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Solution Structure and Stereochemistry of Alkyl- and Silyl-Substituted Allenyl-Propargyllithium Reagents

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Abstract: Analysis of ^{13}C chemical shifts and Li−C couplings showed that allenyllithium (**5A-Li**) was a mixture of monomer and dimer in THF, both with an allenyl structure. Similarly, the metalation products of 2-butyne (**6A-Li**), 4-methylpentyne (**9A-Li**), and 4,4-dimethylpentyne (**21A-Li**) in THF, as well as several 1, 3-dialkyl (**32A-Li**, **33A-Li**, **34A-Li**) propargyl-allenyllithiums formed by metalation or Li/Sn exchange were all monomeric lithioallenes in THF. Compound **6A-Li** was shown to have less than 5% and **21A-Li** less than 3% of the propargyllithium isomers (**6P-Li**, **21P-Li**) present from analysis of residual broadening of the propargyl carbon by Li−C coupling. The reagent prepared by metalation of dicyclopropylacetylene (**8P-Li**) has a propargyl structure, but two related reagents with a cyclobutane spanning the 3,3-positions (**37A-Li** and **39A-Li**) had allenyl structures. Several triorganosilyl-substituted reagents were also investigated. Those with silyl groups at the allenyl position (**28A-Li**, **31A-Li**) are allenyllithiums, those with silyl groups at the propargyl position (**22-Li** to **26P-Li**) showed chemical shifts intermediate between those of allenyl and propargyl isomers, and the shifts were strongly temperature-dependent under some conditions. These compounds are probably equilibrating mixtures of allenyl and propargyllithiums or equilibrating mixtures of unsymmetrically π-complexed structures, with barriers to interconversion ($\Delta G^{\ddagger}_{-150}$) below 4 kcal/mol. Several of the organolithium reagents studied had diastereotopic carbon signals (SiMe$_2$, CMe$_2$, or CPh$_2$ groups), which allowed determination of barriers to configurational inversion of the chiral allenyl fragment. Barriers from 6.1 kcal/mol (**26A-Li** in dimethyl ether) to 14.5 kcal/mol (**39A-Li** in 3:2 THF/ether) were measured.

Introduction

An understanding of the factors that influence the regioselectivity of reactions of allenyl-propargyllithium (A/P−Li) reagents[1a,2−4] requires information about the solution structure of the reagent and the nature of the interaction between the lithium and the carbanionic fragment. We can consider four limiting monomeric structures: localized allenyl (**1**), localized propargyl (**2**), delocalized π-bonded (**3**), or separated ion pair

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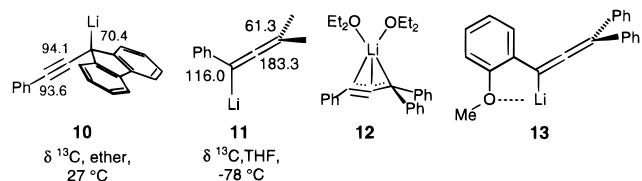
(**4**, SIP). In the discussions to follow we will identify the three carbons as C_A (allenyl), C_C (central), and C_P (propargyl).
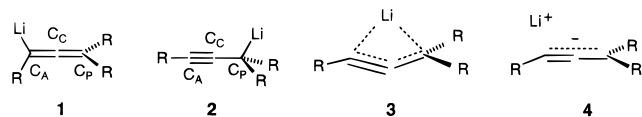
When we began our work, there was only scattered information available on the structures of allenyl-propargyllithium reagents. Proton NMR studies were often ambiguous. For example, the metalation product of 2-butyne gives chemical shifts of δ 2.14 for CH_2 and δ 1.82 for CH_3, consistent with an assignment of structure **6P-Li**, although the structure is actually allenic.[5] The metalation product of 3,3-dimethylallene was correctly assigned structure **7A-Li** on the basis of a δ 4.70 signal for the allenyl proton.[3] More definitive information is provided by ^{13}C NMR spectra. A key early study of the metalation product of allene showed ^{13}C NMR signals consistent only with the allenyl structure **5A-Li**, based on the strong downfield shift (196.4 ppm) of the central carbon, similar to those of allene itself (208.5 ppm).[6] The ^{13}C NMR spectrum of 4-methyl-1,2-pentadienyllithium (**9-Li**) was interpreted in terms of an equilibrating A/P structure.[7] We have re-examined these reagents as well as a number of others and report the results below.
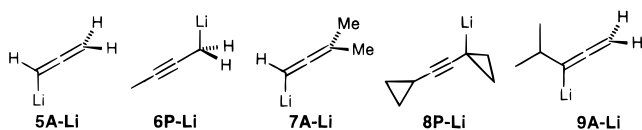
On the basis of a very extensive ^{13}C NMR and UV study of mono, bis, and tris phenylated A/P−Li lithium reagents (including **10**, **11**, **12**, and **13**), Dem′yanov and co-workers conclude that the electronic structure is delocalized, with no separate existence of allenyl and propargyllithiums.[8] Most show ^{13}C shifts that are more propargylic than allenic in nature, in particular, reagents with two aryl groups at the propargyl carbon C_P such as **10** and **12**. On the other hand, a compound with alkyl groups at C_P (**11**), has a greater tendency to be a contact ion pair and shows chemical shifts that are allenic in nature.

X-ray crystal structures have provided some additional information about allenyl-propargyllithiums, although none are simple alkyl-substituted derivatives. An X-ray crystal structure

of the bis-diethyl ether solvate **12** shows a delocalized structure of the propargyl type, with close lithium contacts to all three carbons of the π-system.[9] In contrast, a closely related THF solvate **13** in which the phenyl group on C_A bears a chelating ortho-methoxy substituent, has a dimeric structure with considerable allenic character (the chelated structure does not appear to survive in ether solution).[9] Two bisacetylenic reagents **14** and **15** showing cyclic head-to-tail dimer structures, with multicenter contact between lithium and carbon of the π-propargyl type, have been reported.[10a]
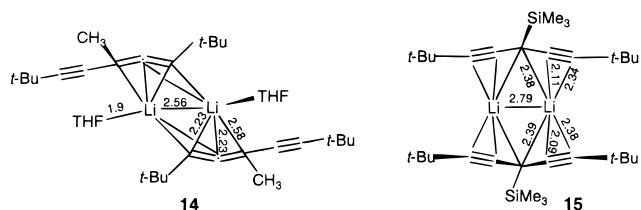
Infrared spectra have also been diagnostic. Absorptions at 1850−1900 cm^{-1} were assigned to allenyl and >2000 cm^{-1} to propargyllithium reagents. Allenyllithium has an absorption at 1895 cm^{-1}.[11,12] The metalation product of dicyclopropylacetylene **8P-H** was identified as a propargyllithium reagent (**8P-Li**) on the basis of an IR absorption at 2160 cm^{-1}.[13] Zinc, boron, titanium, and aluminum allenyl and propargyl structures have also been identified by their IR absorptions.[14,15a]

In connection with synthetic and mechanistic studies of the lithium reagents prepared from 1,4-bis(trimethylstannyl)-2-butyne (**16**) and 2,3-bis(trimethylstannyl)-1,3-butadiene (**18**), we encountered complex regiochemical effects that required precise knowledge of solution structure of the reagents involved. We were able to characterize the monolithium reagent, prepared from **16** by Li/Sn exchange, as the allenyl **17A-Li** and not the propargyl isomer **17P-Li** on the basis of well-defined Li−C coupling to a single carbon and a strongly downfield shifted central carbon analogous to the parent allenyllithium.[6] On the basis of similar considerations, the monolithium reagent prepared from **18** has a vinyllithium structure **19** and not the vinylideneallyllithium structure **20**.[1c]

The data summarized above do not provide a sufficient basis for assigning structures to the many known hydrocarbon- and heteroatom-substituted A/P−Li reagents. We have reported preliminary results[1a,b] of spectroscopic studies on such reagents with alkyl, silyl, phenoxy, alkoxy, carbamoyloxy, phenylthio,

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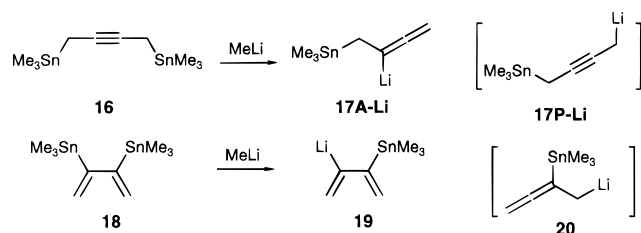
pyridylthio, and phenylseleno substituents at C_P and report here the full details on those with alkyl and silyl substituents. Our study has involved several series of closely related structures to probe substituent effects. We have also examined reagents in solvents of different donor power (ether, dimethyl ether, THF, HMPA). This has allowed us to establish the mode of dimerization in nonpolar solvents and to compare contact and separated ion pair structures in polar solvents. Some of the reagents examined are chiral, and our study has provided information about the racemization process by DNMR studies. The principal tool we have used is variable temperature ^{13}C, ^{6}Li, and ^{7}Li NMR spectroscopy, but some compounds were also examined by IR spectroscopy.

