The Origin of Regioselectivity in an Allenyllithium Reagent[1]

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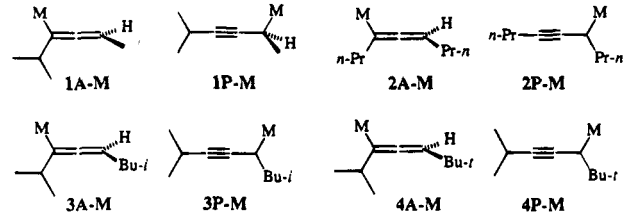
Received June 19, 1995[⊗]

Abstract: A pair of allenyl (5-methyl-4-(trimethylstannyl)-2,3-hexadiene, **1A-Sn**) and propargyl (5-methyl-2-(trimethylstannyl)-3-hexyne, **1P-Sn**) stannanes were prepared and used in a series of lithium−tin exchange experiments (both give the same lithium reagent, **1A-Li**). The experiments were aimed at determining the nature of the reactive allenyl/propargyl anionic species formed. If the lithium−tin exchange was carried out first, followed by trapping with Me_3SiCl (the sequential experiment), the propargyl silane **1P-Si** was the major product (**1A-Si/1P-Si** = 2/98). If the silyl chloride was present during the lithium−tin exchange (*in situ* experiment), highly variable ratios of **1A-Si** and **1P-Si** were formed, with A/P ratios as high as 85/15 in THF−HMPA solvent mixtures. The allenyl- and propargylstannanes **1A-Sn** and **1P-Sn** gave different product ratios when the trimethylstannyl compounds were treated with methyllithium in the *in situ* experiment, but identical product ratios when phenyllithium was used, or when methyl groups on tin were replaced by phenyl groups. The proportion of **1A-Si** product increased as the concentration of Me_3SiCl was increased, and it varied dramatically with substituents on the tin. This kinetic behavior, solvent effects, and the results of double trapping experiments (reaction with a mixture of two silyl chlorides) are consistent with a mechanism in which the intermediate tin ate complex (**1A-SnR$_4$Li** or **1P-SnR$_4$Li**) first fragments to a transient solvent-separated ion pair (SIP), which can be trapped to give mainly **1A-Si**. The SIP rapidly collapses to the stable contact ion pair (CIP), which gives mainly **1P-Si** on reaction with silyl chloride. The stable structure was shown by NMR spectroscopy to have the allenyllithium CIP structure **1A-Li**. Other related allenyllithium reagents (4-lithio-4,5-nonadiene, **2A-Li**; 2,7-dimethyl-3-lithio-3,4-octadiene, **3A-Li**; and 2,6,6-trimethyl-3-lithio-3,4-heptadiene, **4A-Li**) were also prepared by Li/Sn exchange and gave different product ratios for *in situ* and sequential experiments.

Introduction

The origins of regioselectivity in the reactions of delocalized organolithium reagents (allyl or allenyl−propargyl) are very subtle and poorly understood.[2] In addition to the largely unknown effects (and even nature) of aggregation, ion pair status, and solvation, there is the question of localized or delocalized bonding (π- or σ-allyl or allenyl). Synthetic problems are usually solved in an empirical fashion with alterations in solvent polarity, addition of lithium complexation reagents, changes in the electrophile, introduction of chelating[3] or sterically hindering groups,[4] or replacement of lithium with other metals (commonly used are magnesium, aluminum,[2a,5,6a,b] boron,[2a,6a,c,7] zinc,[5,6d] and titanium[8,9]). In this paper we address an unusual regiochemical effect that we have discovered in a family of hydrocarbon allenyllithium reagents. To study this effect, we have used principally 2-methyl-3,4-pentadienyl-3-lithium (**1A-Li**), but 4-lithio-4,5-nonadiene (**2A-Li**), 2,7-dimethyl-3-lithio-3,4-octadiene (**3A-Li**), and 2,6,6-trimethyl-3-lithio-3,4-heptadiene (**4A-Li**) have also been useful. In our study the same lithium reagent was prepared from multiple precursors and trapped with electrophiles either present during the generation of the lithium reagents or added subsequently. We also used NMR spectroscopic studies to provide information about solution structures.[1a]



1-Sn	M = Me_3Sn	**1-SnPh$_2$**	M = $MePh_2Sn$
1-Si	M = Me_3Si	**1-SnPh$_3$**	M = Ph_3Sn
1-SiPr	M = Me_2iPrSi	**1-Li**	M = Li
1-SnPh	M = Me_2PhSn	**1-SnR$_4$Li**	M = Me_3RSn^-

Structures of Allenyllithium−Propargyllithium Reagents. An understanding of the factors which influence regioselectivity

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1995.

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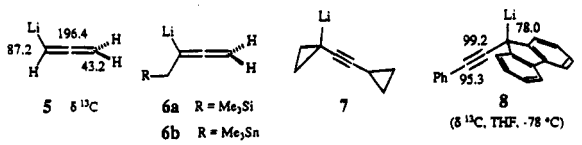
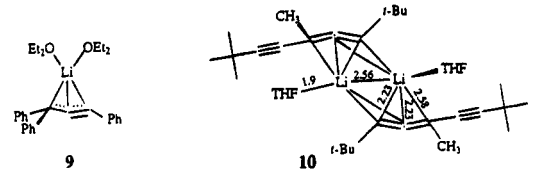
must begin with knowledge about the solution structure of the reagent, starting with reliable information about the location of the lithium (allenyl, propargyl, or π-bonded). When we began our work, there was only scattered information available. Although several simple alkyl-substituted allenyllithium reagents were initially assigned propargyllithium or equilibrating propargyl−allenyl structures (metalation of 2-butyne,[10] 2-hexyne,[6a] 4-methyl-2-pentyne[11]), it is now clear on the basis of IR[12] and NMR[1b,c,13,14a] studies that the parent allenyllithium[13] and most alkyl-substituted homologs have the allenyllithium structure. Most definitive are the ^{13}C chemical shifts: there is a pronounced downfield shift of the central and lithium-bearing carbons compared to propargyl structures.[1c] The metalation product of allene shows ^{13}C signals consistent only with the allenyl structure **5**. The lithium reagents **6**[1b] as well as numerous other alkyl-substituted reagents[1c] are also localized allenyllithiums with well-defined $^{13}C-^{7}Li$ coupling to a single carbon. The 1-alkynyl-1-lithiocyclopropane **7** is an authentic propargyllithium reagent, based on the IR[15] and NMR spectra,[1c] as are metalated 1-phenylthio- and 1-phenylseleno-2-butynes.[1c]

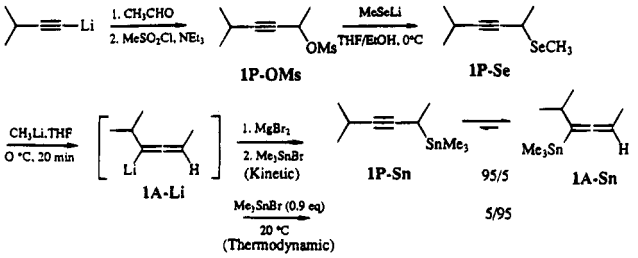


A recent, very-extensive ^{13}C NMR and UV study of mono-, bis-, and tri-arylated allenyllithium−propargyllithium reagents concluded that these are delocalized, with no separate existence of allenyl- and propargyllithiums. Most of the compounds show ^{13}C shifts that are more propargylic than allenic in nature.[16a] In particular, reagents such as **8** and **9** with two aryl groups at the propargyl carbon give chemical shifts which are very propargyl-like. The X-ray structure of **9** shows it to be an η^3-coordinated propargyllithium.[16b] No X-ray crystal structures of simple allenyllithiums have been reported, but dimer **10** has allenic character,[14b] as does a chelated triarylallenyllithium dimer.[16b]

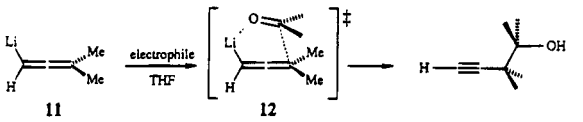


Theoretical studies of allenyllithium and 1-methoxyallenyllithium have suggested an allenyl rather than propargyl structure for the lithium reagent, with some distortion to accommodate lithium contacts at both ends of the anion.[14a,c,d,17] In the ^{13}C NMR spectrum of the 1-methoxyallenyllithium dimer, only C-1 shows coupling to lithium.

Scheme 1



Trapping Studies. A systematic study of the reaction of various electrophiles with 3,3-dimethylallenyllithium **11**[18] has revealed a range of allenyl to propargyl product ratios depending on the nature of the electrophile. A well-defined steric effect was identified for ketones and aldehydes. Acetylenic products are formed exclusively with unhindered carbonyl compounds, which was interpreted in terms of the usual cyclic transition state and S_E2' attack (**12**). Other electrophiles, such as proton, CO_2, and disulfides, gave mostly allenic products. Drawing conclusions about mechanism from ground state structures and reaction products requires knowledge about the energy difference between, and rate of interconversion of, the isomeric structures (Curtin−Hammett principle). Such information is not available for any allenyllithium/propargyllithium reagent.



Results

Syntheses. In an attempt to probe for the possible intervention of allenyl- and propargyllithium species, we studied a pair of isomeric trimethylstannanes (**1A-Sn**, **1P-Sn**), related by a [1,3] sigmatropic shift of the metal group. These and related compounds were prepared as exemplified for **1** in Scheme 1. The syntheses take advantage of the observation that the thermodynamically more stable isomer is **1A-Sn**, but the product of kinetic trimethylstannylation is predominantly **1P-Sn**. Kinetic stannylation was achieved by conversion of the lithium reagent **1A-Li**, prepared by Li/Se exchange of the **1P-Se**, to the Grignard reagent, followed by stannylation with a slight excess of stannyl halide. Equilibration of the propargyl stannanes **1P-Sn**, **1P-SnPh**, and **1P-SnPh$_2$** to allenyl stannanes **1A-Sn**, **1A-SnPh**, and **1A-SnPh$_2$** was achieved by treatment with a catalytic amount of methyllithium or by stannylation of the lithium reagent **1A-Li** with a deficiency (0.9 equiv) of triorganostannane and warming to room temperature. This procedure did not give clean products for the preparation of the triphenylstannyl compound **1A-SnPh$_3$**. Here, treatment of **1P-SnPh$_3$** with 0.5 equiv of 1-lithiopentyne in THF/HMPA (probable formation of the triphenylpentynyl ate complex) proved effective at isomerizing it to **1A-SnPh$_3$** without scrambling of phenyl and allenyl groups.

The isomers **1A-Sn** and **1P-Sn** were subjected to Li/Sn exchange and trapped with electrophiles under two conditions: sequential or *in situ*. In the sequential experiment, the Li/Sn exchange was first completed (MeLi, THF, −78 °C, 10 s or

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Scheme 2

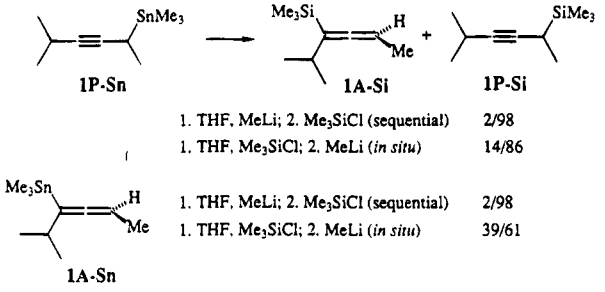
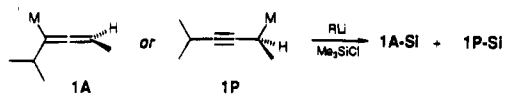


Table 1. Product Ratios from Reaction of Allenyl and Propargyl Stannanes with Me_3SiCl



entry no.	M	RLi	solvent[a]	1A-Si/1P-Si starting from: *in situ* A	*in situ* P	sequential A	sequential P
1	Me_3Sn	MeLi	THF	39/61	14/86	2/98	2/98
2	Me_3Sn	MeLi	THF/2HMPA	81/19	79/21	5/95	4/96
3	Me_3Sn	MeLi	THF/5HMPA	85/15		31/69	48/52
4	Me_3Sn	MeLi	THF/5HMPA[b]	85/15			
5	Me_3Sn	PhLi	THF	27/73	28/72	2/98	2/98
6	Me_2PhSn	MeLi	THF	30/70	26/74	2/98	2/98
7	Me_2PhSn	PhLi	THF	7/93	8/92	2/98	2/98
8	$MePh_2Sn$	MeLi	THF	10/90	9/91	2/98	2/98
9	$MePh_2Sn$	PhLi	THF	4/96		2/98	2/98
10	Ph_3Sn	MeLi	THF	2/98	3/97	2/98	2/98
11	MeSe	RLi[c]	THF		3/97[d]		2/98[e]
12	MeSe	RLi[c]	THF/2HMPA		2/98[d]		5/95[e]

[a] Generally 3 equiv of Me_3SiCl were used. [b] 10 equiv of Me_3SiCl. [c] The Li/Se exchange was performed at 0 °C. [d] *n*-BuLi. [e] MeLi.

longer), and then the electrophile was added. In the *in situ* experiment, methyllithium was added to a *mixture* of tin compound and an excess of the silyl halide, so that reactive intermediates could be trapped before equilibration to ground state structures. Differences in product isomer distribution between the sequential and *in situ* experiments provide direct evidence for the involvement of such intermediates. Scheme 2 shows the results of our initial experiments. The sequential experiments produced products whose A/P ratio of 2/98 was independent of the precursor (**1A-Sn** or **1P-Sn**). The results in Table 1 show further that the product ratio in the sequential experiment was not affected by the presence or nature of the tetraalkyltin species or the method of preparation of the lithium reagent. However, for the *in situ* experiments, there was a dependency on the precursor and method of generation, and both **1A-Sn** and **1P-Sn** formed substantial (but different) fractions of allenyl silane **1A-Si**.

