, *p*-Ph), 2.76 (q, $^3J_{H\text{-}H}$ = 7.2, 1H, Sn-C*H*), 2.07 (m, 2H, Sn-$C(SiMe_3)_2$-CH_2), 1.95 (m, 2H, Sn-$C(SiMe_3)_2$-CH_2), 1.71 (d with Sn satellites, $^3J_{H\text{-}H}$ = 7.2 Hz, $^3J_{Sn\text{-}H}$ = 126 Hz, 3H, Sn-CH-CH_3), 0.37(s, 9H, Si(CH_3)$_3$), 0.39 (s, 9H, Si(CH_3)$_3$), 0.26 (s, 9H, Si(CH_3)$_3$), 0.11 (s, 9H, Si(CH_3)$_3$). ^{13}C (C_6D_6) δ 132.39 (*i*-Ph), 128.89 (*o*-Ph), 125.14 (*p*-Ph), 94.76 (Sn-CH-C*C*), 85.16 (Sn-CH-C*C*), 35.10 (Sn-$C(SiMe_3)_2$-*C*H_2), 35.07 (Sn-$C(SiMe_3)_2$-*C*H_2), 24.18 (Sn-*C*H), 20.18 (Sn-CH-C*H*$_3$), 4.42 (Si(*C*H_3)$_3$), 4.40 (Si(*C*H_3)$_3$), 4.37 (Si(*C*H_3)$_3$), 4.33 (Si(*C*H_3)$_3$). ^{119}Sn (C_6D_6) δ 142.76. MS EI *m/z*: 703.2 (M-CH_3). IR(film) cm^{-1} ν 2920, 2852, 2218, 1252, 896, 847, 753. E.A. Calc'd for $C_{25}H_{47}ISi_4Sn$ C: 43.39; H: 6.86; found C: 43.51; H: 6.91. The quaternary center (Sn-*C*$(SiMe_3)_2$) and the *m*-Ph was not observed by ^{13}C NMR.

(49) $(C_9H_{18}Si)ISnC(SiMe_3)_2CH_2CH_2C(SiMe_3)_2$ A 1-necked 100 mL flask fitted with a rubber septum was charged with 106 μL of iodobenzene (0.95 mmol, 1 eq.), and 5 mL of 1-trimethylsilyl-1-hexyne. A solution containing 400 mg of **10** (0.86 mmol, 0.9 eq.) and 15 mL of 1-trimethylsilyl-1-hexyne was placed in a gas tight syringe equipped with a 20-gauge needle. 15 mL of the red stannylene solution was added to the iodobenzene/alkyne solution at a rate of 8 mL/h using a syringe pump. The last 5 mL of 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 1H NMR spectroscopy indicated the formation of 95% **49** and 5% **29**. Column chromatograply was performed using hexane as solvent yielding 291 mg (45% yield) of analytically pure white powder. ^{1}H NMR (C_6D_6) δ 2.65 (dd with Sn satellites, $^3J_{H\text{-}H}$ = 12.2 Hz, $^3J_{H\text{-}H}$= 2.8 Hz, $^2J_{Sn\text{-}H}$=39.6 Hz, 1 H, SnCH), 2.32 (m, 1H, Sn-CH-C*H*$_2$), 1.91-2.13 (m, 4H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$-C*H*$_2$), 1.81 (m, 1H, Sn-CH-CH$_2$-C*H*$_2$), 1.73 (m, 1H, Sn-CH-C*H*$_2$), 1.49 (m, 1H, Sn-CH-CH$_2$-C*H*$_2$), 0.87 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 3H, Sn-CH-CH$_2$-CH$_2$-C*H*$_3$), 0.42 (s, 9H, Si(C*H*$_3$)$_3$), 0.36 (s, 9H, Si(C*H*$_3$)$_3$), 0.30 (s, 9H, Si(C*H*$_3$)$_3$), 0.26 (s, 9H, Si(C*H*$_3$)$_3$), 0.14 (s, 9H, CC-Si(C*H*$_3$)$_3$). ^{13}C (C_6D_6) δ 109.48 (Sn-CH-*C*C), 89.34 (Sn-CH-C*C*), 35.96 (Sn-CH-*C*H$_2$), 34.20 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 35.12 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 30.19 (Sn-*C*H), 23.06 (Sn-CH-CH$_2$-*C*H$_2$), 14.07 (Sn-CH-CH$_2$-CH$_2$-*C*H$_3$), 4.67 (Si(*C*H$_3$)$_3$), 4.53 (Si(*C*H$_3$)$_3$), 4.43 (Si(*C*H$_3$)$_3$), 4.38 (Si(*C*H$_3$)$_3$), 0.88 (CCSi(*C*H$_3$)$_3$. ^{119}Sn (C_6D_6) δ 130.55. MS EI *m/z*: 729.2 (M-CH$_3$). IR(film) cm^{-1} ν 2923, 2151, 2218, 1251, 896, 845, 757, 654. E.A. Calc'd for $C_{25}H_{57}ISi_5Sn$ C: 40.37; H: 7.72; found C: 40.27; H: 7.86. The quaternary center (Sn-*C*(SiMe$_3$)$_2$) was not observed by ^{13}C NMR.

(**50**) **$(C_6H_9)I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$** A 1-necked 100 mL flask fitted with a rubber septum was charged with 315 mg of 2,4,6-triisopropyliodobenzene (0.95 mmol, 1 eq.), and 5 mL of 2-hexyne. A solution containing 400 mg of **10** (0.86 mmol, 0.9 eq.) and 15 mL of 2-hexyne and 10 mL of benzene was placed in a gas tight syringe equipped with a 20-gauge needle. 25 mL of the red stannylene solution was added to the 2,4,6-triisopropyliodobenzene/alkyne solution at a rate of 8 mL/h using a syringe pump. The last 5 mL of was added at 2 mL/h. The solution was stirred for 8 h yielding a cloudy, white solution containing only C-H activation product by ^{1}H NMR spectroscopy. The volatiles were removed *in vacuo* and the resulting solid purified using flash column chromatography (217 mg, 67 % yield). ^{1}H NMR (C_6D6) δ 2.52 (m, 1H, Sn-C*H*), 2.31 (m, 1H, Sn-CH-C*H*$_2$), 2.11 (m, 2H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$), 2.01 (m, 2H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$), 1.89 (m, 1H, Sn-CH-C*H*$_2$), 1.66 (d with Sn satellites, $^5J_{H\text{-}H}$ = 2.50 Hz, $^5J_{119Sn\text{-}H}$ = 36.49 Hz, 3H, Sn-CH-CC-C*H*$_3$), 1.18 (t, $^3J_{H\text{-}H}$ = 7.0 Hz, 3H, Sn-CH-CH$_2$-CH$_3$), 0.44 (s, 9H, Si(C*H*$_3$)$_3$), 0.38 (s, 9H, Si(C*H*$_3$)$_3$), 0.28 (s, 9H, Si(C*H*$_3$)$_3$), 0.14 (s, 9H, Si(C*H*$_3$)$_3$). ^{13}C (C_6D_6) δ 81.47 (Sn-CH-*C*C), 80.84 (Sn-CH-C*C*), 66.87 (Sn-*C*(SiMe$_3$)$_2$), 35.36 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 34.97 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 31.97 (Sn-*C*H), 28.13 (Sn-CH-*C*H$_2$), 14.79 (Sn-CH-CH$_2$-*C*H$_3$), 4.58 (Sn-CH-CC-*C*H$_3$), 4.52 (Si(*C*H$_3$)$_3$), 4.38 (Si(*C*H$_3$)$_3$), 4.34 (Si(*C*H$_3$)$_3$), 4.32 (Si(*C*H$_3$)$_3$). ^{119}Sn (C_6D_6) δ 132.72. MS EI *m/z*: 657.2 (M). IR(film) cm^{-1} ν 2920, 2852, 2363, 2361, 1252, 897, 847, 754, 654. E.A. Calc'd for $C_{23}H_{51}ISi_5Sn$ C: 39.35; H: 7.35; found C: 39.49; H: 7.50.

Structure Determination of **50**. Colorless plates of **50** were crystallized from a pentane solution at 25 °C. A crystal of dimensions 0.25 x 0.18 x 0.10 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 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 10 s/frame. The integration of the data yielded a total of 107878 reflections to a maximum 2θ value of 56.70° of which 7617 were independent and 7411 were greater than 2σ(I). The final cell constants (Table 1) were based on the xyz centroids of 9449 reflections above 10σI). 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 $P2_1/n$ with Z = 4 for the formula $C_{22}H_{49}Si_4SnI$. 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 = 0.0172 and wR2 = 0.0449 [based on I > 2σ(I)], R1 = 0.0178 and wR2 = 0.0452 for all data. CCDC 677817

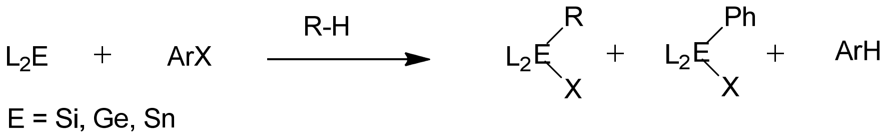
References

(1) Ma, S.; Wang, L. *J. Org. Chem.* **1998**, *63*, 3497.
(2) Ma, S.; Zhang, A.; Yu, Y.; Xia, W. *J. Org. Chem.* **2000**, *65*, 2287.
(3) Acharya, H. P.; Miyoshi, K.; Kobayashi, Y. *Org. Lett.* **2007**, *9*, 3535.
(4) Corey, E. J.; Rucker, C. *Tetrahedron Lett.* **1982**, *23*, 719.
(5) Okamoto, S.; Matsuda, S.; An, D. K.; Sato, F. *Tetrahedron Lett.* **2001**, *42*, 6323.
(6) An, D. K.; Okamoto, S.; Sato, F. *Tetrahedron Lett.* **1998**, *39*, 4861.
(7) Guillerm, G.; Meganem, F.; Lequan, M.; Brower, K. R. *J. Organomet. Chem.* **1974**, *67*, 43.
(8) Kjellgren, J.; Sunden, H.; Szabo, K. J. *J. Am. Chem. Soc.* **2004**, *126*, 474.
(9) Kjellgren, J.; Sunden, H.; Szabo, K. J. *J. Am. Chem. Soc.* **2005**, *127*, 1787.
(10) A 1-necked 100 mL flask fitted with a rubber septum was charged with 315 mg of 2, 6-triisopropyliodobenzene (0.95 mmol, 1 eq.), and 5 mL of 1-phenylpropyne. A solution containing 400 mg of 1 (0.86 mmol, 0.9 eq.) and 15 mL of 1-phenylpropyne and 10 mL of benzene was placed in a gas tight syringe equipped with a 20-gauge needle. 25 mL of the red stannylene solution was added to the iodomesitylene/alkyne solution at a rate of 8 mL/h using a syringe pump. The last 5 mL of 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 1H NMR spectroscopy. The volatiles were removed in vacuo and the resulting solid was recrystallized from pentane at -78 ^{o}C to give a white powder (402 mg, 67 % yield). ^{1}H NMR (C_6D_6) δ: 7.64 (d, $^{3}J_{H-H}$ = 7.0 Hz, 2H, o-Ph), 7.04 (pseudo-t, J = 7.5 Hz, 2H, m-Ph), 6.98 (t, J = 7.0 Hz, 1H, p-Ph), 2.68 (s with br Sn satellites, $^{2}J_{Sn-H}$ = 45.0 Hz, 2H, Sn-CH_2), 2.00 (m, 2H, Sn-C($SiMe_3$)$_2$-CH_2), 1.87 (m, 2H, Sn-C($SiMe_3$)$_2$-CH_2), 0.39 (s, 18H, Si(CH_3)$_3$), 0.15 (s, 18H, Si(CH_3)$_3$) ^{13}C (C_6D_6) δ 132.32 (*i*-Ph), 128.93 (*o*-Ph), 128.06 (*m*-Ph), 125.39 (*p*-Ph), 89.59 (Sn-CH_2-CC), 83.96 (Sn-CH_2-CC), 34.75 (Sn-CH_2), 21.79 (Sn-C($SiMe_3$)$_2$-CH_2), 17.02 (Sn-C($SiMe_3$)$_2$-CH_2), 4.37 (Si(CH_3)$_3$), 4.34 (Si(CH_3)$_3$). ^{119}Sn (C_6D_6) δ 96.59. MS EI m/z: 691.2 (M-CH_3). IR(film) cm-1 ν 2922, 2361, 1251, 898, 848, 753. E.A. Calc'd for $C_{25}H_{47}ISi_4Sn$ C: 42.56; H: 6.71; found C: 42.20; H: 6.79. The quaternary center (Sn-C($SiMe_3$)$_2$) was not observed by ^{13}C NMR. .
(11) Kavara, A.; Cousineau, K. D.; Rohr, A. D.; Kampf, J. W.; Banaszak Holl, M. M. *Organometallics* **2008**, *27*, 1041.