Results

Synthesis of Allenyl-Propargyllithium Reagents. Allenyllithium (**5A-Li**) was prepared by metalation of allene.[6] The hydrocarbon-derived lithium reagents with the allenyl/propargyl grouping at the end of the chain (**6A-Li**, **9A-Li**, **21A-Li**) were prepared according to literature procedures by metalation of the appropriate methyl alkyl acetylenes.[15a,16] Silylation of these gave compounds **22P-H** to **27P-H**, precursors to the lithium reagents **22-Li** to **27-Li** with silyl groups at C_P. The silylation gave only acetylenic products,[16] provided that ether (rather than THF) was used as solvent. The nonterminal reagent **8P-Li** was prepared as reported[13] by metalation of dicyclopropylacetylene **8P-H**.
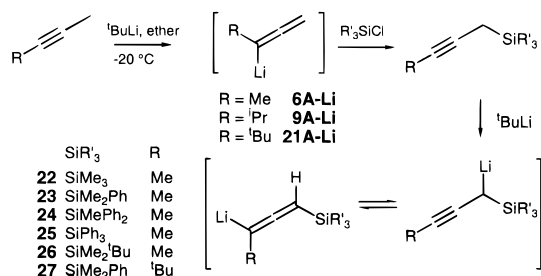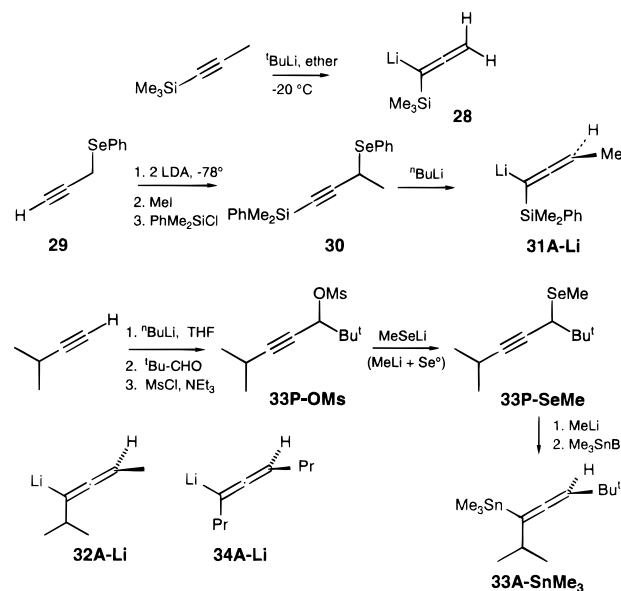

The lithium reagent **28-Li** with trimethylsilyl substitution at C_A was prepared following a literature procedure[17] by metalation of the 1-trimethylsilylpropyne. The reagent **31A-Li** was prepared by Li/Se exchange of **30**, which was prepared by sequential methylation and silylation of the dianion formed from phenyl propargyl selenide (**29**).[1e] The same lithium reagent was also prepared by metalation of 1-phenyldimethylsilyl-1,2-butadiene.

Several of the lithium reagents (**32**, **33**, **34**) were prepared by Li/Se or Li/Sn exchange, following the procedure illustrated for compound **33**.[1d] This route can often be used for the preparation of either the propargyl- (kinetic product of the final stannylation) or allenylstannane (thermodynamic stannylation product).

The cyclobutylidene allene **37** was prepared using a method reported by Bailey, involving an intramolecular addition of an alkyllithium to an acetylene.[18] Compound **39** was prepared using the procedure of Harada.[19] The final reaction gave, in addition to **39A-H**, a significant fraction of the product of hydride (rather than *tert*-butyl) transfer, which was removed by performing a partial metalation of the mixture with *tert*-butyllithium and carbonating the product (which left unreacted **39A-H**). Both **37A-H** and **39A-H** could be metalated using *tert*-butyllithium to give **37A-Li** and **39A-Li**.
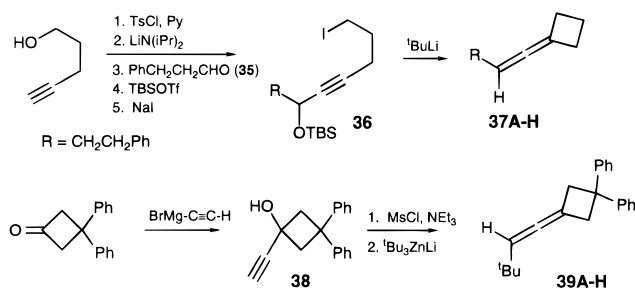

Solvents and NMR Spectral Measurements. The principal goal of the present work was to establish the structures of a series of A/P−Li reagents in commonly used ethereal solvents. Since THF freezes at −109 °C, we frequently used mixtures of THF, diethyl ether (mp −116 °C), and/or dimethyl ether (mp −138.5 °C) for NMR studies (most solutions also contained pentane from the *n*-BuLi or *t*-BuLi used to prepare the reagents). Diethyl ether−THF mixtures are usable to −135 °C, THF/ dimethyl ether mixtures to −145 °C, and ternary THF/ether/ dimethyl ether or binary dimethyl ether/pentane mixtures down to below −160 °C. Dimethyl ether is only a slightly weaker donor solvent than is THF, and diethyl ether is substantially weaker.[1f,20a]

Allenyllithium. The ^{13}C NMR spectrum of the metalation product of allene has been interpreted in terms of an allenyl structure.[6] We have re-examined allenyllithium and found that in 2.5:1:1 Me_2O/THF/pentane the single set of three signals

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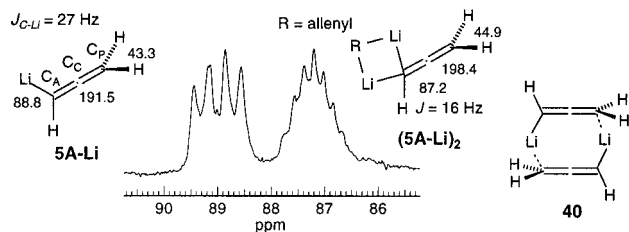
Figure 1. ^{13}C NMR spectra of C_A for 0.26 **5A-Li** in 2.5:1:1 Me$_2$O/THF/pentane at -150 °C.

(43.8, 87.3 and 197.5 ppm) at -80 °C decoalesces into two sets at around -110 °C. The relative areas of the pairs of signals are concentration-dependent, so they cannot represent a pair of isomeric dimers such as a 4-center and head-to-tail dimer (**40**). Both species are clearly allenyl, based on the downfield shift of the central and propargyl carbons, as well as the well defined ^{13}C-^{7}Li coupling of the allenyl carbon (C_A, 88.8 ppm, $J_{C-Li} = 27$ Hz, and 87.2 ppm, $J_{C-Li} = 16$ Hz, Figure 1). The 1:1:1:1 quartet identified the species favored at lower concentration as a monomer **5A-Li**, and the 1:2:3:4:3:2:1 septet must be a cyclic oligomer **(5A-Li)$_n$** (C_A coupled equally to two ^{7}Li). Unfortunately, accurate measurement of the concentration dependence was not possible since a precipitate (identified as 1-propynyl-lithium) formed as spectra were measured. The results of one successful dilution on a homogeneous sample gave an aggregation state difference of two between the monomer and the second species. Thus allenyllithium apparently dimerizes in the normal 4-center fashion of most localized organolithium reagents.

The ratio of monomer to dimer was temperature-dependent. At -140 °C a 0.26 M solution of **5-Li** is an approximately 2:1 molar ratio of monomers to dimers. The fraction of monomer increases on warming until the ratio is 2:3 at -80 °C (estimated from the chemical shift of the averaged signal). Thus the monomer is enthalpically favored but entropically disfavored.

Alkyl-Substituted Allenyllithiums. Alkyl substitution at carbanion centers generally has a destabilizing effect, and placing an alkyl group on C_A is expected to destabilize the allenyl isomer. Both the methyl- (**6-Li**)[5] and isopropyl- (**9-Li**)-substituted[7] compounds have been previously studied by NMR spectroscopy. Our examination of these structures using low-temperature ^{13}C NMR spectra in THF solutions showed **6A-Li** and **9A-Li** to have the C$-$Li coupling and downfield central carbon (C_C) chemical shifts characteristic of allenyllithium structures.
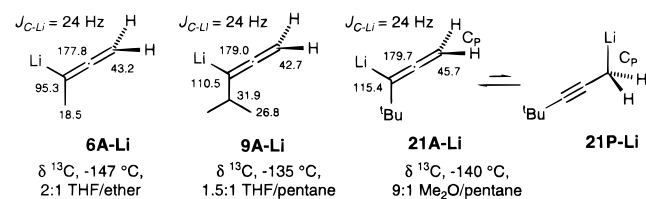
A *tert*-butyl substituent at C_A should maximally destabilize the allenyl structure, not only because of the "normal" alkyl effect but also because the bond angle changes caused by rehybridization at C_A should result in increased strain (B-strain),[21] and because of steric inhibition of solvation of the lithium cation. Nevertheless, **21-Li** has the characteristic chemical shifts of an allenyllithium. We have been able to test this putative "*tert*-butyl effect" with the pair of silyl-substituted compounds **23-Li** and **27-Li** and found that the compound with

(21) For an example of a *tert*-butyl substituent that increased the fraction of propargyl isomer in an allenylzinc reagent, see ref 19.
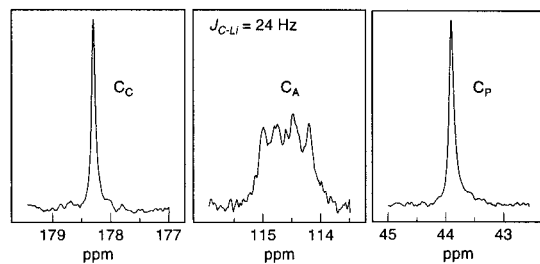

Figure 2. ^{13}C signals of 0.16 M **21-Li** in 9:1 Me$_2$O/pentane at -140 °C. ^{7}Li-^{13}C coupling constants: for C_A, $J = 24$ Hz, for C_P, $J < 0.4$ Hz.

tert-butyl at C_A showed a *larger* fraction of allenyllithium than did the methyl (see below).

We can estimate the maximum fraction of the propargyl-lithium isomer **21P-Li** present as follows. The equilibration between **21A-Li** and **21P-Li** must be intramolecular since C$-$Li coupling is observed. Thus the propargyl carbon C_P would be broadened by C$-$Li coupling in proportion to the fraction of **21P-Li** present. The line width of C_P (3.5 Hz) is only 1.2 Hz greater than that of the central carbon C_C (Figure 2); thus J_{C-Li} for the propargyl carbon is <0.4 Hz ($J = \frac{1}{3}\nu_{1/2}$). If we estimate that the full J_{C-Li} for **21P-Li** is ≥ 16 Hz,[22] the line width of the fully coupled C_P carbon would be >48 Hz (3J). Thus there can be no more than 3% of propargyllithium isomer **21P-Li** present. Compound **6-Li** in 2:1 THF/ether showed an excess broadening of 2 Hz for C_P so that there can be no more than 5% of **6P-Li** in the equilibrium mixture. This analysis presumes that the two isomers are in rapid equilibrium on the NMR time scale.

