

# Carbanion generation through tin-lithium exchange of vinyl-, aryl-, and hetarylstannanes

Chinwon Rim and David Y. Son\*

*Department of Chemistry, Southern Methodist University, Dallas, TX 75275-0314*

*E-mail: [dson@smu.edu](mailto:dson@smu.edu)*

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## Abstract

The synthesis of vinyl-, aryl-, and hetaryllithiums via tin-lithium exchange is described. The majority of the material in this overview dates from the mid-1980's to 2006. The primary focus of this overview is the scope of tin-lithium exchange in regards to the range of functionality that can be tolerated in the organostannane precursors.

**Keywords:** Transmetallation, tin-lithium exchange, carbanions, organostannanes

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## Introduction

Numerous methods exist for the generation of carbanions in organic synthesis, including reactions of a metal or radical anion metal salt with an organic halide, hydrogen-metal exchange, metal-halogen exchange, and transmetallation. In the last category, tin-lithium exchange<sup>1-3</sup> has proved to be a reliable and effective method for the generation of a variety of organolithium reagents. In this case, an organostannane is reacted with an organolithium reagent, resulting in the formation of the new organolithium reagent and concomitant formation of a tetraalkylstannane. In general, an equilibrium is established in which the more stable organolithium compound predominates; thus, reactions of alkylolithiums such as *n*-BuLi with vinyl- and arylstannanes result in effective tin-lithium exchange. The advantages of this method are the rapidity of the reaction even at low temperatures ( $-100^{\circ}\text{C}$ ), the absence of potentially reactive byproducts (e.g. alkyl halides in the case of lithium-halogen exchange), and the variety of synthetic pathways that exist for the preparation of the required organostannane precursors.

This paper presents an overview of recent applications of tin-lithium exchange involving vinyl-, aryl- and hetarylstannanes. Due to an excellent review of this chemistry covering the literature up through 1984,<sup>4</sup> the focus of this overview will be on reports published after this date.

## 1. Vinylstannanes

In 1959, Seyferth reported the generation of vinylolithium from the reaction of phenyllithium and tetravinyltin in ethereal solvents (Equation 1),<sup>2</sup> where tetravinyltin was prepared from the reaction of a vinylic Grignard reagent with tin tetrachloride:<sup>5,6</sup>

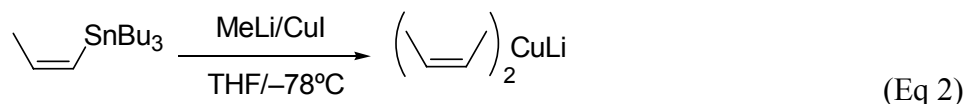


The preparation of vinylolithium in this manner is well established and has been used numerous times in organic and organometallic synthesis. This synthetic method has also been successfully applied to the preparation of functionalized vinylolithiums, where at least one of the three remaining hydrogen atoms is replaced with a non-hydrogen atom. The syntheses of these substituted compounds are the focus of this section.

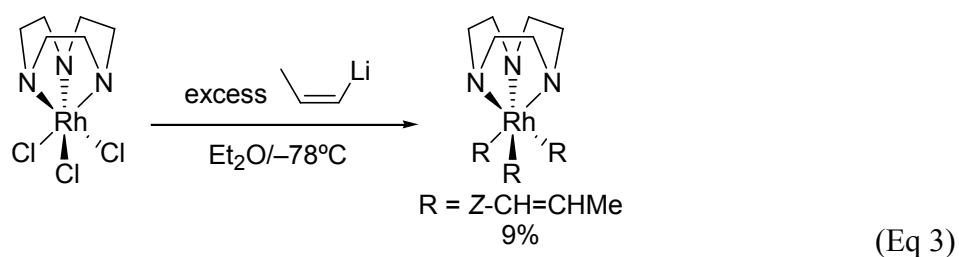
### 1.1 Carbon substituents

Perhaps the simplest derivative of vinylolithium is the replacement of one hydrogen atom of the vinylic group with a methyl group. The first syntheses of *cis*- and *trans*-propenylolithium via tin-lithium exchange were reported in 1964 by Seyferth and coworkers.<sup>7</sup> More recently, the *cis*-

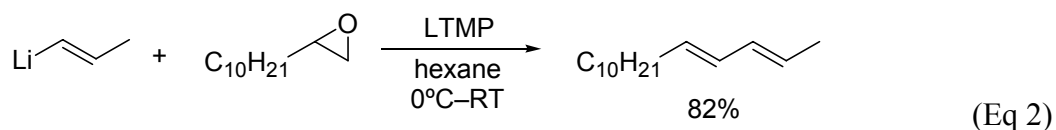
derivative was converted to the corresponding cuprate reagent by treatment with Cu(I) salts (Equation 2).<sup>8</sup> The cuprate reagent was subsequently reacted with a vinyltriflate as part of a cephalosporin synthesis.



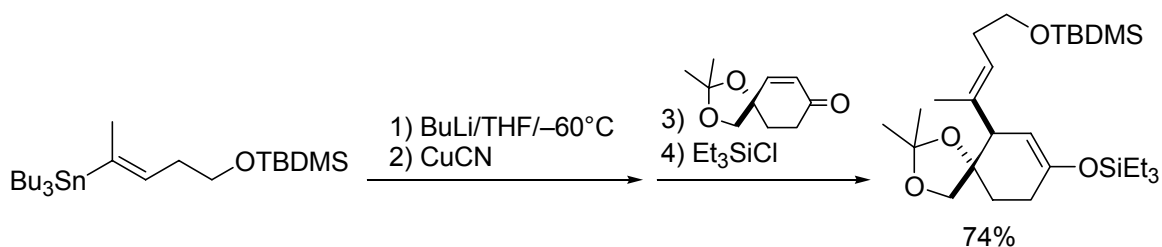
*cis*-Propenyllithium was also used for the synthesis of vinylic Rh(III) compounds in an investigation of the relative migratory abilities of various alkyl groups within the complexes (Equation 3).<sup>9</sup>



Both *cis*- and *trans*-propenyllithium were used for the synthesis of conjugated dienes by reactions with terminal epoxides (for example, see Equation 4).<sup>10</sup> The use of ethereal solvents resulted in the increased formation of byproducts.

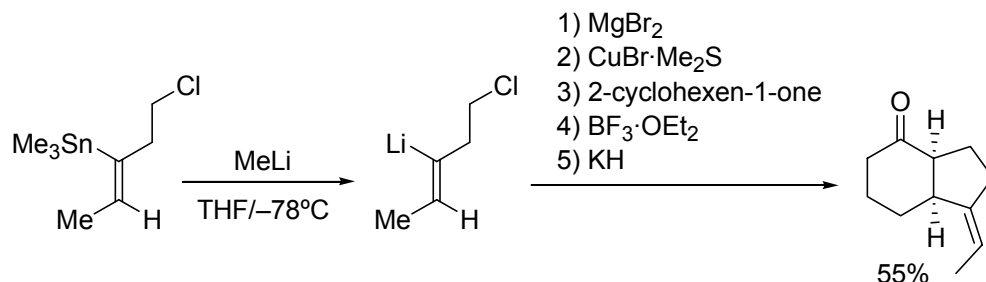


As might be expected, tin-lithium exchange can be extended to other alkyl-substituted vinylstannanes. As part of a synthesis of (–)-fumagillin, the protected vinylstannane shown in Scheme 1 was reacted with BuLi to give the corresponding organolithium compound which in this case was converted to the cuprate. Reaction with a substituted 2-cyclohexen-1-one followed by trapping with Et<sub>3</sub>SiCl gave the corresponding Michael addition product.<sup>11</sup>



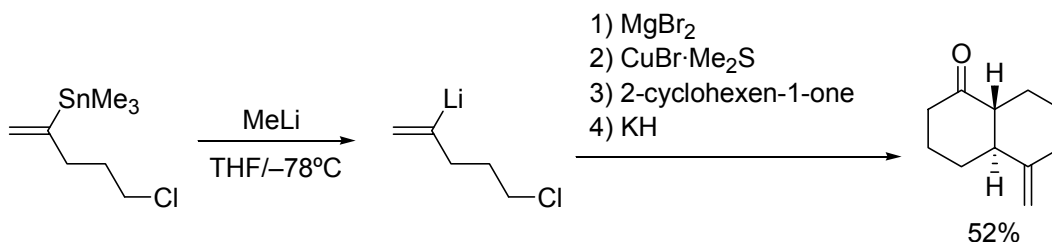
**Scheme 1**

Piers and coworkers utilized tin-lithium exchange of a vinylstannane to synthesize a key intermediate for an annulation reaction (Scheme 2).<sup>12</sup> As in the example above, the vinylstannane was first converted to the cuprate for a Michael addition. This general method was applied for the syntheses of various sesquiterpenoids.



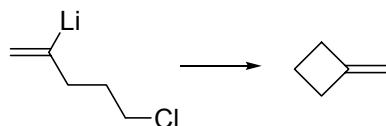
### Scheme 2

In a related study by the same group, 5-chloro-2-trimethylstannyl-1-pentene was transmetalated with methyllithium, converted to the Grignard reagent, and reacted with  $\alpha,\beta$ -unsaturated cyclohexenones and cyclopentenones to ultimately provide the annulation products (for example, see Scheme 3).<sup>13</sup>



### Scheme 3

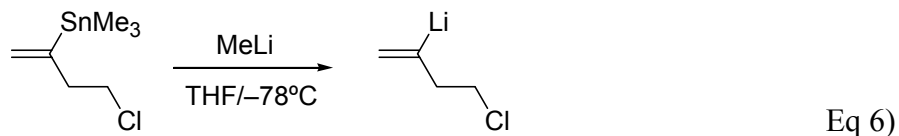
The vinyl lithium intermediate was found to be stable below  $-50^{\circ}\text{C}$ ; at higher temperatures, the reagent cyclized to methylenecyclobutane (Equation 5).



