for $C_{16}H_{16}Zr$: C, 64.1; H, 5.39. Found: C, 62.6; H, 5.28.

Bis(cyclooctatetraenyl)hafnium. To $HfCl_4(THF)_2$ (1.89 g, 4.07 mmol) and magnesium turnings (0.5 g, 21 mmol) suspended in tetrahydrofuran (60 mL) was added cyclooctatetraene (1.1 mL, 9.7 mmol). After being heated to 55 °C for 1 h, the solution developed a dark red color. The solution was stirred for 20 h at 55 °C, and then for 3 h at 70 °C. The cooled solution was filtered, and the remaining red-orange powder was extracted with THF (5 × 20 mL). The combined filtrates were taken to dryness, and the red-orange residue was dried for 6 h at 60 °C under vacuum. The dark brick-red powder was extracted with dichloromethane (3 × 50 mL), and the filtered extracts were combined, concentrated to ca. 50 mL, and cooled to -78 °C to yield small dark-red plates. The crystals were dried for 4 h at 100 °C to remove dichloromethane solvate molecules. Additional crops of crystals were obtained by further concentration and cooling of the supernatant. Yield: 0.72 g (50%). IR (cm^{-1}): 3040 w, 1430 w, 1308 w, 900 s, 860 m, 790 m, 722 s, 540 br, 450 br. ^1H NMR (CD_2Cl_2, -90 °C): δ 5.98 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, -90 °C): δ 97.6 (s).

Crystallographic Studies.[71] Single crystals of $Zr(C_8H_8)_2$ were mounted on a thin glass fiber using oil (Paratone-N, Exxon), transferred to the diffractometer, and immediately cooled to -75 °C in a cold nitrogen gas stream. A suitable crystal was chosen, and preliminary photographs revealed a weak overall diffraction pattern and a broad mosaic spread, probably due to the high thermal motion. Standard peak search and automatic indexing procedures, followed by least-squares refinement using 25 reflections yielded the cell dimensions given in Table I.

Data were collected in one quadrant of reciprocal space ($\pm h$, $+k$, $-l$) by using measurement parameters listed in Table I. Axial photographs clearly indicated the $2/m$ Laue group, and systematic absences for $h0l$, $h + l \neq 2n$ were consistent with space groups $P2/n$ and Pn. The average values of the normalized structure factors suggested the centric choice $P2/n$, but the acentric choice Pn was confirmed by successful refinement of the proposed model. The measured intensities were reduced to structure factor amplitudes and their estimated standard deviations by correction for background, scan speed, and Lorentz and polarization effects. While corrections for crystal decay were unnecessary, absorption corrections were applied, the maximum and minimum transmission factors being 0.951 and 0.892. Systematically absent reflections were deleted, and only those data with $I > 2.58\ \sigma(I)$ were used in the least-squares refinement.

The structure was solved in the centric space group $P2/n$ by using Patterson (SHELXS-86) and weighted difference Fourier methods. The position of the zirconium atom was deduced from a sharpened Patterson map, and subsequent Fourier calculations revealed the positions of the remaining non-hydrogen atoms, which appeared disordered about the 2-fold axis. However, refinement of an ordered model in the acentric space group Pn gave more satisfactory results. The quantity minimized by the least-squares program was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 0.99/(\sigma(F_o)^2 + (pF_o)^2)$. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both real and imaginary components of anomalous dispersion. In the final cycle of least squares, all non-hydrogen atoms were independently refined with anisotropic thermal coefficients, and a group isotropic thermal parameter was varied for the hydrogen atoms, which were fixed in "idealized" positions with C-H = 0.95 Å. Successful convergence was indicated by the maximum shift/error of 0.048 in the last cycle. Final refinement parameters are given in Table I. The final difference Fourier map had no significant features. Refinement of a disordered model in space group $P2/n$ converged to give similar structural features for the $Zr(C_8H_8)_2$ molecule, but was rejected in favor of the ordered model in space group Pn.

Acknowledgment. We thank the National Science Foundation (Grant CHE 89-17586) and the Office of Naval Research under their Young Investigator Award Program for support of this research. We thank Charlotte Stern of the University of Illinois X-ray Crystallographic Laboratory for assistance and Dr. Richard Harlow of DuPont for suggesting that the acentric space group be examined more closely. We thank B.A.S.F. for a generous gift of cyclooctatetraene. G.S.G. is the recipient of an A. P. Sloan Research Foundation Fellowship (1988–1990) and a Henry and Camille Dreyfus Teacher–Scholar Award (1988–1993).

Supplementary Material Available: A table of calculated hydrogen atom coordinates, a full list of anisotropic thermal parameters for $Zr(C_8H_8)_2$, and a complete table of bond distances and angles (4 pages); a listing of final observed and calculated structure factors for $Zr(C_8H_8)_2$ (7 pages). Ordering information is given on any current masthead page.

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[71] For details of the data collection and refinement procedure, see: Jensen, J. A.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* 1988, *110*, 4977–4982.

Formation of Organodilithium Compounds via Lithium–Tin Exchange

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The reaction of methyllithium in THF with 2,5-bis(trimethylstannyl)-1,5-hexadiene (**6**) affords 2,5-dilithio-1,5-hexadiene (**2**) via the intermediacy of lithium stannates. The similar reaction of (2*Z*,4*Z*)-2,5-bis(trimethylstannyl)-2,4-hexadiene (**11**) affords (2*E*,4*E*)-2,5-dilithio-2,4-hexadiene (**3**). The more favorable formation of **3** suggests a greater relative stability over **2**. Ab initio calculations indicate that the symmetrical dilithium-bridged structure found for **3** is more favorable than the unsymmetrical dilithium-bridged structure found for **2**.

Introduction

Lithium bridging is a common structural feature of organopolylithium compounds.[1] Several derivatives of (1*Z*,3*Z*)-1,4-dilithio-1,3-butadiene (**1**) adopt a symmetrical bridged structure **1′** in the solid state.[2-4] Calculations by

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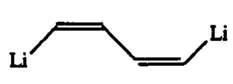
† University of Michigan.

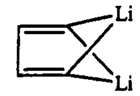
‡ Mu'tah University.

(1) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* 1985, *24*, 353.

(2) Schubert, U.; Neugebauer, W.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* 1982, 1184.

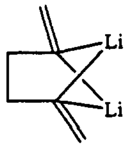


1

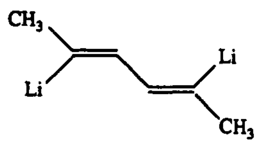


1′

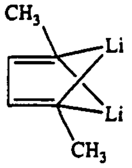
2



2′



3



3′

Schleyer and Kos indicated that structure 1′ is highly stabilized over possible nonbridged geometries.[5] It was originally suggested that structure 1′ is stabilized by a "Möbius-Hückel aromaticity",[5] although subsequent discussions have emphasized the favorable electrostatic interaction between the carbon and lithium atoms of the bridge.[6,7]

In order to assess the importance of conjugation in stabilizing 1,4-dilithio compounds, we have compared the isomeric dilithiohexadienes 2 and 3. Thus, both isomers should be able to form 1,4-bridged structures (2′ and 3′), which might be stabilized by similar electrostatic interactions. On the other hand, cyclic π-conjugation cannot contribute to the stabilization of 2, although it may be important for 3.