The principal subject of this paper is our attempt to understand the two related phenomena revealed by these experiments. These phenomena are as follows: (1) "*in situ* effect" (different products are produced in sequential and *in situ* experiments), and (2) "memory effect" (the isomeric structure of the precursor (A or P stannyl derivative) or the substituents on the tin group affect the A/P product ratios in the *in situ* experiments).

Clearly, there are at least two different organometallic species involved in the formation of the products. One is stable and leads almost exclusively to propargyl silane **1P-Si**, the other(s) is(are) transient and lead(s) to more allenyl product **1A-Si** than does the stable species. It is the nature of the transient ("allenogenic") species trapped during *in situ* experiments that will be the focus of this paper.

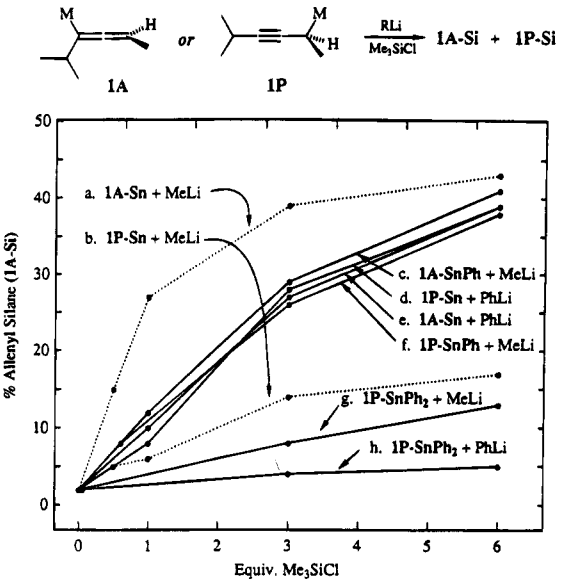
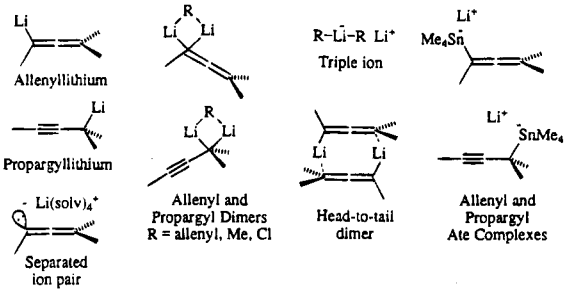


Figure 1. Effect of [Me_3SiCl] on regioselectivity of the trapping reaction of **1-Sn**, **1-SnPh**, and **1-SnPh$_2$** on treatment with methyllithium and phenyllithium *in situ* (THF, −78 °C).

Scheme 3



The principal species that might play a role in the chemistry of allenyllithium−propargyllithium reagents are presented in Scheme 3. The limiting monomeric species are the propargyllithium and allenyllithium reagents and the separated ion pair $R^-//Li^+$. The limiting dimeric species are the two four-center dimers, the head-to-tail dimer, and the triple ion dimer $R_2Li^-Li^+$ (also in allenyl and propargyl forms) as well as possible mixed aggregates with lithium halide or the lithium reagent used for the Sn/Li exchange. Since we will be using the Li/Sn exchange reaction to prepare the lithium reagents, we need to consider the ate complexes A−SnR_4Li and P−SnR_4Li. Pentaorgano tin ate complexes have been spectroscopically[1d,19] and stereochemically[1e] identified as intermediates in the Li/Sn exchange.

With these possibilities in mind, we have performed a large number of sequential and *in situ* single- and double-trapping experiments under various conditions. Some of these data are reported in Table 1 and Figure 1.

An important conclusion from Table 1 is that the sequential experiment produced an identical 2/98 ratio of A/P products under almost all conditions tried (there was a small increase in allenyl product to 5/95 when 2 equiv of HMPA were present). Only when 5 equiv of HMPA were added was a significant fraction of allene produced. For the *in situ* reactions, virtually any experimental variable tried caused changes in the A/P ratio. A more extensive set of experiments, summarized in Figure 1, shows that the fraction of allenyl product produced in the *in situ* experiment is a regular function of the concentration of

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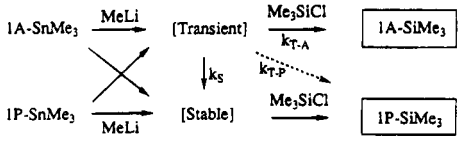
Scheme 4



trimethylchlorosilane. For reactions of **1A-Sn** and **1P-Sn** with methyllithium (but not phenyllithium) the ratio of **1A-Si** to **1P-Si** depends on whether the allenyl or propargyl tin compound was used (curves a and b). In contrast, for the phenyldimethyl- or diphenylmethylstannyl compounds, or when phenyllithium is used in the transmetalation, both isomers give the same product ratio (consider pairs c/f and d/e).

The data in Figure 1 can be interpreted in the following terms. The Li/Sn exchange produces a transient species which undergoes two competitive processes: conversion to the stable species and reaction with trimethylchlorosilane (Scheme 4). The higher the concentration of trapping reagent, the more allenyl product is formed, but this fraction levels out well below 100%. Thus, either the transient species gives a mixture of **1A-Si** and **1P-Si** products (k_{T-A} and k_{T-P}), or the initial Li/Sn exchange produces mixtures of the two intermediates, and the partition ratio k_S/k_{T-A} determines the maximum A/P ratio obtainable. We will provide some evidence below that the latter is probably correct.

The amount of the transient allenogenic species formed is a function of whether the starting tin compound was allenyl or propargyl (curves a and b in Figure 1). The difference between propargyl and allenyl precursors disappears when *either* the trimethylstannyl compounds **1A-Sn** and **1P-Sn** are cleaved with PhLi (rather than MeLi, as in Scheme 1) or the phenyldimethylstannyl compounds **1A-SnPh** and **1P-SnPh** are cleaved with methyllithium. Curves c, d, e, and f all involve formation of an intermediate allenyl or propargyl ate complex with a Me_3PhSn^- substituent, and all show identical product distributions within experimental error, independent of whether the starting material was allenyl or propargyl. In general, the product ratios were identical when the groups on tin in the intermediate ate complex were identical (consider the pairs of entries 5/6, 7/8, and 9/10 in Table 1). Thus, it is possible to observe the *in situ* effect either with or without the memory effect (A or P starting material).

Effect of HMPA. Figure 2 and Table 1 present data which demonstrate that there are large solvent effects. In the presence of 2 equiv of HMPA, the difference between the *in situ* (A/P = 5/95) and sequential experiments (A/P = 79/19) is significantly more pronounced than in THF alone (see Figure 2). Furthermore, there is no longer any dependence on the concentration of Me_3SiCl past 1 equiv (see Table 1, entries 3 and 4), so that all of the transient species formed initially is being trapped. There is also no difference between allenyl and propargyl starting material (no regiochemical memory effect). Up to 2 equiv of HMPA the sequential experiment gives the usual overwhelming proportion of **1P-Si** as product. However, above 2 equiv increasing amounts of allene **1A-Si** are formed, due in part to the presence of Me_4Sn. If the lithium reagent **1A-Li** is prepared by Li/Se exchange of **1P-Se** the increase in the A/P ratio is less pronounced (dotted line in Figure 2).

The graph in Figure 2 stops at 5 equiv of HMPA for the sequential experiment; at higher equivalents the amount of allene continued to rise (**1A-Si/1P-Si** = 62/38 at 10 equiv), but the yields of these silanes (31%) and total recovery of products (67%) dropped below our acceptable limit of 80%. A complicating feature in THF–HMPA solution is that prototropic isomerization to **13A-Li** becomes detectable in the sequential experiment at high HMPA equivalents, as indicated by formation

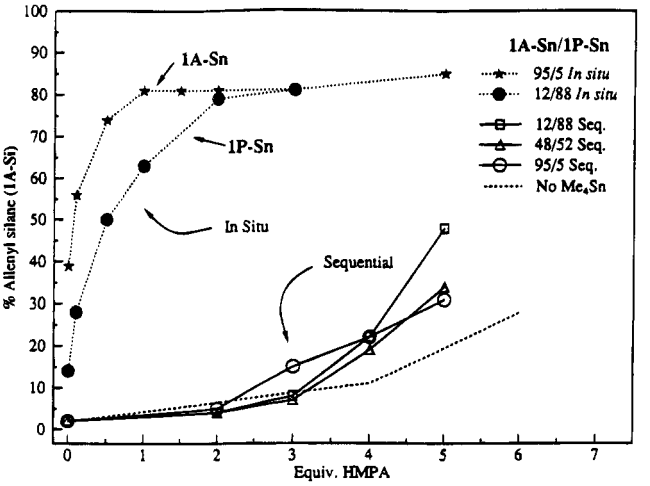
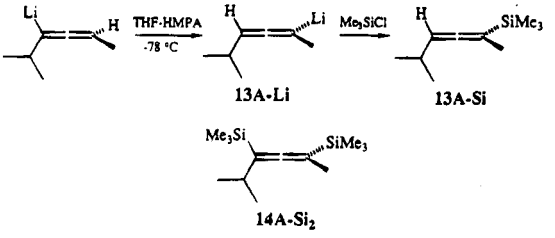


Figure 2. Effect of HMPA on the regioselectivity of silylation of **1-Li** under *in situ* and sequential conditions at −78 °C in THF.

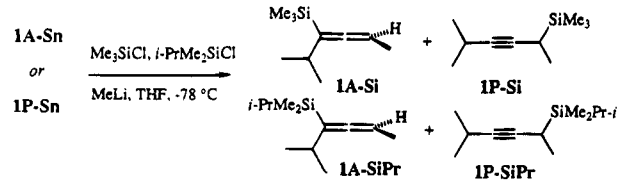
of the isomeric allenyl silane **13A-Si** (up to 10% at 5 equiv of HMPA, 35% at 10 equiv of HMPA for reaction times of <30 s). In addition, in some experiments 3–5% of bis-silylated product (**14A-Si$_2$**) was detected, probably formed by a second metalation of **1A-Si/1P-Si** or **13A-Si** during the quench. To minimize these side reactions, the Me_3SiCl quench was performed within 15 s after addition of the MeLi. The inherent imprecision of such experiments is responsible for the somewhat lower reproduceability of the HMPA experiments. The isomerization to **13A-Li** also effectively prevents NMR spectroscopic studies of **1A-Li** in media containing HMPA, since the time scale of the NMR experiments is at least two orders of magnitude longer than the sequential experiment, and principally **13A-Li** is present in solution.



Double-Trap Experiments. Additional characterization of the transient intermediate was provided by double-trapping experiments, in which *in situ* and sequential experiments were carried out with a mixture of two silyl chlorides, trimethylchlorosilane and dimethylisopropylchlorosilane. This experiment had two goals. One was to characterize the selectivity of the transient and stable species in their reactions with sterically distinct silyl chlorides. For example, a dimeric species or a tin ate complex might be expected to be less reactive and more selective than the monomeric allenyllithium, whereas the separated ion pair would be much more reactive[20] and probably less selective. The second goal was to probe for the presence of the stannyl group in the product-determining transition state. It is clear from the results in Figure 1 that the nature of the stannyl group plays a key role in the formation of the transient species. If the transient species were a tin compound (e.g., the ate complex), then one might expect the methyl/isopropyl

(20) Szwarc, M. *Carbanions, Living Polymers, and Electron Transfer Processes;* Interscience: New York, 1968; Chapter V. Smid, J. *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley-Interscience: New York, 1972; Vol. I, pp 85–151. Hogen-Esch, T. E. *Adv. Phys. Org. Chem.* **1977**, *15*, 153.

Table 2. Results of Double-Trapping Experiments Using Me_3SiCl and *i*-$PrMe_2SiCl$



entry no.	starting material	RLi	solvent	A/P	1A-Si/ 1A-SiPr	1P-Si/ 1P-SiPr
			In Situ Experiments			
1	**1A-Sn**	MeLi	THF	49/51	58/42	92/8
2	**1P-Sn**	MeLi	THF	16/84	55/45	92/9
3	**1A-Sn**	PhLi	THF	36/64	55/45	91/9
4	**1A-SnPh**	MeLi	THF	36/64	56/44	91/9
5	**1P-SnPh**	PhLi	THF	38/62	56/44	91/9
6	**1P-SnPh**	MeLi	THF	34/66	59/41	93/7
7	**1A-Sn**	MeLi	THF/2HMPA	86/14	57/43	78/22
8	**1P-Sn**	MeLi	THF/2HMPA	84/16	57/43	80/20
			Sequential Experiments			
9	**1A-Sn**	MeLi	THF	2/98	*a*	91/9
10	**1P-Sn**	MeLi	THF	2/98	*a*	89/11

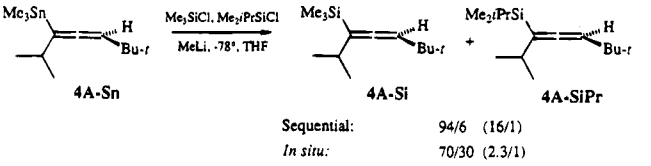
[a] Less than 2% yield of allenyl products.

selectivity to vary with the lithium reagent used for the Li/Sn exchange and with the substituents on the stannyl group.