Chapter 5. Stannylene/Aryl Halide Radical Clocks and Stereoselective Radical Cyclizations

5.1 Introduction

C-H activation reactions employing a reagent consisting of $\overline{\mathrm{SnC(SiMe_3)_2CH_2CH_2C}}\mathrm{(SiMe_3)_2}$ (**10**), $\mathrm{Ge[CH(CH_3)_2]_2}$ (**17**), $\mathrm{Si[N_2(^tBu)_2C_2H_2]}$ (**19**), and an aryl halide have been demonstrated to activate alkanes, amines, arenes, and amines (Eq. 5.1).[1-3] In addition, these stannylene/aryl halide reagents have been shown to be effective for both allylic and propargylic activation.[4-5]

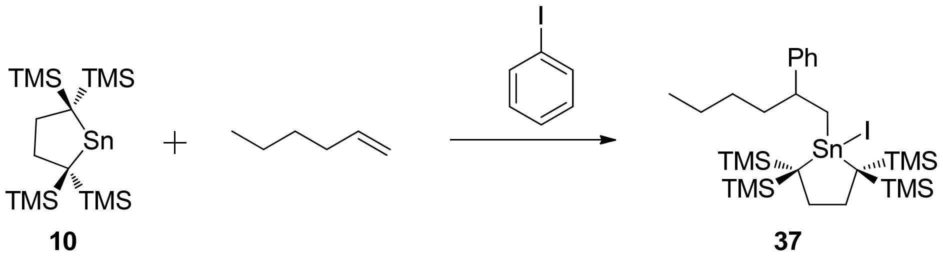


(5.1)

These reactions typically yield a mixture of C-H activation and oxidative addition products, and in the case of alkenes, can also result in addition across the double bond.[4] In order to gain a greater understanding of the reaction mechanism, we desired to perform the reaction using radical clock substrates. Unfortunately, the silylene and germylene reagents employed in our previous studies react directly and rapidly with the radical clocks, both the with alkene functional groups and sometimes other functionality present as well, precluding their application for mechanistic studies.

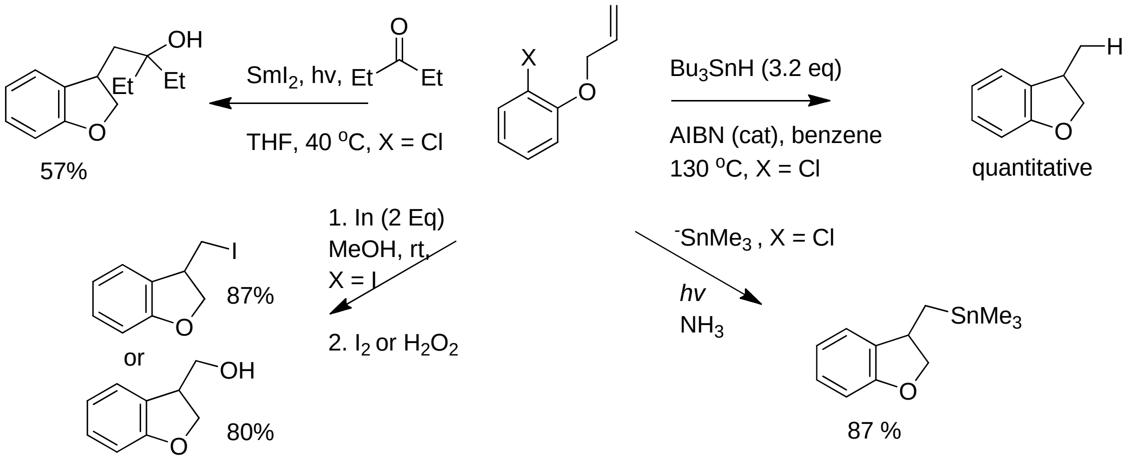
The sterically encumbered "Kuboto" or helmet stannylene, $Sn\overline{C(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$ (**10**), prepared by Kira et al. provided an opportunity to perform the desired radical clock studies.[6-7] Studies from Kira's group indicated that the stannylene did not react with ethylene.[8] Subsequent studies from our group indicated that allylic C-H activation of alkene substrates could be achieved and confirmed that stannylene **10** was tolerant of the alkene functional group.[4] In the course of exploring this chemistry, we also discovered a novel addition chemistry of **10** and aryl halide across the double bond (Scheme 5.1).[4] This set of observations lead us to employ a number of radical clock substrates[9-12] as competitive reaction pathways for the C-H activation, oxidative addition, and double bond addition pathways. These studies enabled us to get a better sense of the reaction rates for this class of C-H activation reactions as well as the rates of the competitive side reactions.

Scheme 5.1 The double bond addition product of **1** and 1-hexene.



In the course of these mechanistic studies, a variety of interesting stereoselective cyclizations were noted. This lead us to also explore this aspect of the chemistry as such cyclizations have been valuable tools in organic chemistry[13-18] and numerous concise syntheses of natural products have employed cyclization strategies.[19-20] The 5-exo radical cyclization of aromatic iodoalkenes has received considerable attention from synthetic community. [21-25] This cyclization mode can be accomplished using tributyltin hydride and AIBN as an initiator, electron transfer reagents such as SmI_2 or Indium metal, under radical nucleophillic substituition or electrochemical conditions. In the tributyltin hydride/AIBN mediated reaction the cyclized radical is trapped with an equivalent of hydrogen resulting in a loss of the iodo functionality, while SmI_2 mediated cyclization can be quenched with aldehydes and ketones to generate functional alcohols (Scheme 5.2). Indium-mediated cyclization yields an iodine or hydroxide substituted cyclization product. Radical nucleophilic substitution conditions using Me_3Sn^- anions in ammonia generate cyclization products with terminal $SnMe_3$ functionality. Tin functionalized heterocycles can be useful due to their applications in cross coupling.[26]

Scheme 5.2 Representative radical methods for 5-exo-trig cyclizations of *ortho* substituted aryl halides.

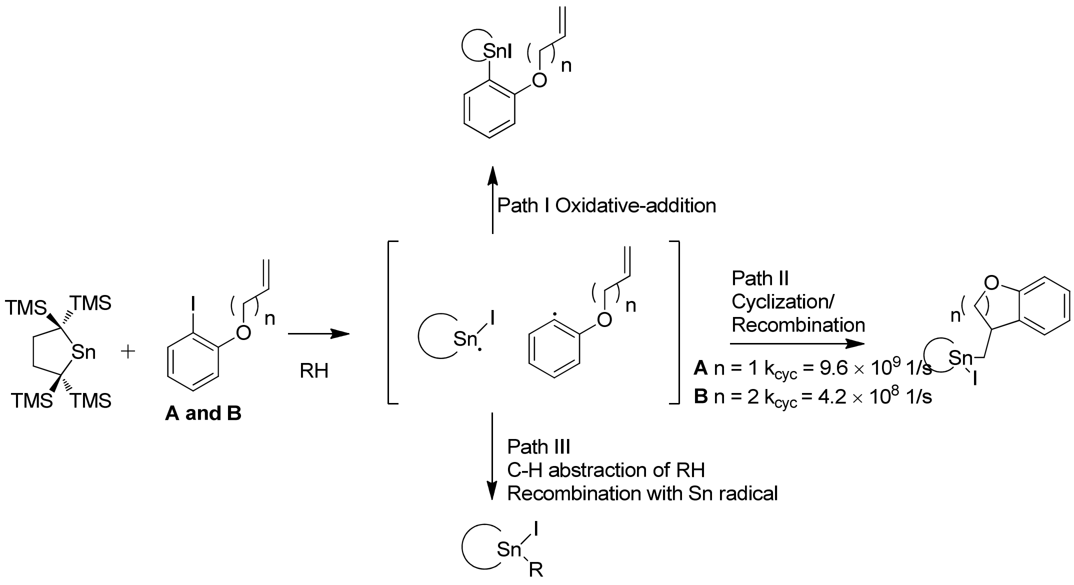


OH
Et
Et
O
57%
SmI2, hv, Et
O
Et
THF, 40 °C, X = Cl
X
O
Bu3SnH (3.2 eq)
AIBN (cat), benzene
130 °C, X = Cl
H
O
quantitative
1. In (2 Eq)
MeOH, rt,
X = I
2. I2 or H2O2
I
87%
O
or
OH
80%
O
-SnMe3 , X = Cl
hv
NH3
SnMe3
O
87 %

5.2 Rate Determination of the C-H Activation Reaction

Radical clocks **A** and **B** have been previously used by Annunziata et al. to determine the rate constants of the reaction between aryl radicals and enolate ions.[27] For our system, we hypothesized that the main reaction pathways include oxidative addition of stannylene onto iodoarene (Path I); cyclization followed by recombination (Path II); or abstraction of substrate hydrogen followed by recombination with the Sn radical (Path III) (Scheme 5.3). From the product distribution, the known cyclization rate of clocks **A** and **B** enabled us to calculate the rates of the competing processes.