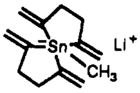
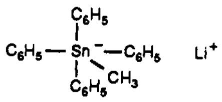
We report here on the formation of 2 and 3 from the corresponding bis(trimethylstannyl)hexadienes 6 and 11, respectively, via the lithium–tin exchange reaction. The considerably more favorable formation of 3 is consistent with a greater relative stability. This result has been confirmed and extended by ab initio calculations.

Results and Discussion

Synthesis. Dilithiohexadienes 2 and 3 may be readily prepared via straightforward routes outlined in Scheme I. Bromination of 1,5-hexadiene 4 followed by dehydohalogenation gave 2,5-dibromo-1,5-hexadiene (5) as the major product, as reported by Sheehan.[8] The reaction of 5 with lithium metal in ether afforded 2,[9] which gave 1,5-hexadiene on quenching with water. Treating 2 with trimethyltin chloride afforded 6.

The hydrostannation of 2,4-hexadiyne 7 with dibutyltin dihydride gives a modest yield of 2,5-dimethyl-1,1-dibutylstannole (8).[10] The stannole may be stereospecifically iodinated with iodine in CS_2 to (2*Z*,4*Z*)-2,5-diiodo-2,4-hexadiene (9).[11] Lithiation of 9 with butyllithium at −78 °C gave 3.[11] The reaction of 3 with trimethyltin chloride gave the corresponding bis(trimethylstannyl)hexadiene 11, while quenching with water gave (2*E*,4*E*)-2,4-hexadiene (10).

Table I. Comparison of Selected ^{13}C and ^{119}Sn NMR Parameters of Lithium Tetraphenylmethylstannate[a] and Lithium Spirostannate (14)[b]

	 14	
δ(Sn)	−344 ppm	−292 ppm
δ(C(Me))	−2.3 ppm	−2.3 ppm
^1J(Sn(Me))	380 Hz	436 Hz
δ(C(vinyl or phenyl))	178 ppm	165 ppm
^1J(Sn(vinyl or phenyl))	351 Hz	376 Hz

[a] Reference 18. [b] This work.

The ^{1}H and ^{13}C NMR spectra of 2 and 3 are completely consistent with their assigned structures. Although the spectra have no unusual features, it was noted that addition of extraneous methyllithium led to small shifts in the chemical shift values of 3. This may be due to changes in aggregation of 3.

Lithium–Tin Exchanges. The preparation of 2 and 3 via the lithium–tin transmetalation reaction seems to offer advantages over the lithium–halide routes. The lithium–tin exchange is a reversible process that leads to the more stable organolithium.[12] Very stable dilithio compounds such as those derived from various 1,3-butadienes can be readily prepared,[13,14] while the exchange reactions leading to less stable dilithio compounds such as *trans*-1,2-dilithioethylene[15,16] and 1,1-dilithio-1-alkenes[17] yield instead only monolithio compounds. Thus, it was hoped that the relative ease of formation of 2 and 3 from 6 and 11, respectively, would be a measure of differences in their stability. For this reason and because of the considerable current interest in the mechanism of the lithium–tin exchange,[18,19] we have examined the reaction of methyllithium with 6 and 11 in detail.

The reaction of 6 with excess methyllithium in THF-d_8/ether at −80 °C gives a pale yellow solution of tetramethyltin and a monolithium compound 12 (see Scheme II). The identity of 12 as a stannate complex follows from its NMR spectra. The ^{1}H NMR spectrum indicates a symmetrical species, while the ^{119}Sn NMR spectrum shows a new signal at $\delta = -308$ ppm, far upfield from that of the precursor 6 (−36 ppm). Such high-field ^{119}Sn chemical shifts are characteristic of higher coordinated tin compounds.[20] Thus, Reich and Phillips report the chemical shift values of various lithium penta(phenyl, methyl)stannates in the range −277 to −311 ppm.[18] Quenching of

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(3) Bauer, W.; Feigel, M.; Müller, G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 6033.

(4) An X-ray structure of the tetraphenyl derivative of 1 shows this bridged structure: Schleyer, P. v. R. Private communication.

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(6) Schleyer, P. v. R. *Pure Appl. Chem.* **1983**, *55*, 355; **1984**, *56*, 151.

(7) Also, see: Streitwieser, A., Jr.; Swanson, J. T. *J. Am. Chem. Soc.* **1983**, *105*, 2502. Streitwieser, A., Jr. *Acc. Chem. Res.* **1984**, *17*, 353.

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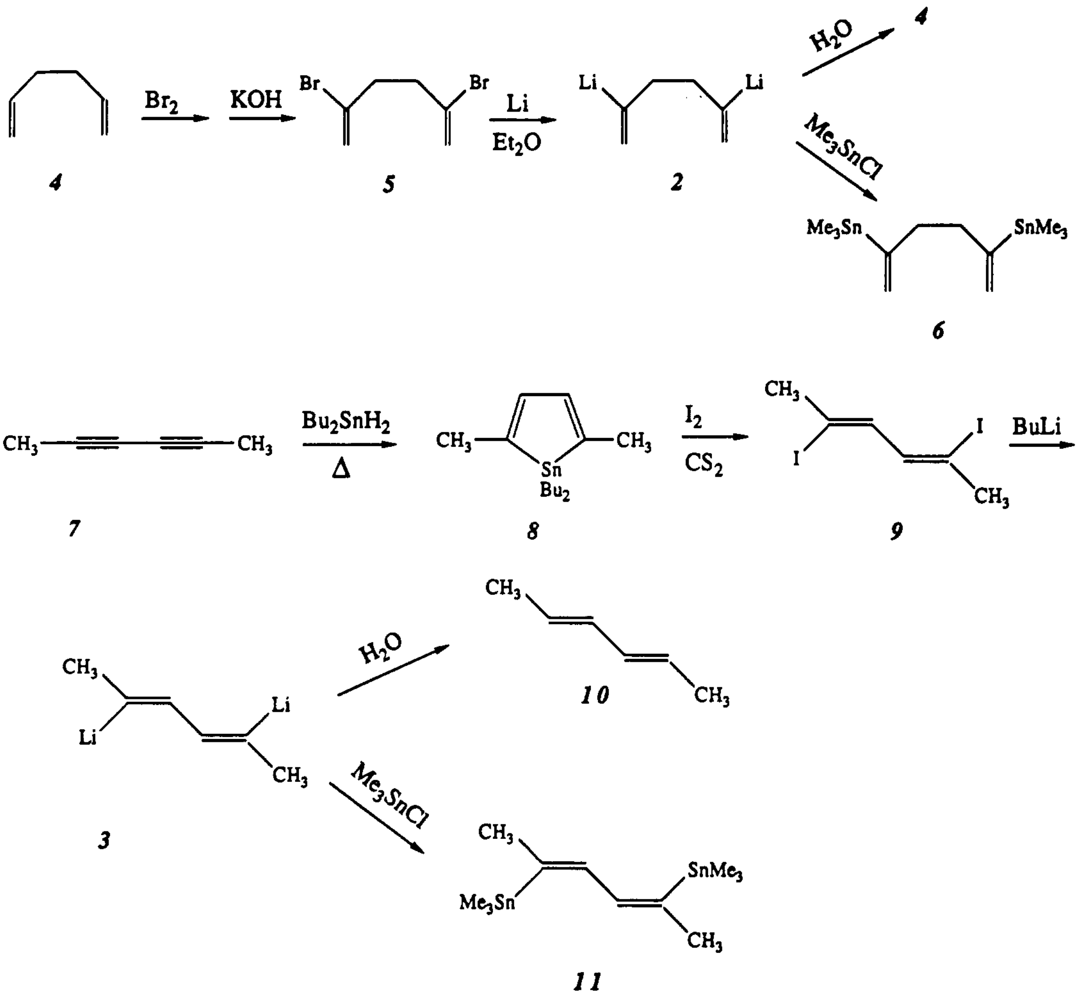
Scheme I



12 with water at −80 °C gave 2-(trimethylstannyl)-1,5-hexadiene (13), the product expected from vinyl cleavage of 12.