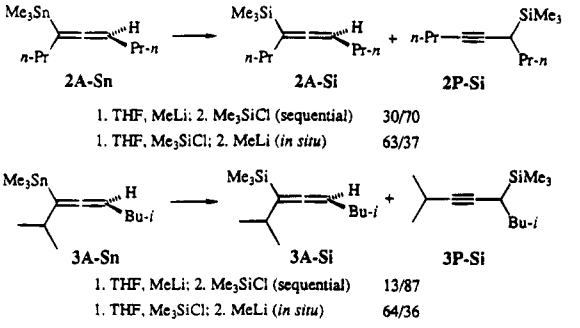
The results of a series of double-trapping experiments are shown in Table 2. The propargyl products in both the *in situ* and sequential experiments in THF favored trimethylsilyl over isopropyldimethylsilyl by a factor of 8:1 to 11:1, with slightly lower ratios (4:1) observed with 2 equiv of HMPA. In sharp contrast, the allenyl silanes were formed in a 1.2 to 1.4 ratio (identical within experimental reproducibility), independent of the lithium reagent, the stannyl group, or the allenyl/propargyl structure of the starting material. Competition experiments of this type may suffer from mixing problems if the rate of reaction is higher than the rate of mixing; the obsered ratios will then be smaller (closer to 1.0) than the true ratios. In the *in situ* experiment, the trapping reagent is homogenously mixed with the precursor before the reaction, so mixing problems are inherently absent, and the low ratios observed here are true values. Only in the sequential experiment could there be a problem, so the 9:1 ratio is a lower limit.

To determine whether the low methyl/isopropyl selectivities at the allenyl center were simply the consequence of reaction at a vinyl center, we carried out two experiments. *m*-Tolyllithium gives a 9:1 ratio under similar conditions, *o*-tolyllithium gives 12:1.

More pertinent are the results with the analog **4A-Sn**. This compound gives no detectable amount (<1%) of propargyl products under any conditions tried, presumably for steric reasons. In the sequential experiment, a 16:1 methyl/isopropyl ratio (**4A-Si:4A-SiPr**) was obtained. In the *in situ* experiment, the ratio was 2.3:1, somewhat higher than the 1.3:1 ratio found for **1A-Sn**. This is as expected, since for **4A-Li** there are two competing sources of the allenyl product: the stable species which gives a ratio of 16:1, and the transient species which gives a ratio near one. For **1A-Sn** the allenyl product seems to be entirely formed from the transient intermediate (only 2% of the allene is formed in the sequential experiment). We conclude that the very low methyl/isopropyl selectivity found for the allenyl products in the *in situ* experiment with **1A-Sn** results from the unusual nature of the transient intermediate which forms them and not because of some inherent propensity of allenyl centers to react with low selectivity. Furthermore, the constant methyl/isopropyl ratio (**1A-Si:1A-SiPr**) found in the *in situ* experiments despite variable allenyl/propargyl ratios suggests strongly that the allenyl product comes predominantly from one source, the transient intermediate, whereas the constant **1P-Si:1P-SiPr** ratio indicates that the propargyl product is being produced by the stable intermediate (k_S and not k_{T-P} of Scheme 4) in both the sequential and *in situ* reactions. By contrast, the variable methyl/isopropyl ratio (**4A-Si:4A-SiPr**) seen for **4A-Sn** indicates that the allenyl product comes from multiple intermediates.



Other Allenes. The substitution pattern of allene **1** is unique among several others tried in that the stable species gives almost exclusively propargyl silane product **1P-Si**, whereas the transient species gives allenyl silane product **1A-Si**. Allenyl stannanes with other substituent groups, such as **2A-Sn** and **3A-Sn**, also show differences in product ratios between sequential and *in situ* experiements, but the effects are less striking since the sequential experiment gives significant allene products. The changes follow those seen for **1**: there is more allene product formed in the *in situ* experiments than when sequential addition is employed.



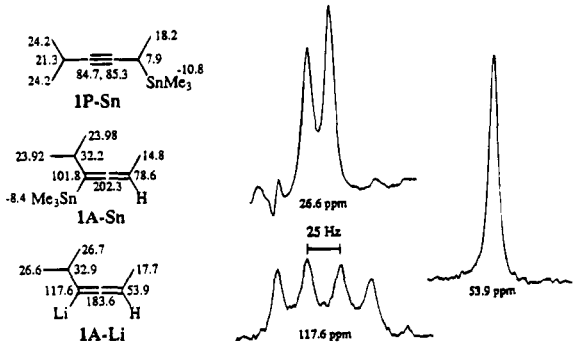
We have also carried out sequential and *in situ* exchanges on the allenyl iodide **1A-I** and the methyl selenide **1A-Se** with trimethylchlorosilane as electrophile. In both cases the sequential and *in situ* experiments gave the same results as the sequential experiment with **1A-Sn**. Thus, these systems do not show the *in situ* effect.

Spectroscopic Studies in THF. An important step in disentangling the role of the various possible species in the chemistry of allenyllithium reagents is the determination of the ground state structure in solution. The lithium reagent **1A-Li** prepared either by Li/Sn exchange of **1A-Sn** or **1P-Sn** or by Li/Se exchange of **1P-Se** gave identical ^{13}C NMR spectra (Scheme 5). The chemical shifts unambiguously define **1A-Li** as an allenyllithium reagent. The well-defined $^{13}C-^{7}Li$ coupling to a single lithium ($J = 25$ Hz) suggests a monomeric structure.[21] Authentic dimers have been detected spectroscopically: they show characteristic 1:2:3:4:3:2:1 multiplets (^{7}Li at natural abundance) in the ^{13}C spectra expected for a four-center structure with lithium primarily coordinated to the allenyl carbon.

The other lithium reagents used in this study (**2A-Li**, **3A-Li**, and **4A-Li**) are also monomeric allenyllithiums as judged from

(21) (a) Coupling constants ($^{7}Li-^{13}C$) of 14 to 25 Hz have been observed for a variety of α-lithio sulfides, selenides and silanes,[1c] and allenyl and propargyllithium reagents.[1g,21b] Thus these partially delocalized organolithium reagents do not follow the *J* vs aggregation correlation ($J = 45$ Hz for monomers) proposed by Bauer, Winchester, and Schleyer.[14e] (b) Holladay, J. E. Ph.D. Dissertation, University of Wisconsin, Madison, 1994.

Scheme 5 ^{13}C NMR data for **1A-Li** at −106 °C in 1:1 ether/THF



chemical shifts and Li−C couplings.[1c,21b] An interesting feature of the ^{13}C NMR spectra of **1A-Li** and **4A-Li** is the diastereotopic isopropyl group resulting from the chiral allenyl system.[22] The two ^{13}C methyl signals of **1A-Li** are diastereotopic to about −60 °C, at which temperature the two peaks merge, probably due to a convergence of chemical shifts rather than a true coalescence. For **4A-Li** the peak separation is larger, and a well-defined coalescence occurs at −38 °C ($\Delta G^{\ddagger}$ = 11 kcal/mol).

Spectroscopic Studies in THF−HMPA. The influence of HMPA on the regiochemical effects being studied here is so dramatic (see Figure 2) that we have devoted considerable effort to understand the solution structure of **1A-Li** and related reagents in THF−HMPA solution. As mentioned above, it was not possible to examine NMR spectra of **1A-Li** in THF/HMPA solution without isomerization to **13A-Li**. We therefore examined the lithium reagent **2A-Li**, prepared by Li/Se exchange of **2P-Se**. Solutions of **2A-Li** did not undergo prototropic isomerization even after extended times (several hours) in HMPA−THF, provided that temperatures were kept near −78 °C or lower.

Figure 3 shows an HMPA titration of **2A-Li** prepared by cleavage of the selenide **2P-Se**. In the early points of the titration, HMPA coordinates to the lithium reagent to form the mono-HMPA contact ion pair (CIP). Past 1 equiv of HMPA small amounts of separated ion pairs (SIP) are formed (quintet at −0.5 ppm in ^{7}Li NMR spectrum), which, however, does not become the major species even at 10 equiv of HMPA. In addition, there is a small signal at δ 1.3, which is more visible in the ^{6}Li NMR spectrum. The ^{13}C NMR spectrum shows the formation of a new species with shifts very similar to those of the lithium reagent in THF. A similar HMPA titration of a solution prepared by Li/Sn exchange (and which thus contained 1 equiv of Me_4Sn) showed complete conversion to a SIP, which was identified as the ate complex **2A-SnMe$_4^-$Li$^+$** from ^{7}Li, ^{119}Sn, and ^{13}C NMR spectra (Scheme 6).

An unambiguous interpretation of the spectra in Figure 3 and a number of other experiments like this one has eluded us. The process occurring on addition of HMPA to **2A-Li** cannot be only the conversion of CIP to SIP. First, in dozens of HMPA titrations that we have performed on many different lithium reagents, when the SIP appears this early in the titration, ion separation is usually complete by 3 equiv of HMPA.[1f,g] Here the lithium reagent is still substantially CIP even at 10 equiv. Secondly, in the ^{13}C NMR spectrum the allenyl carbon still appears to be coupled to ^{7}Li.

(22) Stereochemistry of allenyllithiums: Hoffmann, R. W.; Lanz, J.; Metternich, R.; Tarara, G.; Hoppe, D. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1145. le Noble, W. J.; Chiou, D.-M.; Okaya, Y. *J. Am. Chem. Soc.* **1978**, *100*, 7743. Hoppe, D.; Gonschorrek, C. *Tetrahedron Lett.* **1987**, *28*, 785.

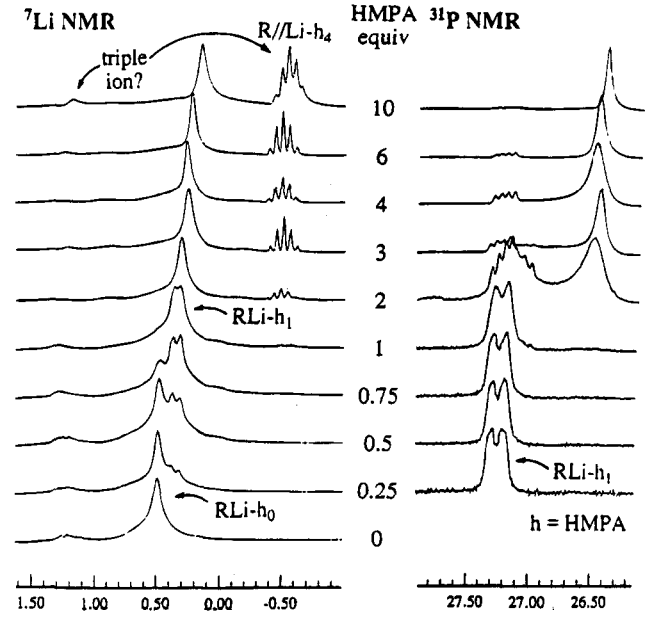
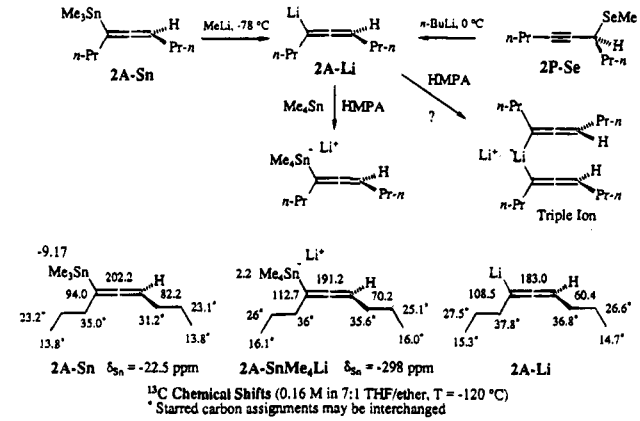


Figure 3. 139.9-MHz ^{7}Li and 145.8-MHz ^{31}P NMR spectra at −120 °C during an HMPA titration of **2A-Li** and Me_2Se (i.e., **2A-Li** prepared from **2P-Se** by treatment with MeLi).

Scheme 6



An appealing interpretation of these data is that this lithium reagent is partially converted to a triple ion (like several others that we have observed, and that have been reported in the literature[23]) rather than to a SIP. A triple ion must have two signals in the Li spectrum with a 1:1 ratio of intensities. Although we do observe two signals (the singlet at δ 1.3 is in a chemical shift region where we have detected other R_2Li^- species, and the quintet at −0.5 for $Li(HMPA)_4^+$ is common to all SIP Li^+ species in THF−HMPA), these are not in a 1:1 ratio. Clearly, in addition to the putative triple ion, there must be other unidentified SIP lithium species present. Possible candidates are a small amount of conversion to the SIP of **2A-Li**; isomerization of the allenyllithium to more conjugated lithium reagents (pentadienyllithiums) which would form separated ion pairs more easily than does **2A-Li**; or some reaction with Me_2Se to form $MeSe^-Li^+$, which is a separated ion under these conditions.[1f,h] However, decomposition must be minor, since recovery of material after quenching of the NMR sample

(23) Gornitzka, H.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 693. Jackman, L. M.; Scarmoutzos, L. M.; Porter, W. *J. Am. Chem. Soc.* **1987**, *109*, 6524. Fraenkel, G.; Hallden-Abberton, M. P. *J. Am. Chem. Soc.* **1981**, *103*, 5657. Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 827. Romesberg, F. E.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* **1991**, *113*, 5751. Olmstead, W. N.; Bordwell, F. G. *J. Org. Chem.* **1980**, *45*, 3299.

with Me_3SiCl was 80 to 90%. The importance of these issues will become clearer when we discuss our mechanistic proposal for the *in situ* trapping experiments.