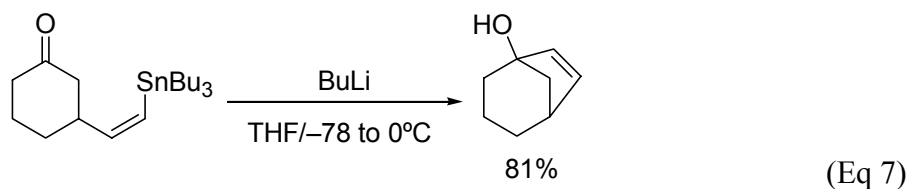
Eq 5)

Piers and coworkers also found that 4-chloro-2-trimethylstannyl-1-butene was smoothly transmetalated with methyllithium to give the corresponding vinyl lithium reagent (Equation 6).<sup>14</sup> This reagent reacted easily with aldehydes and ketones to give the expected alcohol products and also products resulting from cyclization of the resulting chloro-alkoxide intermediate. The vinyl lithium reagent could also be converted to the Grignard and cuprate

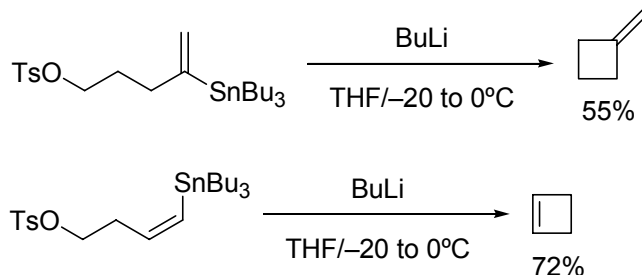
reagents.<sup>14,15</sup> The stability of this reagent is similar to that of the reagent in Scheme 3; this particular vinylstannane reagent cyclizes to methylenecyclopropane at temperatures greater than  $-50^{\circ}\text{C}$ .



Cyclized products were also observed in reactions where tin-lithium exchange could compete with addition or substitution reactions involving the organolithium reagent. For example, the vinylstannane in Equation 7 successfully underwent tin-lithium exchange rather than addition at the carbonyl by BuLi.<sup>16</sup>

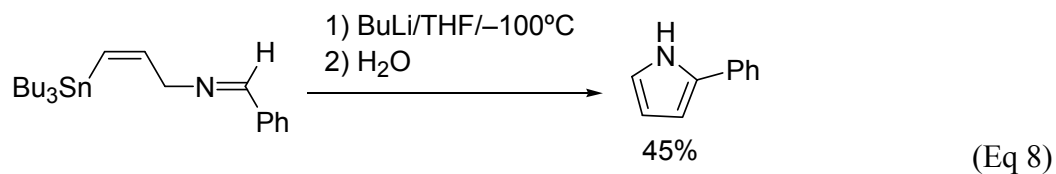


In the same report, tin-lithium exchange was favored over the  $\text{S}_{\text{N}}2$  displacement of primary tosylate groups by BuLi (Scheme 4).

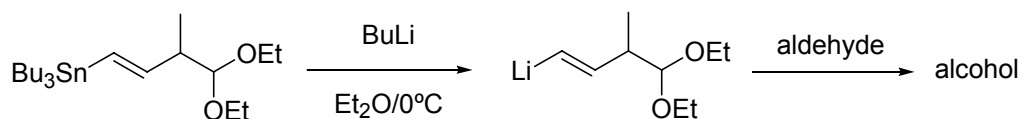


#### Scheme 4

The chemistry shown in Scheme 4 was further extended to the synthesis of a number of different unsaturated four-membered ring compounds.<sup>17</sup> Ring formation of a different sort occurred via the intramolecular addition of a vinyl lithium to the carbon of an imine group, resulting in the formation of 2-phenylpyrrole (Equation 8).<sup>18</sup>

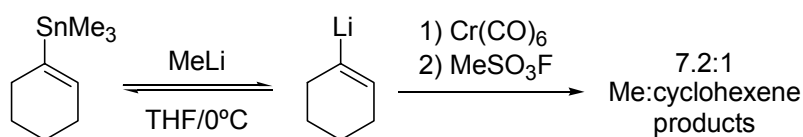


As mentioned earlier, the reaction between an alkyllithium and an organostannane results in an equilibrium that favors the more stable organolithium reagent. For vinylstannanes, this equilibrium generally favors the vinylolithium. However, one report attributed the low yields of vinylolithium functionalizations to the existence of such an equilibrium (Scheme 5). Yields of the alcohols were higher if the vinylstannanes were first converted to the iodo compound and then converted to the vinylolithium by lithium-halogen exchange.<sup>19</sup>



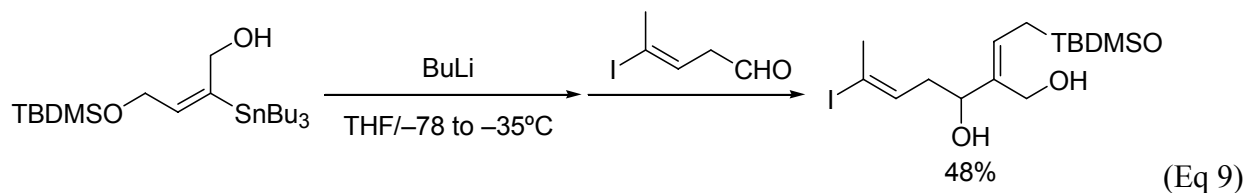
### Scheme 5

The nature of the electrophile is also a key factor for determining the product distribution from tin-lithium exchange, as illustrated in the synthesis of chromium carbene complexes (Scheme 6).<sup>20</sup> Reaction of cyclohexenyllithium with chromium hexacarbonyl followed by methylation gave predominantly the product resulting from reaction with methylolithium rather than cyclohexenyllithium (7.2:1 ratio).



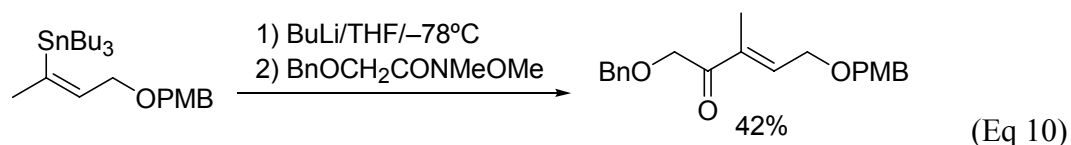
### Scheme 6

Incomplete reaction was also observed in another reaction of a substituted vinylolithium with an aldehyde (Equation 9), with the vinylstannane being recovered in 40% yield.<sup>21</sup> The utilization of a larger excess of BuLi failed to increase the yield of the reaction. This step was part of a larger reaction sequence for the synthesis of caulerpenyne.

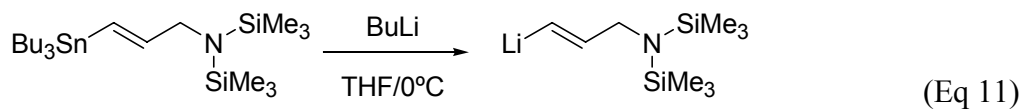


The dianion formed from the transmetalation and deprotonation of a vinylstannane closely related to that in Equation 9 (the silyl ether was *t*-butyldiphenyl) was shown to be sensitive to reaction temperature.<sup>22</sup> A reaction temperature of -35°C was found to be ideal; temperatures below -35°C resulted in incomplete formation of the dianion while temperatures above -35°C led to decomposition. In this study, the dianion was reacted successfully with various carbonyl compounds and epoxy ketones and aldehydes to give the corresponding products in moderate to good yields.

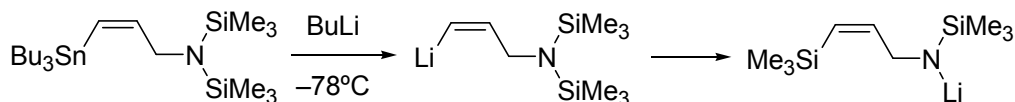
A vinylstannane was also used as an intermediate for the synthesis of bicyclic ring systems via Diels-Alder reactions (Equation 10).<sup>23</sup> The  $\alpha,\beta$ -unsaturated ketone was subsequently converted to the diene by Wittig chemistry.



Tin-lithium exchange of vinylstannanes has also played a key role in the synthesis of various *E*-allylic amines (Equation 11).<sup>24,25</sup> The vinylstannane was synthesized by the hydrostannation of bis(trimethylsilyl)propargyl amine with tributyltin hydride. Smooth transmetalation of the vinylstannane with BuLi gave the corresponding organolithium reagent which was reacted with a variety of electrophiles to give the *E*-allylic amines in excellent yields. The *E*-configuration was retained in all cases.