Apparently, vinyl cleavage is considerably favored over methyl cleavage from 12. We have not been able to detect 1,1-dimethyl-2,5-bis(methylene)stannolane (17) (<5%), the hypothetical product from methyl cleavage. Compound 17 was prepared independently from the reaction of 2 with dimethyltin dichloride.

Warming the solution of 12 to −40 °C led to irreversible changes in the NMR spectra, which indicate an increase in the Me_4Sn concentration and the formation of a new species assigned as spirostannate 14. The ^{119}Sn NMR signal of 14 at $\delta = -334$ ppm indicates a stannate structure. The ^{1}H NMR spectrum of 14, which closely resembles that of 12, indicates a symmetrical species, which has a prominent satellite spectrum due to coupling with $^{119/117}Sn$. The ^{13}C NMR parameters of the carbon atoms bound to tin closely match those of the related lithium tetraphenylmethylstannate (see Table I). Quenching of 14 with water at −80 °C gave a 75% yield of the bis(methylene)stannolane derivative 15 and smaller quantities of 13 (11%) and 16 (14%). Compound 15 is the product expected from vinyl cleavage of 14, while the minor products may have been formed from 15 via reaction of methyllithium during the quench.

The conversion of 12 to 14 involves the chemical exchange of two methyl groups of 12 for a 1,5-hexadienyl moiety. An analogous exchange has been found for lithium (phenyl, methyl)stannates, for which replacement of methyl by phenyl was favored.[18] It appears that the exchange of methyl by vinyl is also favorable. It is also likely that incorporation of a five-membered tin-containing ring in the presumed trigonal-bipyramidal geometry of 14 leads to greater stability.[21]

It has been argued that organotin "ate" complexes have trigonal-bipyramidal structures, as do most main-group hypervalent pentacoordinated compounds.[22] The ^{1}H NMR spectrum of 14 shows only one set of cis and trans vinyl resonances at temperatures down to −80 °C, even though two sets (apical and equatorial) should be observed if the compound were not fluxional. Therefore, pseudorotation must be fast on the NMR time scale.

However, the singlet assigned to the allylic hydrogen atoms of 14 ($\delta = 2.17$ ppm) reversibly separates into two multiplets ($\delta = 2.05$ and 2.23 ppm) at −80 °C with a coalescence temperature about −23 °C. This behavior is reminiscent of that observed for structurally similar spiroarsoranes and spirophosphoranes.[22-24] Thus, pseudorotation of 14 using an equatorial methyl group as a pivot, interconverts the apical and equatorial vinyl groups but the pairs of vicinal hydrogens that are syn or anti to methyl remain so. A second, presumably slower, pseudorotation in which the methyl group becomes apical followed by return to an equatorial position interconverts the syn and anti protons.[23,24] However, an alternative mechanism in-

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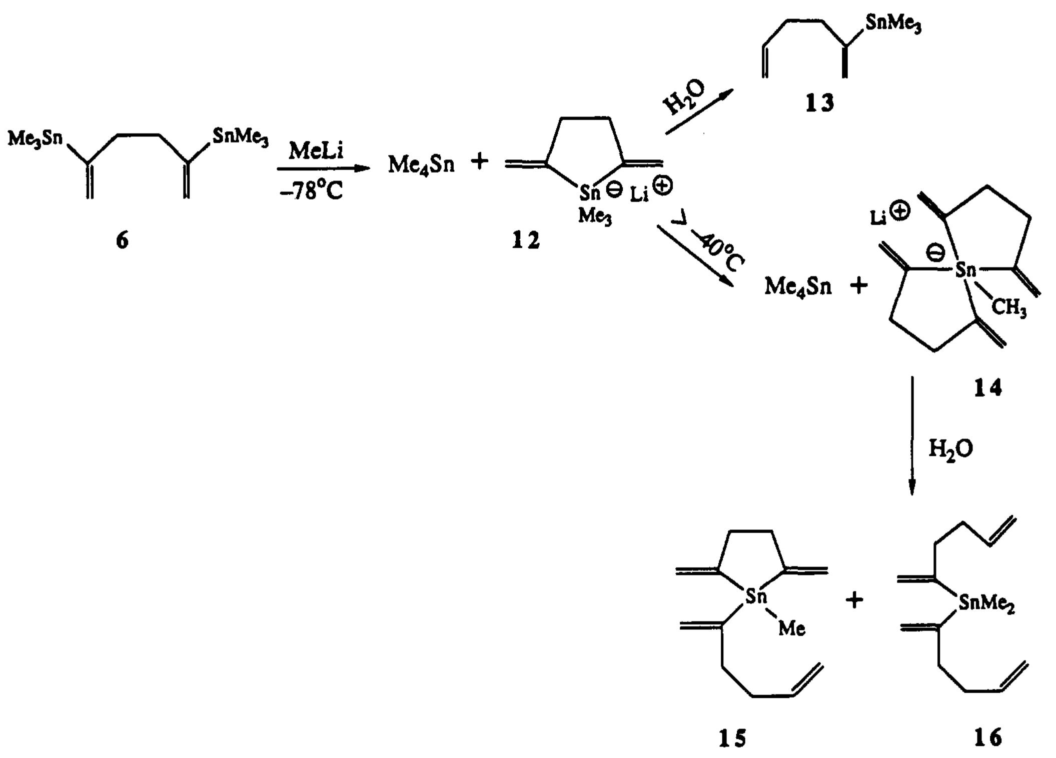
[21] For a similar case, see: Gustavson, W. A.; Principe, L. M.; Min Rhee, W.-Z.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 4126.

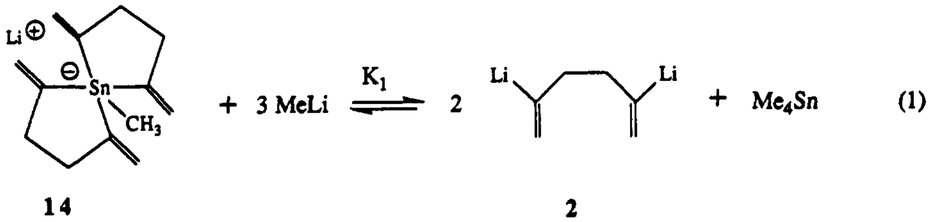
[22] Holmes, R. R. *Acc. Chem. Res.* **1979**, *12*, 257.

[23] Casey, J. P.; Mislow, K. *Chem. Commun.* **1970**, 1410.

[24] Trippett, S. *Phosphorus Sulfur* **1976**, *1*, 89.