1,3-Dialkyl-Substituted Allenyllithiums. We have previously reported on the 1,3-dialkylallenyllithium **32-Li**.[1d] We report here some additional information about this compound and data for **33-Li** and **34-Li**. All are allenyllithiums with well-defined ^{13}C-^{7}Li coupling to C_A and negligible broadening of C_P.
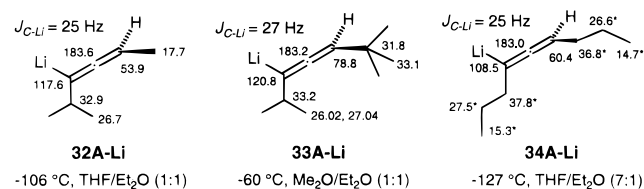

Aggregation. In contrast to the parent allenyllithium **5A-Li**, which is a mixture of monomer and dimer in solvents containing THF, the alkylated allenyllithiums **6A-Li**, **9A-Li**, **21A-Li**, **32A-Li**, **33A-Li**, and **34A-Li** showed no indications of dimerization. In all cases the lithium-bearing carbon was coupled to a single lithium. This is consistent with the general observation that the extent of aggregation decreases with increasing alkyl substitution at carbanion centers.[10b,23,24a] However, in the weaker solvent diethyl ether, both **32A-Li** and **33A-Li** dimerize. All of ^{13}C signals and the ^{6}Li signals are doubled, and the ratio is independent of concentration between 0.64 and 0.01 M (^{6}Li NMR, signals at 0.92 and 0.97 ppm). The C$-$Li NMR signal of **32A-^{6}Li** is a multiplet (Figure 3) best interpreted as the superposition of two 1:2:3:2:1 quintets (offset by 2J) arising from the meso and dl diastereomers of the dimer, as also seen

(22) We have measured J_{C-Li} for two authentic propargyllithium reagents prepared by metalation of phenyl 2-butynyl sulfide, 16 Hz, and phenyl 2-butynyl selenide, 18 Hz.[1a]

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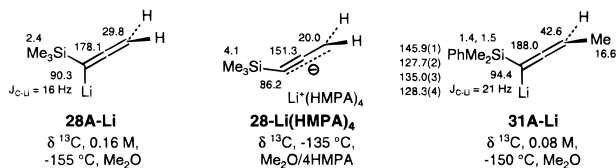
Substituted Allenyl-Propargyllithium Reagents

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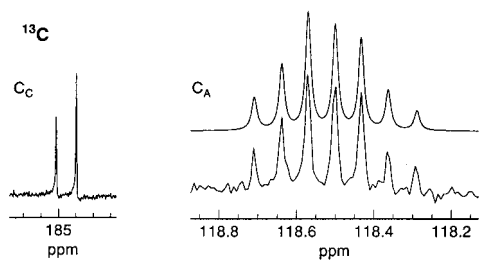
Figure 3. ^{13}C NMR signal of ^{6}Li-labeled C_A of (**32A-Li**)$_2$ in 3.7:1 ether/pentane at -120 °C. Superimposed on the signal for C_A is a simulation of a 5:3 mixture of two 1:2:3:2:1 quintets ($J(^{13}$C-^{6}Li) = 6 Hz).

for 1-methoxy-1-lithio-3-*tert*-butylallene.[10c] The assignment as two superimposed chemically shifted quintets separated by *2J* was confirmed by measuring the spectra at a different field strength. A variable temperature study of (**32A-Li**)$_2$ in ether showed the two sets of signals coalesced between -50 and -46 °C. The isopropyl methyls were diastereotopic and gave four signals at low temperature, which also coalesced in this temperature range.
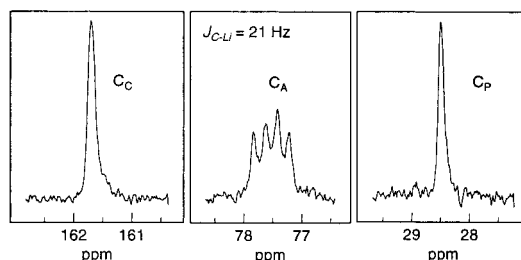
Silyl-Substituted Allenyl-Propargyllithiums. A variety of silyl-substituted allenyl-propargyllithium reagents have been prepared and utilized in synthetic organic chemistry.[14,17,25a−c] We have examined several reagents with a silyl group at either C_P or C_A.

The presence of a carbanion-stabilizing group at either terminus of an A/P−Li reagent might be expected to favor localization of charge and lithium coordination at that carbon. This is in fact what has been observed. For example, the metalation products of phenyl 2-butynyl sulfide and selenide are rare examples of lithium reagents with a propargyl structure.[1a] The consequences of silyl substitution tend to follow this pattern, but the data is more ambiguous than for the S and Se analogues.
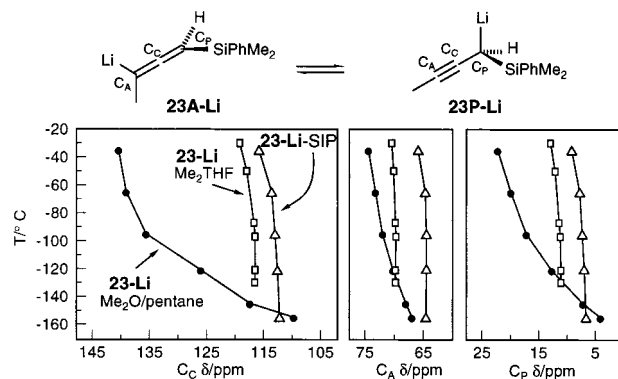
Triorganosilyl Substituents at C_A. Compounds **28A-Li** and **31A-Li** show ^{13}C NMR properties consistent with assignment as allenyllithium reagents. The chemical shifts were only slightly temperature-dependent ($\Delta\delta \sim 1.0$ ppm between -50 and -150 °C). Well-defined C−Li coupling was observed for C_A. Compound **28A-Li** showed strong IR absorptions for an allenyl stretch (1868, 1886 cm^{-1}) and weaker absorptions at a position expected for a propargyllithium (2026 cm^{-1}). Addition of excess HMPA to a dimethyl ether solution of **28A-Li** resulted in complete conversion to a SIP.[1g] The central carbon (C_C) moved almost 27 ppm upfield on ionization, indicating the charge-localizing effect of lithium coordination.

28A-Li
δ ^{13}C, 0.16 M, -155 °C, Me$_2$O

28-Li(HMPA)$_4$
δ ^{13}C, -135 °C, Me$_2$O/4HMPA

31A-Li
δ ^{13}C, 0.08 M, -150 °C, Me$_2$O

Triorganosilyl Substituents at C_P. We examined a family of compounds with substituents at C_P. Of the compounds studied, the *tert*-butyldimethylsilyl analogue **26-Li** shows the simplest behavior. Although the C_C chemical shift is somewhat upfield of that observed for the hydrocarbon allenyllithiums, the other features are those of a true allenyllithium. C_A shows

(25) (a) Hartley, R. C.; Lamothe, S.; Chan, T. H. *Tetrahedron Lett.* **1993**, *34*, 1449−1452. (b) Wang, K. K.; Gu, Y. G.; Liu, C. *J. Am. Chem. Soc.* **1990**, *112*, 4424−4431. Wang, K. K.; Wang, Z.; Sattsangi, P. D. *J. Org. Chem.* **1996**, *61*, 1516−1518. (c) Daniels, R. G.; Paquette, L. A. *Tetrahedron Lett.* **1981**, *22*, 1579−1582.

Figure 4. ^{13}C signals of 0.32 M **26A-Li** in 12:1 Me$_2$O/pentane at -145 °C.

Figure 5. ^{13}C chemical shifts in Me$_2$O (●), 2,5-dimethyltetrahydrofuran (□), and Me$_2$O-8HMPA (△) of C_C, C_A, and C_P of **23-Li**.

coupling to ^{7}Li, and the line widths of C_P and C_C are the same, so there is no indication of any association between Li and C_P (Figure 4).

The other C_P-silyl-substituted reagents have more ambiguous NMR properties. Compound **23A-Li** has chemical shifts intermediate between those of propargyl and allenyllithiums. In some solvents such as dimethyl ether and THF these shifts show temperature dependence too large to be caused by normal changes in solvation,[26] aggregation,[27] or conformation, but instead, they are likely to reflect substantial changes in the electronic structure of the lithium reagent (Figure 5). The reagents **22-Li**, **24-Li**, and **25-Li** show similar behavior. Figure 6 compares the chemical shift behavior of these with authentic allenyllithium (**6A-Li**) and propargyllithium (**41P-Li**) reagents. The most economical explanation is that these lithium reagents are mixtures of the allenyl and propargyl isomers in rapid equilibrium, a conclusion supported by the IR spectrum of **23-Li**, which has absorptions at both 2179 and 1894 cm^{-1}. A bridged structure (**3**) should show only a single intermediate absorption.

The IR spectrum of **23-Li** has absorptions at both 2179 and 1894 cm^{-1}, consistent with formulation as an equilibrium mixture of A and P isomers. A bridged structure (**3**) should show only a single intermediate absorption.

Effect of Ion Pair Separation on Silyl-Substituted Reagents. We have examined the effect of HMPA on all of the silyl-substituted A/P−Li reagents. This experiment provides information about the strength of association between lithium and the carbanion and some insight into the effect of lithium coordination on the electronic structure of the carbanion. A typical HMPA titration is presented in Figure 7. With up to 1

(26) Jackman, L. M.; Scarmoutzos, L. M. *J. Am. Chem. Soc.* **1987**, *109*, 5348−5355.