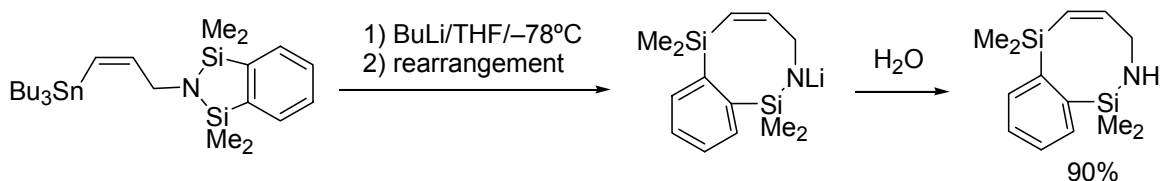


The transmetalation of the analogous *Z*-isomer gave an interesting result. Treatment of the vinylstannane with BuLi at -78°C resulted in an instantaneous rearrangement to a lithium amide, which was then reacted with various electrophiles to give the rearranged product.<sup>18</sup>



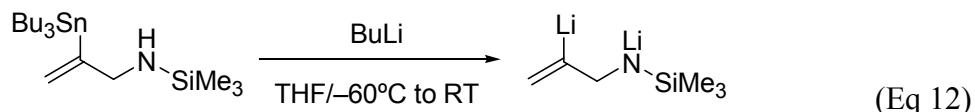
### Scheme 7

Scheme 8 illustrates another migration that was described in the same report. In this case, the rearrangement resulted in ring expansion.



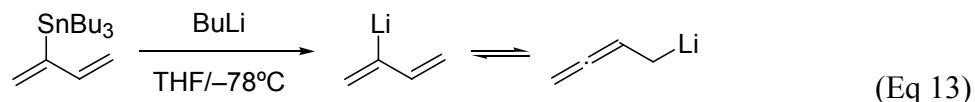
### Scheme 8

The synthesis of 2-substituted allylic amines was accomplished via a method similar to that shown in Equation 11 (Equation 12).<sup>26</sup> In this case, treatment of the vinylstannane with two equivalents of BuLi resulted in the formation of the dianion, which was stable up to room temperature. Reacting the dianion with a variety of electrophiles resulted in the isolation of the corresponding products in good to excellent yields. In general, reaction occurred at the vinylic carbon rather than at the nitrogen.

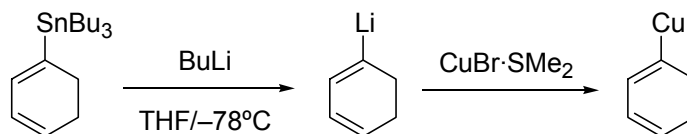


The chemistry described in Equation 12 could also be extended to derivatives with different alkyl groups on the nitrogen.<sup>27</sup> The behavior of these dianionic species at elevated temperatures has also been studied at length.<sup>28</sup>

Lithio-butadienes can also be generated easily by tin-lithium exchange reactions. 2-Lithio-1,3-butadiene was generated from the reaction of 2-tributylstannyl-1,3-butadiene with BuLi in THF (Equation 13).<sup>29</sup> The resulting butadienyl anion, which exists in equilibrium with the allenyl anion, was reacted with various carbonyl compounds to give the corresponding alcohols in good yields. The 1,3-butadienyl product was the predominant product in almost all cases.



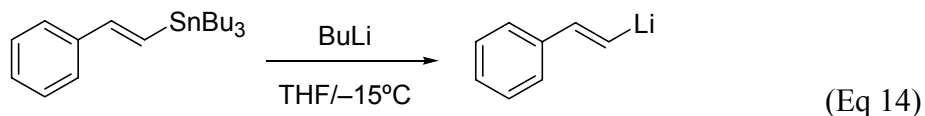
Cyclohexadienyllithium was generated in a similar manner (Scheme 9).<sup>30</sup> In this case, the organolithium was converted to the copper reagent and coupled with a vinyl triflate.



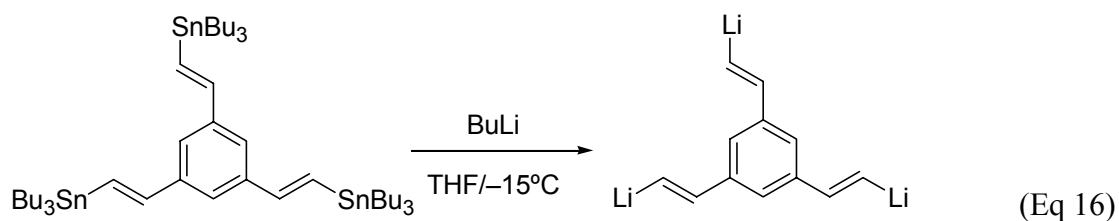
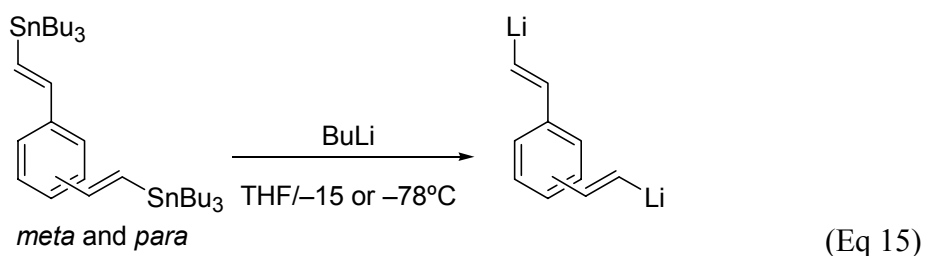
### Scheme 9



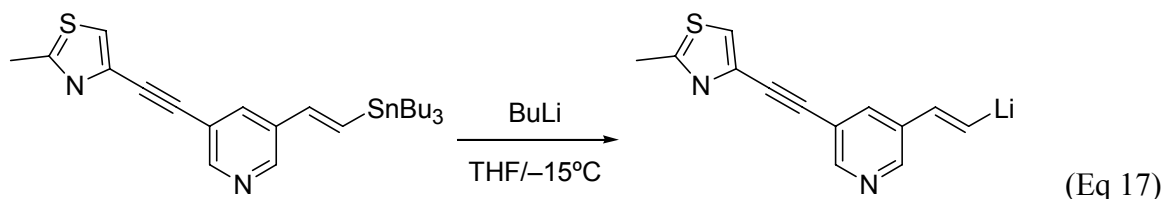
Styryllithium reagents could also be prepared by tin-lithium exchange. (*E*)- $\beta$ -Styryllithium was first prepared in 1964 by transmetallation of (*E*)- $\beta$ -trimethyl(styryl)stannane or (*E*)- $\beta$ -triphenyl(styryl)stannane with methyllithium or phenyllithium, respectively.<sup>31</sup> More recently, the same reagent was prepared by transmetallation of (*E*)- $\beta$ -tributyl(styryl)stannane with BuLi (Equation 14).<sup>32</sup> The (*Z*)-isomer was also transmetallated successfully, which was in contrast to the earlier report.<sup>31</sup>



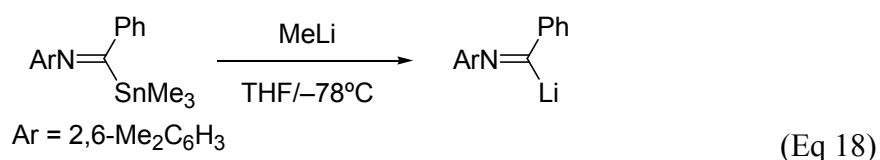
The *meta*- and *para*- dilithiated reagents were also prepared successfully (Equation 15), as was the 1,3,5-trilithiated reagent (Equation 16).<sup>32</sup> In all cases, configuration about the double bond was retained. It is possible that in reactions with electrophiles, tin-lithium exchange in these reactions occurred in a stepwise fashion, rather than through the dianionic or trianionic species. The vinylstannanes in this report were synthesized by either hydrostannation of the ethynylbenzenes or reaction of the ethynylbenzene with a tributylstannyl cuprate reagent.



This same methodology was applied to the synthesis of a vinylpyridyl reagent (Equation 17).<sup>33</sup> The generated lithium reagent was reacted with chlorotrimethylsilane and then desilylated. The starting vinylstannane was synthesized by hydrostannation of the ethynylpyridine with tributyltin hydride.



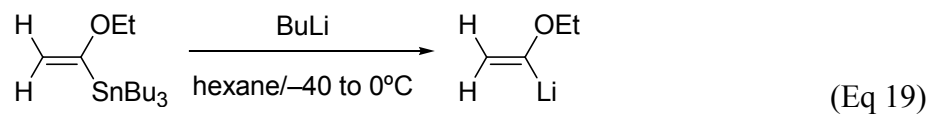
Finally, although all of the examples covered thus far have involved C–C=C–Sn species, tin-lithium exchange can also take place with C–X=C–Sn species, where X is a non-carbon atom. One example would be the transmetalation of aryl-substituted imidoystannanes (Equation 18).<sup>34</sup> Reactions of the organolithium compound with various electrophiles gave the corresponding products in good yields.



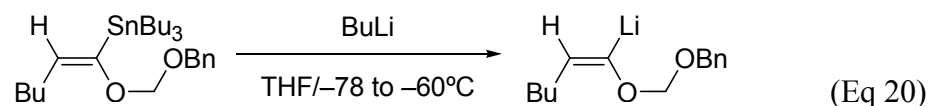
## 1.2 Oxygen or sulfur substituents

Tin-lithium exchange as a route to alkoxy-substituted vinylolithiums is well-known, and the early literature in this field has been reviewed.<sup>4</sup> In general, transmetalation of the corresponding vinylstannanes occurs smoothly.