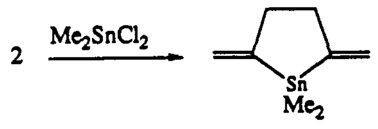
Scheme II





14 2

$$K_1 = \frac{[2]^2[Me_4Sn]}{[14]\,[MeLi]^3} \sim 0.05M^{-1}$$



17

volving scission of the vinyl–tin bond followed by recombination cannot be excluded on the basis of available data.

Warming solutions of 14 to 25 °C led to the formation of small concentrations of the dilithium compound 2. Similar equilibrium mixtures of 2, 14, MeLi, and Me_4Sn were obtained by treating 17 with excess methyllithium or by adding 1 equiv of Me_3SnCl to 2. With an initial concentration of 0.84 M methyllithium and 0.07 M 6, the equilibrium constant for the formation of 2 from 14 (eq 1) was found to be approximately 0.05 M^{-1} at 25 °C. Although this value has only qualitive significance,[25] it is clear that the formation of 2 from 14 is not particularly favorable.

The lithium–tin exchange of 11 with methyllithium was very similar to that of its unconjugated isomer (see Scheme III). The reaction of 11 with excess methyllithium at −80 °C gave a 1:1 mixture of Me_4Sn and stannate complex 18. The ^{119}Sn NMR spectrum of 18 showed a signal at $\delta = -295$ ppm, far upfield from that of 11 at $\delta = -48$ ppm. The symmetrical ^{1}H NMR spectrum with prominent $^{119/117}$Sn satellite peaks is completely consistent with structure 18, while a low-temperature aqueous quench gave the expected (2*Z*,4*E*)-2-(trimethylstannyl)-2,4-hexadiene (19).

Warming the solution of 18 to −30 °C led to the formation of Me_4Sn and a new stannate (δ(Sn) = −331 ppm), which was assigned structure 20 on the basis of its ^{1}H NMR spectrum. Aqueous quenching of 20 at −78 °C afforded a mixture of 19, 21, and a thermally labile product assigned stannole structure 22 on the basis of spectra and the analogy to the formation of 15 from 14.

Warming the solution of 20 to 25 °C led to quantitative formation of tetramethyltin and 3. The spectra of 3 prepared in this manner from 11 were identical with those of samples prepared from diiodide 9, which contained excess methyllithium. Signals assigned to 20 could not be detected. Thus, the equilibrium constant for formation of dilithio compound 3 from the organotin precursors and methyllithium must be extremely large (eq 2). This is consistent with the prior data for the unsubstituted compound 1.[14]

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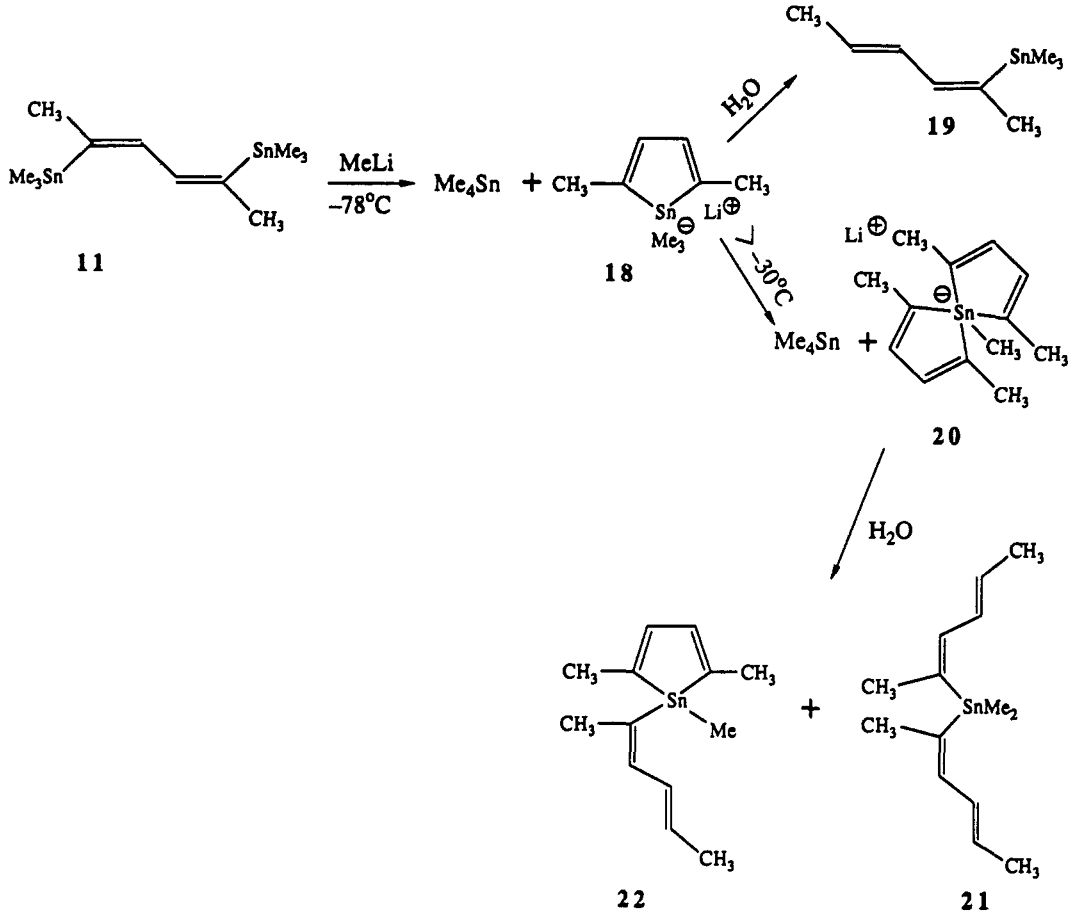
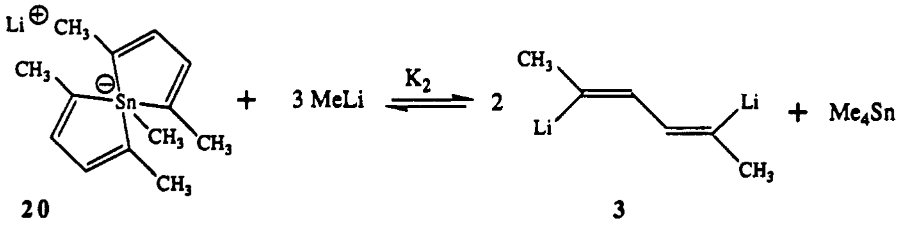
[25] A complete expression for the equilibrium constant would require knowledge of different aggregation states of various organolithium species. These data are not available.

Scheme III





(2)

$$K_2 = \frac{[3]^2[\mathrm{Me_4Sn}]}{[20]\,[\mathrm{MeLi}]^3} > 10^2 M^{-1}$$

The routes whereby organotin compounds 6 and 11 are converted to dilithio compounds 2 and 3 are analogous. However, the formation of the conjugated dilithiohexadiene 3 is considerably more favorable than that of its unconjugated isomer 2 under identical conditions. This is seen most clearly by inspecting eq 3 obtained by combining eqs 1 and 2 (Scheme IV). We estimate $K_3 > 10^3$. The large value of K_3 is consistent with a greater relative stability of 3 over 2. However, any relative difference in energy of stannates 20 and 14 will also affect K_3. We felt it would be prudent to probe independently the differences between 2 and 3. Therefore, we have undertaken an ab initio MO study of 2 and 3.