Discussion

The chemical properties of the transient species, as defined by the *in situ* experiments above, are as follows:

(1) Regioselectivity. The transient intermediate reacts with trimethylchlorosilane to give allenyl silane **1A-Si**. The stable species gives **1P-Si**.

(2) Lifetime. The lifetime of the intermediate is certainly under 10 s at −78 °C and probably well under 1 s.[24] The intermediate converts to the stable species at about the same rate as it reacts with Me_3SiCl. The stable species has an indefinite lifetime.

(3) Solvent Effects. Polar solvents favor trapping of the intermediate. More of the intermediate is formed and/or is trapped in HMPA−THF than in THF.

(4) Regiochemical Memory Effect. In the reaction of the trimethyltin derivatives with MeLi, the allenyl (**1A-Sn**) precursor gives substantially more of the transient intermediate than does the propargyl (**1P-Sn**) precursor (Figure 1). This difference disappears in HMPA, or when one or more phenyl groups are attached to tin.

(5) Effect of Substituents on Tin. The amount of transient intermediate formed is strongly affected by the tin group and the lithium reagent used for the Li/Sn exchange. The substituents on tin in the intermediate ate complex determine the amount of the intermediate formed (Figure 1). Most notably, the *in situ*/sequential difference disappears for compounds with three phenyls on the tin (entries 9 and 10 in Table 1).

(6) Steric Selectivity. The intermediate has almost no selectivity (1.2:1) in its reaction with two silyl halides (Me_3SiCl and $Me_2iPrSiCl$) differing in steric hindrance to substitution. The stable species has ≈10:1 selectivity (Table 2).

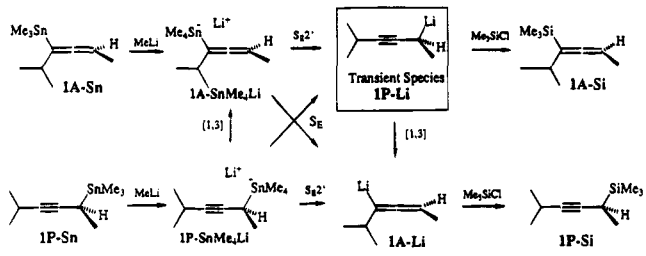
(7) Absence of Tin Effect on Double Trapping. The stable species contains neither tin nor another metalloid. As judged by the double-trapping experiments, the transient intermediate also does not contain tin, since the steric selectivity was independent of precursor. However, this conclusion is tentative since selectivity is low, and different intermediates could fortuitously give identical ratios (Table 2).

(8) Effect of High HMPA Concentrations on the Sequential Experiment. Under conditions where the ate complex is stable (5 equiv of HMPA), a substantial amount of the intermediate is trapped even in the sequential experiment (Figure 2).

We have considered the following candidates for the transient species: (1) dimer or higher aggregate, or mixed aggregate with methyllithium, phenyllithium, or LiCl (formed during the reaction); (2) tin ate complex; (3) propargyllithium; and (4) separated ion pair (SIP). In each case we propose that the stable species is the spectroscopically identified monomeric allenyllithium **1A-Li**.

Aggregates. A number of features of the transient intermediate argue against its being a dimer or mixed aggregate. First, the *in situ* effect is enhanced in THF−HMPA, conditions where extent of aggregation should be reduced. For example, LiCl is converted from a dimer in THF to a separated ion pair in THF−HMPA; LiBr is also separated by HMPA.[1f] The allenyllithium reagent **1A-Li** shows no indication of aggregation in THF.

Scheme 7



Second, the *in situ* effect is also observed when PhLi is used for the cleavage. PhLi is only marginally aggregated in THF (1:1 dimer:monomer at 0.1 M).[1i,j,14e]

Perhaps the most significant argument against a dimer as the crucial intermediate is that in almost all cases where a kinetic distinction has been made, dimers and higher aggregates are *less* reactive than monomers.[1j,25,26] It is inherent in the nature of the *in situ* experiment that the intermediate must be more reactive than the stable structure present in solution, the monomeric allenyllithium. Thus, one would not anticipate higher aggregates to be kinetically active, nor would one expect the low methyl/isopropyl selectivity for a less reactive species.

Tin Ate Complex. Several features of the reaction show that the tin ate complexes are directly and intimately involved in determining the *partition* of the reaction path between the transient and stable intermediates. Could one or both of the ate complexes be the actual reactive intermediates? The double-trapping experiments provide significant (although not conclusive) arguments against a direct involvement of the tin ate complexes. The low methyl/isopropyl selectivity is not what would be expected for a nucleophilic organometallic reagent with a bulky R_4Sn^- group as the metal center, nor would one expect the selectivity to be independent of the R groups on tin.

We have previously addressed the general question of the reactivity of tin ate complexes compared to lithium reagents. For example, the reactivity of PhLi toward *n*-BuI in THF at −78 °C is *reduced* when Ph_2Me_2Sn or Ph_3MeSn is added.[1d] NMR studies reveal that in these solutions the ate complexes $Ph_3Me_2Sn^-Li^+$ and $Ph_4MeSn^-Li^+$ are the principal species present.

Propargyllithium. Early in this work we formulated the working hypothesis shown in Scheme 7. Here the transient intermediate is the unstable propargyllithium reagent **1P-Li** (formed from the intermediate ate complex **1A-SnR$_4$Li**), which gives allenyl product **1A-Si**, whereas the allenyllithium **1A-Li** (shown by the NMR studies to be the ground-state structure) gives the propargyl product **1A-Si**. In the sequential experiment, transient **1P-Li** isomerized to **1A-Li**, and hence only **1P-Si** was formed. A basic premise is that the reaction of the ate complex with the lithium cation, like many electrophile substitutions of allylic and allenic/propargylic organometallic reagents,[6c,9,18,27] occurs predominantly with allylic inversion. Similarly, the reactions with Me_3SiCl also occur by an S_E2' mechanism.

As will be discussed below in connection with the closely related SIP mechanism discussed next, Scheme 7 provides an excellent rationalization for the essential role played by the ate complexes in the reaction. It also rationalizes the A/P regioselectivities. Two important features of the reaction are not well predicted by this mechanism, however. First, it seems unlikely that a propargyllithium species would show methyl/

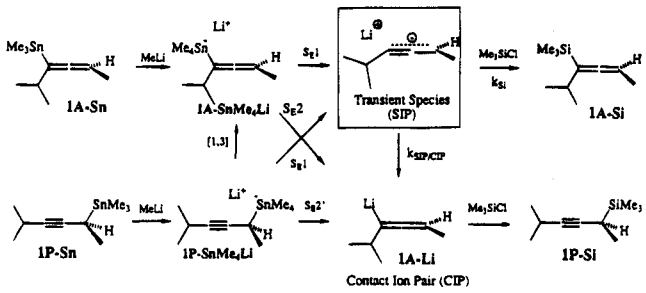
(24) The lifetime of the transient species must be well under 1 s, since, even when MeLi and **1A-Sn** were mixed for only the time it takes to travel a few centimeters down a forcefully depressed syringe needle before trapping with trimethylchlorosilane (simple stopped flow experiment), the products of the sequential experiment were obtained.

(25) McGarrity, J. F.; Ogle, C. A.; Brich, Z.; Loosli, H.-R. *J. Am. Chem. Soc.* **1985**, *107*, 1810.

(26) West, P.; Waack, R.; Purmont, J. I. *J. Am. Chem. Soc.* **1970**, *92*, 840.

(27) Marshall, J. A.; Perkins, J. *J. Org. Chem.* **1994**, *59*, 3509.

Scheme 8



isopropyl selectivity (double-trap experiments) so different from other lithium reagents such as allenyllithium and *o*- and *m*-tolyllithium. However, we have no direct arguments to rule out such behavior. Secondly, HMPA should increase the rate of equilibration of the transient propargyllithium to the allenyllithium by loosening the association between anion and cation. One might thus anticipate a reduction or complete absence of the sequential/*in situ* dichotomy in HMPA. In actual fact, the opposite is true. We thus turn to the final mechanism.

Solvent Separated Ion Pair. In this mechanism, which we believe to be the correct one, the CIP allenyllithium **1A-Li** (shown by the NMR studies to be the ground-state structure) gives the propargyl product **1P-Si**, and a transient SIP gives the allenyl products (Scheme 8). Both direct spectroscopic observation[1d] and stereochemical studies at the tin center[1e] have directly implicated ate complex intermediates in the Li/Sn exchange. We propose the ate complexes **1A-SnR$_4$Li** and **1P-SnR$_4$Li** as the first significant intermediates in the reaction. Facile equilibration between the isomeric ate complexes by [1,3] sigmatropic rearrangement seems probable and would explain the production of identical products from **1A-Sn** and **1P-Sn** for reactions in which a phenyl group is attached to the tin in the intermediate ate complex. For reactions between methyllithium and **1A-Sn** or **1P-Sn**, which proceed through less stable tetramethyltin ate complexes, incomplete equilibration would result in the different behavior for A and P precursors.

Direct information about the mechanism of the conversion of the tin ate complexes to lithium reagents is sparse. However, the reaction invariably occurs with retention of configuration at carbon, where this can be detected,[1e,28] and thus can be considered an electrophilic substitution with Li^+ as the electrophile. Like all substitutions, we can envision two limiting mechanisms: (a) a bimolecular S_E2 or S_E2' reaction of Li^+ with the ate complex which would lead directly to either the propargyl or allenyllithium CIP reagent or (b) unimolecular dissociation (S_E1) of the weak C−SnR$_4$ bond to produce a carbanion and a molecule of the tetraorganostannane. In this connection it is important to recognize that all ate complexes in THF studied to data have been separated ion pairs: Ph_2I^+,[1j] $Ph_3Hg^+Li^-$,[1j,f] $PhEt_3B^-Li^+$,[1k] $Ph_3Te^-Li^+$,[1j] $R_3Se^-Li^+$,[1l] and $R_3Ph_2Sn^-Li^+$.[1f] Thus, S_E1 fragmentation of the tin bond should lead initially to a separated lithium ion pair. Spectroscopic studies of the lithium reagent **1A-Li** unambiguously identify the CIP as the stable species in THF (the situation in THF−HMPA is murkier), therefore the SIP would quickly collapse to the CIP ($k_{SIP/CIP}$). If the reaction is carried out in the presence of Me_3SiCl, some of the SIP is trapped before ion pair collapse occurs to form allenyllithium **1A-Li** (k_{Si}); the fraction trapped will be a function of the concentration of silyl chloride as shown in Figure 1. It is the delicate balance between the S_E2 and S_E1 processes for the various A and P ate complexes and subsequently the competition between the $k_{SIP/CIP}$ and k_{Si} processes that is responsible for the complex dependence of the A/P trapping ratios of the *in situ* experiment.

We discuss below the chemical behavior of the *in situ* trapping experiments and the properties of the transient SIP intermediate as outlined in the first part of the Results section.

(1) Regioselectivity. As shown in Scheme 8, observed regioselectivities seem appropriate. The spectroscopically observed species is the allenyllithium structure, and reaction under sequential conditions occurs almost exclusively at the propargyl end by and S_E2' reaction. There is significant evidence for S_E2' reaction of allenyl−propargyl titanium,[9] boron,[6a,c] and other organometallic species.[27,29] The general tendency for many allenyllithium/propargyllithium reagents to react with unhindered carbonyl compounds remote from the *usually presumed* site of metal coordination[18] also tends to support S_E2' processes, although the ease of 1,3-shifts in the more polar organometallic compounds (Li, Mg) makes direct correlation between the equilibrium structure of the organometallic and the site of reaction problematic. The regiochemical preferences for non-chelating electrophiles, such as silyl chlorides and alkyl halides, are even less predictable. They appear to be governed by many factors, including the site of metal coordination, steric effects, solvation effects, and HSAB-related effects.

From the observation that lithium is coordinated at the allenyl end in a variety of hydrocarbon allenyllithiums, we can conclude that the site of highest electron density in the free anion is the allenyl end. Thus, it is expected that in the absence of an interfering coordinated metal ion, there would be a preference for reaction at the allenyl end (barring overwhelming steric effects), as observed for the transient species. Pertinent in this connection are the double-trap experiments with **4A-Li**, which show that the methyl/isopropyl selectivity can be either high or low at the same site, depending on whether a sequential or *in situ* experiment is performed.

The intervention of SIP intermediates has been proposed to explain numerous stereochemical, regiochemical, and reactivity effects. For example, large changes in the stereochemistry of protonation of a 9,10-dihydro-9-lithioanthracene in ether and ether−HMPA (from 99:1 to 1:99) have been ascribed to the different behavior of CIP and SIP species.[30] It has been proposed that the striking effects of HMPA on the ratio of 1,2- to 1,4-addition of many lithium reagents to α,β-unsaturated carbonyl compounds are due to the intervention of SIP's.[31]

(2) Lifetime. The collapse of a SIP to a CIP should have activation energies comparable to that of lithium−oxygen coordination energy of a single molecule of THF (since at least one molecule of THF must be removed from the $Li(THF)_4^+$ counterion of the SIP to form the presumed R−$Li(THF)_3$ CIP), hence rates must be very fast on the laboratory time scale.[32]

$$R^- Li(solv)_4^+ \xrightarrow{-solv} R^- Li(solv)_3^+ \longrightarrow R\text{-}Li(solv)_3$$

(3) Solvent Effects. The larger *in situ*/sequential difference

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in THF–HMPA compared with THF (Figures 1 and 3) would be expected on the basis that collapse of the $R^-Li(HMPA)_4^+$ ion pair to a CIP requires desolvation of at least one HMPA molecule from Li^+, which has barriers in the neighborhood of 6–9 kcal/mol (measurable by DNMR techniques)[1f] whereas exchange of solvent molecules in THF is near the DNMR detection limit (≈6 kcal/mol), but can be detected in favorable cases.[1m,32] Thus, the transient SIP intermediate should have a longer lifetime in HMPA than in THF. Furthermore, the $Li(HMPA)_n^+$ counterion will be a much weaker electrophile than $Li(THF)_n^+$, so the S_E2 and S_E2' processes, which bypass the transient SIP, should be slower in HMPA.