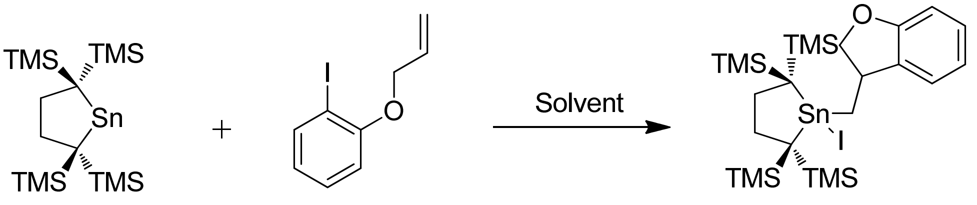
Scheme 5.3 The product distribution of the reaction of stannylene with aryl halide radical clocks that have known cyclization rates. Based upon previous studies of the C-H activation mechanism, the incipient "aryl radical" formed in this process is believed to be part of an inner-sphere complex with the stannylene formed via an iodine bridge. It is this incipient radical which can progress towards oxidative-addition (path I), cyclization/recombination (path II), or C-H abstraction (path III).



SnI
n
O
Path I Oxidative-addition
TMS
TMS
Sn
TMS
TMS
+
I
n
O
A and B
RH
Sn
I
n
O
Path II
Cyclization/
Recombination
A n = 1 k_cyc = 9.6 × 10^9 1/s
B n = 2 k_cyc = 4.2 × 10^8 1/s
n
O
Sn
I
Path III
C-H abstraction of RH
Recombination with Sn radical
Sn
I
R

The reaction between **10** (0.013 M) and radical clock **A** followed the cyclization/recombination path (II) for all substrates studied (cyclohexene, 1-hexene, TMS-hexyne, THF and pentane) (Scheme 5.4). This indicated that the oxidative-addition and C-H activation pathways were substantially slower than the cyclization rate of 9.6 x 10^9 s^{-1}. The crystal structure of the cyclization product is illustrated in Fig. 5.1.

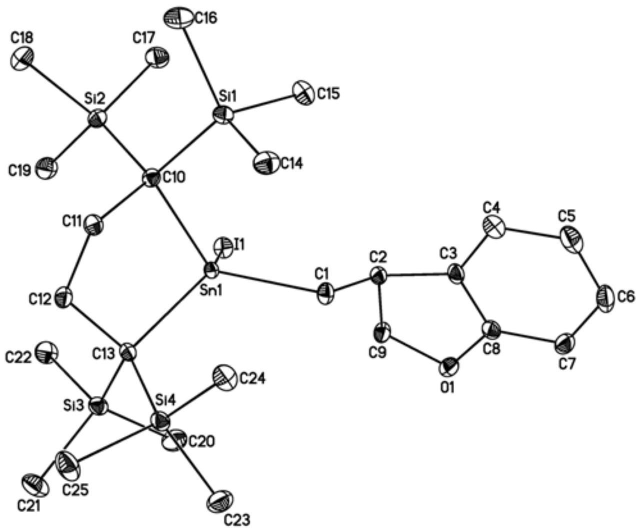
Scheme 5.4 The reaction of **10** and radical clock A gave cyclization product **51** regardless of substrate employed.


TMS
TMS
Sn
TMS
TMS
+
I
O
Solvent
TMS
TMS
O
Sn
I
TMS
TMS

10 **A** **51**

Quantitative in:
cyclohexene
TMS-hexyne
THF
pentane

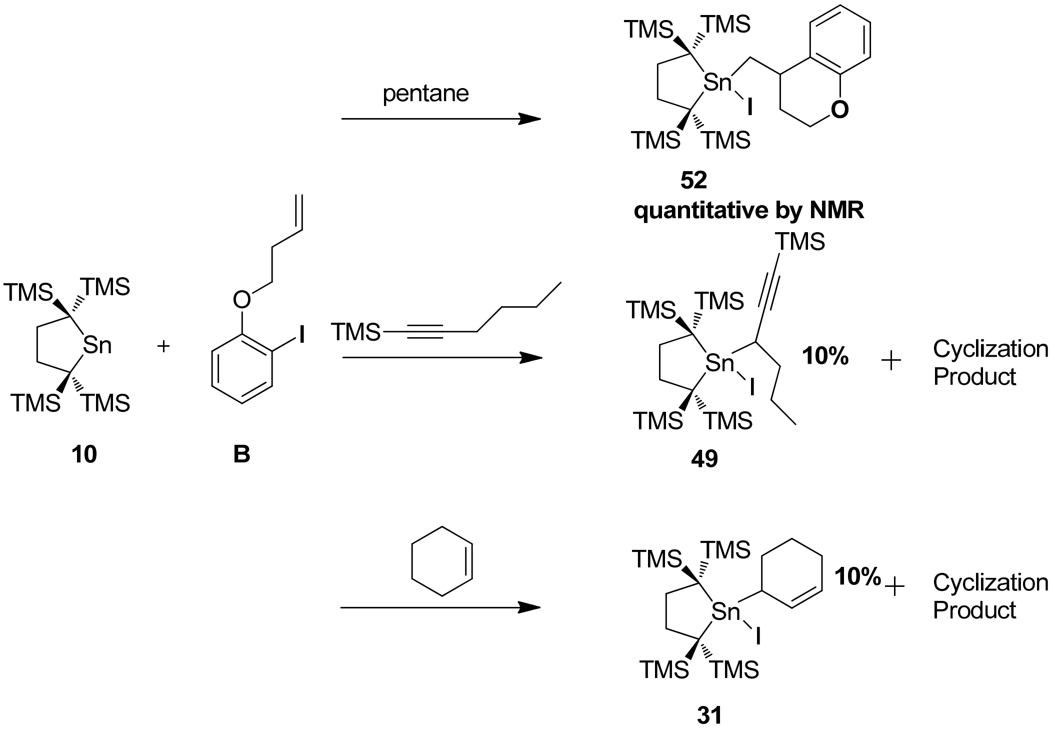
Figure 5.1 ORTEP diagram of $(C_8H_7O)I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$ (**51**) (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Sn-C1, 2.172(2); Sn-I, 2.7345(2); C1-C2, 1.536(3); Sn-C10, 2.183(2); Sn-C13, 2.184(2); Sn-C10-C13, 92.27(7); Sn-C1-C13 116.48(7) Sn-C1-C10, 119.77(7);Sn-C1-I1, 100.89(5); C2-C1-C3, 170.7(1).


C16
C18
C17
Si2
Si1
C15
C19
C10
C14
C11
I1
C4
C5
C2
C3
C1
C12
Sn1
C6
C9
C8
C7
C22
C13
O1
C24
Si3
Si4
C20
C25
C21
C23

Since clock **A** had outcompeted all of the reactions of interest, a slower radical clock was then selected which had a cyclization rate roughly one order of magnitude slower (Scheme 5.5). When testing this system using pentane as the substrate, the 5-exo-trig cyclization product was still formed quantitatively; however, when the reaction was carried out in cyclohexene or TMS-hexyne the C-H activation product was observed as 10% of the product manifold. Employing Eq. 5.2, the rate constant for C-H abstraction from cyclohexene and TMS-hexyne was calculated to be 1.1 $*10^{8}$ $M^{-1}s^{-1}$.

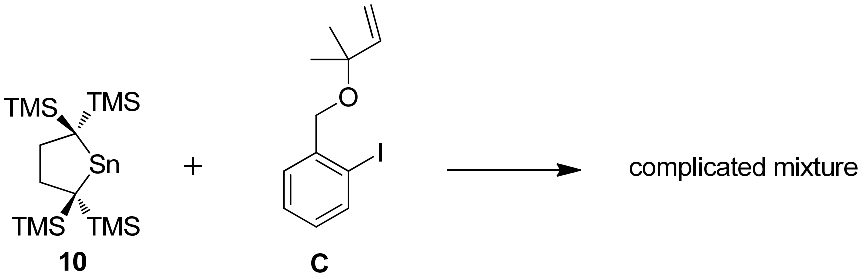
$$\frac{[\text{Cyclization}]}{[\text{CH - Activation}]} = \frac{k_{cy}}{k_{CH}\,[\text{substrate}]} \qquad (5.2)$$

Scheme 5.5 Reaction of **10** with radical clock **B** resulted in both cyclization and C-H activation products.

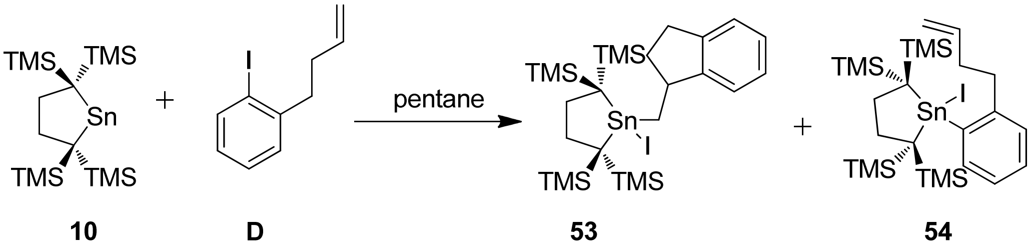

TMS
TMS
Sn
TMS
TMS
10
O
I
B
pentane
TMS
TMS
Sn
I
TMS
TMS
O
52
quantitative by NMR
TMS
TMS
TMS
Sn
I
TMS
TMS
49
10%
+
Cyclization Product
TMS
TMS
TMS
Sn
I
TMS
TMS
31
10%
+
Cyclization Product

Attempts to measure the rate of C-H activation of alkanes and ethers by synthesizing a radical clock **C** with a slower cyclization rate (7.6 x 10^{7} s^{-1}) were complicated by side-reactions (Scheme 5.6).[27] It was previously reported that this radical clock was sensitive to nucleophiles.[27] It was reported that the reaction of enolate ions with photolytically generated phenyl radicals from radical clock **D** was accompanied by the formation of o-iodo benzyl alcohol.[27] Thus, we suspect that the cause of the erratic reactivity of slower radical clock **D** was the nucleophillicity of our stannylene reagent. This is consistent with the observation that **1** does not tolerate methyl esters functionality in C-H activation reactions.[28]

Scheme 5.6 Cyclization with clocks **C** did not proceed predictably to yield measurable rates for C-H abstractions of alkanes and ethers.


TMS
TMS
Sn
TMS
TMS
10
+
O
I
C
complicated mixture

We have also performed cyclization with 1-(but-3-en-1-yl)-2-iodobenzene (**D**), Scheme 5.7.[29] Cyclization was the major product (>95%) with substrates cyclohexene, TMS-hexyne, THF and pentane at the identical concentrations to the procedure used for radical clock **A**. No C-H activation products were observed in these reactions, but a small amount (~5%) of oxidative addition product was formed, Scheme 5.7.


TMS
TMS
Sn
TMS
TMS
+
I
pentane
TMS
TMS
Sn
I
TMS
TMS
+
TMS
TMS
Sn
I
TMS
TMS
10
D
53
54

Scheme 5.7 Reaction of **10** with radical clock D produces a mixture of cyclization and oxidative addition products.