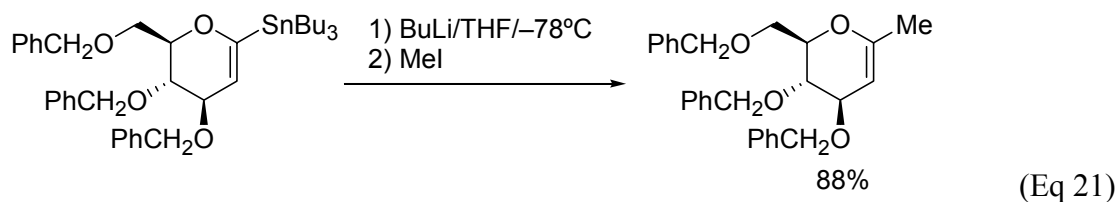
$\alpha$ -Alkoxyvinylolithium reagents are of interest due to their utility as acyl anion equivalents. One of the simplest of such species,  $\alpha$ -ethoxyvinylolithium, was synthesized using tin-lithium exchange and crystallized from hexane at room temperature (Equation 19). Single crystal X-ray crystallography revealed that  $\alpha$ -ethoxyvinylolithium exists in a polymeric structure in the solid state.<sup>35</sup>



Tin-lithium exchange was also used effectively for the synthesis of an (alkoxy)alkyl-substituted vinylolithium (Equation 20).<sup>36</sup> The vinylolithium reagent was formed in essentially quantitative yield.

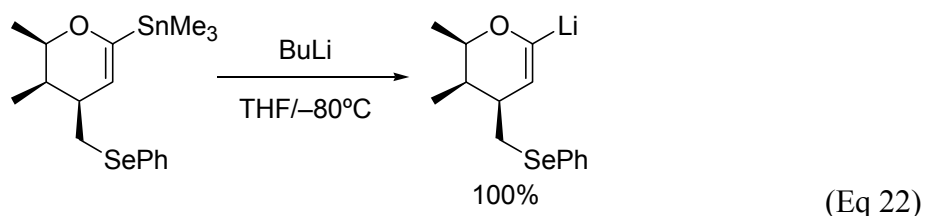


Cyclic derivatives also undergo facile tin-lithium exchange. Transmetalation of the vinylstannane shown in Equation 21 followed by methylation provided a new approach to C-glycosides.

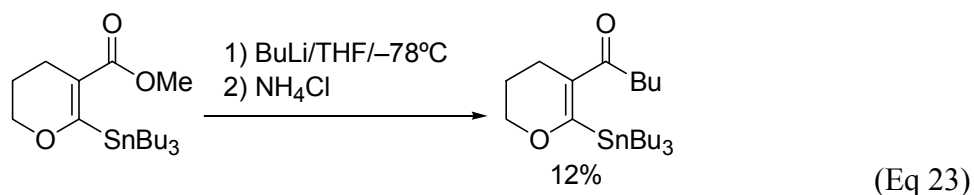


Another research group independently reported the same transmetalation under the same conditions, reacting the vinyl lithium reagent from Equation 21 with chlorotrimethylsilane, methyl iodide, and various aldehydes to give the corresponding products in good yields.<sup>37</sup>

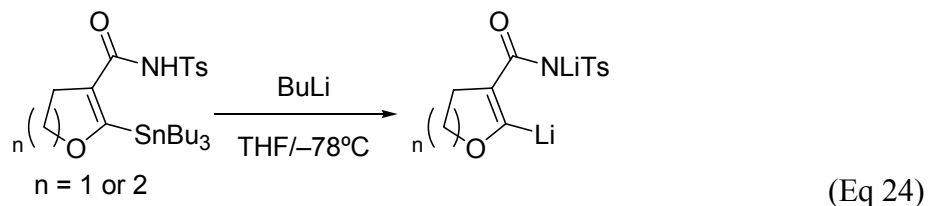
In another example, the cyclic compound shown in Equation 22 reacted cleanly with BuLi, giving the vinyl lithium reagent in quantitative yield.<sup>38</sup> The neighboring aryl selenoether group did not present any problems in the transmetalation step.



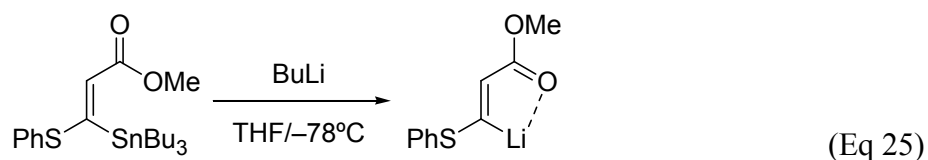
As noted earlier, a functional group that can react with alkyllithium can compete with tin-lithium exchange. This is illustrated by the reaction shown in Equation 23. In this particular instance, the ester group proved to be more reactive than the vinylstannane, resulting in the formation of the ketone in low yield (12%).<sup>39</sup> No other products could be identified.



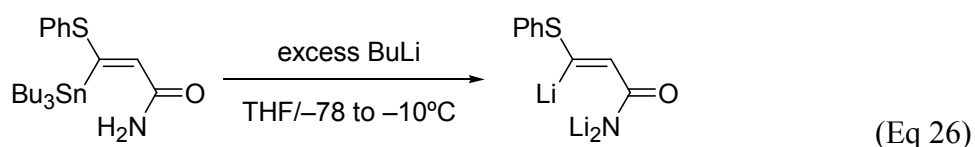
Dianionic species were formed from the reaction of the cyclic compounds shown in Equation 24 with BuLi.<sup>40</sup> The vinyl lithium compound is generated by tin-lithium exchange and the amide group is deprotonated with a second equivalent of BuLi.



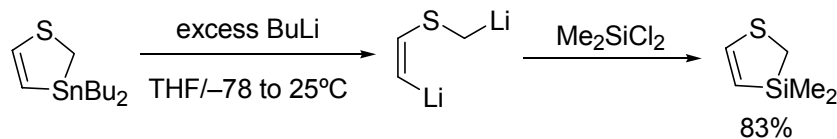
Sulfur-substituted vinyl lithium compounds are not as common as their oxygen-containing counterparts. In Equation 23, the ester group competed with tin-lithium exchange. However, for the sulfur-substituted compound in Equation 25, tin-lithium exchange was the primary reaction occurring, with subsequent reactions with electrophiles proceeding in moderate yields.<sup>39</sup> This difference in reactivity was attributed to the ability of the carbonyl to chelate the vinyl anion, a stabilization that is apparently not possible with the vinyl anion generated from the stannane in Equation 23.



As in Equation 24, amide protons can be deprotonated under the conditions of transmetalation. For example, treatment of the arylthio-substituted vinylstannane in Equation 26 with an excess of BuLi resulted in the formation of the trianion.<sup>40</sup> Protonation or deuteration proceeded in high yields.



When a tin atom is part of a ring structure, the possibility exists of double transmetalation. The cyclic thioether in Scheme 10 ring-opened to the dianion on treatment with an excess of BuLi.<sup>41</sup> The dianion reacted readily with dichlorodimethylsilane to give the cyclic product in 83% yield.

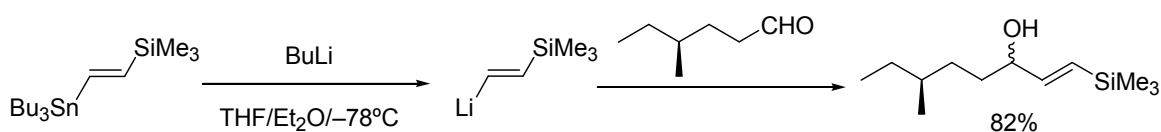


## Scheme 10

### 1.3 Silicon substituents

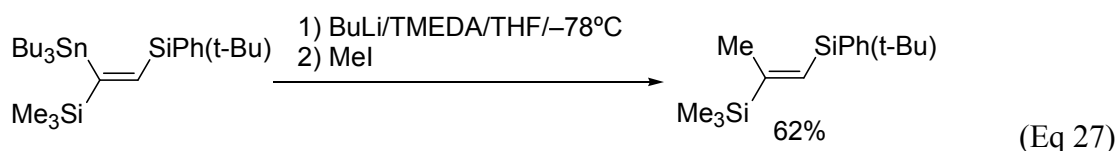
Silylvinyl lithiums have been routinely prepared via tin-lithium exchange.<sup>42-44</sup> More recent examples illustrate this application. (*E*)-1-Tributylstannyl-2-(trimethylsilyl)ethylene was reacted with BuLi to give the lithium reagent which was then reacted with (4*S*)-methylhexanal to give the corresponding alcohol in 82% yield (Scheme 11).<sup>45</sup> This step was part of the total synthesis

of the antifungal agent papulacandin D. In a similar fashion, the (*Z*)-isomer can be transmetallated with BuLi and reacted with aldehydes to give the corresponding alcohols.<sup>46</sup>

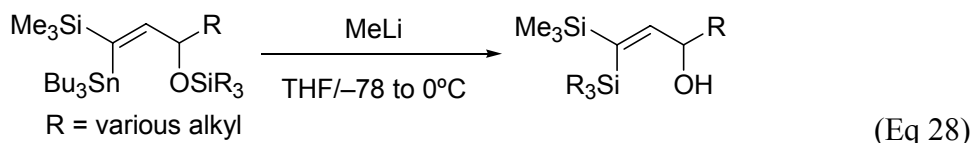


**Scheme 11**

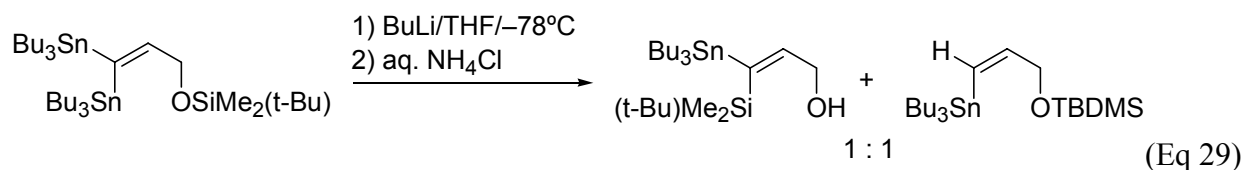
In another example, the doubly silylated vinylstannane shown in Equation 27 was treated with BuLi/TMEDA and methylated to give the product in 62% yield.<sup>47</sup>