(4) Regiochemical Memory Effect. Figure 1 shows that **1A-Sn** gives substantially more allenyl product than does **1P-Sn** (curves a and b). The balance between the S_E2 and S_E1 processes will be different for the A and P ate complexes **1A-SnR$_4$Li** and **1P-SnR$_4$Li**. In particular, the propargyl ate complex **1P-SnR$_4$Li** is less stable than the allenyl isomer **1A-SnR$_4$Li** and might be expected to undergo faster S_E1 fragmentation. On the other hand, S_E2' attack on **1P-SnR$_4$Li** leads to the more stable allenyllithium reagent **1A-Li** and might be faster. Apparently, the latter effect dominates, and the propargyl tin precursor **1P-Sn** produces less of the transient intermediate than does **1A-Sn**, with the intermediate ate complex (**1P-SnR$_4$Li**) undergoing faster direct substitution to give allenyllithium **1A-Li**.

(5) Effect of Substituents on Tin. There are two effects of replacing tin–methyl groups by tin–phenyl in the ate complex intermediate. For the first substitution the memory effect is lost (A and P become identical). With additional substitutions the sequential/*in situ* difference decreases, until with Ph_3MeSn both experiments give identical results (**1A-Si/1P-Si** = 2/98). In the context of the mechanism in Scheme 8, this can be rationalized as follows: the association constants of ate complexes in the $Ph_nMe_{5-n}Sn^-Li^+$ series show a steady state increase from $n = 0$ (Me_5SnLi) to $n = 4$ ($MePh_4SnLi$).[1d] For the latter, ate complex formation is complete (by NMR detection) in THF, whereas for the former there is no detectable ate complex in THF (it does form when HMPA is added). It may be, therefore, that the more stable, higher phenylated, allenyl tin ate complexes no longer fragment by the S_E1 pathway, which leads to the transient intermediate, but proceed to the CIP predominantly or entirely by the direct S_E2 reaction.

(6) Steric Selectivity. The classical investigations of Swarc and Hogen-Esch have shown that SIP's can be 3–5 orders of magnitude more reactive than CIP's,[20] and thus low selectivities in the methyl versus isopropyl silane double trapping experiments would be predicted for a SIP.

(7) Absence of Tin Effect on Double Trapping. In Scheme 8, the ate complexes determine the ratio of transient to stable intermediates formed, but all of the reactions are those of lithium reagents.

(8) Effect of High Concentrations of HMPA on the Sequential Experiment. In the presence of >2 equiv of HMPA, the sequential experiment begins to give significant allenyl products (Figure 2). Under these conditions, the NMR spectroscopic studies show that there is significant conversion of **1A-Li**/Me_4Sn to the ate complex **1A-SnR$_4$Li** (R = Me). Thus, the sequential experiment begins at the ate complex portion of the mechanism in Scheme 8 and takes on the character of an *in situ* reaction for that fraction of the material which is present as an ate complex.

The HMPA titration of these allenyllithium reagents shows substantial amounts of separated lithium ions even in the absence of tetramethylstannane. The mechanism of Scheme 8 requires that the sequential experiment give allenyl product **1A-Li** to the extent that separated ions are present. As discussed in the Results section, we are unable to fully account for the amount of separated lithium cations observed; no SIP allenyllithium could be detected in the ^{13}C NMR spectra. It should, however, be emphasized that the NMR experiments were performed at −120 to −130 °C, whereas the trapping experiments were performed at −78 °C. Lower temperatures favor SIP's,[20] so it is expected that the low-temperature NMR samples would have a higher fraction of SIP's than was actually present in the trapping experiments.

There are other problems in attempting to directly correlate the NMR data with sequential trapping experiments. As trimethylchlorosilane reacts, lithium chloride forms. The lithium chloride will also be complexed to HMPA,[1f] and this will change the concentration of the various species in ways that are difficult to predict.

Other "Nascent" Lithium Reagent Effects. There are scattered reports in the literature of unusually reactive intermediates produced during *in situ* experiments which perform transformations distinct from those of the equilibrated species. Most closely related to the effect discussed above is the observation of intra- and intermolecular migrations of stannyl groups during reaction of aryl bromides with magnesium.[33] These rearrangements have been ascribed to the intermediacy of free carbanions in the reduction. Similar migrations do not occur with the fully formed Grignard reagents.

The report by Meyers, Lutomski, and Laucher that addition of several "aged" organolithium reagents (vinyl, allyl, or benzyl) to 1-naphthyloxazoline proceeded much more slowly than when the lithium reagent was prepared *in situ* by reaction of methyllithium with the appropriate stannane may also be related.[34] We do not, however, think it likely that this effect can be easily explained by the same mechanism that we are proposing here. First, the reactions were carried out over 24 h at −78 °C. A transient SIP intermediate will complete its reactions in fractions of a second, or it will have decayed to the CIP. Second, the Meyers effect was observed for a range of lithium reagents which are likely to differ greatly in their ease of ion-pair separation (e.g., allyl and vinyl). The extent to which our mechanism operates (or whether it operates at all) is crucially dependent on the SIP/CIP behavior. In fact, we have not been able to detect any difference between *in situ* and sequential experiments using ArLi or R_3SnAr precursors using several different tests.[1n] Presumably, in these cases no SIP is generated during the Li/Sn exchange, or the SIP collapses to CIP faster than capture by external electrophiles.

An interesting regiochemical effect has been reported by Baudouy, DelBecq, and Gore.[35] These workers found that the ratio of regioisomeric products varied depending on the time between the addition of the metalating agent to **15** and the addition of the electrophile (trimethylsilyl chloride). They ascribed the effect to the intervention of regioisomeric propargyl–allenyl lithium reagents, but did not further investigate the process.

(32) Barriers of 8–10 kcal/mol have been observed for exchange of ether and THF complexed to lithium bis(trimethylsilyl)amide in hydrocarbon solvent: Lucht, B. L.; Collum, D. B. *J. Am. Chem. Soc.* **1994**, *116*, 6009. Slow exchange of THF and other ethers (ΔG ≈ 6 kcal/mol) has been observed for a chelated α-lithio silane.[1m]

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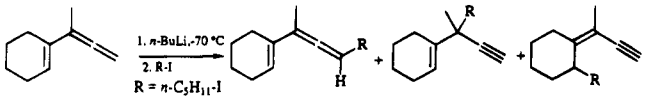

Unusually reactive alkoxide intermediates were detected by the rapid-injection NMR technique of McGarrity.[25] This "nascent alcoholate" was probably not a SIP but a monomeric alkoxide, rather than the more stable (and less reactive) higher aggregates that alkoxides form in THF.

Also relevant is the observation by Suzuki, Norita, and Noyori that slightly different allenyl/propargyl ratios were formed during the reactions of 3-lithio-4-methyl-1,2-butadiene prepared either by metalation or by lithium−tin exchange.[11] The phenomenon was not further investigated. This is not an *in situ* effect and may be unrelated to our experiment.

Conclusion. We have provided evidence that a transient intermediate in the lithium−tin exchange reaction can be trapped with trialkylsilyl chlorides. The evidence supports the assignment of a separated ion pair structure to this intermediate. These results suggest that similar phenomena should be considered whenever reactive organometallic reagents are generated *in situ*, or when intramolecular trapping of such intermediates is performed (such reactions are inherently *in situ* processes).[36] This adds yet another complication to interpretation of results from studies of the metal halogen exchange by use of radical cyclization probes, since one has to consider a second carbanionic intermediate (the SIP) in addition to the stable lithium reagent and possible intermediate free radicals.[36a]

Experimental Section

General. All reactions involving lithium reagents were run in oven- or flame-dried flasks under a dry nitrogen atmosphere. Tetrahydrofuran (THF) and ether were freshly distilled from benzophenone ketyl. Solvent grade dichloromethane was distilled. Hexamethylphosphoric triamide (HMPA) was distilled from CaH_2 at reduced pressure and stored under nitrogen over molecular sieves.

Phenyllithium (halide free),[1f] tetramethylstannane,[37a] bromotrimethylstannane,[37b] bromodiphenylmethylstannane,[37c] and dichlorodimethylstannane[38] were synthesized using known procedures.

Commercial methyllithium (as a complex with lithium bromide or low halide content) and *n*-butyllithium (halide free) were used. Lithium reagents were titrated with *n*-PrOH (or *i*-PrOH) in THF or ether using 1,10-phenanthroline as an indicator.[39]

Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker AM-500, AC-300, WP-270, or WP-200 spectrometer. Spectra were referenced to Me_4Si or the residual solvent peak ($CHCl_3$ = 7.26 ppm). IR spectra were obtained on a Beckman Acculab 7, IR 4230, or Mattson Polaris FT-IR spectrometer and mass spectra (MS) were obtained on an AEI MS-902 or Kratos MS-80 spectrometer. Elemental analysis was performed by Galbraith Laboratories. Bath temperatures are reported for Kugelrohr distillations. Melting and boiling points are uncorrected. Short column chromatography refers to rapid elution of the compound mixture through a column of SiO_2 (60−200 mesh).

GC analysis was performed on a Varian 3700 gas chromatograph with a flame ionization detector. The column was a Varian BP1−0.5 bonded phase vitreous silica capillary column 25 m in length, 0.33 mm bore, with a bonded phase of dimethylsiloxane. Relative response factors (RRF) were calculated as molar amount/GC peak area using PhBr or 4-bromo-*tert*-butylbenzene having RRF = 1.00.

Caution: Organoselenium (*Stench!*) and organotin compounds are toxic and should be handled with due care. Organotin and organoselenium compounds were rotary evaporated and otherwise handled in hoods with the user wearing gloves. Adequate precautions must be taken to avoid all forms of exposure to HMPA.

General Procedure for the Synthesis of Propargyl Alcohols. 5-Methyl-3-hexyn-2-ol (1P-OH).[40] *n*-Butyllithium (33.8 mL, 2.12 M in hexane, 71.6 mmol) was added to a solution of 3-methyl-1-butyne (8.0 mL, 78 mmol) at 0 °C in THF (100 mL) in a 250-mL, oven-dried, N_2-purged flask equipped with a magnetic stir bar and septum. After 20 min the bright yellow solution was cooled to −78 °C and acetaldehyde (4.15 mL, 74.3 mmol) was added by a cooled syringe. The solution was stirred an additional 20 min at −78 °C and, following slight warming, quenched with 5 mL of glacial acetic acid. The contents were diluted in ether (150 mL), washed with saturated $NaHCO_3$ (2 × 50 mL), and dried through a cone of $NaSO_4$. The solvent was removed by rotary evaporation to give **1P-OH** as a light yellow liquid (7.14 g, 63.6 mmol, 89% yield). The compound was generally used without further purification; however, it did readily distill at 57−60 °C at 37 mm Hg. ^1H NMR: ($CDCl_3$, 270 MHz) δ 1.14 (d, J = 6.9 Hz, 6H), 1.40 (d, J = 6.6 Hz, 3H), 1.7 (br s, 1H), 2.55 (sept d, J = 6.9, 1.7 Hz, 1H), 4.49 (qd, J = 6.5, 1.7 Hz, 1H); ^{13}C NMR (C_6D_6, 68 MHz) δ 20.7 (CH), 23.1 (CH_3), 25.0 (CH_3), 58.3 (CH), 82.6 (C), 89.3 (C); IR (neat) 3350 (OH), 2970, 2865, 2240 cm^{-1}; MS $(M - H)^+$ = 111.0816[44] (calcd for $C_7H_{12}O - H$ = 111.0807).

General Procedure for the Synthesis of Methanesulfonate Esters. Synthesis of 5-Methylhex-3-yn-2-ol Methanesulfonate Ester (1P-OMs).[41] Methanesulfonyl chloride (5.42 mL, 70.0 mmol) was added dropwise to a solution of alcohol **1P-OH** (7.14 g, 63.6 mmol) and triethylamine (13.3 mL, 95.5 mmol) at 0 °C in dichloromethane (250 mL). After 15 min the solution was transferred cold to a separatory funnel and washed with ice water (50 mL), 1% cold HCl (50 mL), saturated $NaHCO_3$ (50 mL), and brine (50 mL) and dried through a cone of $NaSO_4$. The solvent was removed by rotary evaporation resulting in 10.8 g (56.7 mmol, 89% yield) of **1P-OMs** which was used without further purification. ^1H NMR ($CDCl_3$, 200 MHz) δ 1.11 (d, J = 6.5 Hz, 6H), 1.54 (d, J = 6.5 Hz, 3H), 2.55 (sept d, J = 6.5, 2 Hz, 1H), 3.05 (s, 3H), 5.21 (qd, J = 6.5, 2 Hz, 1H).