The amount of oxidative addition product increased with increasing concentration of reagents (52% at 0.22 M of stannylene). The rate of cyclization for radical clock **D** was previously measured via laser flash photolysis in benzene at 30°C to be 4 x 10^8 s^{-1}.[30] The absence of C-H activation products in this reaction seems to contradict the results obtained with radical clock **B** whose cyclization rate was determined to be 4.2 x 10^8 s^{-1} by Annunziata et al.[27] Laser flash photolysis studies on the rate of cyclization underestimate the rate of cyclization as compared to the photochemical method in DMSO at 25 °C by Annunziata et al (6.3 x 10^9 s^{-1} by flash photolysis for radical clock **A** vs 9.6 x 10^9 by Annunziata et al.). Thus, it is reasonable that the difference in medium, temperature and the value for abstraction of hydrogen from tri-*n*-butylstannane used to calibrate the radical clocks (4.2 x 10^8 M^{-1} s^{-1} vs 5.9 x 108 M^{-1} s^{-1}) is responsible for the discrepancy in the measurement of cyclization rates.

5.3 Discussion of the C-H Activation Rate

Previous studies have determined the rate constants of phenyl radicals generated from decomposition of phenylazotriphenylmethane (PAT) with aliphatic substrates.[31] This rate was found to be 0.35 x 10^5 M^{-1} s^{-1} for primary, 3.3 x 10^5 M^{-1} s^{-1} for secondary and 16 x 10^5 M^{-1} s^{-1} for tertiary abstractions. The same group determined the rate of the reaction of phenyl radical with oxygen to be 5 x 10^9 M^{-1} s^{-1}. The reaction rate of phenyl radical with THF was measured to be 6 x 10^7 s^{-1}.[29] These results are consistent with our observations that allylic and propargylic C-H abstraction is three orders of magnitude faster than the aliphatic C-H abstraction and one order magnitude faster than abstraction α to the oxygen. This can be explained using the Hammond postulate and the bond dissociation energies which are related to radical stability values.[32-33] There is ~20 kcal/mol difference in bond dissociation energies between allylic and aliphatic sites(105.1 kcal/mol for primary aliphatic, 95. 1 kcal/mol for secondary aliphatic, 93.2 for tertiary aliphatic, 82.3 kcal/mol for allylic sites).[34] According to the Hammond postulate, in the case of late transition state that resembles the products the radical stability values become important factor determining the rate and selectivity of radical reactions.

Lappert has studied the oxidative addition reaction of bromobenzene to amide stannylene, $Sn[N(SiMe_3)_2]_2$, and concluded that this reaction proceeds via radical pathway.[35] This is consistent with our studies of C-H activation with ER_2/PhX (E = divalent group 14 reagent, X = I, Br).[1-2,4] We have generally observed that the reaction of ER_2 and aryl halide produces the mixture of C-H activation and oxidative addition products, indicating that the oxidative addition is competitive with the C-H activation. The amount of oxidative addition depends on the concentration, with the increase of this product with the increase in concentration. In the case of reaction of **10** with radical clock **D**, the rate of C-H activation is not competitive with the oxidative addition or 5-exo-trig cyclization regardless of the solvent employed. The presence of only cyclization product under dilute conditions suggests that the cyclization rate of the radical clock **D** is faster than cyclization with the radical clock **B**.

5.4 Implication for the Mechanism of C-H Activation with Divalent Group 14 Reagent/Aryl Halide

Previous studies in the the Banaszak Holl lab have elucidated the important mechanistic details about C-H activation with group 14 reagent/aryl halide.[1-2] Table 5.1

shows the summary of the mechanistic data. Second order of the germylene and first order in aryl halide indicated the formation of activated complex between 2 divalent species and aryl halide, Table 5.1. The inner sphere electron transfer from one of the divalent species onto aryl halide was supported by the primary and secondary isotope effects, which were consistent with the formation of aromatic radical anions.[2] The radical clock study sheds light on the steps that follow, namely the formation of phenyl radicaloid species and its subsequent reactivity, Scheme 5.7.

Table 5.1 The summary of previous mechanistic data on our C-H activation.

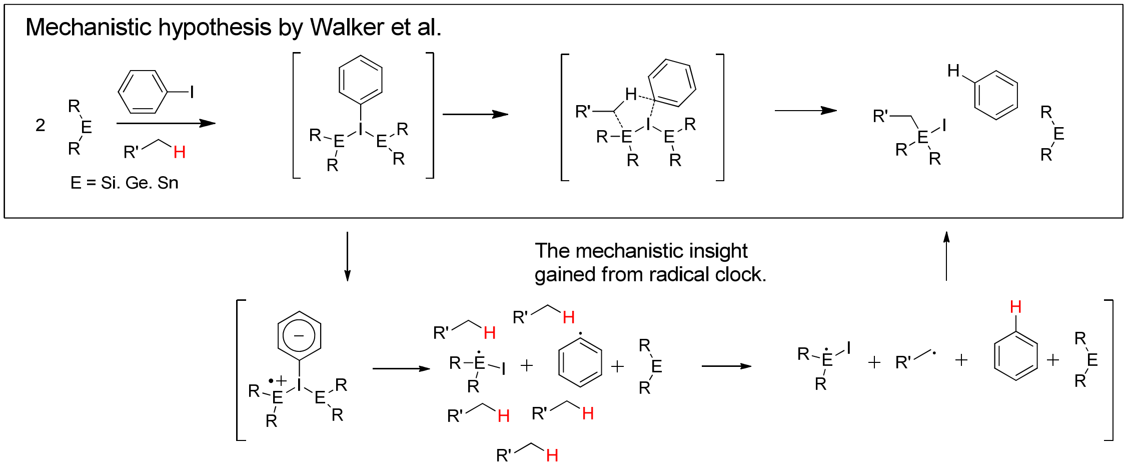
1. Reaction Second Order in Germylene Species
2. First Order in Iodoarene
3. Primary and Secondary Isotope Effects

Divalent Species	Substrate	Ar-X	k_h/k_d
$Ge[N(SiMe_3)_2]_2$	THF/THF-*d8*	C_6H_5I	4.1 ± 0.2
$Ge[CH(SiMe_3)_2]_2$	THF/THF-*d8*	C_6H_5I	5.1 ± 0.2
"	Et_2O	C_6H_5Br/C_6D_5I	1.6 ± 0.1
"	Et_2O	C_6H_5Br/p-C_6H_4DI	1.3 ± 0.1
"	Et_2O	C_6H_5Br/m-C_6H_4DI	1.3 ± 0.1
Kira Stannylene	Toluene/Toluene-*d7*	2,4,6-tri-isopropyliodobenzene	4.9 ± 0.5

The reactivity of radical clocks **A**, **B** and **C** with **10** with alkene and alkyne substrates has been instrumental in understanding the timescale and the nature of intermediates that are proposed after the electron transfer step. The formed phenyl radicaloid species may add across the tethered or terminal double bonds or it may abstract the hydrogen atom of the solvent. These processes are in the order of 10^7 to 10^8 M^{-1} s^{-1}.

The allylic, propargylic or aliphatic radical species recombine with the divalent species radical to form the C-H activation or cyclization products, Scheme 5.8.

Scheme 5.8 The radical clock study elucidated the nature of the intermediates and timescales that are associated with formation of the phenyl radicaloid species.

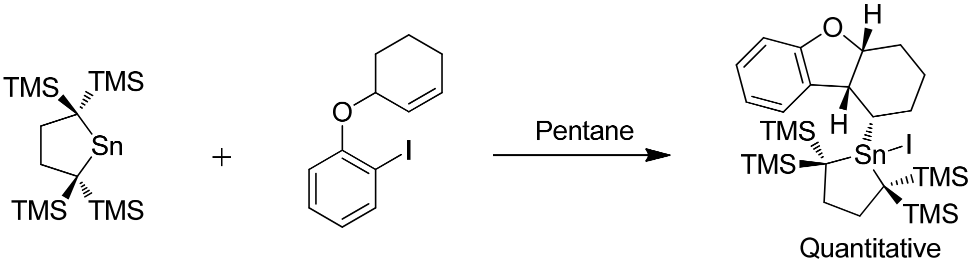

Mechanistic hypothesis by Walker et al.
E = Si. Ge. Sn
The mechanistic insight gained from radical clock.

5.5 Stereoselective Radical Cyclizations

In order to demonstrate synthetic utility of this method we have performed radical cyclization with several alkene and alkyne substrates.

Cyclizations with **10** and 1-(cyclohex-2-en-1-yloxy)-2-iodobenzene also resulted in quantitative cyclization product **55**, Scheme 5.9. The stereochemistry of cyclization product with 1-(cyclohex-2-en-1-yloxy)-2-iodobenzene has been determined with 2 dimensional ^{1}H NMR experiments, Plot 5.1. Oxidation of product **55** to obtain an alcohol of identical relative stereochemistry would result in benzofuran substrates that are difficult to synthesize with other methods.[36-37]

Scheme 5.9 Cyclization with 1-(cyclohex-2-en-1-yloxy)-2-iodobenzene resulted in quantitative cyclization yielding only *trans* diastereomer.



10 **55**

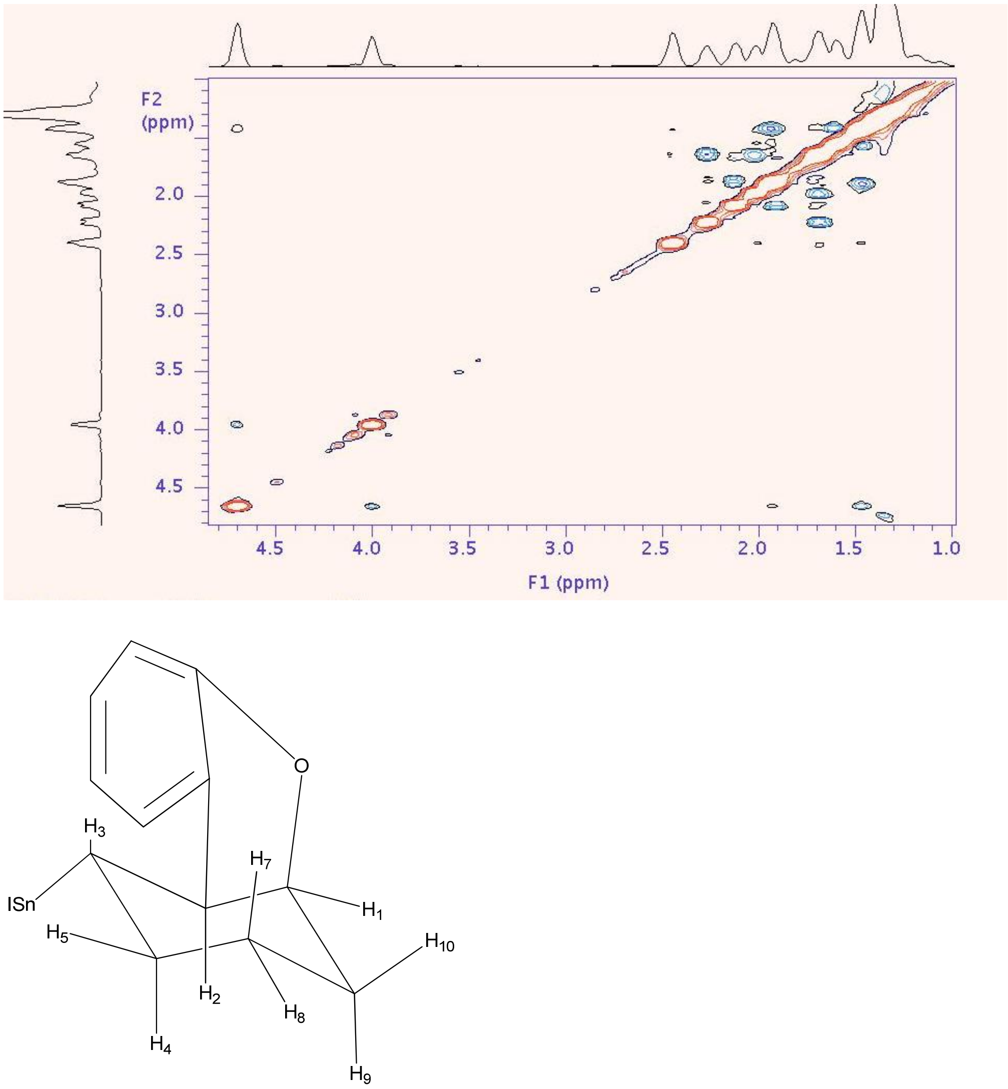
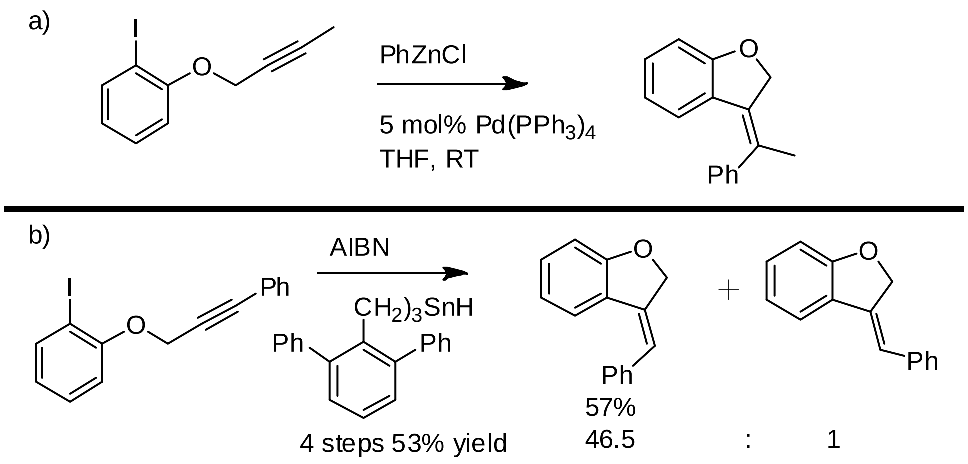