(27) The monomer and dimer of allenyllithium differ by 1.5 ppm (C_A), 6.9 ppm (C_C), and 1.3 ppm (C_P). The PhLi ipso carbon varies from 174.2 ppm for the ether tetramer and 187.1 ppm for the ether dimer to 196.7 for the THF monomer.[1h]
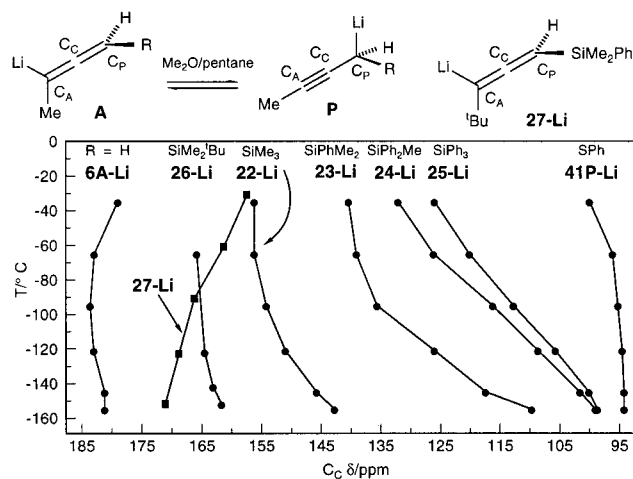
Figure 6. Temperature dependence of C_C in A/P—Li reagents (Me_2O solvent) with alkyl substitution at C_A and proton (**6A-Li**), silyl (**22-Li** to **27-Li**), or thio (**41P-Li**) substitution at C_P.
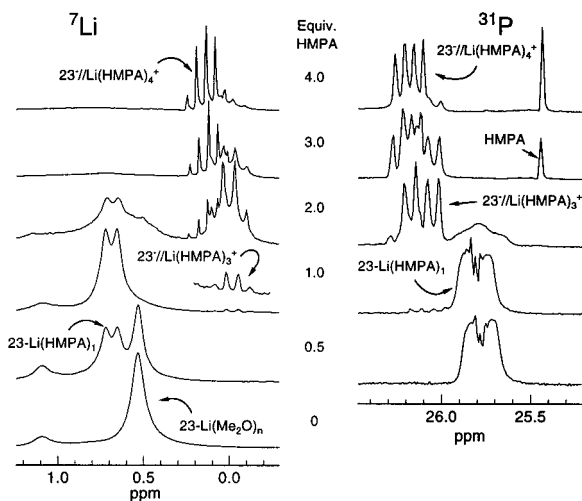
Figure 7. ^7Li and ^{31}P NMR spectra of an HMPA titration of **23-Li** in Me_2O at −150 °C.

equiv of HMPA, only the mono-HMPA CIP was present. The lithium signals of the **23-Li(Me_2O)$_n$** and the **23-Li(HMPA)$_1$** species are unusually broad, and the ^{31}P signal shows the characteristic broadening of a T_1-relaxed P—Li-coupled 1:1:1:1 quartet.[28−30] The broadening is not due to chemical exchange (T_2) effects, since the natural abundance ^6Li triplet is clearly resolved in the center of the broad doublet. The relatively short T_1 of the ^7Li nucleus in these compounds explains why it has been difficult to resolve ^{13}C-^7Li coupling. The observation of only a mono-HMPA CIP at 0.5 equiv of HMPA rules out a temperature-dependent CIP/SIP equilibrium as an explanation for the chemical shift behavior of **22-Li** to **25-Li** (Figure 6).

All of the silyl-substituted lithium reagents were fully converted to SIP's on addition of 4−6 equiv of HMPA (Figure 8). The strength of C—Li association is similar to that of lithiomethanes bearing two carbanion-stabilizing groups such as $Me_3Si(PhS)CHLi$ or $(PhS)_2CHLi$.[1i] The free carbanion of the

(28) NMR signals of nuclei coupled to a ^7Li nucleus with a short T_1 value show a characteristic peak shape in which the outer two pairs of the 1:1:1:1 quartet first collapse to a broad doublet.[29,30] Frequently the natural abundance ^6Li signals (1:1:1 triplet) can be seen in the valley between the peaks (for a ^{31}P example see Figure 7, for a ^{13}C example see ref 24b).

(29) Gillespie Bacon, J.; Gillespie, R. J.; Quail, J. W. *Can. J. Chem.* **1963**, *41*, 3063−3069.

(30) Fraenkel, G.; Subramanian, S.; Chow, A. *J. Am. Chem. Soc.* **1995**, *117*, 6300−6307.
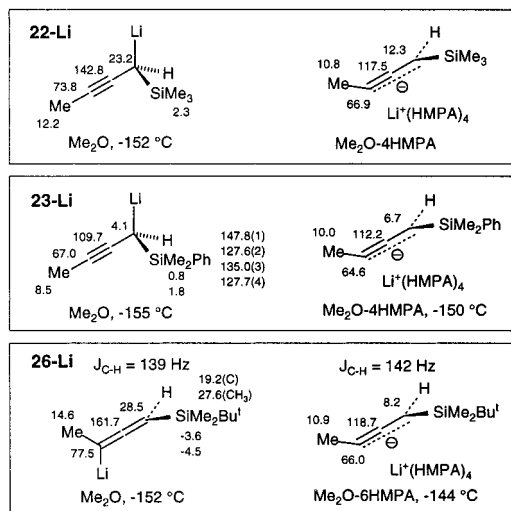
Figure 8. Comparison of CIP and SIP structures for triorganosilyl-substituted A/P—Li reagents.

SIP has propargyl-like chemical shifts (see Figure 5), consistent with charge localization at the Si-bearing carbon. This is true even for the *tert*-butyldimethylsilyl compound **26-Li**, for which the CIP is strongly allenic; here lithium coordination significantly changes the structure.

Barrier to Interconversion of Propargyl and Allenyllithiums. For many σ-allyl or σ-A/P—Li organometallics the position of electrophilic substitution is determined by the position of the organometallic group, usually in an S_E2N sense.[15b,17c,31] For others the interconversion between isomers is faster than the rate of substitution, and the Curtin-Hammett principle applies. This can be detected either by a lack of correlation between product ratios and organometallic regio-isomer ratios[25b] or by the observation of product ratios that vary with electrophile.[3,15a] One of the goals of the current study was to measure the energy barrier to interconversion of pairs of isomeric allenyl and propargyllithium reagents to help establish whether the site of metalation has an influence on product regiochemistry. This requires reagents in which both isomers are present in significant amount, so that DNMR techniques can be used to measure interconversion rates, or place an upper or lower limit on the rate.

The silyl-substituted reagents **22-Li** to **26-Li** are suitable substrates. The most sensitive indicator of incipient decoalescence between the A and P signals would be the C_C signal because of the large chemical shift difference (∼70 ppm, 6300 Hz) between the two isomers. Although excess broadening was typically seen for C_C, in none of these reagents was decoalescence of the A and P isomer NMR signals detected even at the lowest temperatures (−160 °C) accessible. The three allenyl signals of the trimethylsilyl-substituted analogue **22-Li**, chosen because it appears to be an almost 1:1 mixture of A and P structures, are shown in Figure 9. C_A shows some signs of splitting, and C_P shows excess broadening at −150 °C, probably from residual ^{13}C-^7Li J coupling.[28] C_C gave excess broadening of ∼15 Hz, which allows estimation of a rate constant of at least 10^6 s^{-1} and $\Delta G^{\ddagger} < 3.6$ kcal/mol for A/P isomerization (we assume that the chemical shifts of C_C in the A and P isomers are 165 and 98 ppm; with a shift of 142 ppm this means A/P = 66/34). This barrier is also an upper limit on the free-energy difference between localized A and P structures such as **1** and **2** and bridged structures such as **3**.

(31) Marshall, J. A.; Perkins, J. *J. Org. Chem.* **1994**, *59*, 3509.
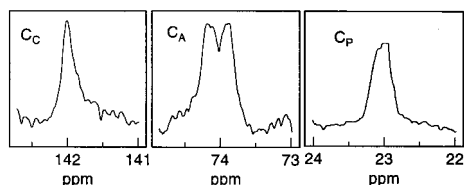
Figure 9. ^{13}C NMR spectrum of **22-Li** in 5:2:1:1 $Me_2O/Et_2O/THF/$ pentane at -150 °C.
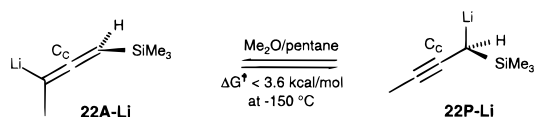

Alkyl-substituted A/P−Li reagents are likely to have a higher barrier to A/P isomerization than silyl-substituted ones such as **22-Li** because of charge stabilization by the silyl group. Racemization of related lithium reagents, a process related to the 1,3-shift, has a 5 kcal higher barrier in alkyl (**33A-Li**) compared with a silyl analogue (**26A-Li**). Simple alkyl substitution seems unlikely to provide a system in which both isomers are significantly present (**6-Li** and **21-Li** are optimally substituted, but are >95% allenyl). We turned to angle strain to alter the balance between the A and P isomers. The lithium reagent **8-Li** has been reported to be a propargyllithium on the basis of its IR and ^{1}H NMR spectra.[13] On the basis of the chemical shifts of C_P (-7.5 ppm) and C_C (99.8 ppm), about 40 and 90 ppm upfield of those found in typical allenyllithiums, we can confirm this assignment. Thus the increase in ring strain on going from formally an sp^3 to an sp^2 cyclopropyl carbon, approximately 13 kcal/mol,[32] is sufficient to overwhelm the normal preference for an allenyllithium structure.
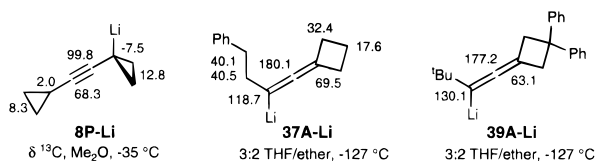
A lighter touch is needed, so we examined two cyclobutylidene systems, in which the propargyl isomer should be favored by approximately the difference in strain between cyclobutane and methylenecyclobutane (1.4 kcal/mol). Compound **37-Li** shows chemical shifts nearly identical to those of other allenyllithium reagents. Even **39-Li**, in which we have maximally destabilized the allenyl isomer by combining cyclobutane angle strain effect with the (presumed) *tert*-butyl effect, is unambiguously allenic. We have thus been unable to measure the barrier to interconversion of alkyl or silyl-substituted A and P isomers.