MO Studies. Molecular geometries were optimized at the SCF (HF) level by using analytic gradients with the GAUSSIAN86 program[26] and the split-valence basis set 4-31G. This computational level is designated as HF/4-31G. The geometries were fully optimized within the designated symmetry constraints, thus requiring 14 structural variables for the C_{2v} structures and 22 for the C_2 structures. Vibrational frequencies were calculated at all stationary points from analytic second derivatives. The criterion of all-real vibrational frequencies was used to distinguish local

Table II. Ab Initio Energies and Energy Differences for Various Conformers of 2,5-Dilithio-1,5-hexadiene (2) and (2*E*,4*E*)-2,5-Dilithio-2,4-hexadiene (3)

structure[a]	symmetry	HF[b]	ΔHF[c]	imag freq[d]
2a	C_{2v}	-246.338 42	93.6	3
2b	C_2	-246.348 44	67.3	0
3a	C_{2v}	-246.369 81	11.2	2
3b	C_{2v}	-246.374 06	0	0

[a] Optimized HF/4-31G structures in Figures 1 and 2; structures 2a and 2b are conformers of the dimethylene isomer; structure 3a (not shown) is simply the energetically less favorable rotomer of the isomer 3b. [b] Energies in au at the HF/4-31G level. [c] Energy differences in kJ mol^{-1} at the above level. [d] Number of imaginary vibrational frequencies at the above level.

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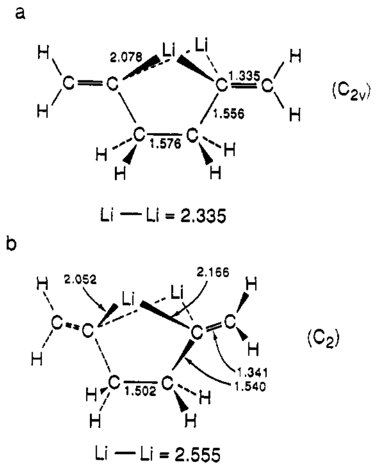
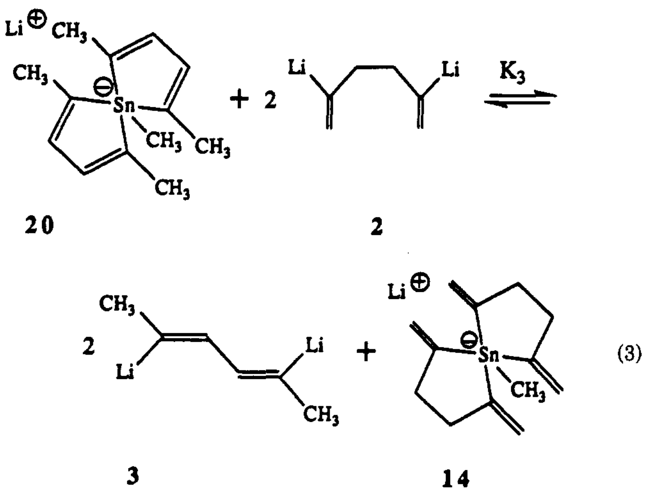


Figure 1. Optimized geometries for conformers of 2,5-dilithio-1,5-hexadiene at the HF/4-31G level with bond distances (key values only) in angstroms: (a) structure **2a**, symmetry C_{2v}; (b) structure **2b**, symmetry C_2 (stable conformer).

Scheme IV



$$K_3 = \frac{K_2}{K_1} = \frac{[14]\,[3]^2}{[20]\,[2]^2} > 10^3$$

minima from saddle-point structures.

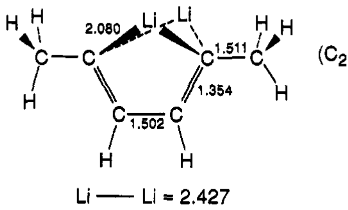


Figure 2. Optimized geometry of the most stable rotamer, structure **3b**, of (2*E*,4*E*)-2,5-dilithio-2,4-hexadiene at the HF/4-31G level with bond distances in angstroms.

Four stationary points were located at the HF/4-31G level, with their energies being given in Table II and their structures (except for structure **3a**) in Figures 1 and 2. Two of these, structures **2a** and **2b** (Figure 1), correspond to conformers of 2,5-dilithio-1,5-hexadiene and thus incoporate an unconjugated hydrocarbon moiety. The remaining two structures, **3a** (not shown) and **3b** (Figure 2), correspond to rotamers of (2*E*,4*E*)-2,5-dilithio-2,4-hexadiene and thus incoporate a conjugated hydrocarbon moiety. The energetically most stable structure (Table II) is **3b**, which is a dimethyl analogue of Kos and Schleyer's structure **1′**. We note, as did they, the significant alternation in C—C bond lengths. The rotamer **3a** is 11.2 kJ mol^{-1} higher in energy than **3b**, with this difference essentially being twice the internal rotation barrier in propene.[27] Structure **3a** possesses two imaginary vibrational frequencies, indicating its instability with respect to a pair of methyl-group rotations, while the preferred conformer **3b** has C–H bonds eclipsed with the C=C double bonds (as in propene). The structures lacking a conjugated hydrocarbon moiety are higher yet in energy, with the C_{2v} structure **2a** being 93.6 kJ mol^{-1} higher than **3b**. This structure has three imaginary vibrational frequencies and hence is unstable with respect to a significant symmetry lowering to form its structurally stable conformer **2b** with only C_2 symmetry (Figure 1b). Note that the terminal =CH$_2$ groups in **2b** are rotated approximately 40° from their positions in **2a**. This is primarily a rotation relative to the C—C unit at the base of the molecule rather than a twist about each =CH$_2$ group. These instabilities are associated in part with the eclipsing of the CH$_2$ groups at the base of the molecule and in part with the unfavorable orientation of the ethylene side groups with respect to the C—C bonds. Thus, the energy lowering of 26.3 kJ mol^{-1} in going from **2a** to **2b** is partly attributable to the sum of one ethane and two propene internal rotation barriers (see below).

The most striking energy difference, namely the 67.3 kJ mol^{-1} difference between the nonconjugated local minimum **2b** and the conjugated local minimum **3b**, represents in part the energy difference between 1,5-hexadiene and 2,4-hexadiene, which has been estimated as 39.7 kJ mol^{-1}.[28] Thus, there is another 28 kJ mol^{-1} of the difference to be accounted for. A major portion of this is probably associated with the asymmetric Li bridges in **2b**, which presumably contribute less stability to the molecule than do the symmetric bridges in structure **3b**. We note that the C–Li separations in **2b** are 2.052 and 2.166 Å (two each), as contrasted to 2.080 Å (four) in **3b**.

There is an apparent tendency for each Li to be within an interaction distance of not just one but both carbons of each ethylene subunit; in structure **3b** each Li is only 2.363 Å from the more distant C atoms in each such subunit, while in the unstable structure **2a** the distance is 3.151 Å. This latter distance is drastically reduced, to 2.631 Å, by the twisting displacement leading to structure **2b** having only C_2 symmetry. Stabilizing interactions will not be as strong as in **2b**, however, as can be inferred from the positions of the Li atoms in **2b** relative to the C atom framework (see top view of **2b** in Figure 2).