Figure 5.2 Noesy spectrum of product **55** shows through space interaction of H_1 and H_2 (4.72 ppm to 4.0 ppm). In addition, interaction of proton at 2.42 ppm with 1.62 ppm indicates NOE between H_3 and H_7.

5.6 Cyclization with (2-iodophenyl) Alkynes

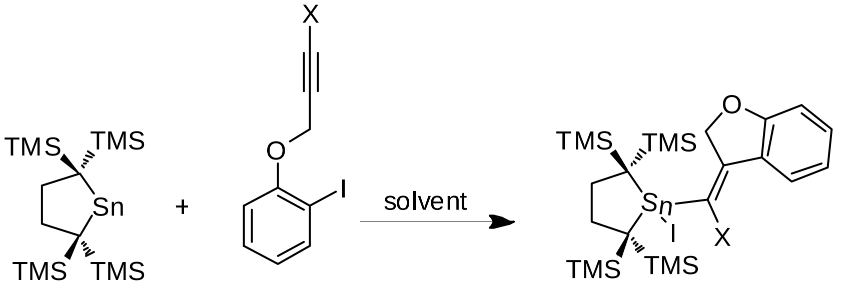
Literature routes for cyclization of 2-(iodophenyl) alkynes include palladium catalyzed and tin radical mediated methods. Palladium catalyzed route proceeds via *cis* carbopalladation and the reductive elimination generates the product with electrophile in the *cis* position, Scheme 5.10a.[38] Similarly, Nickel catalyzed method gives products of syn addition across the double bond.[39] The ordinary Bu_3SnX mediated cyclization gives mixture of stereoisomers while the bowl shaped tin reagent introduced by Sasaki et al. provide alkene products with E stereochemistry, Scheme 5.10b.[40] It should be noted that the bowl shaped tin reagent synthesized in 4 steps, 53% yield introduces a stoichiometric amount of hydrogen resulting in a loss of the iodo functionality.

Scheme 5.10 Literature routes for stereoselective cyclization of (2-iodophenyl)-alkynes.



The reaction of **10** with 1-iodo-2-(prop-2-yn-1-yloxy)benzene produces a mixture containing 50:50 E/Z stereoisomers, Scheme 5.11. When methyl substituted alkyne in pentane was employed 95 to 5 mixture favoring E stereoisomer was obtained. The stereospecificity of the reaction with methyl substituted alkyne eroded as solvent polarity was increased, Scheme 5.11. The TMS protected alkyne generated a single product of anti addition across the triple bond. This is consistent with the radical cyclizations that utilize bulky tin substituents introduced by Sasaki et al. When we used phenyl substituted 2-(iodophenyl) alkynes initial cyclization product was obtained and characterized with X-ray crystallography, Figure 5.3. Our attempts to characterize this product with NMR spectroscopy and other methods were not successful due to facile polymerization of this product. We also synthesized *para* substituted O-Me and CF_3 2-(iodophenyl) alkynes to find that the similar polymerization side reaction consumes the product. We are in process of characterizing this tin and aromatic substituted furan containing polymer and will report our finding in due course.

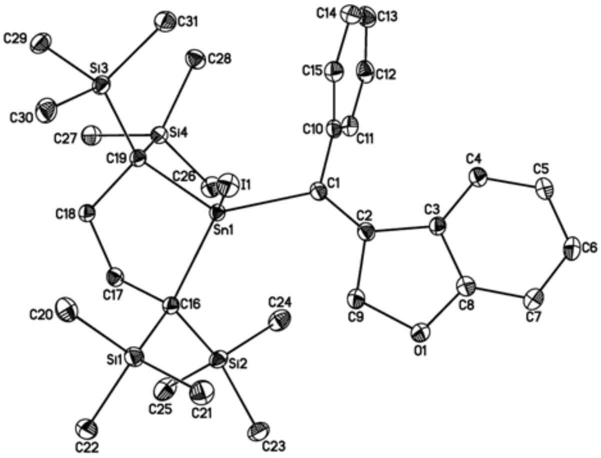
Scheme 5.11 Radical cyclization of (2-iodophenyl) alkynes.



X	Solvent	Trans/cis	Product
H	pentane	1	**56**
Me	toluene	2.3	**57**
Me	pentane	19	**57**
TMS	pentane	trans only	**58**
Ph	pentane	polymer formation	**59**
p-CF_3Ph	pentane	polymer formation	
p-OMe	pentane	polymer formation	

In comparison to the method by Sasaki et al., our method provides a route that preserves functionality and selectivity with TMS and alkyl substituted alkynes. The room temperature/pentane conditions employed are comparatively milder than those of Sasaki et al. However, phenyl substituted alkynes are not compatible with our reaction conditions. Only aryl halides and not alkyl or vinyl halides are compatible with our conditions since initial step in this reaction is not halide abstraction but electron transfer onto the aryl ring followed by the leaving of iodide and formation of aryl radical.[2] The reaction of alkyl and vinyl halides with **10** only gives products of oxidative addition onto divalent tin reagent. The products we obtain are similar to the method utilizing $SnMe_3$ anions in liquid ammonia.[24] While **10** presents a disadvantage from atom economy standpoint, the products of our reactions would be expected to exhibit lesser toxicity due to steric bulk around tin atom.[41] The room temperature/pentane conditions are much milder than use of liquid ammonia and trimethyltin anions.

Figure 5.3 ORTEP diagram of $(C_{12}H_{15}OSi)I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$ (**59**) (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Sn-C1, 2.165(2); Sn-I, 2.7877(2); C1-C2, 1.344(2);C1-C10 1.487 (2); Sn-C19, 2.191(2); Sn-C16, 2.915(2); Sn-C16-C19, 92.67(6); Sn-C1-C9 90.65(7);Sn-C1-I1,93.03(4); C2-C1-C10, 120.81(1).


C31
C29
Si3
C28
C30
C27
Si4
C19
C26
I1
C18
Sn1
C17
C16
C20
C24
Si1
Si2
C25
C21
C22
C23
C14
C13
C15
C12
C10
C11
C1
C2
C3
C4
C5
C6
C9
C8
C7
O1

5.7 Summary

In conclusion we have demonstrated new radical cyclization method that utilized bulky Kira stannylene and ortho-iodo aromatic alkynes and alkenes. This route has been used to prepare heterocycles with defined stereochemistry and Tin functionality. This radical cyclization has been used to determine the rate of C-H activation of alkenes and alkynes to be 1.1 $x10^8 M^{-1}s^{-1}$.

Experimental

Manipulations involving $\overline{\mathrm{SnC(SiMe_3)_2CH_2CH_2C}}\mathrm{(SiMe_3)_2}$ (**10**) were performed using inert atmosphere techniques. Solvents were dried over sodium benzophenone ketyl and degassed. **10** was synthesized according to literature procedures.[7] Starting haloalkenes and alkynes were synthesized according to literature methods.[39,42] ^{1}H and ^{13}C NMR spectra were acquired on a Varian 500 MHz instruments (499.904 and 125.714 MHz respectively). ^{1}H and ^{13}C NMR 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.[43] 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.

(51) $\mathbf{(C_8H_7O)I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2}$

A 1-necked 100 ml flask fitted with a rubber septum was charged with 61.7 mg (0.24 mmol, 1.1 eq) of 1-(allyloxy)-2-iodobenzene and 20 ml of pentane. 100 mg (0.22 mmol, 1eq) of **1** was added in one portion and the solution was stirred overnight until the red color disappeared completely. The volatiles were removed *in vacuo* and the resulting solid was recrystallized from pentane at -78 °C to give a white powder (75 mg, 83 % yield). ^{1}H NMR (C_6D_6) δ: 7.24 (d, $^3J_{H\text{-}H}$ =7.21 Hz, 1H, O-C-C*H*), 6.99 (pseudo-t, $^3J_{H\text{-}H}$ = 7.21 Hz, 1H, O-C=CH=C*H*), 6.87 (d, $^3J_{H\text{-}H}$ = 8.01 Hz, 1H, O-C-CH=CH=CH=C*H*), 6.82 (pseudo-t, $^3J_{H\text{-}H}$ = 7.61 Hz, 1H, O-C=CH=CH=C*H*), 4.87 (pseudo-t, $J_{H\text{-}H}$ = 8.81 Hz, 1H, O-CH_2), 4.39 (dd, $J_{H\text{-}H}$ = 9.21 Hz, $J_{H\text{-}H}$ = 5.2 Hz, 1H, O-CH_2), 4.01 (m, 1H, Sn-CH$_2$-C*H*), 2.28 (dd with br Sn satellites, $^2J_{H\text{-}H}$ = 13.2 Hz, $^3J_{H\text{-}H}$ = 2.0 Hz, $^2J_{Sn\text{-}H}$ = 13.4 Hz, 1H, Sn-C*H*$_2$), 2.07 (m, 2H, Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 1.92 (m, 3H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$ and Sn-C*H*$_2$), 1.76 (m, 1H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$), 0.37 (s, 9H, Si(C*H*$_3$)$_3$), 0.33 (s, 9H, Si(C*H*$_3$)$_3$), 0.02 (s, 9H, Si(C*H*$_3$)$_3$), 0.01 (s, 9H, Si(C*H*$_3$)$_3$). ^{13}C (C$_6$D$_6$) δ 160.84 (O-C), 133.67 (Sn-CH$_2$-CH-*C*), 129.28 (O-C=CH=*C*H), 124.25 (O-C=*C*H), 121.45 (O-C=CH=CH=*C*H), 110.78 (O-C=CH-CH=CH=*C*H), 79.77 (O-*C*H$_2$), 42.60 (Sn-CH$_2$-C*H*), 35.17 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 34.95 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 32.33 (Sn-*C*H$_2$), 4.61 (Si(*C*H$_3$)$_3$), 4.58 (Si(*C*H$_3$)$_3$), 4.51 (Si(*C*H$_3$)$_3$), 4.42 (Si(*C*H$_3$)$_3$). ^{119}Sn (C$_6$D$_6$) δ 129.61. MS EI *m/z*: 709.3 (M-CH$_3$). IR(film) cm^{-1} ν 2922, 2852, 1595, 1463, 1377, 1251, 962, 901, 844.