Configurational Stability of Allenyl-Propargyllithiums. We have examined the configurational stability in ethereal solvents of several of the lithium reagents discussed above. Compounds **32A-Li** and **33A-Li** bear isopropyl groups that lose their diastereotopic nonequivalence when the lithium reagents racemize on the NMR time scale. For **32A-Li** in 1:1 THF/ether the diastereotopic ^{13}C methyl signals ($\Delta\delta = 0.1$ ppm), peaks merge at about -60 °C, probably due to a convergence of chemical shifts, rather than a true coalescence. For **33A-Li** the peak separation is larger ($\sim$1 ppm). One of the signals is coincident with a THF signal, but a coalescence can be detected between -60 and -20 °C. In 1:1 Me_2O/Et_2O the isopropyl methyl signals are free of solvent interferences and spectra suitable for
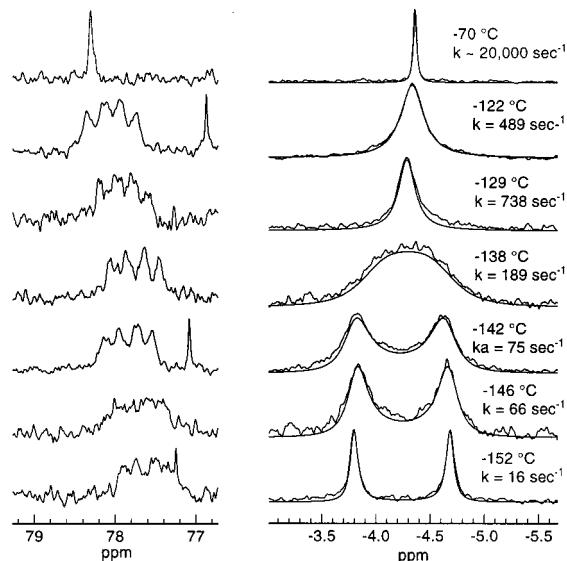
Figure 10. Variable temperature ^{13}C NMR spectra of **26A-Li** in Me_2O. The left stack shows C_A.

line shape analysis were obtained (see Figure 11).[1j,33] The coalescence temperature is slightly concentration-dependent (0.13 M to 0.5 M) but is not significantly affected by the presence of Li$^+$ species (0.16 M **33A-Li**, 0.32 M of the separated ion pair lithium fluorenide[1g]). The lithium−carbon coupling in **33A-Li** is dynamically averaged by intermolecular exchange already at -90 °C, some 50 °C below the coalescence of the methyl groups.

The cyclobutylidene allenyllithium **39A-Li** shows diastereotopic phenyl groups. Coalescence of ipso carbons (δ 152.3, 152.9) occurred at 25 °C. The data for racemization of this lithium reagent are not sufficiently accurate for measurement of activation parameters, but $\Delta G^{\ddagger} = 14.5$ kcal/mol.

We have also measured the inversion barrier for the silyl-substituted reagents **26A-Li** and **31A-Li**, detected by coalescence of the SiMe$_2$ groups. The SiMe$_2$ and C−Li regions of the ^{13}C NMR spectra of **26A-Li** are shown in Figure 10, together with simulations. Only the five lowest temperatures were used in the analysis (See Figure 11). There is no appreciable broadening of the Li−C-coupled multiplet even well after coalescence of the SiMe$_2$ group. The inversion of **31A-Li** is also an intramolecular process.

Discussion

The thermodynamic stability differences between allenyl and propargyl structures in the absence of perturbing substituents are small. Methylacetylene actually has a more favorable heat of formation ($\Delta H_f°_{298} = 44.3$ kcal/mol) than allene (45.9 kcal/mol).[34] A free-energy comparison using the position of the equilibrium for the Cope rearrangement of **41** and **43** gives a preference of 0.93 kcal/mol at 198 °C for the allenyl isomer.[35]

The preference of elements more electropositive than carbon for the allenyl position (bonding to C_A) is more pronounced. Trimethylallenylsilane and trimethylpropargylsilane equilibrate at 555 °C to give 86.1% of the allenyl isomer, $\Delta G°_{555} = 2.9$

(32) The strain of methylenecyclopropane is 13 kcal/mol higher than that of cyclopropane: Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978; pp 66, 94.

(33) See Supporting Information.

(34) Stull, D. R.; Prophet, H. *JANAF Thermochemical Tables*, 2nd ed.; National Bureau of Standards, Washington, D.C., 1971.
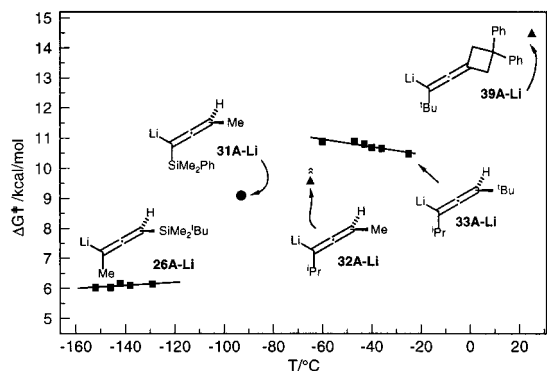
Figure 11. Barriers to configurational inversion of **26A-Li** ($\Delta G^{\ddagger}_{-138}$ = 6.1 kcal/mol, $\Delta H^{\ddagger}$ = 6.8 ± 0.4 kcal/mol, $\Delta S^{\ddagger}$ = −5 ± 3 eu in Me$_2$O), **3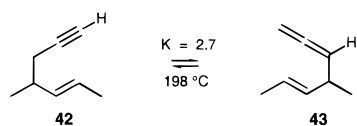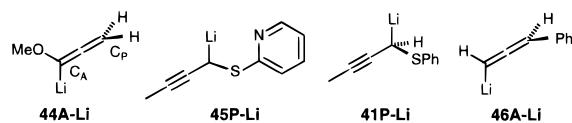1A-Li** ($\Delta G^{\ddagger}_{-93}$ = 9.1 kcal/mol, 5:3:2 Me$_2$O/THF/Et$_2$O), **32A-Li** ($\Delta G^{\ddagger}_{-65}$ > 9.6 kcal/mol, THF), **33A-Li** ($\Delta G^{\ddagger}_{-43}$ = 10.8 kcal/mol, $\Delta H^{\ddagger}$ = 11.2 ± 0.2 kcal/mol, $\Delta S^{\ddagger}$ = 12 ± 3 eu in 1:1 Me$_2$O/Et$_2$O), and **39A-Li** ($\Delta G^{\ddagger}_{25}$ ≥ 14.5 kcal/mol in 3:2 THF/ether).

kcal/mol.[36] There are examples of propargyl stannanes and boranes where "complete" equilibration to the allenyl isomer was observed.[1d,31]

A PES study showed gas-phase acidities (ΔG°_{acid}) of 373 kcal/mol for allene and 375 kcal/mol for the CH$_3$ of methylacetylene.[37] These authors concluded that C$_3$H$_3$ in the gas phase has an allenyl structure (=C−H bent, CH$_2$ planar) rather than propargyl (CH$_2$ pyramidal, CH linear). These results are consistent with several high-level computational studies of the anion, which have predicted an allenyl-like structure, with no local minimum for the propargyl structure.[9,10c−d,38] For the lithium reagent an allenyl rather than propargyl structure was also found, with significant distortion from linearity to accommodate lithium contacts at both ends of the anion as in **3**.

We have examined a sufficiently wide range of alkyl-substituted A/P−Li reagents to show that allenyl structures are favored in solution by a significant margin. Since **8-Li** has a propargyl structure and **37-Li** has an allenyl structure, the difference between A and P isomers is less than the extra strain of a methylene cyclopropane (about 14 kcal/mol) but more than the destabilization of a methylenecyclobutane (1.4 kcal/mol) plus the destabilization of a partially delocalized carbanion center by a methyl or *tert*-butyl group (>1 kcal/mol).[39] When carbanion-stabilizing groups (Ph (**11A-Li**),[8] MeO (**44A-Li**),[10c] SiR$_3$ (**28A-Li**), SAr[1a]) are placed at C$_A$ only allenyllithium structures are seen.

Placement of anion-stabilizing groups at C$_P$ gives systems in which the natural propensity for allenyl structures conflicts with the presumed effect of the substituents. For a single substituent like PhS (**41P-Li**), 2-PyS (**45P-Li**), and PhSe or double substitution by phenyl (**10**, **12**),[8] the carbanion-stabilizing effect dominates since propargyllithium structures result.[1a] For silyl substitution (**23-Li**) the NMR results indicate that intermediate structures are usually present. For a phenyl group at C$_P$ (**11**, **46A-Li**), the structure seems to be allenic.[8,40]

^{13}C Chemical Shifts and Couplings. The allenyl-propargyl nature of these lithium reagents is well defined by the chemical shifts of the central and lithium bearing carbon atoms, as indicated by the agreement between the shifts and other data ($J_{C−Li}$, IR). In a number of these reagents, the lithium cation was localized on a single carbon to the limits of detection by the Li−C coupling criterion. Nevertheless, there was significant evidence for delocalization of charge to the nonmetalated carbon. Thus, for allenyllithium **5A-Li** the terminal carbon (C$_P$) is shifted upfield by 30 ppm from that in allene.[6] This is similar to that found in a substantially localized allyllithium reagent (**47**, probably an aggregate) in pentane solvent.[41a]
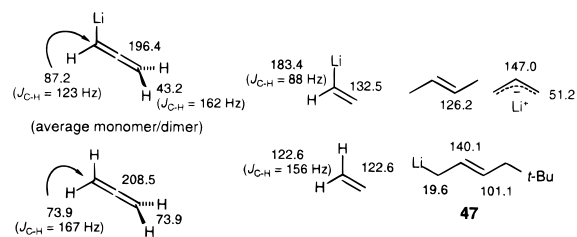
Many lithium reagents having Li on an sp^2-hybridized carbon (such as phenyllithium,[1h,41b] vinyllithium[6]) show strong downfield shifts of the Li-bearing carbon. The allenyllithium reagents also show this effect, although it appears to be smaller (13 ppm) than that for aryl and vinyllithium reagents The origin of these shifts is related to the favorable HOMO−LUMO relationship at sp^2 carbanionic carbons.[41b,42] Such effects are largely absent at sp^3 centers (such as C$_P$ in a propargyllithium reagent) as a result of orbital symmetry effects (overlap between filled and unoccupied orbitals after a 90° rotation).

Structures of Allenyl-Propargyllithium Reagents with Intermediate ^{13}C Chemical Shifts. Five of the A/P−Li reagents investigated (**22-Li**, **23-Li**, **24-Li**, **25-Li**, and **29-Li**) have intermediate chemical shift values for C$_C$. We have considered three explanations: (1) a CIP/SIP equilibrium; (2) a bridged structure such as **3**; (3) and an equilibrium between allenyl and propargyllithium reagents.

Although the temperature dependence is as expected for a CIP/SIP equilibrium,[43] the observation of unambiguously contacted mono-HMPA complexes for **23-Li** rules out the presence of sufficient SIP species to cause the chemical shift changes observed. Lithium reagents that are partially ion-separated in THF or other ether solvents will quantitatively form a SIP on addition of even 1 equiv of HMPA (e.g., LiI[1g]).

Computational studies of several A/P−Li reagents have predicted global minima with structures such as **3**, and several

(35) Owens, K. A.; Berson, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 5973−5985.