An interesting rearrangement was observed with silyl-substituted vinylstannanes possessing a silyl ether in the allylic position. Treatment of the vinylstannane with BuLi resulted in the silyl group migrating from the oxygen to the vinylic carbon, giving the alcohol in high yield after quenching (Equation 28).<sup>48</sup>



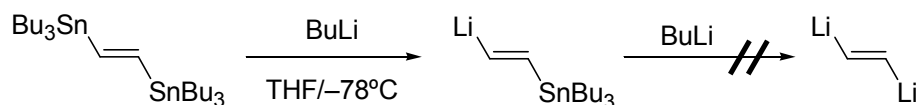
As might be expected, only the (*Z*)-lithio species can undergo this rearrangement, as illustrated by the experiment shown in Equation 29.<sup>49</sup>



#### 1.4 Tin substituents

In this section we include examples of tin-lithium exchange involving vinylstannanes with more than one tin atom connected to the vinylic moiety. The syntheses and reactions of these compounds have been established, with the results indicating that tin-lithium exchange does occur but that multiple tin-lithium exchanges, yielding polyolithiated species, are not possible

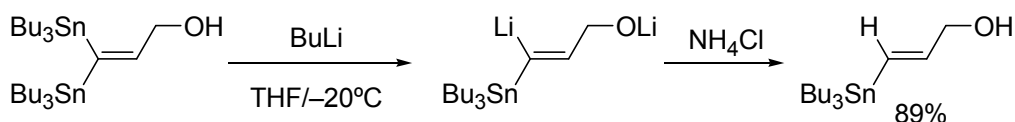
(e.g. Scheme 12<sup>43</sup>).<sup>4</sup> On the other hand, stepwise tin-lithium exchange is possible which can result in heterosubstitution of the double bond.



**Scheme 12**

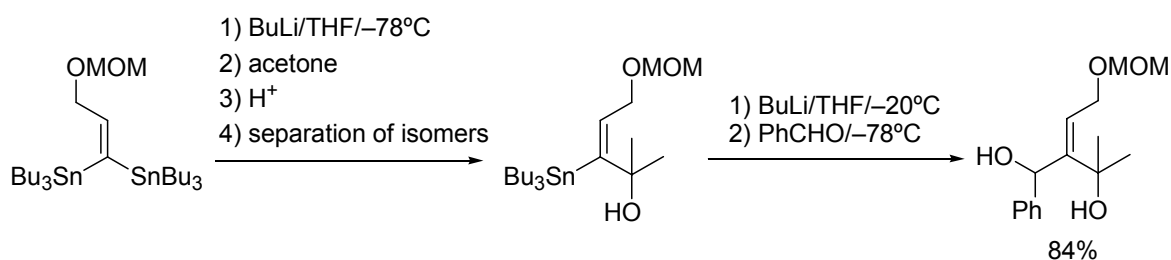
As part of ongoing studies regarding the reactions of 1,1-bis(trialkylstannyl)alkenes with alkyllithium,<sup>50</sup> Mitchell and coworkers investigated the efficiency of mono-transmetallation with regard to several variables including alkyl substituents on the double bond and solvent.<sup>51</sup> In many cases, the equilibrium did not lie heavily to  $\alpha$ -stannylvinyl lithium formation. Furthermore, isomerization of the mono-lithiated product was observed. Additional studies included the spectroscopic characterization, decomposition reactions, and functionalizations of the  $\alpha$ -stannylvinyl lithium reagents.<sup>51,52</sup>

The mono-transmetallation of 1,1-bis(trialkylstannyl)alkenes was utilized effectively for the synthesis of various substituted ethylenes.<sup>49</sup> For example, the reaction of the alcohol in Scheme 13 with two equivalents of BuLi gave the dianion, which was then quenched to give exclusively the (*E*)-isomer. The transmetallation was sluggish at  $-78^\circ\text{C}$  but occurred rapidly at  $-20^\circ\text{C}$ .



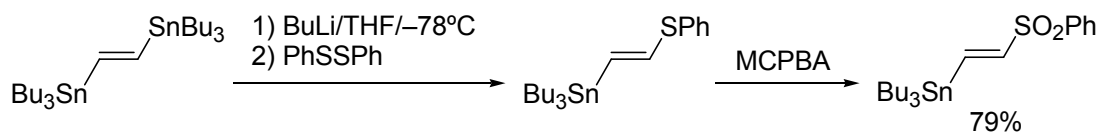
**Scheme 13**

Transmetallation of the TBDMS-ether compound gave a 1:1 mixture of the (*Z*)-isomer and a product resulting presumably from rearrangement of the (*Z*)-lithio intermediate (75% total yield, Equation 29).<sup>49</sup> Other similar ethers gave a mixture of (*E*)- and (*Z*)-isomers under the same reaction conditions. In the same report, the sequential replacement of the tributylstannyl groups was also demonstrated (Scheme 14).

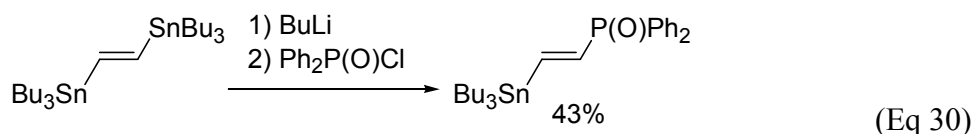


**Scheme 14**

1,2-Bis(trialkylstannyl)alkenes also undergo mono-transmetallation, as demonstrated in the synthesis of vinyl sulfones and phosphine oxides from (*E*)-1,2-bis(tributylstannyl)ethene (Scheme 15 and Equation 30).<sup>53</sup>

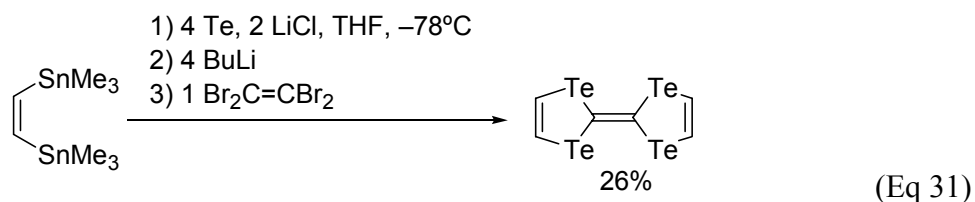


Scheme 15

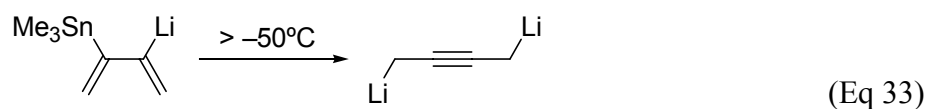
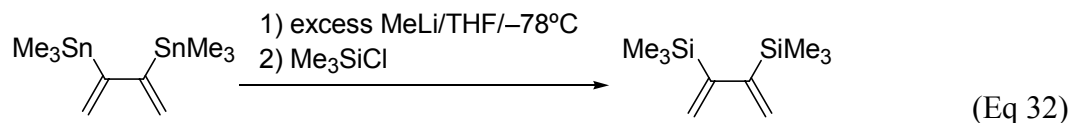


In a later report, a different group was unable to reproduce the high yield of sulfide in Scheme 15 using the same methodology.<sup>54</sup> The best yields obtained using various experimental conditions were 28-32%. The authors determined that the transmetallation proceeded quantitatively; therefore, the sulfenylation was the low-yielding step.

The double transmetallation of (*Z*)-1,2-Bis(tributylstannyl)ethane was used for the synthesis of tetratellurafulvalene (Equation 31).<sup>55,56</sup> Various factors were examined in order to optimize the yield, and it was found that using an excess of BuLi in the presence of LiCl gave the highest yield of product (26%). Additives such as TMEDA or HMPA were not as effective. Using MeLi in place of BuLi gave much lower yields of product, indicating that the basicity of the alkyllithium played a crucial role in determining the equilibrium distribution of organolithium reagents. It was unclear whether the reaction proceeded via a stepwise transmetallation process or via the dilithiated reagent.