(**52**) **$(C_{10}H_{11}O)I\overline{SnC(SiMe_3)_2CH_2CH_2C(}SiMe_3)_2$**

A 1-necked 100 mL flask fitted with a rubber septum was charged with 130.1 mg of 1-(but-3-en-1-yloxy)-2-iodobenzene (0.47 mmol, 1 eq.), and 5 mL of pentane. A solution containing 200 mg of **1** (0.43 mmol, 1 eq.) and 10 mL of pentane was placed in a gas tight syringe equipped with a 20-gauge needle. 10 mL of the red stannylene solution was added to the 1-(but-3-enyloxy)-2-iodobenzene/alkane solution at a rate of 3 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 as indicated by ^{1}H NMR spectroscopy. The volatiles were removed by heating at 80 °C in a Kugel Rohr apparatus *in vacuo* (280 mg, 88.0 % yield). ^{1}H NMR (C$_6$D$_6$) δ: 7.30 (d, $^3J_{H\text{-}H}$ = 7.60 Hz, 1H, Ph), 6.99 (pseudo-d, $J_{H\text{-}H}$ = 4.00 Hz, 2H, Ph), 6.84 (m, 1H, Ph), 4.11 (dd, $J_{H\text{-}H}$ = 10.0 Hz, $J_{H\text{-}H}$ = 2.4 Hz, 1H, O-C*H*$_2$), 3.97 (m, 1H, O-C*H*$_2$), 3.57 (m, 1H, Sn-C*H*$_2$), 2.30 (dd, $J_{H\text{-}H}$ = 12.8 Hz, $J_{H\text{-}H}$ = 1.60 Hz, 1H, O-CH$_2$-C*H*$_2$), 2.17-1.78 (m, 4H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$-C*H*$_2$), 2.11 (m, 1H, Sn-CH$_2$-C*H*), 1.89 (m, 2H, O-CH$_2$-C*H*$_2$ and Sn-C*H*$_2$), 0.39 (s, 9H, Si(C*H*$_3$)$_3$), 0.34 (s, 9H, Si(C*H*$_3$)$_3$), 0.15 (s, 9H, Si(C*H*$_3$)$_3$), 0.06 (s, 9H, Si(C*H*$_3$)$_3$). ^{13}C (C$_6$D$_6$) δ 155.6 (Ph), 129.3 (Ph), 121.2 (Ph), 118.2 (Ph), 63.15 (O-*C*H$_2$), 35.49 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 35.03 (Sn-C(SiMe$_3$)$_2$-

*C*H$_2$), 34.09 (Sn-CH$_2$-*C*H), 33.75 (Sn-*C*H$_2$), 30.57 (O-CH$_2$-*C*H$_2$), 4.71 (Si(*C*H$_3$)$_3$), 4.67 (2 x Si(*C*H$_3$)$_3$), 4.57 (Si(*C*H$_3$)$_3$). ^{119}Sn (C$_6$D$_6$) δ 133.4 MS EI *m/z*: 723.5 IR(film) cm^{-1} 2918, 1928, 1606, 1580, 1485, 1248, 960, 901. E.A. Calc'd for $C_{26}H_{51}IOSi_4Sn$ C: 42.33; H: 6.97; found C: 42.42; H: 7.13.

(**53**) **$(C_{10}H_{11})ISnC(SiMe_3)_2CH_2CH_2C(SiMe_3)_2$**

A 1-necked 100 ml flask fitted with a rubber septum was charged with 61.7 mg (0.24 mmol, 1.1 eq) of 1-(but-3-en-1-yl)-2-iodobenzene and 20 ml of pentane. 100 mg (0.22 mmol, 1eq) of **1** was added in one portion and red solution was stirred overnight until red color disappeared completely. The volatiles were removed using a Kugel-Rohr apparatus *in vacuo* to obtain elementally pure material. This material contained ~10% of oxidative addition product. (120 mg, 77 % yield). ^{1}H NMR (C$_6$D$_6$) δ: 7.32 (pseudo-d, $^3J_{H-H}$ = 7.50 Hz, 1H, Ph), 7.14-7.07 (m, 3H, Ph), 3.85 (m, 1H, Sn-CH$_2$-C*H*), 2.83 (m, 1H, Ph-C*H*$_2$), 2.68 (m, 2H, Ph-C*H*$_2$ and Sn-C*H*$_2$), 2.43 (dd with Sn satellites, $^2J_{H-H}$ = 12.5 Hz, $^3J_{H-H}$ = 2.50 Hz, $^4J_{Sn-H}$ = 18.5 Hz, 1 H, Ph-CH$_2$-C*H*$_2$), 2.16-1.94 (m, 4H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$-C*H*$_2$), 1.87-1.77 (m, 2H, Ph-CH$_2$-C*H*$_2$ and Sn-CH$_2$), 0.42 (s, 9H, Si(C*H*$_3$)$_3$), 0.40 (s, 9H, Si(C*H*$_3$)$_3$), 0.20 (s, 9H, Si(C*H*$_3$)$_3$), 0.12 (s, 9H, Si(C*H*$_3$)$_3$). ^{13}C (C$_6$D$_6$) δ 149.5 (Ph), 144.1 (Ph), 127.33 (Ph), 127.27 (Ph), 125.4 (Ph), 123.7 (Ph), 45.32 (Sn-CH$_2$-*C*H), 36.36 (Sn-CH$_2$), 35.39 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 35.08 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 32.47 (Ph-CH$_2$-*C*H$_2$), 31.67 (Ph-*C*H$_2$), 4.68 (Si(*C*H$_3$)$_3$). ^{119}Sn (C$_6$D$_6$) δ 135.14. MS EI (mixture of cyclization and oxidative addition) *m/z*: 707.7 (M-CH$_3$). IR(film) cm^{-1} (mixture of cyclization and oxidative addition) 2902, 2859, 1457, 1407, 1248, 1005, 961, 903, 836.

(**54**) **$(C_{10}H_{11})ISnC(SiMe_3)_2CH_2CH_2C(SiMe_3)_2$**

A 1-necked 100 ml flask fitted with a rubber septum was charged with 61 mg (0.24 mmol, 1.1 eq) of 1-(but-3-en-1-yl)-2-iodobenzene and 1 ml of pentane. 100 mg (0.22 mmol, 1eq) of **1** was added in one portion and red solution was stirred overnight until red color disappeared completely. ^{1}H NMR indicated presence of cyclization and oxidative addition products. ^{1}H NMR (C_6D_6) δ: 7.72 (d with Sn satellites, $^3J_{Sn-H}$ = 37.0 Hz, $^3J_{H-H}$ = 7.0 Hz, 1H, Sn-C-C*H*), 7.12-7.00 (m, 3H, Ar), 6.01 (m, 1H, *H*C=CH$_2$), 5.22 (d, J_{H-H} = 17.0 Hz, 1H, HC=C*H*$_2$), 5.08 (d, J_{H-H} = 9.5 Hz, 1H, HC=C*H*$_2$), 3.00 (pseudo-t, J_{H-H} = 8.00 Hz, 2H, Ar-CH$_2$-C*H*$_2$), 2.17-1.95 (m, 4H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$-C*H*$_2$), 2.64 (m, 1H, Ar-C*H*$_2$), 1.79 (m, 1H, Ar-C*H*$_2$), 0.47 (s, 18H, Si(C*H*$_3$)$_3$), 0.21 (s, 18H, Si(C*H*$_3$)$_3$). ^{13}C (C_6D_6) δ 149.8 (Sn-*C*), 146.8 (CH$_2$-*C*), 138.0 (H*C*=CH$_2$), 135.9 (Sn-C-C*H*), 130.8 (Ph), 130.0 (Ph), 123.7 (Ph), 116.5 (HC=*C*H$_2$), 41.53 (Ph-CH$_2$-C*H*$_2$), 36.4 (Ph-*C*H$_2$), 35.6 Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 4.04 (Si(*C*H$_3$)$_3$). ^{119}Sn (C_6D_6) δ 33.3

(55) $\mathbf{(C_{12}H_{13}O)I\overline{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2}$

A 1-necked 100 ml flask fitted with a rubber septum was charged with 71 mg (0.24 mmol, 1.1 eq) of 1-(cyclohex-2-enyloxy)-2-iodobenzene and 20 ml of pentane. 100 mg (0.22 mmol, 1eq) of **10** was added in one portion and the solution was stirred overnight until the red color disappeared completelyand a white precipitate was obtained. The volatiles were removed *in vacuo* and the resulting white powder was recrystallized from pentane at -78 °C. (103.9 mg, 63.1 % yield). ^{1}H NMR (C_6D_6) δ: 7.65 (d, $^3J_{H-H}$ = 7.50 Hz, 1H, Ph), 7.00 (pseudo-t, J_{H-H} = 7.50 Hz, 1H, Ph), 6.88 (m, 2H, Ph), 4.71 (pseudo-d, J_{H-H} = 4.50 Hz, 1H, O-C*H*), 4.01 (pseudo-t with br Sn satellites, $^3J_{Sn-H}$ = 35.0, J_{H-H} = 7.50 Hz, 1H, Ph-C*H*), 2.46 (m, 1H, Sn-C*H*), 2.27 (m, 1H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$), 2.12 (m, 1H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$), 2.03 (m, 1H, Sn-CH-C*H*$_2$), 1.93 (m, 2H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$ and O-CH-C*H*$_2$), 1.69 (m, 2H, Sn-C(SiMe$_3$)$_2$-C*H*$_2$ and Sn-CH-C*H*$_2$), 1.60 (m, 1H, Sn-CH-CH$_2$-C*H*$_2$), 1.46 (m, 2H, O-CH-C*H*$_2$ and Sn-CH-CH$_2$-C*H*$_2$), 0.44 (s, 9H, Si(C*H*$_3$)$_3$), 0.42 (s, 9H, Si(C*H*$_3$)$_3$), 0.14 (s, 9H, Si(C*H*$_3$)$_3$), 0.02 (s, 9H, Si(C*H*$_3$)$_3$). ^{13}C (C_6D_6) δ 161.1 (Ar), 134.2 (Ar), 129.0 (Ar), 124.56 (Ar), 121.9 (Ar), 111.5 (Ar), 84.32 (O-*C*H), 46.62 (Ar-*C*H), 44.33 (Sn-*C*H), 37.21 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 34.77 (Sn-C(SiMe$_3$)$_2$-*C*H$_2$), 29.93 (Sn-CH-*C*H$_2$), 28.05 (O-CH-*C*H$_2$), 22.88 (Sn-CH-CH$_2$-*C*H$_2$), 4.77 (Si(*C*H$_3$)$_3$), 4.56 (Si(*C*H$_3$)$_3$), 4.52 (Si(*C*H$_3$)$_3$), 3.88

($Si(CH_3)_3$).^{119}Sn (C_6D_6) δ 153.83. MS EI *m/z*: 749.3 ($M-CH_3$). IR(film) cm^{-1}. E.A. Calc'd for $C_{28}H_{53}IOSi_4Sn$ C: 44.04; H: 7.00; found C: 44.12; H: 7.15.