(36) Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, *95*, 8678−8685.

(37) Oakes, J. M.; Ellison, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 2969−2975. Robinson, M. S.; Polak, M. L.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C. *J. Am. Chem. Soc.* **1995**, *117*, 6766−6778.

(38) Wilmshurst, J. K.; Dykstra, C. E. *J. Am. Chem. Soc.* **1980**, *102*, 4668.

(39) For related behavior of some allyltitanium derivatives, see Kasatkin, A.; Sato, F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2848−2849.

(40) Maercker A.; Fischenich, J. *Tetrahedron* **1995**, *51*, 10209−10218.

(41) (a) Fraenkel, G.; Halasa, A. F.; Mochel, V.; Stumpe, R.; Tate, D. *J. Org. Chem.* **1985**, *50*, 4563−4565. (b) Jones, A. J.; Grant, D. M.; Russell, J. G.; Fraenkel, G. *J. Phys. Chem.* **1969**, *73*, 1624−1626.

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(43) Buncel, E.; Menon, B. C.; Colpa, J. P. *Can. J. Chem.* **1979**, *57*, 999−1005. Buncel, E.; Menon, B. *J. Org. Chem.* **1979**, *44*, 317−320. Hogen-Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* **1966**, *88*, 307−318.

| | $-RlnK = (1/T)\Delta H° - \Delta S°$ | | |
Reagent	$\Delta H°$ (kcal/mol)	$\Delta S°$ (e.u.)	std. dev.
22-Li	0.65 ± 0.008	6.9 ± 0.05	0.999
23-Li	1.1 ± 0.04	6.3 ± 0.07	0.99
24-Li	2.0 ± 0.19	9.0 ± 1.3	0.99
25-Li	2.1 ± 0.18	8.9 ± 1.2	0.99
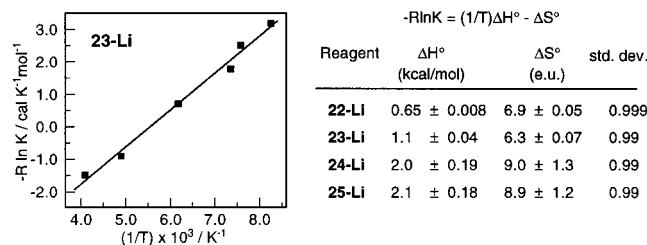
Figure 12. Thermodynamic parameters for the A/P equilibration of **22-Li** to **25-Li**.

crystal structures with this type of bonding have been reported (**12**, **14**, **15**).[10a,9] Since the high-level calculations were performed without appropriate solvents on Li, it is not clear whether such structures should also be present in solution. Some evidence for bridged structures has been obtained for 1-methoxyallenyllithium,[10c] in which ⁶Li-¹H HOESY cross-peaks were detected for the protons on the $C=CH_2$ terminus in the THF-solvated dimer. Since this structure lacks a proton at C_A (as do most of our structures), it is hard to evaluate the degree of bridging actually present from the qualitative observation of a cross-peak. C–Li coupling is seen only for C_A. Our failure to detect ¹³C-⁷Li coupling in all except one of the C_P-silyl-substituted reagents (although such coupling can be routinely observed in "normal" A and P organolithium reagents) suggests a qualitatively different type of structure, perhaps **3**.

Some direct evidence against a bridged structure and in favor of equilibrating isomers for these reagents comes from IR spectra. Although not all features of the pertinent region between 1800 and 2200 cm⁻¹ are fully explained in all of these reagents, compound **41P-Li**, which is clearly propargyl in its ¹³C chemical shifts, shows absorption only at ~2150 cm⁻¹. Reagent **6A-Li**, on the other hand, shows only a band at ~1890 cm⁻¹. Compound **23-Li** has absorptions at both 2179 and 1894 cm⁻¹ in THF. A bridged structure should show a single intermediate absorption.

Origin of the Temperature-Dependent Chemical Shifts for 22-Li–26-Li. We feel that an equilibrium between allenyl and propargyllithium reagents best explains the intermediate ¹³C chemical shifts observed in those solvents where the shifts are temperature-dependent. Why do low temperatures favor the propargyl isomer?

A thermodynamic analysis of the equilibrium between A and P structures was performed, using an estimated δ of 165 ppm for C_C in the allenyl (**23A-Li**) and 98 ppm for the propargyl isomer (**23P-Li**) (Figure 12). A principal source of uncertainty in the thermodynamic parameters is the estimation of the C_C δ, which ranges from 191.5 ppm for monomeric allenyllithium **5A-Li** to 162 ppm for **26A-Li**. For each compound the propargyl isomer is enthalpically favored, whereas the allenyl isomer is entropically favored.

The observed effects can be summarized as follows: (1) higher temperatures favor the allenyl isomer; (2) solvents less polar than THF or Me_2O such as ether and 2,5-dimethyltetrahydrofuran favor the propargyl isomer and the temperature dependence is lost; (3) SIP's show propargyl-like ¹³C chemical shifts; (4) substitution of Me by Ph on silicon favors the propargyl isomer; and (5) substitution of Me by t-Bu on silicon favors the allenyl isomer.

To explain the temperature dependence, we suggest a difference in solvation between the A and P isomers. Even a fractional decrease in the average number of solvent molecules in the A isomer would explain the small $\Delta H°$ and $\Delta S°$ changes. Perhaps the more highly directional, formally sp²-hybridized,

carbanion orbital at C_A results in stronger C–Li bonding and reduces the level of lithium solvation as compared to that of the formally sp³-hybridized propargyl carbanion carbon C_P. Higher temperatures would favor the isomer with the lower degree of lithium solvation. Stronger C–Li covalency at C_A would also explain the tendency for more allenyl character in the contact vs the separated ion pairs seen in most of the systems studied. The absence of temperature dependence for **23-Li** in 2,5-dimethyltetrahydrofuran and ether solution suggests that either the A/P equilibrium has no enthalpic component in these solvents or perhaps here symmetrically bridged structures such as **3** are present.

When methyl groups on silicon are replaced by the more electron-withdrawing phenyl groups, the fraction of propargyl isomer increases (compare **22-Li** to **23-Li**, **24-Li** and **25-Li**); consistent with the hypothesis that carbanion-stabilizing groups (such as Ph, PhS, PhSe, or R_3Si) at C_P favor the propargyl isomer. On the other hand, substitution of methyl on silicon by *tert*-butyl results in a reagent (**26-Li**) with predominant or exclusive allenyl character. This effect can be rationalized on the basis of solvation effects: the larger $SiMe_2Bu^t$ group hinders solvation of the lithium in the propargyl isomer compared with $SiMe_3$.

Configurational Stability of Allenyl-Propargyllithiums. Only scattered information is available about the stereodynamics of A/P–Li reagents. An early report concerns **8P-Li**, in which the ¹H NMR AA′BB′ pattern of the cyclopropyl group in benzene at room temperature coalesced and became an A_4 pattern as THF was added. Okamura and co-workers metalated diastereomeric allenes (**49** and its isomer) and found that deuteration gave identical products.[44] However, treatment of sulfoxide **48** and its isomer with MeLi to give **49**, a reaction that probably goes through an allenyllithium intermediate, proceeded stereospecifically with retention of configuration, implying some stereochemical lifetime of the lithium reagent before protonation occurs.[45]
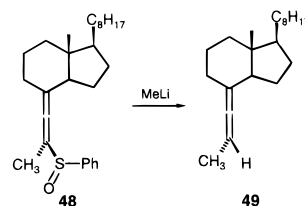
Both the in situ metalation-trimethylsilylation of **50**[46] and the KO^tBu/DO^tBu isotope exchange of **51**[47] occurred with retention of configuration. Thus the heteroatom-substituted lithium or potassium carbanion intermediates have substantial configurational stability: an estimate of 22 kcal/mol was made for inversion of the chloroallenyl anion formed from **51**. It is expected from analogies with inversion of heterosubstituted lithium reagents and nitrogen pyramidal inversion that RO- and Cl-substituted reagents would show exceptionally high barriers.
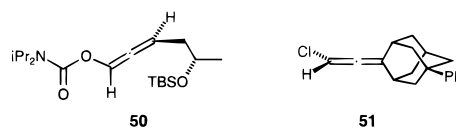
Our stereodynamic measurements were in part a byproduct of structural studies and so were not taken under uniform conditions of solvent and concentration, nor do the compounds

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form a pleasing series. We report the results (Figure 11) because there is little data available on racemization barriers for A/P−Li reagents. Our measurement of the inversion barrier for **33A-Li** is the first information on the configurational stability of an alkyl-substituted allenyllithium. The barrier of 10.7 kcal/mol in 1:1 Me_2O/Et_2O is close to that calculated for the inversion barrier of naked allenyl anion (9 kcal/mol).[38] Although the barrier to configurational inversion of organolithium reagents is often (but not always[1i*,48]) lowered by going to more strongly coordinating solvents,[49,13a] the inversion/diastereomer interconversion barrier of **32A-Li** in ether, where the principal aggregate appears to be a dimer, is not dramatically different from that in THF.

The Li−C coupling of **33A-Li** disappears at approx 50 °C lower temperature than the coalescence of the methyl groups, so there are fast intermolecular exchange processes of the C−Li bond (probably through transient dimers), which must occur with predominant retention of configuration at carbon. We thus cannot determine whether the racemization of **33A-Li** is intra or intermolecular.

This behavior is in contrast to that of **26A-Li** and **31A-Li**, for which the configurational inversion is intramolecular since the Li−C-coupled multiplet survives even after coalescence of the $SiMe_2$ group (Figure 10). Although direct comparison of the silyl and alkyl-substituted systems is problematic because the intra- or intermolecular nature of the racemization in the latter is unknown, it is certain that the barrier to intramolecular inversion of **33A-Li** is at least as high as the one measured ($\Delta G^{\ddagger} = 10.8$ kcal/mol). The substantial lowering in $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ on replacing an alkyl by a silyl must result principally from loosening of C−Li coordination, a consequence of the carbanion-stabilizing effect of the silyl group. It is interesting that **31A-Li** shows substantially higher configurational stability than does **26A-Li**. Presumably silyl substitution at C_A in **31A-Li** reinforces the natural localization of charge at C_A, whereas in **26A-Li** the silicon substituent tends to equalize charges on C_A and C_P.