In summary, the structures and energies that we have obtained from electronic structure calculations suggest the importance of stabilizing interactions between dilithium bridges and *both* carbons of an ethylene subunit. The more favorable dilithium-bridging **3** relative to **2** appears to be a consequence of the more favorable juxtaposition of the ethylene subunits to the lithium atoms rather than to π-conjugation.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of argon. Solvents were dried by using standard procedures. THF-d_8 was dried by treating with Na/K alloy. The mass spectra were determined by using a VG-70-S spectrometer, while the NMR spectra were obtained by using either a Brucker WH-360 or AM-300 spectrometer, on solutions in CDCl$_3$ or THF-d_8 as noted. The ^{1}H NMR and ^{13}C NMR spectra were

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[27] Lide, D. R., Jr.; Mann, D. E. *J. Chem. Phys.* **1957**, *27*, 868.

[28] Wolkoff, P.; Holmes, J. L.; Lossing, F. P. *Can. J. Chem.* **1980** *58*, 251.

calibrated by using signals from the solvents referenced to Me_4Si, while Me_4Sn was used to calibrate the ^{119}Sn NMR spectra. The combustion analyses were determined either by the Spang Microanalytical Laboratory, Eagle Harbor, MI, or by Galbraith Laboratories, Knoxville, TN. Analytical and preparative glpc were performed by using an Antek 300 chromatograph equipped with a thermal conductivity detector. A $^1/_4$ in. × 2 m column packed with 20% Apiezon L on Chromosorb W was used at temperatures between 150 and 250 °C.

2,5-Dilithio-1,5-hexadiene (2). Lithium wire (0.15 g, 21.6 mmol) was added portionwise with stirring over 3 h to a solution of 2,5-dibromo-1,5-hexadiene (1.0 g, 4.1 mmol) in 15 mL of ether at 0 °C. After stirring for an additional 30 min, 3.0 mL of this solution was transferred to a second flask. After removal of the solvent in vacuo, 1.0 mL of THF-d_8 was added and the ^1H NMR spectrum was recorded. ^1H NMR (THF-d_8): δ 5.59 (d, J = 6.7 Hz, 2 H), 5.09 (br d, J = 6.7, 2 H), 2.25 (s, 4 H), 3.36, 1.05 ($C_4H_{10}O$). ^{13}C NMR (THF-d_8): δ 206 (*C*Li), 143 (*C*H_2=C), 54.7 (*C*H_2). The remaining solution was transferred to a flask containing excess water in ether at −78 °C. Removal of solvent gave only 1,5-hexadiene which was identified by ^1H NMR spectroscopy.

2,5-Bis(trimethylstannyl)-1,5-hexadiene (6). A solution of 2,5-dilithio-1,5-hexadiene, prepared from 8.4 g (34 mmol) of 2,5-dibromo-1,5-hexadiene and 1.3 g (excess) of lithium–2% sodium in 100 mL of diethyl ether at 0 °C, was added slowly to 12.5 g (5.8 mL, 51 mmol) of trimethyltin bromide in 60 mL of diethyl ether. After stirring at 0 °C for 15 min, the reaction mixture was allowed to warm to 25 °C over 1 h. The mixture was then added to excess water, and the organic layer was separated and dried over anhydrous $MgSO_4$. Removal of solvent followed by distillation gave 7.4 g (71%) of product, bp 74–85 °C (0.25 Torr). ^1H NMR ($CDCl_3$): δ 5.85 (d, J = 3.3 Hz, $^3J(^{119}SnH)$ = 155 Hz, 2 H), 5.18 (d, J = 3.3 Hz, $^3J(^{119}SnH)$ = 74 Hz, 2 H), 2.35 (s, 4 H), 0.18 (s, $J(^{119}SnH)$ = 51 Hz, 18 H). ^{119}Sn NMR (THF-d_8): δ −36. Anal. Calcd for $C_{12}H_{26}Sn_2$: C, 35.35; H, 6.43. Found: C, 35.47; H, 6.44.

1,1-Dimethyl-2,5-bis(methylene)stannolane (17). A solution of 2,5-dilithio-1,5-hexadiene, prepared from 4.15 g (17.3 mmol) of 2,5-dibromo-1,5-hexadiene and 0.6 g of lithium metal in 75 mL of diethyl ether at 0 °C, was added to solution of dimethyltin dichloride (3.8 g, 17 mmol) in 70 mL of diethyl ether at 0 °C. The solvent was removed under vacuum, and the residue was extracted with pentane. Pot-to-pot distillation (70 °C, 0.1 Torr) gave 0.65 g (17%) of product. ^1H NMR ($CDCl_3$): δ 5.79 (d, J = 3.2 Hz, $J(^{119}SnH)$ = 146 Hz, 2 H), 5.26 (d, J = 3.2 Hz, $J(^{119}SnH)$ = 65 Hz, 2 H), 2.38 (s, $J(^{119}SnH)$ = 43 Hz, 4 H), 0.30 (s, $J(^{119}SnH)$ = 61 Hz, 6 H). Anal. Calcd for $C_8H_{14}Sn$: C, 41.98; H, 6.16. Found: C, 41.88; H, 6.05.

1,1-Dibutyl-2,5-dimethylstannole (8). A solution of 2,4-hexadiyne (11.2 g, 0.14 *m*) and dibutyltin dihydride (33.4 g, 0.14 *m*) in 150 mL of heptane was allowed to reflux for 20 h. After removal of the solvent 4.25 g of product (bp 105 °C, 0.05 Torr) was distilled off. Slow heating of the residue under vacuum gave an additional 3.3 g of product for a combined yield of 17%. ^1H NMR ($CDCl_3$): δ 0.88 (t, J = 7 Hz, 6 H), 1.13 (t, J = 7 Hz, 4 H), 1.33 (m, 4 H), 1.58 (m, 4 H), 2.04 (s, $J(^{119}SnH)$ = 41 Hz, 6 H), 6.49 (s, $J(^{119}SnH)$ = 128 Hz, 2 H). MS, *m/e*: 314 (M^+ for $C_{14}H_{26}{}^{120}Sn$), 257 ($M^+ - C_4H_9$).[29] Anal. Calcd for $C_{14}H_{26}Sn$: C, 53.71; H, 8.37. Found: C, 53.78; H, 8.32.

(2*Z*,4*Z*)-2,5-Diiodo-2,4-hexadiene (9). Iodine (23.0 g, 0.09 *m*) was added portionwise with stirring over 2 h to a solution of 1,1-dibutyl-2,5-dimethylstannole (15.8 g, 0.05 *m*) in 170 mL of carbon disulfide at 25 °C. The color changed to dark purple during the addition, following which the solvent was removed in vacuum and the residue was extracted with 200 mL of pentane. The extracts were washed successively with 250 mL of a 10% aqueous solution of $Na_2S_2O_3$ followed by 100 mL of H_2O and then dried over anhydrous Na_2SO_4. Distillation gave 14.7 g (88% yield) of (2*Z*,4*Z*)-2,5-diiodo-2,4-hexadiene (bp 73–76 °C, 0.016 Torr) as an oil, which crystallized to a pale yellow solid, mp 36–39 °C. ^1H NMR ($CDCl_3$): δ 2.60 (s, 6 H), 6.20 (s, 2 H). MS, *m/e* (relative intensity): 334 (3, M^+ for $C_6H_8I_2$), 80 (100, $M^+ - I_2$). Anal. Calcd for $C_6H_8I_2$: C, 21.58; H, 2.41. Found: C, 21.37; H, 2.31.