(**57**) **$(C_{10}H_9O)ISnC(SiMe_3)_2CH_2CH_2C(SiMe_3)_2$**

A 1-necked 100 ml flask fitted with a rubber septum was charged with 64 mg (0.24 mmol, 1.1 eq) of 1-(but-2-yn-1-yloxy)-2-iodobenzene and 20 ml of pentane. 100 mg (0.22 mmol, 1eq) of **10** was added in one portion and the solution was stirred overnight until the red color disappeared completely. The volatiles were removed *in vacuo* and the resulting solid was recrystallized from pentane at -78 °C to give a white powder (80 mg, 78 % yield). ^{1}H NMR (C_6D_6) δ: 7.36 (d, J = 8.0 Hz, 1H, Ar), 6.95 (pseudo-t, J = 7.5 Hz, 1H, Ar), 6.85 (d, J = 8.0 Hz, 1H, Ar), 6.73 (pseudo-t, J = 7.5 Hz, 1H, Ar), 5.55 (s, 2H, O-CH_2), 2.34 (pseudo-t with br Sn satellites, J_{H-H} = 3 Hz, $^3J_{Sn-H}$ = 37.0 Hz, 3H, Sn-C-CH_3), 2.05 (m, 2H, Sn-$C(SiMe_3)_2$-CH_2-CH_2), 1.93 (m, 2H, Sn-$C(SiMe_3)_2$-CH_2-CH_2), 0.43 (s, 18H, Si(CH_3)$_3$), 0.20 (s, 18H, Si(CH_3)$_3$). ^{13}C (C_6D_6) δ 146.6 (Ar), 137.0 (Ar), 131.4 (Ar), 126.8 (Ar), 121.3 (C=C), 120.6 (Ar), 111.7 (C=C), 111.5 (Ar), 77.08 (O-CH_2), 35.60 (Sn-$C(SiMe_3)_2$-CH_2), 4.53 ($Si(CH_3)_3$), 3.97 ($Si(CH_3)_3$). ^{119}Sn (C_6D_6) δ 27.93. MS CI with methane *m/z*: 721.1 3 ($M-CH_3$). (IR(film) cm^{-1} 2554, 1600, 1463, 1253, 897, 841.

(**58**) **$(C_{12}H_{15}OSi)ISnC(SiMe_3)_2CH_2CH_2C(SiMe_3)_2$**

A 1-necked 100 ml flask fitted with a rubber septum was charged with 31.3 mg (0.095 mmol, 1.1 eq) of (3-(2-iodophenoxy)prop-1-yn-1-yl)trimethylsilane and 7 ml of pentane. 40 mg (0.086 mmol, 1eq) of **10** was added in one portion and the solution was stirred overnight until the red color disappeared completely. The volatiles were removed *in vacuo* and the resulting oil contained a single product as judged by ^{1}H NMR spectroscopy. ^{1}H NMR (C_6D_6) δ: 7.63 (d, $^3J_{H-H}$ = 7.5 Hz, 1H, Ar), 6.70 (pseudo-t, J = 7.5 Hz, 1H, Ar), 6.65 (d, $^3J_{H-H}$ = 9.0 Hz, 1H, Ar), 6.73 (pseudo-t, J_{H-H} = 9.0 Hz, 1H, Ar), 5.60 (s, 2H, O-CH_2), 2.15-1.90 (m, 4H, Sn-$C(SiMe_3)_2$-CH_2-

CH_2), 0.55 (s, 18H, $Si(CH_3)_3$), 0.46 (s, 18H, $Si(CH_3)_3$), 0.05 (s, 9H, CC-$Si(CH_3)_3$). ^{13}C (C_6D_6) δ 168.1 , 142.2, 132.7 , 129.6 , 126.9 , 120.9 , 112.5 , 93.5 (Ar and C=C), 67.57 (O-CH_2), 36.79 (Sn-$C(SiMe_3)_2$-CH_2), 5.56 ($Si(CH_3)_3$), 4.64 ($Si(CH_3)_3$), 4.50 ($Si(CH_3)_3$), 4.31 ($Si(CH_3)_3$). 0.00 ($Si(CH_3)_3$). ^{119}Sn (C_6D_6) δ – 1.14 MS CI with methane *m/z*: 794.5 (M^+), 779.5 (M-CH_3). (IR(film) cm^{-1} 3000, 2361, 2337, 1463, 1377, 1251, 892, 847.

Radical cyclization in pentane, THF, cyclohexene and TMS-hexyne

A 1 necked 50 ml flask fitted with a rubber septum was charged with 0.71 mol of radical clock and 5 ml of solvent. **1**, 30 mg (0.065 mol, 1eq), was added in one portion and the red solution was stirred overnight until red color disappeared completely. The volatiles were removed *in vacuo* and the resulting mixture was analyzed using ^1H NMR spectroscopy.

References

(1) Miller, K. A.; Bartolin, J. M.; O'Neill, R. M.; Sweeder, R. D.; Owens, T. M.; Kampf, J. W.; Banaszak Holl, M. M.; Wells, N. J. *J. Am. Chem. Soc.* **2003**, *125*, 8986.
(2) Walker, R. H.; Miller, K. A.; Scott, S. L.; Cygan, Z. T.; Bartolin, J. M.; Kampf, J. W.; Banaszak Holl, M. M. *Organometallics* **2009**, *28*, 2744.
(3) Bartolin, J. M.; Kavara, A.; Kampf, J.; Banaszak Holl, M. M. *Organometallics* **2006**, *25*, 4738.
(4) Kavara, A.; Cousineau, K. D.; Rohr, A. D.; Kampf, J. W.; Banaszak Holl, M. M. *Organometallics* **2008**, *27*, 1041.
(5) Kavara, A.; Kampf, J. W.; Banaszak Holl, M. M. *Organometallics* **2008**, *27*, 2896.
(6) Kira, M.; Yauchibara, R.; Hirano, R.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 7785.
(7) Iwamoto, T.; Masuda, H.; Ishida, S.; Kabuto, C.; Kira, M. *J Organomet. Chem.* **2004**, *689*, 1337.
(8) Kira, M.; Ishida, S.; Iwamoto, T. *Chem. Rec.* **2004**, *4*, 243.
(9) Jin, J.; Newcomb, M. *J. Org. Chem.* **2007**, *72*, 5098.
(10) Lalevée, J.; Allonas, X.; Fouassier, J.-P.; Ingold, K. U. *J. Org. Chem.* **2008**, *73*, 6489.
(11) Roschek, B.; Tallman, K. A.; Rector, C. L.; Gillmore, J. G.; Pratt, D. A.; Punta, C.; Porter, N. A. *J. Org. Chem.* **2006**, *71*, 3527.
(12) Buckmelter, A. J.; Kim, A. I.; Rychnovsky, S. D. *J. Am. Chem. Soc.* **2000**, *122*, 9386.
(13) Majumdar, K. C.; Basu, P. K.; Chattopadhyay, S. K. *Tetrahedron* **2007**, *63*, 793.
(14) Russell Bowman, W.; Fletcher, A. J.; Potts, G. B. S. *J. Chem. Soc., Perk. T. 1* **2002**, 2747.
(15) Majumdar, K. C.; Basu, P. K.; Mukhopadhyay, P. P. *Tetrahedron* **2004**, *60*, 6239.
(16) Hodgson, D. M.; Winning, L. H. *Org. Biomol. Chem.* **2007**, *5*, 3071.
(17) Zimmerman, J.; Sibi, M. In Enantioselective Radical Reactions **2006**, p 107.
(18) Robertson, J.; Pillai, J.; Lush, R. K. *Chem. Soc. Rev.* **2001**, *30*, 94.
(19) Jasperse, C. P.; Curran, D. P.; Fevig, T. L. *Chem. Rev.* **1991**, *91*, 1237.
(20) Salom-Roig, X. J.; Dénès, F.; Renaud, P. *Synthesis* **2004**, 1903.
(21) Beckwith, A. L. J.; Gara, W. B. *J. Chem. Soc., Perk. T. 2* **1975**, 795.
(22) Ogawa, A.; Sumino, Y.; Nanke, T.; Ohya, S.; Sonoda, N.; Hirao, T. *J. Am. Chem. Soc.* **1997**, *119*, 2745.
(23) Yanada, R.; Obika, S.; Nishimori, N.; Yamauchi, M.; Takemoto, Y. *Tetrahedron Lett.* **2004**, *45*, 2331.
(24) Vaillard, S. E.; Postigo, A.; Rossi, R. A. *J. Org. Chem.* **2002**, *67*, 8500.

(25) Beckwith, A. L. J.; Gara, W. B. *J. Chem. Soc., Perk. T. 2* **1975**, 593.
(26) Seregin, I. V.; Gevorgyan, V. *J. Am. Chem. Soc.* **2006**, *128*, 12050.
(27) Annunziata, A.; Galli, C.; Marinelli, M.; Pau, T. *Eur. J. Org. Chem.* **2001**, *2001*, 1323.
(28) Kavara, A. Banaszak Holl, M. M. Unpublished results.
(29) Garst, J. F.; Boone, J. R.; Webb, L.; Lawrence, K. E.; Baxter, J. T.; Ungvary, F. *Inorg Chim Acta* **1999**, *296*, 52.
(30) Johnston, L. J.; Lusztyk, J.; Wayner, D. D. M.; Abeywickreyma, A. N.; Beckwith, A. L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc* **1985**, *107*, 4594.
(31) Kryger, R. G.; Lorand, J. P.; Stevens, N. R.; Herron, N. R. *J. Am. Chem. Soc.* **1977**, *99*, 7589.
(32) McKean, D. C. *Int. J. Chem. Kin.* **1989**, *21*, 445.
(33) Hammond, G. S. *Cc/Eng. Tech. Appl. Sci.* **1985**, 16.
(34) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465.
(35) Lappert, M. F.; Misra, M. C.; Onyszchuk, M.; Rowe, R. S.; Power, P. P.; Slade, M. J. *J. Organomet. Chem.* **1987**, *330*, 31.
(36) Shankaran, K.; Snieckus, V. *J. Org. Chem.* **1984**, *49*, 5022.
(37) Tietze, Lutz F.; Schuster, Heiko J.; Hampel, Sonja M.; Rühl, S.; Pfoh, R. *Chem.Eur. J.* **2008**, *14*, 895.
(38) Wang, R. T.; Chou, F. L.; Luo, F. T. *J. Org. Chem.* **1990**, *55*, 4846.
(39) Durandetti, M.; Hardou, L.; Clement, M.; Maddaluno, J. *Chem. Comm.* **2009**, 4753.
(40) Sasaki, K.; Kondo, Y.; Maruoka, K. *Angew. Chem. Int. Ed.* **2001**, *40*, 411.
(41) Smith, P. *Chemistry of Tin*; Chapman & Hill, 1998.
(42) Molander, G. A.; Harring, L. S. *J. Org. Chem.* **1990**, *55*, 6171.
(43) Harris, R. K.; Becker, E. D.; De Menezes, S. M. C.; Goodfellow, R.; Granger, P. *Pure Appl. Chem.* **2001**, *73*, 1795.