General Procedure for the Synthesis of Propargyl Selenides. Synthesis of 5-Methyl-2-(methylseleno)-3-hexyne (1P-Se).[42] MeLi (47.2 mL, 1.5 M, 70.8 mmol) was added to a magnetically stirred suspension of gray selenium powder (5.59 g, 70.8 mmol) in THF (110 mL) at 0 °C in an oven-dried, N_2-purged, 250-mL flask outfitted with a septum. The solution developed a deep red color and turned colorless at the end point of the MeLi addition. After 20 min a solution of **1P-OMs** (10.8 g, 56.6 mmol) in absolute ethanol (35 mL) was added by cannula. The resulting orange solution was stirred at 0 °C for 20 min and chloroacetic acid in EtOH (about 1 equiv) was added to facilitate removal of excess methaneselenolate. The contents of the flask were diluted in 1:1 ether/hexane (150 mL) and washed with water (50 mL), NaOH (3 M, 20 mL), saturated $NaHSO_4$ (50 mL), and brine (50 mL) and dried through $NaSO_4$. Solvent removal by rotary evaporation followed by short column chromatography (2% ether in hexane) gave 6.86 g (36.3 mmol, 64% yield) of **1P-Se** as a light yellow liquid. bp: 56−59 °C at 4.5 mmHg; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.14 (d, J = 6.9 Hz, 6H), 1.55 (d, J = 5.8 Hz, 3H), 2.11 (S, J_{Se-H} = 10.4 Hz, 3H), 2.57 (sept d, J = 6.9, 2 Hz, 1H), 3.63 (qd, J = 6.9, 2 Hz, 1H); ^{13}C NMR (C_6D_6, 15 MHz) δ 4.2 (CH_3), 20.9 (CH_3), 21.3 (CH_3), 23.5 (CH), 23.8 (CH), 81.3 (C), 89.5 (C); IR (neat) 2237, 2225 cm^{-1}; MS M^+ = 190.0261 (calcd for $C_8H_{14}Se$ = 190.0257).

Magnesium Dibromide Etherate.[43] Magnesium turnings (2.45 g, 101 mmol) and ether (90 mL) were added to an oven-dried 250-mL 3-necked flask equipped with a magnetic stir bar, addition funnel, and reflux condenser and the flask was purged with nitrogen. 1,2-

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Dibromomethane (8.69 mL) was added dropwise (exothermic reaction). The solution was refluxed for 2.5 h, and the contents transferred by cannula to a dry, stoppered, 250-mL flask containing 100 mL of benzene (dried through silica gel) and used as a 0.5 M solution.

General Procedure for the Synthesis of Propargylstannanes. 5-Methyl-2-(trimethylstannyl)-3-hexyne (1P-Sn). Selenide **1P-Se** (1.69 mL, 10.0 mmol) was added to a solution of MeLi·LiBr (6.8 mL, 1.5 M, 10 mmol) in THF (100 mL) at 0 °C. The bright yellow solution was stirred 20 min at 0 °C. Magnesium dibromide etherate (40 mL, 0.5 M, 20 mmol) was added and the solution was warmed to room temperature for 30 min. Me_3SnBr (1.28 mL, 11 mmol) was added using a heated syringe and the solution was stirred 45 min at room temperature. The contents were diluted in ether/hexane (100 mL), washed with water (3 × 20 mL) and brine (20 mL), and dried through $NaSO_4$. Removal of solvent resulted in the recovery of **1P-Sn** as a light yellow liquid (2.03 g, 7.82 mmol, 78% yield) in 95% isomeric purity. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.12 (s, J_{Sn-H} = 153.2, 150.9 Hz, 9H), 1.11 (d, J = 6.8 Hz, 6H), 1.28 (d, J = 7.3 Hz, 3H), 1.88 (qd, J = 7.4, 2.3 Hz, 3H), 1.88 (qd, J = 7.4, 2.3 Hz, 1H), 2.52 (sept d, J = 6.7, 2.4 Hz, 1H); ^{13}C NMR (C_6D_6, 68 MHz) δ −10.8 (J_{Sn-C} = 326.3, 312.5 Hz CH_3), 7.9 (J_{Sn-C} = 335, 320 Hz, CH), 18.2 (CH_3), 21.3 (CH_3), 24.2 (CH), 84.7 (C), 85.3 (C); IR (neat) 2220 cm^{-1}; MS M^+ = 258.0601 (calcd for $C_{10}H_{20}Sn$ = 258.0586). Anal. Calcd for $C_{10}H_{20}Sn$: C, 46.38; H, 7.78. Found: C, 46.36; H, 7.95.

Dimethyldiphenylstannane. To an oven-dried, N_2-purged, 250-mL round bottom flask equipped with a stir bar and reflux condenser were added Mg^0 (3.25 g, 134 mmol) and Et_2O (50 mL). A solution of PhBr (13.65 mL, 130 mmol) in Et_2O (75 mL) was added slowly via cannula, and the reaction mixture was allowed to stir for 2 h. The phenyl Grignard was transferred via cannula to another dried, purged, 250-mL round-bottom flask equipped with a stir bar and reflux condenser. Dichlorodimethylstannane[38] (7.7 g, 35 mmol) was dissolved in Et_2O (10 mL) and THF (20 mL) and was transferred to the Grignard reagent via cannula. A reaction was immediately evident by the formation of the Grignard salt. After refluxing for 4 h, the reaction was cooled to 0 °C and 15 mL of a saturated NH_4Cl solution was added. The contents were transferred to a separatory funnel containing 1:1 ether/hexane (150 mL), and the organic layer was washed with H_2O (3 × 75 mL) and brine (75 mL). The organic layer was dried over Na_2SO_4, and the solvents were removed by rotary evaporation. The compound was passed through a plug of silica gel using pentane as the eluent, and the pentane was removed by rotary evaporation, yielding 10.2 g (33.7 mmol, 96%) of a fluorescent, yellow-green liquid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.50 (s, 6H, $^2J_{Sn-H}$ = 56.0, 53.3 Hz), 7.3−7.6 (m, 10H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ −10.1 (Sn−Me, J_{Sn-C} = 365.6, 348.4 Hz), 128.3 (J_{Sn-C} = 48.3 Hz), 128.6 (J_{Sn-C} = 10.2 Hz), 136.2 (J_{Sn-C} = 36.2 Hz), 140.7 (quat).

Bromodimethylphenylstannane. Dimethyldiphenylstannane (5.58 g, 17.7 mmol) in 125 mL of MeOH was added to a 500-mL round-bottom flask equipped with a stir bar and a 125-mL addition funnel. The flask was cooled to −40 °C using a dry ice/ethanol bath. A solution of Br_2 (0.91 mL, 17.7 mmol) in CH_3Cl (100 mL) was added dropwise via the addition funnel over the course of 1 h. The reaction mixture was allowed to stir at −40 °C for an additional 30 min. Solvents were removed by rotary evaporation, and the product was isolated by Kugelrohr distillation (0.09 mmHg: PhBr distilled at ambient temperature, and the product distilled at 50−55 °C). Distillation afforded 5.20 g (17.0 mmol, 96%) of a clear, colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.92 (s, 6H, $^2J_{Sn-H}$ = 58.7, 56.1 Hz), 7.3−7.7 (m, 5H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ −2.1 (Sn−Me, J_{Sn-C} = 384.0, 367.5 Hz), 128.8 (J_{Sn-C} = 59.1 Hz), 130.0 (J_{Sn-C} = 12.1 Hz), 135.1 (J_{Sn-C} = 49.0 Hz), 139.9 (quat).

2-(Dimethylphenylstannyl)-5-methyl-3-hexyne (1P-SnPh). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.34 (s, J_{Sn-H} = 56.2, 53.6 Hz, 3H), 0.35 (s, J_{Sn-H} = 56.2, 53.6 Hz, 3H), 1.10 (d, J = 6.8 Hz, 6H), 1.32 (d, J = 7.3 Hz, 3H), 2.10 (qd, J = 7.3, 2.3 Hz, 1H), 2.52 (sept d, J = 6.8, 2.3 Hz, 1H), 7.20−7.35 (m, 3H), 7.48−7.53 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$), δ −11.6, −11.3, 8.4, 18.1, 20.8, 23.6, 84.2, 85.6, 128.1, 128.5, 136.2, 140.8; IR (neat) 2220 cm^{-1}.

2-(Diphenylmethylstannyl)-5-methyl-3-hexyne (1P-SnPh$_2$). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.56 (s, J_{Sn-H} = 56.2, 53.6 Hz, 3H), 1.08 (d, J = 6.8 Hz, 6H), 1.41 (d, J = 7.3 Hz, 3H), 2.37 (qd, J = 7.3, 2.3 Hz, 1H), 2.52 (sept d, J = 6.8, 2.3 Hz, 1H), 7.33−7.45 (m, 6H), 7.50−7.60 (m, 4H); ^{13}C NMR: (68 MHz, $CDCl_3$) δ −11.9, 9.2, 18.4, 20.8, 23.6, 83.9, 86.1, 128.2, 128.8, 137.0, 139.3; IR: (neat) 2210 cm^{-1}.

5-Methyl-2-(triphenylstannyl)-3-hexyne (1P-SnPh$_3$). ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.02 (d, J = 6.8 Hz, 6H), 1.52 (d, J = 7.3 Hz, J_{Sn-H} = 70.9, 67.8 Hz, 3H), 2.48 (sept d, J = 6.9, 2.2 Hz, 1H), 2.63 (q d, J = 7.3, 2.3 Hz, 1H), 7.36 (m, 9H), 7.61 (m, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 10.3 (J_{Sn-C} = 375, 362.5 Hz), 18.9 (J_{Sn-C} = 32.8 Hz), 21.3, 23.7, 84.1, 87.0, 128.5, 128.9 (J_{Sn-C} = 30 Hz), 129.4, 137.7 (J_{Sn-C} = 34.2 Hz), 138.4 (J_{Sn-C} = 490, 469 Hz); IR (neat) 2205 cm^{-1}.

General Procedure for the Synthesis of Allenylstannanes. Synthesis of 5-Methyl-4-(trimethylstannyl)-2,3-hexadiene (1A-Sn). Selenide **1P-Se** (2.33 g, 12.3 mmol) in THF (30 mL) was added to a 0 °C solution of MeLi (8.4 mL, 1.5 M, 12.6 mmol) in THF (30 mL). The dark orange solution was stirred at 0 °C for 20 min then cooled to −78 °C. A −78 °C solution of Me_3SnBr (1.36 mL, 11.7 mmol) in 20 mL of THF was added to the allenyllithium reagent by cannula. The solution was stirred for 15 min, allowed to warm to room temperature, and stirred 45 min. The contents of the flask were diluted in 150 mL of 1:1 Et_2O/hexane, washed with H_2O (3 × 35 mL) and 35 mL of brine, and dried through Na_2SO_4. Removal of solvent by rotary evaporation gave a clear yellow liquid (9.57 g crude). Vacuum distillation (75−77 °C at 6−7 mmHg) gave a clear, colorless liquid of **1A-Sn**, yield 1.63 g (6.31 mmol, 54%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.16 (s, J_{Sn-H} = 55.0, 51.9 Hz, 9H), 1.02 (d, J = 6.7 Hz, 3H), 1.03 (d, J = 6.7 Hz, 3H), 1.61 (d, J = 6.8 Hz, J_{Sn-H} = 24.2 Hz, 3H), 2.36 (sept d, J = 6.7, 2.4 Hz, 1H), 4.66 (qd, J = 6.8, 2.4 Hz, 1H); ^{13}C NMR (C_6D_6, 68 MHz) δ −8.4 (J_{Sn-C} = 358, 342 Hz, CH_3), 14.8 (CH_3), 23.98 (CH_3), 32.2 (CH), 78.6 (J_{Sn-C} = 56 Hz, CH), 101.8 (C), 202.3 (C); IR (neat) 1980 cm^{-1}; MS M^+ = 258.0560 (calcd for $C_{10}H_{20}Sn$ 258.0586). Anal. Calcd for $C_{10}H_{20}Sn$: C, 46.38; H, 7.78. Found: C, 46.05; H, 7.91.

3-(Dimethylphenylstannyl)-2-methyl-3,4-hexadiene (1A-SnPh). The general procedure was followed using **1P-Se** (1.09 g, 5.78 mmol), MeLi (3.85 mL, 1.50 M, 5.78 mmol), $Me_2PhSnBr$ (1.68 g, 5.49 mmol), and 40 mL of THF. The product was obtained in a quantitative crude yield and purified using flash chromatography (hexane, 1% triethylamine). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.38 (s, J_{Sn-H} = 55.4, 53.1 Hz, 6H), 1.01 (d, J = 6.7 Hz, 3H), 1.02 (d, J = 6.7 Hz, 3H), 1.63 (d, J = 6.8 Hz, J_{Sn-H} = 26.5 Hz, 3H), 2.37 (sept d, J = 6.7, 2.4 Hz, 1H), 4.74 (qd, J = 6.8, 2.4 Hz, 1H), 7.3−7.4 (m, 3H), 7.49−7.52 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ −9.06 ($SnCH_3$), 14.55 (CH_3, C^6), 23.69 (CH_3, C^1), 23.79 (CH_3, $C^{1\prime}$), 31.78 (CH, C^2), 78.82 (CH, C^5), 128.1, 128.3, 130.0, 136.0 (the signal-to-noise was insufficient to see the two quaternary carbons).