(2*Z*,4*Z*)-2,5-Bis(trimethylstannyl)-2,4-hexadiene (11). A solution of 2.5 N butyllithium in hexane (3.2 mL, 8 mmol) was added dropwise to a solution of (2*Z*,4*Z*)-2,5-diiodo-2,4-hexadiene (1.17 g, 3.5 mmol) in 40 mL of diethyl ether at −78 °C. After stirring for 2 h, the mixture was added dropwise, with stirring, to a solution of trimethyltin chloride (1.60 g, 8 mmol) in 40 mL of diethyl ether at −78 °C. After 10 min, the reaction mixture was allowed to warm to 25 °C. The solvent was removed in vacuo, and the residue was extracted with pentane. Distillation gave 0.60 g (46%) of product, bp 58 °C (0.03 Torr), which crystallized to a colorless solid, mp ~30 °C. ^1H NMR ($CDCl_3$): δ 0.19 (s, $J(^{119}SnH)$ = 53 Hz, 18 H), 1.96 (s, $J(^{119}SnH)$ = 48 Hz, 6 H), 6.58 (s, $J(^{119}SnH)$ = 133 Hz, 2 H). ^{119}Sn NMR (THF-d_8): δ −48. Anal. Calcd for $C_{12}H_{36}Sn_2$: C 35.35; H, 6.43. Found: C, 35.35; H, 6.37.

(2*E*,4*E*)-2,5-Dilithio-2,4-hexadiene (3). To a solution of 0.2 g (0.75 mmol) of (2*Z*,4*Z*)-1,5-diiodo-2,4-hexadiene in 6.0 mL of ether at −78 °C was added dropwise 0.6 mL of 2.5 N (1.5 mmol) butyllithium in hexane with stirring over 1 h. After stirring for an additional 1 h at −78 °C and for 1 h at 0 °C, the solvent was removed in vacuo and 1.0 mL of THF-d_8 (predried over K/Na) was added. The H NMR spectra showed only the product with residual ether and THF. ^1H NMR (THF-d_8): δ 7.14 (s, 2 H), 1.97 (s, 6 H), 3.34, 1.07 ($C_4H_{10}O$). ^{13}C NMR (THF-d_8): δ 183.5 (br), 143.2, 34.0. This solution was added to 0.21 mmol of methyllithium at −78 °C. The NMR spectra showed more peaks in addition to the previous spectrum. ^1H NMR (THF-d_8): δ 7.10 (s, 2 H), 2.00 (s, 6 H), −2.1 (CH_3Li). ^{13}C NMR (THF-d_8): δ 187 (br), 141.6, 33.8, −15.5 (CH_3Li). Similar addition of butyllithium to an independently prepared sample of **3** gave a solution that showed peaks at δ 7.08 and 2.04 ppm in the ^1H NMR spectrum. Addition of water to any of the above samples gave only (2*E*,4*E*)-2,4-hexadiene, as identified by ^1H NMR spectroscopy.

Reaction of 11 with Methyllithium. Methyllithium in ether (1.4 N, 0.6 mL, 0.84 mmol) was placed in a flame-dried flask equipped with a septum and magnetic stirrer. Removal of the solvent in vacuo left white solid, to which was added 1.0 mL of THF-d_8. After cooling to −78 °C, (2*Z*,4*Z*)-2,5-bis(trimethylstannyl)-2,4-hexadiene (100 mg, 0.25 mmol) was added to produce a yellow solution. The ^1H and ^{119}Sn NMR spectra were consistent with assignment as a mixture of Me_4Sn, MeLi, and **18**. ^1H NMR (THF-d_8): δ −2.15 (MeLi), −0.51 (s, $J(^{119}SnH)$ = 39 Hz, 9 H), 0.0 (Me_4Sn), 1.78 (s, $J(^{119}SnH)$ = 32 Hz, 6 H), 6.04 (s, $J(^{119}SnH)$ = 114 Hz, 2 H). ^{119}Sn NMR (THF-d_8): δ −295.4, 0.0 (Me_4Sn). On warming to −30 °C, the color darkened to green. The ^1H and ^{119}Sn NMR spectra showed that **18** had been transformed to a new mixture, which was consistent with assignment as a mixture of Me_4Sn, MeLi, and **20**. ^1H NMR (THF-d_8): δ −2.15 (MeLi), −0.35 (s, $J(^{119}SnH)$ = 47 Hz, 3 H), 0.0 (Me_4Sn), 1.88 (s, $J(^{119}SnH)$ = 35 Hz, 12 H), 6.15 (s, $J(^{119}SnH)$ = 114 Hz, 4 H). ^{119}Sn NMR (THF-d_8): δ −310.9, 0.0 ($SnMe_4$). On warming to 25 °C, the color changed to dark green. The ^1H NMR spectra showed only Me_4Sn, MeLi, and **3**, ^1H NMR (THF-d_8): δ −2.15 (MeLi), 0.0 (Me_4Sn), 1.97 (s, 6 H), 7.14 (s, 2 H). Recooling to −78 °C followed by the addition of water gave only (2*E*,4*E*)-2,4-hexadiene, as identified by ^1H NMR spectroscopy.

Aqueous Quench of the Reaction of 11 with Methyllithium. A solution of 1.4 mmol of methyllithium in 3.0 mL of THF was prepared as above. To this solution was added (2*Z*,4*Z*)-2,5-bis(trimethylstannyl)-2,4-hexadiene (0.32 g, 0.78 mmol) at −78 °C. The yellow solution was allowed to stir at −78 °C for 30 min, after which it was transfered via cantula to a solution of H_2O (0.2 g) in 2 mL of THF at −78 °C. After warming to 25 °C, the solvent was removed under vacuum to give a yellow oil, which was purified by glpc to give (2*Z*,4*E*)-2-(trimethylstannyl)-2,4-hexadiene (**19**). ^1H NMR ($CDCl_3$): δ 0.18 (s, $J(^{119}SnH)$ = 60 Hz, 9 H), 1.73 (d, J = 7 Hz, 3 H), 1.94 (s, $J(^{119}SnH)$ = 53 Hz, 3 H), 5.6 (m, 1 H), 6.0 (m, 1 H), 6.55 (d, J = 12 Hz, 1 H). Anal. Calcd for $C_9H_{18}Sn$: C, 44.13; H, 7.41. Found: C, 44.24; H, 7.29.

An identical quench of a solution of **11** and methyllithium, which had been warmed to −30 °C for 30 min, followed by cooling to −78 °C gave 66% **19**, 24% **22**, and 10% **21**, analyzed by glpc. Compound **22** showed extensive decomposition on the column at $T > 200$ °C.

1-((2*Z*,4*E*)-2-Hexa-2,4-dienyl)-1,2,5-trimethylstannole (22). ^1H NMR ($CDCl_3$): δ 0.42 (s, $J(^{119}SnH)$ = 55 Hz, 3 H), 1.72 (d, J = 8 Hz, 3 H), 2.05 (s, 3 H), 2.09 (s, $J(^{119}SnH)$ = 44 Hz, 6 H),

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[29] MS of vinylstannanes shows weak molecular ions and prominent peaks for loss of alkyl. See: Occolowitz, J. L. *Tetrahedron Lett.* **1966**, 5291.