Chapter 6. Conclusions

6.1 Conclusions

C-H activation reactions utilizing a sterically bulky stannylene **10/**aryl halide reagent combination have been demonstrated for ethers, aromatics, alkenes and alkynes. Addition across the double bond has been observed with terminal alkenes and cyclopentene. The effects of steric bulk and electronics have been analyzed and it was found that sterically bulky aryl halides suppress the formation of oxidative addition byproduct. The electronic influence of substituents on aryl halide was found to operate mainly through inductive effects. Sigma electron withdrawing substituents in the *para* position of the aryl halide suppress oxidative addition formation. A moderate degree of steric control of C-H activation with substrates possessing different C-H bonds was accomplished using sterically bulky aryl halides. In addition, new radical cyclization reaction chemistry has been introduced with (2-iodopheny) alkenes and alkynes. The rate of alkene and alkyne C-H activation was found to be comparable, on the order of $1.1 *10^8$ $M^{-1}s^{-1}$.

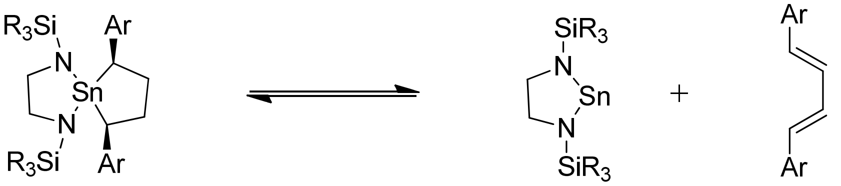
A broader understanding of advantages and limitations of the C-H activation with group 14 divalent reagent/aryl halide was achieved. It is now understood that the divalent reagent affects formation of a unique, transient phenyl radicaloid species that abstracts the substrate C-H bond or adds across an alkene/alkyne substrate. C-H activation or cyclization reactions produce aliphatic, vinylic, allylic and propargylic tin compounds.

We have demonstrated that primary and allylic tin compounds can be used in palladium catalyzed cross-coupling reactions.

6.2 Future Work

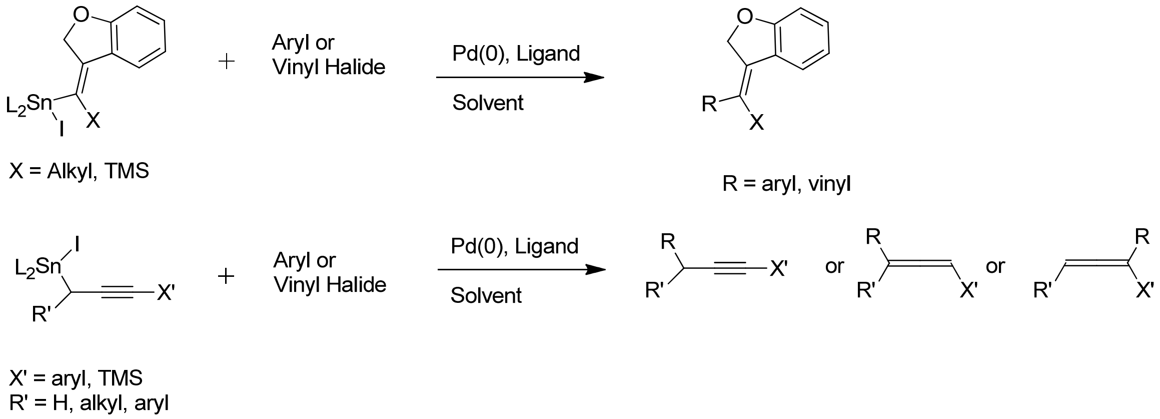
The first challenge to this chemistry is the practicality of synthesizing the sterically bulky stannylene. The arduous synthesis of air sensitive stannylene **10** represents a serious obstacle for anyone desiring to utilize this chemistry for practical applications. Thus, an easily accessible, air stable precursor to a novel sterically bulky stannylene is to be desired. Specifically, the study of reversible 1+4 cyclizations of some easily accessible, literature reported stannylenes would be of interest, Scheme 6.1.[1] The reactions of silylenes but not stannylenes have been previously explored with the type of dienes shown in Scheme 6.1.[2] The optimization with respect to sterics and electronics of aryl and silicon protecting groups is proposed in order to effect the stannylene formation at higher temperatures.

Scheme 6.1 Proposed reaction scheme for an air stable stannylene precursor.



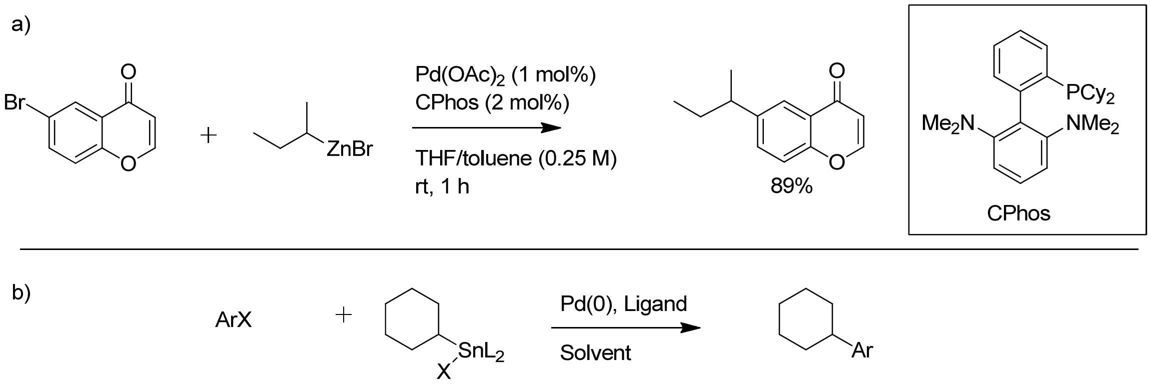
The second challenge involves designing reactions that bestow utility for C-H activation products. The rredominant use of organotin compounds in the literature has been carbon-carbon bond formation via transition metal catalyzed cross-coupling and Lewis Acid mediated allylation of aldehydes and ketones.[3] To date we have accomplished cross-coupling with compounds containing allylic tin moiety and primary tin-carbon compounds. However, we have not cross-coupled any of our vinylic, propargylic nor compounds containing secondary tin-carbon bonds. Cross-coupling of vinylic and propargylic tin compounds is precedented in the literature and experimentation to establish appropriate conditions to obtain benzofuran products with stereodefined exocyclic double bond, propargylic and allenic product would advance the utility of C-H activation and cyclization products, Scheme 6.2. Establishing the appropriate conditions for coupling propargylic tin compounds can yield diverse products including functionalized alkynes and allenes.

Scheme 6.2 Cross-coupling of vinylic and propargylic organotin compounds.



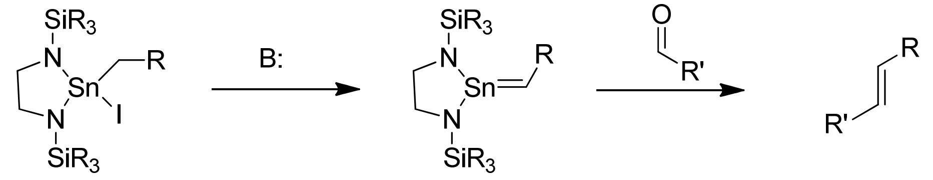
In contrast to the cross-coupling of vinylic, aryl, allylic and propargylic organometallics cross-coupling of substrates containing unfunctionalized secondary tin-carbon bond remains one of the challenges for transition metal catalysis. Recently, Buchwald has published a palladium catalyzed method for cross-coupling of secondary organozinc compounds, Scheme 6.3.[4] In terms of catalyst loading and mildness of the reaction conditions, Buchwald's procedure represents the state of the art in cross coupling techniques. Buchwald's work underlies the importance of designing the right ligand set that promotes the desired product formation and suppresses β-hydrogen elimination and alkane isomerization. Experiments for future work are proposed that would cross-couple secondary organotin compounds with variety of aryl, vinyl and even alkyl halides, Scheme 6.3b.

Scheme 6.3 a) State of the art cross-coupling of secondary organozinc compounds with aryl halides by Buchwald's group b) Proposed work future work on cross coupling of secondary organotin compounds obtained by C-H activation.


a)
Br
O
O
+
ZnBr
Pd(OAc)2 (1 mol%)
CPhos (2 mol%)
THF/toluene (0.25 M)
rt, 1 h
89%
PCy2
Me2N
NMe2
CPhos
b)
ArX
+
SnL2
X
Pd(0), Ligand
Solvent
Ar

The C-H activation and cyclization reactions yield aliphatic, allylic and propargylic tin compounds that possess bulky substituents and iodo functionality on tin atom. Exploring useful reactions by taking advantage of the sterically bulky substituents and iodo functionality on tin would tap the unique potential of the C-H activation products. In the proposed reaction scheme, Scheme 6.4, treating C-H activation with base and aldehyde and ketone provides new olefin forming method. Compounds containing a double bond between carbon and tin have been synthesized before by Tokitoh et al, but these compounds don't have any practical application as of yet.[5]

Scheme 6.4 Proposed novel olefination chemistry using C-H activation products.


SiR3
N
Sn
R
I
N
SiR3
B:
SiR3
N
Sn
R
N
SiR3
O
R'
R
R'

Overall, C-H activation with group 14 divalent reagent is an exciting area with many attractive possibilities that should be explored in the future.

References

(1) Schaeffer, C. D.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1974**, *96*, 7160.
(2) West, R. D. M. *Pure. Appl. Chem.* **1996**, *68*, 785.
(3) Espinet, P.; Echavarren, A. M. *Angew. Chem. Int. Ed.* **2004**, *43*, 4704.
(4) Han, C.; Buchwald, S. L. *J. Am. Chem. Soc.* **2009**, *131*, 7532.
(5) Tokitoh, N.; Okazaki, R. *Coordin. Chem. Rev.* **2000**, *210*, 251.