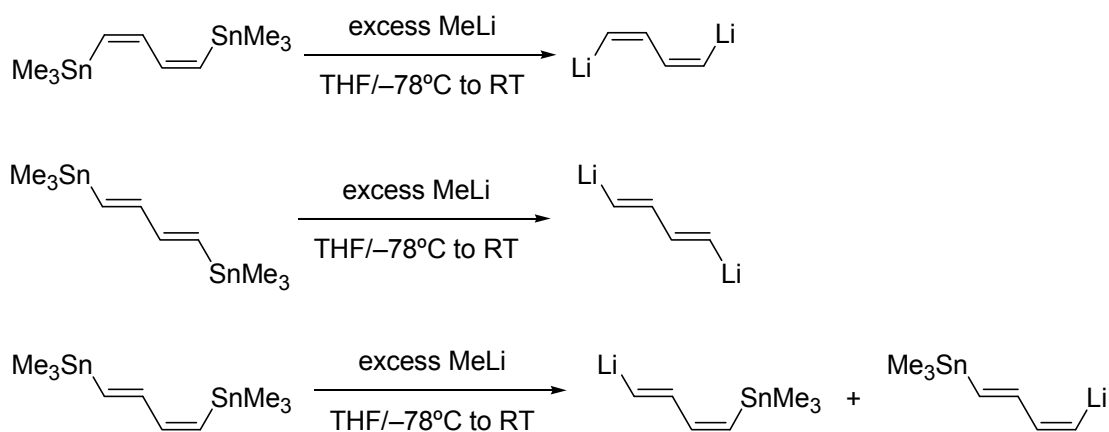


2,3-Bis(trimethylstannyl)-1,3-butadiene undergoes stepwise transmetallation. As in the example above, double substitution can be attained by adding an excess of alkyllithium to the initial reaction mixture (Equation 32).<sup>57</sup> This approach is effective because tin-lithium exchange is faster than the reaction of alkyllithium with many electrophiles. Various mono- and difunctionalizations were performed. Of note is that the intermediate monolithium compound converted to a dilithiated ethynyl compound at temperatures above  $-50^{\circ}\text{C}$  (Equation 33).

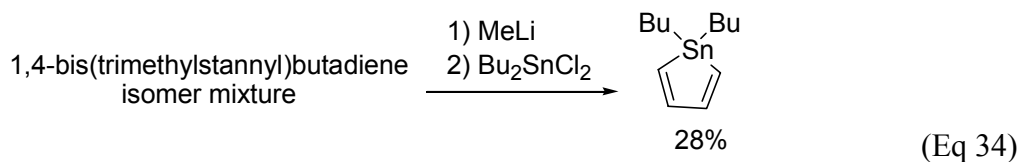


### 1.5 Multiple tin-lithium exchange

The possibility of dilithiated vinylic reagents has been discussed earlier in regards to vinylic systems with two tin substituents attached to the double bond. In general, transmetallation occurs in stepwise fashion for these systems. However, dilithiated species can be obtained in certain polyene systems with tin substituents on separate double bonds. For example, (*Z,Z*)- and (*E,E*)-1,4-bis(trimethylstannyl)-1,3-butadiene were conveniently converted to the stable dilithiated species on treatment with excess MeLi (Scheme 16).<sup>58</sup> Treatment of the (*E,Z*)-isomer resulted only in the formation of the monolithiated species. The (*Z,Z*)-dilithiated species was found to be considerably more stable than the (*E,E*)-isomer. Interestingly, it was found that under certain reaction conditions, (*E,E*)- and (*E,Z*)-1,4-bis(trimethylstannyl)-1,3-butadiene isomerized to the (*Z,Z*)-isomer, which was then converted easily to the stable (*Z,Z*)-dilithiated reagent under the same conditions. Thus, a convenient source of the (*Z,Z*)-dilithiated reagent is simply a mixture of the various 1,4-bis(trimethylstannyl)-1,3-butadiene isomers (Equation 34).

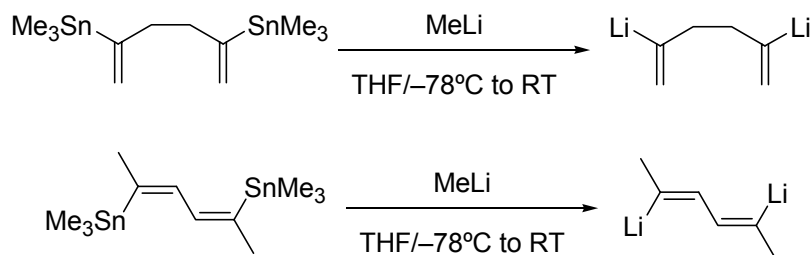


Scheme 16



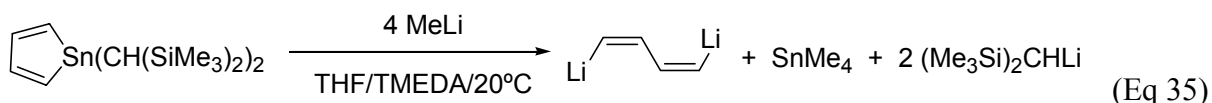


A similar study was carried out with the bis(trimethylstannyl) dienes in Scheme 17.<sup>59</sup> Reaction with excess methyllithium led to the corresponding dilithiated compounds on warming to room temperature. The intermediate ate species were detectable by NMR spectroscopy. The formation of the dilithiated compound from 2,5-bis(trimethylstannyl)-1,5-hexadiene was found to be considerably less favorable than the formation of the corresponding compound from (Z,Z)-2,5-bis(trimethylstannyl)-2,4-hexadiene, attributed to the more favorable dilithium bridging in the latter as determined by *ab initio* calculations.



### Scheme 17

As shown in Equation 34, a dilithiobutadiene compound could be used to synthesize a stannole. It should also be apparent that the reverse could also occur: the synthesis of a dilithiobutadiene from a stannole via double tin-lithium exchange. The application of this process is shown in Equation 35.<sup>60</sup> The excess of MeLi was necessary to drive the equilibrium completely to the right. NMR spectroscopy indicated the formation of products to be quantitative.

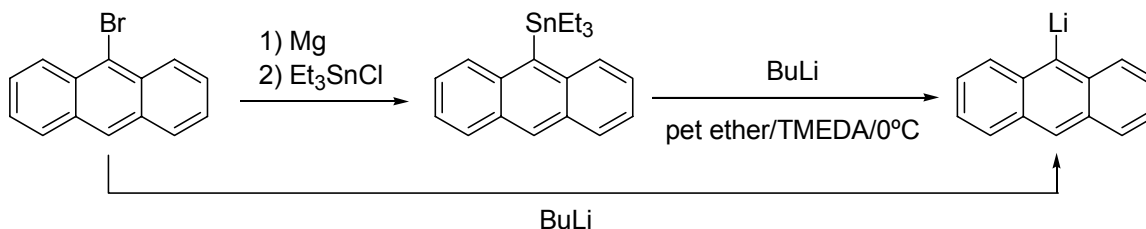


## 2. Aryl- and hetarylstannanes

Compared to vinylstannanes, tin-lithium exchange in aryl- and hetarylstannanes is far less common. The reason for this is not because tin-lithium exchange does not readily occur, but because lithium-halogen exchange of aryl- and hetaryl halides is an excellent route to the organolithium. Furthermore, the organostannane precursors are often synthesized from the halide via Grignard chemistry or lithium-halogen exchange. Nevertheless, various reports of aryl- and hetarylstannane tin-lithium exchange exist, and an overview is presented here.

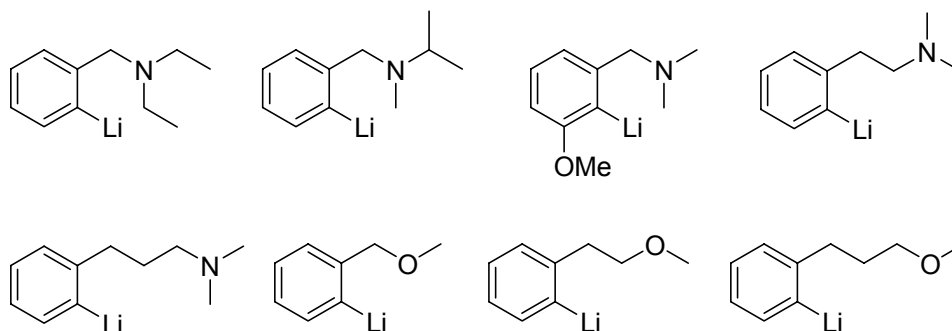
## 2.1 Arylstannanes

The lack of a definitive advantage of tin-lithium exchange in arylstannanes is illustrated by the synthesis of 9-lithioanthracene (Scheme 18).<sup>61</sup> In this case, the precursor stannane was synthesized from 9-bromoanthracene using Grignard chemistry. Furthermore, 9-bromoanthracene could be converted directly to the lithium reagent in high yield by lithium-halogen exchange. The transmetalation route to 9-lithioanthracene was used to isolate the compound in crystalline form.