3-(Diphenylmethylstannyl)-2-methyl-3,4-hexadiene (1A-SnPh$_2$). The general procedure was followed using selenide **1P-Se** (0.535 g, 2.83 mmol) in 7 mL of THF and MeLi (1.9 mL, 1.5 M, 2.85 mmol) in 7 mL of THF. The orange solution was stirred at 0 °C for 20 min then cooled to −78 °C. $Ph_2MeSnBr$, dissolved in 10 mL of THF at −78 °C, was added by cannula and the mixture stirred for 20 min then warmed to room temperature for 45 min. The yield of the crude product was 0.796 g (2.08 mmol, 78% yield). Further purification was accomplished by running the compound through a plug of silica gel (pentane as eluent) and HPLC purification (MeOH as eluent). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.55 (s J_{Sn-H} = 55.3, 52.9 Hz, 3H), 1.00 (d, J = 6.7 Hz, 3H), 1.01 (d, J = 6.7 Hz, 3H), 1.57 (d, J = 6.9 Hz, 3H), 2.38 (sept d, J = 6.7, 2.4 Hz, 1H), 4.75 (qd, J = 6.9, 2.4 Hz, 1H), 7.3−7.65 (m, 10H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.50 (CH_3), 26.63 (CH_3), 31.83 (CH), 79.64 (CH), 100.49 (C), 203.56 (C). IR (neat) 1934 cm^{-1}.

2-Methyl-3-(triphenylstannyl)-3,4-hexadiene (1A-SnPh$_3$). To a 50-mL round-bottom flask purged with N_2 and equipped with a rubber septum and magnetic stir bar was added 20 mL of THF. The flask was cooled to −78 °C, 1-pentyne (0.099 mL, 1 mmol) and MeLi (0.56 mL, 1.26 M, 0.7 mmol) were added, the solution was stirred at −78 °C for 2−3 min, and HMPA (0.696 mL, 4.0 mmol) was added. A solution of **1P-SnPh$_3$** (0.65 g, 1.46 mmol) in 10 mL of THF at −78

(44) The parent ions were not observed for the propargyl alcohols. The $(M - H)^+$ ion for 5-methyl-3-hexyn-2-ol has been reported: Fleming, I.; Takaki, K.; Thomas, A. P. *J. Chem. Soc., Perkin Trans. I* **1987**, 2269.

Table 3. Trapping Studies in THF

	S.M.[c] **1**	RLi	I/S[b]	**1-Si A/P**	yield	**1-Sn A/P**	recovery
1	**A-Sn**	MeLi	I	39/61	85		85
2	**P-Sn**	MeLi	I	14/86	94		94
3	**A-Sn**	MeLi	S	2/98	82		82
4	**P-Sn**	MeLi	S	2/98	99		99
5	**A-Sn**	PhLi	I	27/73	70	90/10	80
6	**P-Sn**	PhLi	I	28/72	81	30/70	*a*
7	**A-SnPh**	MeLi	I	30/70	89	*a*	*a*
8	**P-SnPh**	MeLi	I	26/74	107	*a*	*a*
9	**A-SnPh**	PhLi	I	7/93	25	*a*	*a*
10	**P-SnPh**	PhLi	I	8/92	36	*a*	*a*
11	**A-SnPh$_2$**	MeLi	I	9/91	79	*a*	*a*
12	**P-SnPh$_2$**	MeLi	I	9/91	108	*a*	*a*
13	**A-SnPh$_2$**	PhLi	I	4/96	22	*a*	*a*
14	**P-SnPh$_2$**	PhLi	I	4/96	18	*a*	*a*
15	**A-SnPh$_3$**	MeLi	I	3/97	52	*a*	*a*
16	**P-SnPh$_3$**	PhLi	I	2/98	90	*a*	*a*

[a] Starting material does not come off GC at operating temperature. [b] I = *in situ*, S = sequential. [c] S.M. = starting material.

°C was added by cannula to the acetylide solution. The pale orange solution was allowed to stir for 30 min at −78 °C and NH_4OAc (3 mL, 1 M in MeOH, 3 mmol) was added. The solution was poured into a separatory funnel containing 40 mL of 1:1 Et_2O/pentane and the organic layer washed with 3 × 15 mL of H_2O and dried by passing through a cone of Na_2SO_4. The solvent was removed by rotary evaporator to give a yellow oil. Short column chromatography through SiO_2 using pentane as eluent gave 0.323 g (50%) of **1A-SnPh$_3$** as a light yellow oil of ≈95% isomeric purity. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.02 (d, J = 6.7 Hz, 3H), 1.03 (d, J = 6.7 Hz, 3H), 1.56 (d, J = 7.1 Hz, J_{Sn-H} = 28 Hz, 3H), 2.42 (sept d, J = 6.7, 2.4 Hz, 1H), 4.78 (qd, J = 6.9, 2.3 Hz, J_{Sn-H} = 45 Hz, 1H), 7.35 (m, 9H), 7.57 (m, 6H); ^{13}C NMR (68 MHz, C_6D_6) δ 14.5, 23.8, 23.9, 32.4, 80.8, 100.6, 128.9, 129.3, 137.5 (J_{Sn-C} = 34.6 Hz), 139.4, 204.8; IR (neat) 1940 cm^{-1}.

Standard Procedure for *in Situ* Single- and Double-Trap Reactions. To an oven-dried, nitrogen-purged, 5 mL long neck round-bottom flask equipped with a magnetic stir bar was added freshly distilled THF (1.5 mL), stannane (0.1 mmol), chlorosilane(s) (0.3 mmol), and HMPA (0−1 mmol). The flask was immersed in a dry ice−ethanol bath to the level of the septum while under positive nitrogen pressure. The nitrogen line was removed and 1.0 to 1.2 mmol of MeLi (≈0.05 M LiBr) or phenyllithium (halide free) was added. The solution was stirred for 10 min at −78 °C then 150 μL of 30% KOH solution was added and the dry ice bath was removed. Upon warming, pentane (3−4 mL), the GC standard, and Na_2SO_4 were added. Analytical GC analysis was performed without any further workup. Under some conditions, particularly those involving HMPA, 4 mL of water was added and analysis was done on the pentane layer without removing the septum. The results are summarized in Tables 3, 5, and 6.

Standard Procedure for Sequential Single-Trap Reactions with Silanes. To an oven-dried, nitrogen-purged, 5-mL long neck round-bottom flask equipped with a magnetic stir bar was added THF (1.5 mL), stannane (0.1 mmol), and HMPA (0−1 mmol). The flask was immersed in a dry ice−ethanol bath to the level of the septum while under positive nitrogen pressure. The nitrogen line was removed and MeLi (low halide content, ~0.05 M) or phenyllithium (halide free) was added by syringe followed 10 to 15 s later by Me_3SiCl (0.3 mmol). The solution was stirred for 10 min at −78 °C then 150 μL of 30% KOH solution was added and the dry ice bath was removed. Upon warming, pentane (3−4 mL), the GC standard, and Na_2SO_4 were added. Analytical GC analysis was performed without any further workup. Under some conditions, particularly those involving HMPA, 4 mL of water was added followed by analysis on the pentane layer without removing the septum. The results are summarized in Tables 3 and 4.

Standard Procedure for Sequential Double-Trap Reaction with Silanes. Note: Sequential double-trapping experiments are intrinsically prone to mixing problems; to circumvent this the allenyllithium reagent was added to the electrophile under inverse conditions. THF was added to two oven-dried, nitrogen-purged flasks, a 5-mL conical flask (0.5 mL of THF), and a 5-mL round-bottom flask (1.0 mL of THF) with stir bar and septa. Me_3SiCl (38.0 μL, 0.3 mmol) and isopropyldimethylchlorosilane (47.2 μL, 0.3 mmol) were added to the round-bottom flask and the stannane added to the conical flask. Both flasks were submerged in dry ice−ethanol baths while under positive nitrogen pressure. MeLi was added to the stannane in the conical flask and it was swirled by hand or mixed using the stir bar. The contents of the conical flask were transferred to the round-bottom flask via a jacketed syringe at −78 °C. Caution: This must be performed in a glovebag under nitrogen in humid weather or the syringe barrel will freeze when it is opened. The inverse addition of the lithium reagent could alternatively be accomplished using a cannula in which the receiving end was coiled under the THF solution to ensure the lithium reagent was at −78 °C when it reached the electrophile. The workup after 10 min of stirring at −78 °C followed that of the *in situ* reactions. The results are summarized in Table 6.

Table 4. Sequential Trapping Studies in THF/HMPA

	S.M.[b] **1**	HMPA equiv	**1-Si (A/P)**	yield **1-Si**	recovery **Si**[a]
1	**A-Sn**	0	2/98	82	82
2	**A-Sn**	2.0	5/95	77	80
3	**A-Sn**	3.0	15/85	85	88
4	**A-Sn**	4.0	22/78	83	87
5	**A-Sn**	5.0	31/69	76	87
6	**P-Sn**	0.0	2/98	92	93
7	**P-Sn**	2.0	4/96	78	78
8	**P-Sn**	3.0	8/92	88	90
9	**P-Sn**	4.0	22/78	82	84
10	**P-Sn**	5.0	48/52	79	81
11	**A+P-Sn**	2.0	4/96	85	85
12	**A+P-Sn**	3.0	8/92	87	89
13	**A+P-Sn**	4.0	19/81	79	83
14	**A+P-Sn**	5.0	34/66	73	78
15	**P-Se**	4.0	16/84	73	79
16	**P-Se**	6.0	28/72	48	79

[a] Yield of **1A-Si** + **1P-Si** + **13A-Si** + **14A-Si$_2$**. [b] S.M. = starting material.

Table 5. *In Situ* Trapping Studies in THF/HMPA

	S.M.[c] **1**	HMPA equiv	**1-Si (A/P)**	yield **1-Si**	recovery **Si**[a]
1	**A-Sn**	0	39/61	85	85
2	**A-Sn**	0.1	56/44	88	88
3	**A-Sn**	0.5	74/26	75	76
4	**A-Sn**	1.0	81/19	65	66
5	**A-Sn**	1.5	81/19	69	70
6	**A-Sn**	2.0	81/19	77	79
7	**A-Sn**	3.0	81/19	89	89
8	**A-Sn**	5.0	85/15	95	99
9	**A-Sn**	10.0	85/15	33	65[b]
10	**P-Sn**	0.0	14/86	94	94
11	**P-Sn**	0.1	23/77	80	81
12	**P-Sn**	0.5	50/50	73	74
13	**P-Sn**	1.0	63/37	81	82
14	**P-Sn**	2.0	79/21	59	59
15	**P-Sn**	3.0	81/19	80	82

[a] Yield of **1A-Si** + **1P-Si** + **13A-Si**. [b] **1A-Si** + **1P-Si** + **13A-Si** + **1A-Sn**. [c] S.M. = starting material.

General Procedure for Calculation of Relative Response Factors. An *in situ* single-trap reaction was run using the stannane of choice with either trimethylchlorosilane or isopropyldimethylchlorosilane as described above. The solutions were diluted in 15 mL of ether/pentane, washed with water (3 × 20 mL) and brine (20 mL), and dried through Na_2SO_4. Solvent was removed by rotary evaporation. The compound was dissolved in $CDCl_3$ and GC standard added. High-resolution ^{1}H NMR analysis (270 MHz, 16−340 scans, recycle delay 10 s) was immediately followed by analytical GC analysis. The relative response factor (RRF) was calculated from the relative concentration of (standard/**1A-Si**) in the ^{1}H NMR spectrum multiplied by the GC areas of (**1A-Si**/standard). Results: bromobenzene ≡ 1.00, **1A-Si**, **1P-Si** = 1.60, **1A-SiPr**, **1P-SiPr** = 1.84, **1A-Sn**, **1P-Sn** = 1.75; 4-*tert*-butylbromobenzene ≡ 1.00, **2-Si** = 0.93, **3-Si** = 1.35, **3-SiPr** = 1.35, **4-Si** = 1.31, **4-SiPr** = 1.56.

Table 6. Double-Trapping Studies

	1	RLi	I/S[d]	HMPA equiv	A/P	1A-Si/SiPr	1P-Si/SiPr	yield	recovery
1	**A-Sn**	MeLi	I	0	48/52	58/42	93/7	84	84
2	**P-Sn**	MeLi	I	0	16/84	55/45	92/8	54	54
3	**A-Sn**	MeLi	S	0	2/98	62/38	88/12	83	83[c]
4	**P-Sn**	MeLi	S	0	*a*	*a*	91/9		
5	**A-Sn**	PhLi	I	0	36/64	55/45	91/9	38	86
6	**A-SnPh**	MeLi	I	0	36/64	56/44	91/9	26	*b*
7	**P-Sn**	PhLi	I	0	38/62	56/44	91/9	43	61
8	**P-SnPh**	MeLi	I	0	34/66	61/39	93/7	83	*b*
9	**P-SnPh**[3]	PhLi	I	0	>2/98		91/9	38	*b*
10	**P-SnPh**[3]	PhLi	S	0	>2/98		91/9	42	*b, c*
11	**A-Sn**	MeLi	I	2.0	88/12	56/44	82/18	48	69
12	**P-Sn**	MeLi	I	2.0	79/21	57/43	84/16	58	64
13	**A-Sn**	MeLi	S	2.0	13/87	54/46	82/18	32	*c*

[a] Peak interference prevented analysis. [b] Starting material does not come off GC at operating temperature. [c] Sequential technique does not allow proper determination. [d] I = *in situ*, S = sequential.