5.62 (m, 1 H), 5.95 (m, 1 H), 6.49 (s, $J(^{119}\mathrm{SnH}) = 142$ Hz, 2 H), 6.63 (d, $J = 10$ Hz, 1 H). MS, *m/e*: 281 ($M^+ - 15$), 215 ($M^+ - 81$).[29]

Bis((2*Z*,4*E*)-2-hexa-2,4-dienyl)dimethylstannane (21). ^{1}H NMR ($CDCl_3$): δ 0.33 (s, $J(^{119}\mathrm{SnH}) = 53$ Hz, 6 H), 1.73 (d, $J = 8$ Hz, 6 H), 1.99 (s, $J(^{119}\mathrm{SnH}) = 49$ Hz, 6 H), 5.60 (m, 2 H), 5.99 (m, 2 H), 6.62 (d, $J = 10$ Hz, 2 H). MS, *m/e*: 297 ($M^+ - 15$), 231 ($M^+ - 81$).[29] Exact mass calcd for ($M^+ - 15$) $C_{13}H_{21}{}^{110}Sn$: 297.0665. Found: 297.0677.

Reaction of 6 with Methyllithium. A solution of methyllithium (0.84 mmol) in 1.0 mL of THF-d_8 was prepared in the usual manner. After cooling to −78 °C, **6** (100 mg, 0.2 mmol) was added to produce a yellow solution. The ^{1}H and ^{119}Sn NMR spectra were consistent with assignment as a mixture of Me_4Sn, MeLi, and **12**. ^{1}H NMR (THF-d_8): δ −2.15 (MeLi), −0.47 (s, $J(^{119}\mathrm{SnH}) = 43$ Hz, 9 H), 0.0 (Me_4Sn), 2.10 (s, 4 H), 4.80 (d, $J = 6$ Hz, 2 H), 5.38 (d, $J = 6$ Hz, 2 H). ^{119}Sn NMR (THF-d_8): δ ($J = -307.9$ Hz), 0.0 (Me_4Sn).

On warming to 0 °C, the color darkened. The ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were consistent with assignment as a mixture of Me_4Sn, MeLi, and **14**. ^{1}H NMR (THF-d_8): δ −2.15 (MeLi), 0.18 (s, $J(^{119}\mathrm{SnH}) = 54$ Hz, 3 H), 0.0 (Me_4Sn) 2.17 (s, $J(^{119}\mathrm{SnH}) = 35$ Hz, 8 H), 4.95 (d, $J = 5.7$ Hz, $J(^{119}\mathrm{SnH}) = 51$ Hz, 4 H), 5.49 (d, $J = 5.7$ Hz, $J(^{119}\mathrm{SnH}) = 118$ Hz, 4 H). On cooling to −78 °C, the δ 2.17 ppm singlet reversibly separates into two multiplets δ 2.05 and 2.23 ppm, T (coalescence) ~ -23 °C. ^{13}C NMR (THF-d_8): δ 177.7 ($^1J(^{119}\mathrm{SnC}) = 351$ Hz, *C*Sn), 113.6 ($^2J(^{119}\mathrm{SnC}) = 36$ Hz, C=CH_2), 44.5 (CH_2), −2.3 ($^1J(^{119}\mathrm{SnC}) = 399$ Hz, SnCH_3). ^{119}Sn NMR (THF-d_8): δ ($J = -334.1$), 0.0 (Me_4Sn). On warming to 25 °C, the color changes to dark yellow. The ^{1}H NMR spectra showed additional small peaks due to **2** in addition to those of **14**. The equilibrium mixture of **14** and **2** could also be generated by treating **16** with methyllithium or by treating **2** with 1 equiv of Me_3SnCl.

Aqueous Quench of the Reaction of 6 with Methyllithium. 2,5-Bis(trimethylstannyl)-1,5-hexadiene (0.32 g, 0.78 mmol) was added at −78 °C to a solution of 1.4 mmol of methyllithium in 3.0 mL of THF. The yellow solution was allowed to stir at −78 °C for 5 min, after which it was transferred to a solution of H_2O (0.2 g) in 2 mL of THF at −78 °C. After warming to 25 °C, the solvent was removed under vacuum and the residue was extracted with pentane. On removal of the solvent, the resulting yellow oil was purified by glpc to give 2-(trimethylstannyl)-1,5-hexadiene (**13**). ^{1}H NMR ($CDCl_3$): δ 0.14 (s, $J(^{119}\mathrm{SnH}) = 53$ Hz, 9 H), 2.15 (q, $J = 7.7$ Hz, 2 H), 2.36 (t, $J = 8$ Hz, 2 H), 4.94 (dm, $J = 10$ Hz, 1 H), 5.00 (dm, $J = 17$ Hz, 1 H), 5.16 (m, $J(^{119}\mathrm{SnH}) = 71$ Hz, 1 H), 5.62 (m, $J(^{119}\mathrm{SnH}) = 150$ Hz, 1 H), 5.79 (symm, 1 H). Anal. Calcd for $C_9H_{18}Sn$: C, 44.13; H, 7.41. Found: C, 44.47; H, 7.50.

In the same manner as above, a solution that had been warmed to 25 °C for 10 min and then cooled to −78 °C was added to 1 mL of THF containing 0.2 g of H_2O at −78 °C. Removal of solvent left a yellow oil. Analysis by glpc showed it to be 11% **13**, 75% **15**, and 14% **16**. ^{1}H NMR ($CDCl_3$) for 1-(2-hexa-1,5-dienyl)-1-methyl-2,5-bis(methylene)stannolane (**15**): δ 0.31 (s, $J(^{119}\mathrm{SnH}) = 57$ Hz, 3 H), 2.18 (q, $J = 7.3$ Hz, 2 H), 2.35–2.50 (m, 6 H), 4.96 (dm, $J = 10$ Hz, 1 H), 5.02 (dm, $J = 17$ Hz, 1 H), 5.32 (m, $J(^{119}\mathrm{SnH}) = 81$ Hz, 1 H), 5.35 (d, $J = 3$ Hz, $J(^{119}\mathrm{SnH}) = 64$ Hz, 2 H), 5.73 (m, $J(^{119}\mathrm{SnH}) = 175$ Hz, 1 H), 5.74 (symm, 1 H), 5.91 (d, $J = 3$ Hz, $J(^{119}\mathrm{SnH}) = 149$ Hz, 2 H). Exact mass (*m/e*) calcd for ($M^+ - 15$) $C_{12}H_{17}{}^{120}Sn$: 281.0352. Found: 281.0364.[29] Anal. Calcd for $C_{13}H_{20}Sn$: C, 52.93; H, 6.83. Found: C, 52.43; H, 6.66. ^{1}H NMR ($CDCl_3$) for bis(2-hexa-1,5-dienyl)dimethylstannane (**16**): δ 0.22 (s, $J(^{119}\mathrm{SnH}) = 64$ Hz, 6 H), 2.13 (q, $J = 7.3$ Hz, 4 H), 2.34 (t, $J = 7.31$ Hz, 4 H), 4.9–5.05 (m, 4 H), 5.16 (symm, 2 H), 5.70 (symm, 2 H), 5.77 (symm, 2 H). MS, *m/e*: 297 ($M^+ - 15$), 231 ($M^+ - 81$).[29] Exact mass (*m/e*) calcd for ($M^+ - 15$) $C_{13}H_{21}{}^{120}Sn$: 297.0665. Found: 297.0657.

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