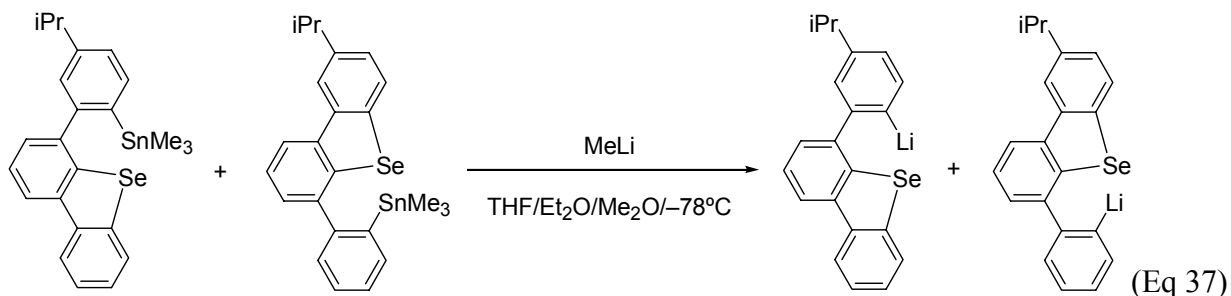
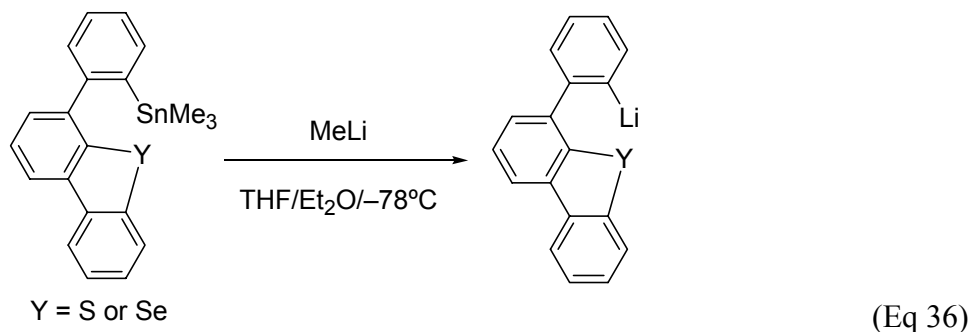
**Scheme 18**

Tin-lithium exchange is a good route to aryllithiums if the byproducts from lithium-halogen exchange are undesirable. This was illustrated in chelation studies of the aryllithiums in Figure 1, which were synthesized by tin-lithium exchange from the corresponding trimethylstannyl compounds.<sup>62,63</sup> The bromide byproducts from lithium-halogen exchange of the aryl bromides would have interfered with the intended spectroscopic studies.

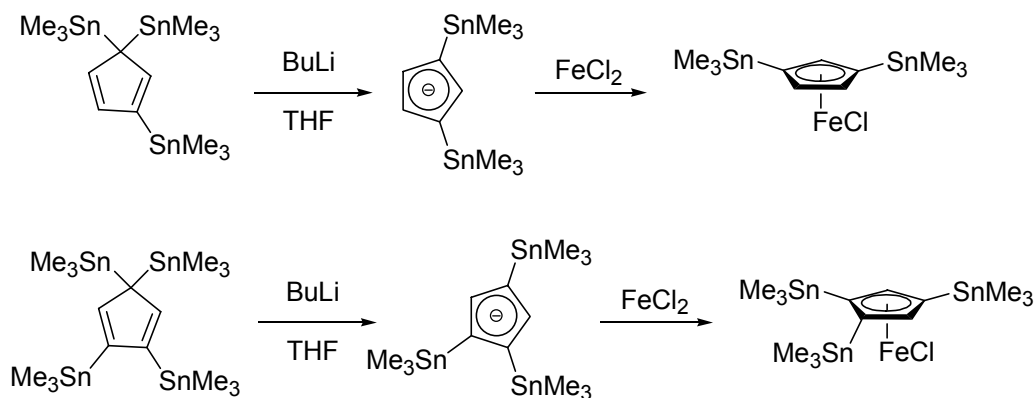


**Figure 1**

Halide-free aryllithium reagents were also obtained for the selenium and sulfur derivatives shown in Equation 36 and Equation 37.<sup>64</sup> The aryllithiums generated in Equation 37 interconvert through an intermediate ate complex.



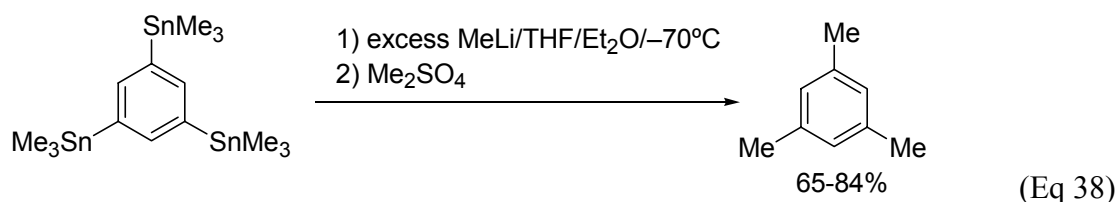
Though not initially aromatic, the cyclopentadienylstannanes shown in Scheme 19 lead to arylstannanes by tin-lithium exchange.<sup>65</sup> In both cases, tin-lithium exchange occurs preferentially at the allylic carbon to give the aromatic cyclopentadienyl anions, which then react with ferrous chloride to give the corresponding products. These compounds were later used in the synthesis of stannyl-substituted ferrocenes.



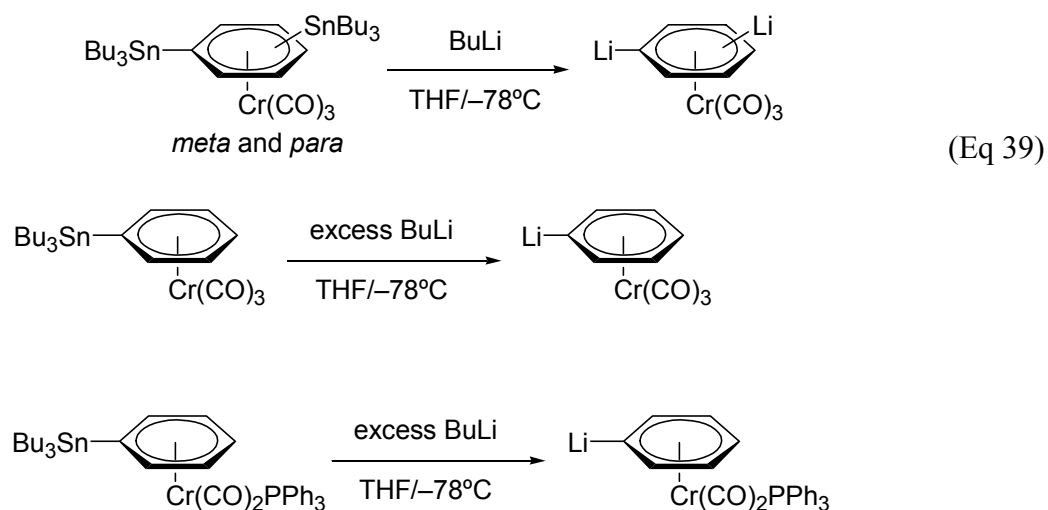
### Scheme 19

Multiple tin-lithium exchanges are also possible in arylstannanes. For example, the reaction of 1,3,5-tris(trimethylstannyl)benzene with excess MeLi followed by reaction with dimethylsulfate gave mesitylene in 65-84% yield (Equation 38).<sup>66</sup> Although this result indicated that the trilitio compound had formed, other observations suggested that the reaction proceeded in a stepwise fashion. For example, reacting 1,3,5-tris(trimethylstannyl)benzene with excess

MeLi gave a mixture consisting of a mixture of mono- and dilithiated compounds, as indicated by  $^{119}\text{Sn}$  NMR spectroscopy.

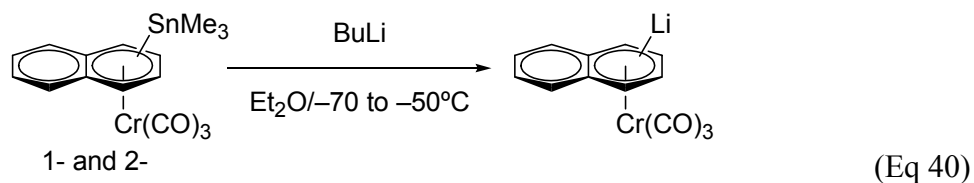


Tin-lithium exchange also takes place in arylstannanes where the aryl group is bound to a transition metal. Both the *meta* and *para* bis(tributylstannyl)benzene chromium complexes smoothly underwent transmetallation to give the dilithium compounds (Equation 39), which were reacted with various electrophiles in good yield.<sup>67</sup> Attempted reaction in ether led to poor yields. Replacing one of the carbonyl groups in the *para* arylstannane complex with the more electron-rich  $\text{Bu}_3\text{P}$  decreased the amount of dilithium compound formed.<sup>68</sup> In this case, reactions with electrophile led to a mixture of both mono- and disubstituted product, with the disubstituted product formed in greater yield. This difference in reactivity apparently does not affect the efficiency of a single tin-lithium exchange, as both chromium complexes shown in Scheme 20 underwent transmetallation in good yield.<sup>68</sup>

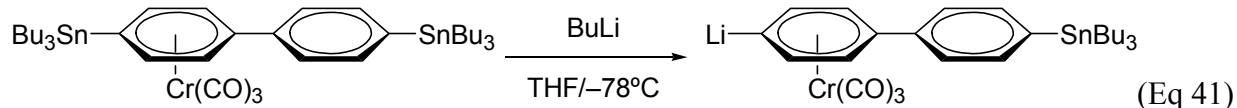


### Scheme 20

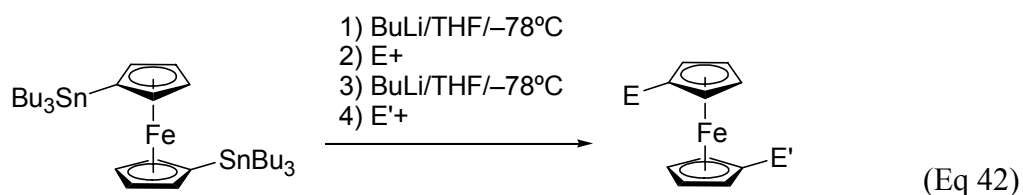
In a related study, trimethylstannylnaphthyl chromium complexes also underwent tin-lithium exchange smoothly (Equation 40).<sup>69</sup>



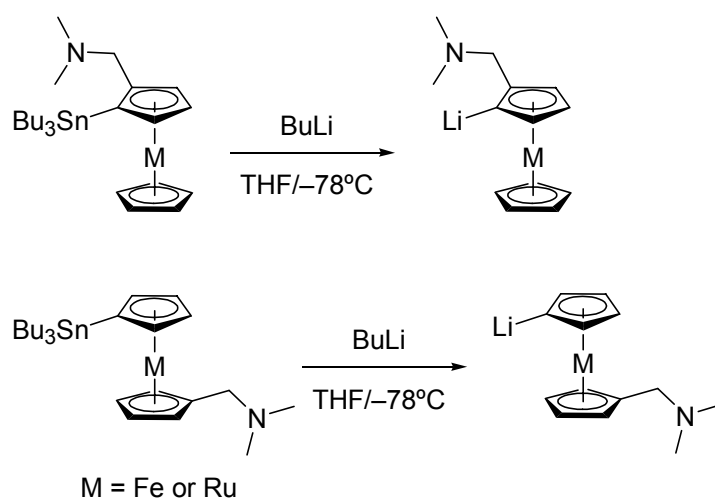
Interestingly, it was found that aryl-Cr complexation activates tin-lithium exchange as demonstrated in the reaction shown in Equation 41.<sup>67</sup> Tin-lithium exchange occurred regioselectively at the aryl group bound to chromium.