Summary. Alkyl-substituted A/P−Li reagents show a pronounced tendency for localized structures, with lithium predominantly coordinated to the allenyl carbon C_A (**5A-Li**, **6A-Li**, **9A-Li**, **21A-Li**, **32A-Li**, **33A-Li**, **34A-Li**, **37A-Li**, **39A-Li**). Placement of an anion-stabilizing group like triorganosilyl (**28A-Li**, **31A-Li**) at C_A reinforces this tendency. Placement of anion-stabilizing substituents at C_P reduces the preferences for allenyl structures and may lead either to pure propargyl compounds (**41P-Li**), or to intermediate structures (**22-Li** to **26-Li**). Several of these show a pronounced temperature dependence of their chemical shifts, suggesting that they are mixtures of allenyl and propargyl isomers in rapid equilibrium on the NMR time scale. Since decoalescence could not be achieved even below −150 °C, $\Delta G^{\ddagger}$ for A/P interconversion must be less than 4 kcal/mol. Placement of silyl groups at either C_A or C_P leads to easier ion separation, so that SIPs are formed when more than 1 equiv of HMPA is added. All of the A/P−Li reagents except the parent (**5A-Li**) and possibly **8P-Li** are monomeric in THF or dimethyl ether; **32A-Li** and **33A-Li** are dimeric in ether.

Ring-strain effects result in a propargyl structure when a three-membered ring spans C_P (**8P-Li**). However, similar 4-ring structures (**37A-Li**, **39A-Li**) are still allenyllithiums.

All of the A/P−Li reagents investigated with diagnostic diastereotopic groups (**23-Li**, **24-Li**, **26A-Li**, **32A-Li**, **33A-Li**, and **39A-Li**) underwent slow racemization on the NMR time scale at low temperatures, with free energies of activation barriers ranging from 6.1 to 14.5 kcal/mol.

Experimental Section

General. All reactions involving lithium reagents were run in oven (125 °C) or flame dried flasks under a dry nitrogen atmosphere. Tetrahydrofuran (THF) and ether were freshly distilled from sodium benzophenone ketyl. Methyl ether (boiling point −20 °C) was freshly distilled from alkyllithium reagents. Hexamethylphosphoric triamide (HMPA) was distilled from CaH_2 at reduced pressure and stored under N_2 over molecular sieves. Common lithium reagents were titrated with *n*-PrOH or *i*-PrOH in THF or ether using 1,10-phenanthroline as indicator.[50] Reported reaction temperatures are those of the cooling bath with −78 °C being maintained by a dry ice/ethanol bath and −20 °C maintained by a freezer. Bath temperatures are reported for Kugelrohr distillations.

Precautions. HMPA has long been recognized to have low to moderate acute toxicity in mammals.[51a] Inhalation exposure to HMPA, however, has been shown to induce nasal tumors in rats.[51b,c] Adequate precautions must be taken to avoid all forms of exposure to HMPA. Organoselenium and organotin compounds are toxic and should be handled with care in a fume hood.

NMR Spectroscopy. Multinuclear low-temperature NMR experiments were run on a wide-bore AM-360 spectrometer at 90.56 MHz (^{13}C), 139.962 MHz (^{7}Li), 52.998 MHz (^{6}Li), or 145.784 MHz (^{31}P) or an AM-500 spectrometer at 125.6 MHz (^{13}C) with the spectrometer unlocked (the field was generally very stable, and only occasionally did an experiment have to be abandoned due to a field shift). Gaussian multiplication (GM) was performed using the Gaussian broadening parameter (GB) equal to the duration of the FID and the line broadening parameter (LB) equal to −(digital resolution)/GB.

Various techniques were utilized to make unambiguous ^{13}C chemical shift assignments including the following: DEPT 90, DEPT 135, QUATD, and ^{1}H-coupled ^{13}C. QUATD is a pulse sequence that dephases all carbons with one-bond ^{1}H coupling leaving only quaternary carbons, and additionally provides long-range ^{1}H decoupling. QUATD proved to be a most important tool since two of the three carbons of the allenyl-propargyl framework of many of the compounds studied are quaternary carbons. Additionally ^{13}C-^{7}Li couplings usually had improved signal-to-noise when one of these techniques was employed.

General Procedure for NMR Spectroscopy of Lithium Reagents. Samples of the lithium reagent in THF or other solvents (total 4.0 mL for 10 mm tubes, 0.5 mL for 5 mm tubes) were prepared in thin-walled NMR tubes, which were oven-dried, fitted with a septum, and flushed with N_2. The outside top portions of the tubes were lightly greased to make a better seal for the septa, which were held securely by Parafilm. Silicon grease was placed on the septa tops to seal punctures, and the tubes were stored at −78 °C until the experiment was performed. The field was adjusted to a $CDCl_3$ lock sample, the spectrometer unlocked, and the probe cooled (−90 to −155 °C). Temperatures were measured using the internal ^{13}C shift thermometer tris(trimethylsilyl)methane[1k] or a calibrated RTD (resistance temperature device) accurate to 0.1 °C. The reading was taken 5−10 min after the RTD element had been

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lowered into the probe. (The reading fluctuated within −0.1 °C at this point.) The sample was inserted and the spectrometer tuned. Since deuterated solvents were not used, the magnet was shimmed on the free induction decay (FID) signal of a restricted acquisition of C-3 of THF, CH$_2$ of ether, or the carbon signal of methyl ether. The probe was then tuned to the nucleus of interest, and spectra were measured.

Referencing ^{13}C, ^{7}Li, and ^{31}P NMR Spectra. ^{13}C spectra were referenced to solvent peaks (previously referenced to tetramethylsilane). The following values were used: THF (C-2 = 67.96 ppm), methyl ether (60.08), and ether (CH$_2$ = 66.51). The ^{7}Li and ^{31}P chemical shift references were sealed capillary tubes containing LiCl (0.3 M MeOH, δ 0.00) and PPh$_3$ (1 M THF, δ −6.00), respectively. These tubes were oven-dried before use.

Starting Materials. Commercially available materials were used except as follows: *n*-Bu^{6}Li was synthesized from 1-chlorobutane and ^{6}LiE.[52] Dicyclopropylacetylene (**8P-H**),[13b] 3,3-diphenylcyclobutanone,[53] and the trimethylstannyl and/or methylseleno procursors to lithium reagents **32-Li**, **33-Li**, and **34-Li**[1d] were prepared by literature procedures.

General Procedure for the Synthesis of Propargyl Silanes: Synthesis of 1-Phenyldimethylsilyl-2-butyne, 23P-H.[55,56] To an oven-dried, nitrogen-purged flask with a magnetic stir bar and septum was added *ether* (70 mL), 2-butyne (1.6 mL, 20 mmol), and *t*-BuLi (10.7 mL, 1.78 M, 19 mmol) at −78 °C. The flask was warmed to −20 °C for 1 h and cooled to −78 °C, and PhMe$_2$SiCl (2.5 mL, 19 mmol) was added. The solution was warmed to 0 °C and diluted in hexane (70 mL), washed with water (3 × 20 mL) and brine (20 mL), and dried over Na$_2$SO$_4$. The solvent was removed by rotary evaporation to give 2.475 g (13.1 mmol, 69% yield) of **23P-H** as a clear colorless liquid, which was purified by flash chromatography (5% ether/hexane as eluent) or kugelrohr distillation (60−80 °C bath temperature, 0.25 mmHg). The reaction must be run in ether; reactions in THF resulted in up to 20% allene product. ^{1}H NMR (200 MHz, CDCl$_3$) δ: 0.36 (s, 6H), 1.64 (q, *J* = 2.86 Hz, 2H), 1.76 (t, *J* = 2.86 Hz, 3H), 7.32−7.36 (m, 3H), 7.52−7.57 (m, 2H). ^{13}C NMR (90.56 MHz, CDCl$_3$) δ: −3.48 (CH$_3$), 3.56 (CH$_3$), 6.22 (CH$_2$), 74.51 (C), 75.87 (C), 127.75 (CH), 129.21 (CH), 133.55 (CH), 137.96 (C). IR: v 2224, 2096. MS M$^+$ calcd 188.1021; exp 188.1026.[56b]

3-Phenylseleno-1-dimethylphenylsilyl-1-butyne (30).[1e] A solution of lithium diisopropylamide (2.2 mmol) was prepared by addition of n-BuLi (1 mL, 2.2 mmol, 2.21 M) to a solution of freshly distilled diisopropylamine (0.3 mL, 2.2 mmol) in THF (10 mL) at −78 °C. Propargyl phenyl selenide (138 μL, 1.0 mmol) was added to the solution at −78 °C, followed in 10 min by MeI (65.4 μL, 1.0 mmol). The solution was stirred at −78 °C for 10 min, and PhMe$_2$SiCl (176 μL, 1.0 mmol) was added. After 10 min, the reaction mixture was allowed to warm to −20 °C for 40 min. Ether/hexane (1:1, 30 mL) was added, and the reaction mixture was washed with H$_2$O (5 × 15 mL), NH$_4$Cl solution (2 × 15 mL), and brine (2 × 15 mL) and dried over Na$_2$SO$_4$. Siloxane was removed by preparative TLC, eluting the plate 4× with distilled hexane as solvent. The plate was allowed to dry after each elution. The product **30** was a light yellow oil (180.5 mg, 53% yield). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 0.35 (s, 6 H), 1.63 (d, *J* = 4.8 Hz, 3 H), 3.95 (q, *J* = 4.8 Hz, 1 H), 7.25−7.70 (m, 10 H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: −0.82 (SiMe), 22.33 (CH$_3$), 25.47 (CH), 86.29 (C-2), 109.16 (C-1), 129.18 (i-SePh), 133.68 (o-SePh), 127.80 (m-SePh),

128.31 (p-SePh), 137.10 (i-SiPh), 135.84 (o-SiPh), 128.84 (m-SiPh), 129.29 (p-SiPh). MS M$^+$ calcd C$_{18}$H$_{20}$SeSi 344.0499; exp 344.0506.