Isolation and Characterization of 3-(Trimethylsilyl)-2-methyl-3,4-hexadiene (1A-Si) and 2-(Trimethylsilyl)-5-methyl-3-hexyne (1P-Si). Using a scaled-up version of the general *in situ* exchange of **1A-Sn** in THF (above), **1P-Si** and **1A-Si** were prepared from **1A-Sn** (0.114 mL, 0.5 mmol), MeLi (0.476 mL, 1.26 M, 0.6 mmol), TMSCl (0.191 mL, 1.5 mmol), and 7.5 mL of THF. After the reaction mixture had stirred at −78 °C for 10 min, the solution was poured into a separatory funnel containing 20 mL of a 1:1 mix of Et_2O/pentane. The organic layer was washed with 2 × 20 mL of 10% aqueous KOH and 3 × 20 mL of H_2O and dried by passing through a cone of Na_2SO_4. Removal of the solvent by rotary evaporator (cold water bath) gave a pale yellow liquid. Preparatory reverse-phase HPLC on a 21 mm × 25 cm Altex Ultrapshere-ODS column using MeCN as eluent with a flow rate of 8 mL/min gave a fraction at t = 16.8 min which contained **1P-Si** and a fraction at t = 21.5 min which contained **1A-Si**. Each fraction was separately placed into a separatory funnel containing 20 mL of pentane, the contents swirled, and the pentane layer (top layer) separated. The pentane layer was washed with 2 × 10 mL of H_2O and dried by passing through a cone of Na_2SO_4. Removal of the solvent by rotary evaporator (cold water bath) gave 29 mg (35%) of **1P-Si** as a clear colorless liquid and 25 mg (30%) of **1A-Si** as a clear colorless liquid.

Spectral data for 1A-Si: GC RT = 3.33 min at 120 °C; ^{1}H NMR ($CDCl_3$, 200.13 MHz) δ 0.06 (s, 9H), 0.98 (d, J = 6.8 Hz, 3H), 1.00 (d, J = 6.8 Hz, 3H), 1.58 (d, J = 7.0, 3H), 2.18 (sept d, J = 7.0, 2.0 Hz, 1H), 4.78 (qd, J = 6.8, 2.0 Hz, 1H); ^{13}C NMR (C_6D_6, 125.13 MHz) δ −8.4 ($SiCH_3$), 14.1 (CH_3), 23.8 and 24.0 (*i*-Pr CH_3), 29.2 (*i*-Pr C), 81.8 (C_P), 103.5 (C_A), 206.1 (C_C); IR (neat) 1930 cm^{-1}; MS M$^+$ = 168.1338 (calcd for $C_{10}H_{20}Si$ = 168.1329).

Spectral data for 1P-Si: GC RT = 3.46 min at 120 °C; ^{1}H NMR ($CDCl_3$, 200.13 MHz) δ 0.03 (s, 9H), 1.09 (d, J = 7.3 Hz, 3H), 1.10 (d, J = 6.8 Hz, 6H), 1.59 (qd, J = 6.8, 2.2 Hz, 1H), 2.50 (sept d, J = 7.3, 2.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ −3.5, 13.3, 15.4, 21.2, 24.0, 82.8, 85.9; IR (neat) 2220 cm^{-1}; MS M$^+$ = 168.1338 (calcd for $C_{10}H_{20}Si$ = 168.1329).

Isolation and Characterization of 3-(Dimethylisopropylsilyl)-2-methyl-3,4-hexadiene (1A-SiPr) and 2-(Dimethylisopropylsilyl)-5-methyl-3-hexyne (1P-SiPr). Using a scaled-up version of the general *in situ* exchange of **1A-Sn** in THF (above), **1A-SiPr** and **1P-SiPr** were prepared from **1A-Sn** (0.114 mL, 0.5 mmol), MeLi (0.476 mL, 1.26 M, 0.6 mmol), *i*PrMe$_2$SiCl (0.235 mL, 1.5 mmol), and 7.5 mL of THF. After the reaction mixture had stirred at −78 °C for 10 min, the solution was poured into a separatory funnel containing 20 mL of 1:1 Et_2O/pentane. The organic layer was washed with 2 × 20 mL of 10% aqueous KOH and 3 × 20 mL of H_2O and dried by passing through a cone of Na_2SO_4. Removal of the solvent by rotary evaporator (cold water bath) gave a yellow liquid. Preparatory reverse-phase HPLC on a 21 mm × 25 cm Altex Ultrasphere-ODS column using MeCN as eluent with a flow rate of 8 mL/min gave a fraction at t = 22.0 min which contained **1P-SiPr** and a fraction at t = 29.0 min which contained **1A-SiPr**. Each fraction was separately placed into a separatory funnel containing 20 mL of pentane, the contents swirled, and the pentane layer (top layer) separated. The pentane layer was washed with 2 × 10 mL of H_2O and dried by passing through a cone of Na_2SO_4. Removal of the solvent by rotary evaporator (cold water bath) gave 24 mg (24%) of **1P-SiPr** as a clear colorless liquid and 25 mg (25%) of **1A-SiPr** as a clear colorless liquid.

Spectral data for 1A-SiPr: GC RT = 6.01 min at 120 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.00 (s, 3H), 0.01 (s, 3H), 0.88 (m, 1H), 0.93 (d, J = 5.3 Hz, 6H), 0.98 (d, J = 6.8 Hz, 3H), 1.00 (d, J = 6.8 Hz, 3H), 1.58 (d, J = 6.8, 3H), 2.12 (sept d, J = 6.8, 1.2 Hz, 1H), 4.76 (qd, J = 6.8, 1.3 Hz, 1H); ^{13}C NMR (C_6D_6, 125.13 MHz) δ −4.81 and −4.75 ($SiCH_3$), 14.1 (CH_3), 17.9 (Si*i*-Pr), 23.8 and 24.1 (*i*-Pr CH_3), 29.3 (*i*-Pr C), 81.8 (C_P), 101.7 (C_A), 206.5 (C_C); IR (neat) 1940 cm^{-1}; MS M$^+$ = 196.1656 (calcd for $C_{12}H_{24}Si$ = 196.1647).

Spectral data for 1A-SiPr: GC RT = 6.51 min at 120 °C; ^{1}H NMR ($CDCl_3$, 200.13 MHz) δ −0.04 (s, 3H), −0.01 (s, 3H), 0.01 (s, 6H), 0.88 (m, 1H), 0.96 (br d, J = 3 Hz, 6H), 1.10 (d, J = 7.3 Hz, 6H), 1.68 (qd, J = 7.3, 2.3 Hz, 1H); 2.50 (sept d, J = 6.8, 2.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ −7.2, 11.2, 12.7, 15.7, 17.9, 18.1, 21.2, 24.0, 83.0, 85.9; IR (neat) 2280 cm^{-1}.

Isolation and Characterization of the Prototropic Isomerized Trimethylsilane 13A-Si and the Bis(trimethylsilyl) Allene 14A-Si$_2$. The combined product mixtures of three sequential HMPA reactions were washed with water (3 × 15 mL) and brine (15 mL) and dried through Na_2SO_4. Some pentane was removed by rotary evaporation, and the resultant liquid was subjected to preparatory GC analysis (oven temperature = 110 °C). The compounds **1A-Si**, **1P-Si**, and **13A-Si** were collected in an ice-cooled collection vial (RT 3.0−3.5 min) followed by **14A-Si$_2$** (RT 10 min). A homonuclear decoupled ^{1}H NMR experiment was used to make an unambiguous assignment for **13A-Si** in the mixture of the three isomers. Product **14A-Si$_2$** was obtained pure.

Spectral data for 13A-Si: GC RT = 3.54 min at 120 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.05 (s, 9H), 0.96 (d, J = 6.5 Hz, 6H), 1.66 (d, J = 3.0, 3H), 2.21 (sept d, J = 6.5, 5.3 Hz, 1H), 4.77 (dq, J = 5.3, 3.0 Hz, 1H).

Spectral data for 14A-Si$_2$: GC RT = 7.77 min at 120 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.06 (s) and 0.06 (s) (both integrated together for 18H), 1.00 (d, J = 6.7 Hz, 3H), 1.01 (d, J = 6.7 Hz, 3H), 1.62 (s, 3H), 2.14 (sept, J = 6.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.93 MHz) δ −6.25 ($SiCH_3$), −5.29 ($SiCH_3$), 10.3 (CH_3), 19.2 and 19.6 (*i*-Pr CH_3), 23.7 (*i*-Pr C), 80 (C_P), 91 (C_A), 201 (C_C).

Synthesis of Trimethyl-*m*-tolylsilane and Isopropyldimethyl-*m*-tolylsilane. To an oven-dried, N_2-purged flask fitted with a septum was added *m*-bromotoluene (61 μL, 0.5 mmol) in dry THF (10 mL). The solution was cooled to −78 °C, and 0.55 mL of 1.83 M *t*-BuLi/pentane (1.0 mmol) was added. The *m*-tolyllithium was quenched with 0.75 mmol (1.5 equiv) of the appropriate trapping agent (95 μL of Me_3SiCl or 118 μL of *i*-PrMe$_2$SiCl), and the reaction mixture was warmed to room temperature. The solution was taken up in 1:1 ether/hexane (10 mL) and washed with H_2O (2 × 10 mL) and once with brine (10 mL). The solution was dried over anhydrous $MgSO_4$, and the solvents were removed by rotary evaporation.

Spectral data for trimethyl-*m*-tolylsilane: GC RT = 1.89 min at 130 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.26 (s, 9H, $SiMe_3$), 2.35 (s, 3H, −Me), 7.13−7.35 (m, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ −1.1 ($SiMe_3$), 21.5 (Me), 127.7, 129.6, 130.3, 134.0, 137.0 (quat), 140.3 (quat); MS M$^+$ = 164.1016 (calcd for $C_{10}H_{16}Si$ = 164.1021).

Spectral data for isopropyldimethy-*m*-tolylsilane: GC RT = 3.58 min at 130 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.23 (s, 6H, $SiMe_2$), 0.95 (s, 7H, $CHMe_2$, signals coincident), 2.35 (s, 3H, Me), 7.13−7.36 (m, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$), δ −5.3 ($SiMe_2$), 13.8 (SiCH), 17.6 (*i*PrMe's), 21.5 (Me), 127.5, 129.5, 131.0, 134.6, 136.8 (quat), 138.4 (quat); MS M^+ = 192.1334 (calcd for $C_{12}H_{20}Si$ = 192.1334).

Relative response factors: trimethyl-*m*-tolylsilane ≡ 1.00, isopropyldimethyl-*m*-tolylsilane = 0.85.

***m*-Tolyllithium Double-Trap Experiments.** The procedure was analogous to that for the allenyl/propargyl *in situ* trapping experiments. The experiment was performed by adding 0.10 mL (0.2 mmol) of 1.92 M *t*-BuLi/pentane to a −78 °C solution of 12 μL (0.1 mmol) of *m*-bromotoluene and 0.6 mmol each of Me_3SiCl (76 μL) and *i*-$PrMe_2SiCl$ (95 μL) in 6 mL of dry THF. GC analysis showed a 9.2:1 preference for trapping by Me_3SiCl over *i*-$PrMe_2SiCl$.

^{13}C, ^{7}Li, and ^{31}P NMR Spectra of an HMPA Titration of 2A-Li + Me_2Se. A 10-mm NMR tube was dried in an oven at 125 °C, the top was lightly greased and fitted with a septum, and the tube was purged with N_2 for 20 min. To the NMR tube was added THF (3.7 mL) and **2P-Se** (68 μL, 0.32 M). The tube was cooled to 0 °C, MeLi (0.25 mL, 1.51 M, 0.38 mmol) was added, and after 10 min the tube was cooled to −78 °C. The HMPA titration was performed by removing the tube from the probe of the instrument, placing it into a dry ice/ethanol bath, and adding aliquots of HMPA using a microliter syringe. The tube was removed from the bath and shaken for very brief intervals to allow the HMPA to dissolve. ^{7} Li and ^{31}P reference spectra were obtained using a second NMR tube containing two sealed capillaries, one containing LiCl in methanol (0 ppm) and the other Ph_3P in THF (−6 ppm). The spectra were referenced at 0 (for ^{7}Li only), 0.5, and 5 equiv of HMPA. The carbon spectra were referenced to C_2 of THF (67.96 ppm). Following the experiments the sample was quenched with Me_3SiCl (0.12 mL, 0.96 mmol). The solution was warmed to room temperature and 30 μL of 4-*tert*-butyltoluene was added. The solution was diluted with 20 mL of ether/pentane, washed with water (3 × 10 mL) and brine (10 mL), and dried through a plug of Na_2SO_4. GC analysis of the organic phase identified **2A-Si** (0.17 mmol), **2P-Si** (0.050 mmol), **2A-H**, and **2P-H** (≈0.07 mmol). The silane yield was 69% and the total recovery was 91%.

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Foundation for support of this work.

Supporting Information Available: ^{1}H NMR spectra for compounds **1P-OH**, **1P-OMs**, **1P-Se**, **1A-Sn**, **1P-Sn**, **1P-SnPh**, **1P-$SnPh_2$**, **1A-$SnPh_3$**, **1P-$SnPh_3$**, **1A-Si**, **1P-Si**, **1A-SiPr**, and **1P-SiPr**; ^{1}H NMR spectra, experimental procedures, and characterization of **2P-OH**, **2P-OMs**, **2P-Se**, **2A-Sn**, **3P-OH**, **3P-OMs**, **4P-OH**, **4P-OMs**, and **4A-Sn**; experimental procedures and characterization of **2A-Si**, **2P-Si**, **3P-Se**, **3A-Sn**, **3A-Si**, **3P-Si**, **3A-SiPr**, **3P-SiPr**, **4P-Se**, **4A-Si**, and **4A-SiPr**; and spectra and experimental details for an HMPA titration of **2A-Li** prepared from **2A-Sn** by treatment with MeLi (29 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instruments.

JA951987L