Cp-SnR<sub>3</sub> groups can also be transmetalated. Tributylstannyl substituents on the Cp rings of ferrocenes could be sequentially transmetalated, allowing unsymmetrical substitution (Equation 42).<sup>70,71</sup> This stepwise substitution sequence was utilized to synthesize ferrocene-bridged triiron complexes.<sup>70</sup>



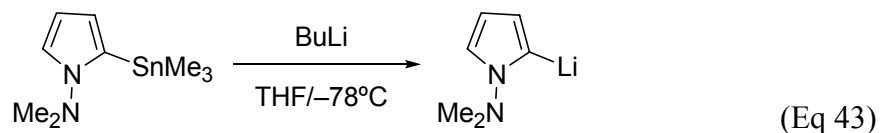
A more recent report describes the transmetalation of stannyl-substituted ferrocenes, and also ruthenocenes (Scheme 21).<sup>71</sup>



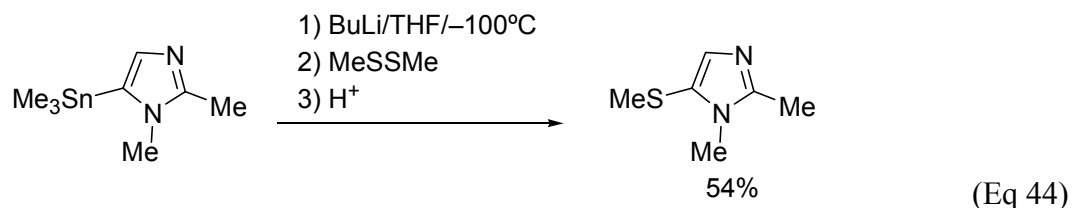
Scheme 21

## 2.2 N-Containing hetarylstannanes

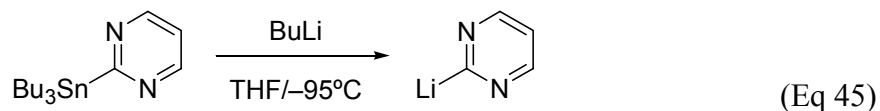
There appears to be no unusual reactivity regarding tin-lithium exchange in nitrogen-containing hetarylstannanes. An early report described the transmetalation of the trimethylstannyl-substituted pyrrole in Equation 43.<sup>72</sup> The organolithium compound, subsequently reacted with aldehydes, proved to be useful for the synthesis of 2-acylpyrroles.



Tin-lithium exchange also occurred smoothly in an imidazole derivative (Equation 44), with the generated organolithium compound used to synthesize a methyl sulfide.<sup>73</sup>

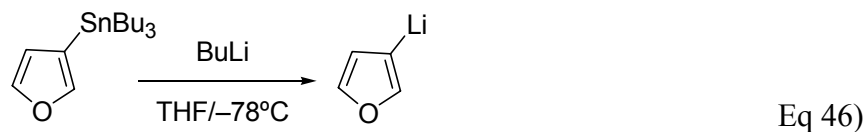


Finally, tin-lithium exchange occurs readily in stannyl-substituted pyrimidines. Reaction of 2-tributylstannylpyrimidine with BuLi gave the organolithium compound (Equation 45), which was then reacted with various carbonyl compounds to give the alcohols in moderate to good yields.<sup>74</sup>

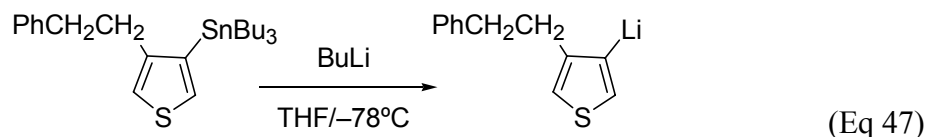


## 2.3 Thiophenes and furans

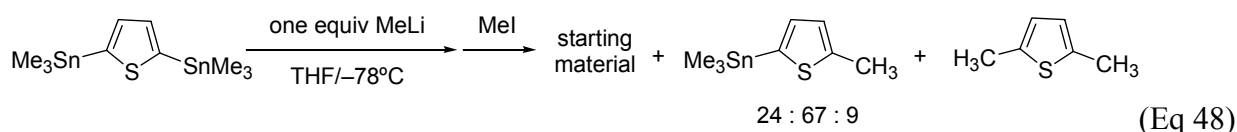
Tin-lithium exchange in 3-tributylstannylfuran occurs smoothly under standard conditions (Equation 46).<sup>75</sup> The generated organolithium compound can be used as is, or converted to the cuprate before further reaction.



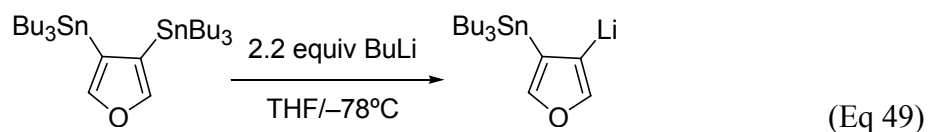
Tin-lithium exchange has also been reported to occur in a 3-tributylstannylthiophene under the same conditions (Equation 47).<sup>76</sup> Reaction of the generated organolithium compound with electrophiles such as acetone, DMF, or PhSeBr gave the expected products in moderate yields.



Transmetalation of bis(stannyl) derivatives has also been reported. The transmetalation of 2,5-bis(trimethylstannyl)-furan and -thiophene was first reported in 1983. Reaction of these compounds with one equivalent of MeLi followed by addition of MeI gives a mixture of starting material, monosubstituted product, and disubstituted product (e.g. Equation 48).<sup>77</sup> It is unclear whether the disubstituted product was synthesized via the dilithium compound or through a stepwise process. The monolithiated thiophene reagent was later used in the synthesis of a functionalized steroid.<sup>78</sup>



Tin-lithium exchange in 3,4-bis(tributylstannyl)furan proceeded to give the monometallated product (Equation 49).<sup>79</sup> Two equivalents of BuLi were required for complete conversion. A larger excess of BuLi gave no dilithiated product. The monolithiated product was reacted with various electrophiles in reasonable yields, and the products were then employed in Stille coupling reactions.<sup>79,80</sup>



### 3. Conclusions

As can be seen, tin-lithium exchange is an extremely efficient method for the generation of various functionalized organolithium compounds. This method is particularly effective for the synthesis of vinyllithiums, compounds which are not always simple to make using lithium-halogen exchange. Although this overview was limited to the generation of vinyl-, aryl- and hetaryllithiums, tin-lithium exchange is also well-known for stannanes in which the tin is attached to  $sp^3$ -hybridized carbon. Clearly, tin-lithium exchange is a valuable tool for both organic and inorganic chemists.

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## Biographical Sketches

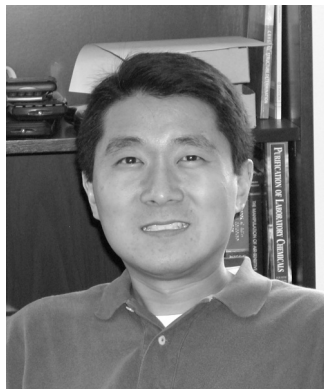
### Chinwon Rim



**Ms. Chinwon Rim** is a native of South Korea and completed a B.S. degree in chemistry at the University of Houston in 1998. In 2002, she completed a M.S. in chemistry at Southern

Methodist University under the supervision of Professor David Son. Since 2002 she has been working on her Ph.D. at the same institution with Professor Son. Ms. Rim has investigated the hyperbranched polymerization of organosilicon thiophene and furan derivatives, transmetallation as a synthetic route to new substituted vinylolithium reagents, and metal-ligand interactions of thioether ligands. She is currently working on the selective amination of cyanuric chloride.

### **Professor David Y. Son**



**Professor David Y. Son** obtained a B.S. in chemistry at Andrews University (Berrien Springs, MI) in 1989. He obtained a Ph.D. in 1993 at the Massachusetts Institute of Technology under the supervision of Professor Dietmar Seyferth. After completing a two-year National Research Council postdoctoral fellowship at the Naval Research Laboratory in Washington, D.C., Professor Son joined the faculty at Southern Methodist University in 1996, where he is now an associate professor. Professor Son's research interests include organosilicon dendrimers and hyperbranched polymers, transmetallation chemistry, and the design of ligands for late transition metal complexes.