^{13}C NMR Spectroscopy of Allenyllithium (5A-Li) in Methyl Ether. Allene gas (−0.3 mL) and methyl ether (3.5 mL) were condensed into a 10 mm NMR cooled to −78 °C. *t*-BuLi (0.4 mL) was added to dry the reagent and solvent. The contents were distilled at room temperature into a second 10 mm NMR tube at −78 °C. *t*-BuLi (0.38 mL, 1.70 M, 0.64 mmol) was added, and the solution was warmed to −20 °C for 20 min. A white precipitate formed immediately, and the solution slowly developed a yellow color. The white solid remained even after the addition of 2 mL of THF; upon standing it settled to the bottom of the NMR tube and did not interfere with spectroscopy. An additional 0.64 mL of *t*-BuLi was added, and volume was adjusted to form a 0.27 M solution with a Me$_2$O/THF ratio of 2.5:1. Two sets of signals were present (Figure 1). Coupling $J_{C−Li}$ in the monomer could be resolved at −140 °C (*J* = 26 Hz). Coupling in both monomer ($J_{C−Li}$ = 27 Hz) and dimer ($J_{C−Li}$ = 16 Hz) was resolved at −150 °C. Assignments were verified using DEPT 90, 135, and QUATD experiments. In a variable temperature experiment the signals of monomer (δ 41.2, 88.7, 191.7) and dimer (δ 44.8, 87, 198.5) began to broaden at −130 °C and were fully coalesced at −80 °C (δ 43.8, 87.3, 197.6). Following the experiment, the solution was quenched with PhMe$_2$SiCl. Aqueous workup followed by removal of solvent resulted in 178 mg (95% yield) of a 95:5 ratio of propargyl/allenyl silanes **5P-SiMe$_2$Ph** and **5A-SiMe$_2$Ph**. ^{1}H NMR of dimethylphenylpropargylsilane, **5P-SiMe$_2$Ph** (200 MHz, CDCl$_3$) δ: 0.40 (s, 9H), 1.72 (d, *J* = 2.9 Hz, 2H), 1.86 (t, *J* = 2.9 Hz, 1H), 7.33−7.42 (m, 3H), 7.51−7.60 m, 2 H).[57] The NMR sample also contained 25% of PhMe$_2$SiOSiMe$_2$Ph.

The solid (which formed in all experiments in THF or Me$_2$O) was identified by decanting the solution, adding fresh THF and PhMe$_2$-SiCl. The product was identified as 1-dimethylphenylsilyl-1-propyne. ^{13}C NMR (75.5 MHz, CDCl$_3$) δ −0.77 (SiCH$_3$), 3.72 (CH$_3$), 81.78 (C), 104.80 (C), 127.80 (CH), 129.25 (CH), 133.61 (CH), 137.46 (C).

Sample Experimental Procedure for Metalation and Spectroscopy of 2-Alkynes: ^{13}C NMR of 3-Lithio-2,2-dimethyl-3,4-pentadiene (21A-Li), 0.64 M in Methyl Ether and Ether. *t*-BuLi (0.38 mL, 1.8 M, 0.70 mmol) was added to a −78 °C solution of 2,2-dimethyl-3-pentyne (**21P-H**, 86 μL, 0.64 mmol) in methyl ether (3.6 mL) in a 10 mm NMR tube. The solution was warmed to −20 °C for 20 min and then cooled to −78 °C. ^{13}C NMR identified a clean solution of **21A-Li**. The line widths for C$_C$ and C$_P$ were 3.53 and 4.77 Hz (LB = 1 Hz), and C$_A$ was coupled to lithium (δ 114.6, 1:1:1:1 q, *J* = 24 Hz at −140 °C, Figure 2). Assignments were verified using DEPT 135, QUATD, and ^{1}H-coupled experiments. **21A-Li** ^{7}Li NMR δ: 0.63. ^{13}C NMR (90.56 MHz) δ: 43.93 (C$_P$), 114.6 $J_{C−Li}$ = 24 Hz (C$_A$), 178.26 (C$_C$); the *tert*-butyl signal assignment were ambiguous. **21P-H** (90.56 MHz, THF −125 °C) δ: 3.18 (C$_P$), 74.15 and 89.99 (C$_A$ and C$_C$). In ether **21P-H** partially metalated in the presence of *t*-BuLi to give a single allene species. ^{13}C-^{7}Li coupling was not resolved. **(21A-Li)$_2$** δ: 46.8 (C$_P$), 114.8 (C$_A$), 176.2 (C$_C$); the *tert*-butyl signals were not distinguishable from solvent signals.

One of the NMR solutions was trapped with PhMe$_2$SiCl (0.12 mL, 0.73 mmol). An aqueous workup afforded a 66% yield of a 6:1 molar ratio of **27P-H** and phenyldimethylsiloxane.

Sample Experimental Procedure for Spectroscopic Studies of 1-Triorganosilyl-2-butynes: ^{13}C NMR of 1-Lithio-1-dimethylphenylsilyl-2-butyne/3-Lithio-1-dimethylphenylsilyl-1,2-butadiene (23-Li), 0.16 M in Methyl Ether. *t*-BuLi (0.4 mL, 1.7 M, 0.67 mmol) was added to a −78 °C solution of **23P-H** (133 μL, 0.64 mmol) in methyl ether (3.3 mL), or other solvent. The NMR tube was warmed to −20 °C for 20 min then cooled back to −78 °C. ^{13}C spectra were obtained at the following temperatures: −155, −145, −121, −95, −65, and −35 °C (see Table 1 and Figures 5 and 6). Chemical shift assignments were verified using QUATD, DEPT 135, DEPT 90, and ^{1}H-coupled experiments. Lithium coupling was not observed, although C$_P$ did broaden (line width 40 Hz, residual ^{7}Li coupling) at −150 °C.

A variable concentration study was performed in 1:1 THF/pentane in a 5 mm NMR tube. Dilutions were accomplished by adding 500 μL

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Table 1. Variable Temperature ^{13}C NMR δ for 23-Li[a]

T (°C)	−35	−65	−95	−121	−145	−155
C_P	22.24	19.90	17.16	12.72	7.2	4.1
C_C	140.44	139.10	135.60	126	117.43	109.7[b]
C_A	74.41	73.22	72.02	70.18	68.03	67.00
methyl	11.62	11.39	10.93	10.11	9.06	8.53
$SiMe_2$	0.73	0.72	0.84	1.01	1.48/0.97	1.83/0.85
ipso	147.22	147.21	147.26	147.39	147.61	147.76
ortho	134.64	134.66	134.70	134.78	134.88	134.96
meta	127.38	127.38	127.41	127.47	127.53	127.57
para	127.49	127.53	127.60	127.65	127.71	127.74

[a] Measured in parts per million.

of 1:1 THF/pentane with a microliter syringe then removing 0.5 mL of the solution with a 1 mL syringe. Between 0.64 and 0.08 M at −90 °C, C_A changed from 12.1 to 13.9 ppm, C_C from 125.9 to 130.3 ppm, C_P from 69.0 to 70.2, and the CH_3 signal from 9.9 to 10.5 ppm.

Experiments were performed in 2,5-dimethyltetrahydrofuran as described above and are reported in Figure 5.

An HMPA titration was performed during one experiment by removing the sample from the probe and placing the NMR tube into a −78 °C bath then adding small aliquots of HMPA through the septum and replacing the NMR tube into the probe. The reagent fully separated in the presence of 4 equiv of HMPA to form a propargyllithium separated ion **23⁻//Li(HMPA)₄**+ (Figure 8). In the presence of 8 equiv of HMPA, the chemical shifts of **23⁻//Li(HMPA)₄**+ did not move significantly over a temperature range of −155 to −35 °C. (see Table 2 and Figure 5). The separated ion was stable to proton transfer during the course of the experiment. ^{7}Li NMR (139.96 MHz, Me_2O) δ: 0.50 ppm (Me_2O), 0.01 ppm (4-HMPA, quintet); referenced to LiCl in methanol (0 ppm). The C−H coupling constant ($^1J_{C-H}$) for C_P was 138 Hz for the CIP at −69 °C and 142 Hz for the separated ion.

Several of the NMR experiments were quenched with CH_3OD. A 3:2 THF/ether solution gave a 76% yield of **23A-D** and **23P-D** in a

Table 2. Variable Temperature ^{13}C NMR Data for **23⁻//Li(HMPA)₄**+ in 8 Equiv of HMPA

T (°C)	−35	−65	−95	−120	−155
C_P	9.19	7.75	7.35	7.00	6.68
C_C	115.78	113.58	113.02	112.57	112.23
C_A	65.96	64.75	64.55	64.55	64.61
Me	9.69	9.81	9.86	9.94	10.00
$SiMe_2$	2.08	2.34	2.41	2.49	2.56
ipso	151.57	151.82	151.68	151.45	151.15

0.1.8:1 (A/P) ratio. ^{1}H NMR (200 MHz, $CDCl_3$) **23P-D** δ: 0.36 (s, 9H), 1.64 (q, peak interference, 1H), 1.75 (d, J = 2.74 Hz, 3H), 7.28−7.38 (m, 3H), 7.50−7.57 (m, 2H). **23A-D** δ: 0.35 (s, 9H), 1.61 (d, J = 4.0 Hz, J_{D-H} −0.6 Hz, 3H), 5.02 (q, J = 4.0 Hz, J_{D-H} −0.6 Hz, 1H), 7.28−7.38 (m, 3H), 7.50−7.57 (m, 2H). ^{13}C NMR (90.56 MHz, $CDCl_3$) **23P-D** δ: −3.49 ($SiCH_3$), 3.54 (CH_3), 5.90 (J_{C-D} = 19 Hz, C_P), 74.51 and 75.85 (C_A, C_C), 127.74 (*ortho*), 129.20 (*para*), 133.63 (*meta*), 137.93 (*ipso*). **23A-D** δ: −2.31 ($SiCH_3$), 12.95 (CH_3), 78.2 (J_{C-D} = 18 Hz, C_A), 80.51 (C_P), 127.93 (*ortho*), 129.01 (*para*), 133.53 (*meta*), 138.69 (*ipso*), 212.12 (C_C). IR: 1932 (s), 2100 (w) 2220 (w).

Supporting Information Available: Preparative procedures for precursors, reproductions of ^{13}C and ^{1}H NMR spectra, and chemical shift data for **6A-Li, 8P-Li, 9A-Li, 22-Li, 23-Li, 25-Li, 26-Li, 27-Li, 28A-Li, 31A-Li, 32A-Li, 33A-Li, 34A-Li, 37A-Li,** and **39A-Li**; IR spectra of **6A-Li, 23-Li,** and **41P-Li**. This material is available free of charge via the Internet at http://pubs.acs.org.

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