Polylithiumorganic Compounds, 24[◇]

The Reaction of Substituted Vinylsilanes with Lithium Metal

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Vinylsilanes are known to react with lithium metal to form either 1,2-dilithioethanes by reduction or 1,4-dilithiobutanes by reductive dimerization. The reaction of the substituted vinylsilanes **3**, (*Z*)-**13b**, **17b**, **c**, **42b**, **c**, **44**, and **51** with lithium has been investigated. Depending on the substituents on the vinylsilane and the solvent employed, several new reaction pathways are observed, which have been proved by independent syntheses of the reactive intermediates (*E*)-**14b**, **18d**, and **25–27**. Thus, besides the known elimination of lithium hydride, either a 1,4-proton shift of **25** to **26** or a Grovenstein-Zimmerman rearrangement of **45** to **47** can occur as follow-up reactions. Furthermore, two different types of dimerization of the silyl-substituted vinyllithium compounds have been identified. Either the vinyllithium compound **18d** adds to the starting vinylsilane leading to the monolithiumorganic species **41**, or lithium metal catalyzed dimerization to the 1,4-dilithio-2-butene derivative **49** takes place, which is without precedence.

Introduction

Vinylsilanes like **1**[3] or **3**[4] with monosilyl- and geminal disilyl-substituted C−C double bonds afford, when brought to reaction with lithium metal in THF, the products of reductive dimerization, i.e. the 1,4-dilithiobutanes **2** and **4**. This type of reaction is known as Schlenk dimerization.[5] Symmetrically tetrasilyl-substituted C−C double bonds as in **5** on the other hand add lithium metal with formation of 1,2-dilithioethanes. As stable intermediates in these reactions radical anions, like **7**, can be observed, which are then reduced once again, here to the dianion **6**.[6] These two types of reaction are analogous to the reductions of the corresponding styrene derivatives 1,1-diphenylethylene[7] and stilbene,[5a] obviously silyl groups have the same ability to stabilize negative charges in these polyanions as have aromatic substituents. The comparison holds even true for the structures observed for either 1,2-dilithio-1,1,2,2-tetrakis-(trimethylsilyl)ethane (**6**) and 1,2-dilithio-1,2-diphenylethane (**8**), both show a double lithium bridge in *trans* configuration, interacting with the solvent (Figure 1).[8][9]

Recently, Khotimskii and coworkers reported a similar Schlenk dimerization of trimethylvinylsilane (**9**) with lithium metal in THF,[10] interestingly, when employing hexane as the solvent a 1:1 mixture of the corresponding vinyllithium compound **11** and the acetylide **12** was formed, besides lithium hydride. For this reaction no mechanistic explanation was given, however, the result resembles the reactivity of ethylene[11][12] and alkyl-substituted alkenes[13] towards lithium metal, the reaction pathway is mainly determined by the solvent employed: ethylene forms quantitatively vinyllithium when using special catalysts as shown by Rautenstrauch[11a] and Bogdanovic,[11b] when using dioxane or DME (1,2-dimethoxyethane) as the solvent dili-

Scheme 1

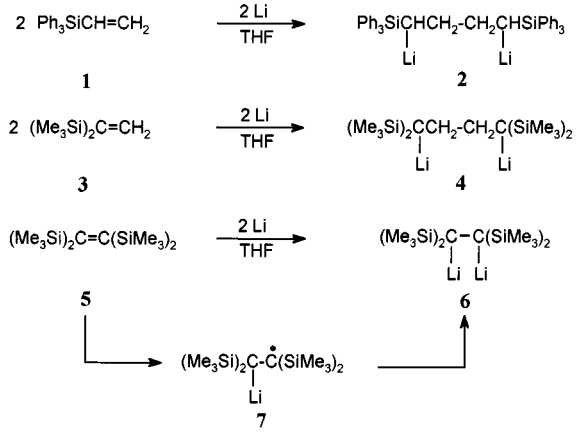
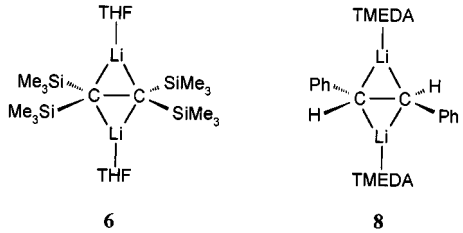


Figure 1. Structures of **6** and **8** in the solid state (TMEDA = *N,N,N′,N′*-tetramethylethylene diamine)



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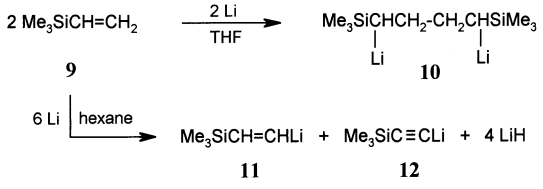
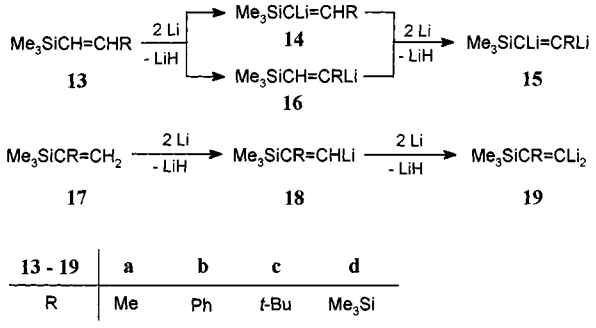
thioacetylide (lithium carbide) is formed as the final product.[12] In all these reactions polylithiumorganic intermediates have to be postulated. We have shown for 1,1-dilithioethanes, as well as *cis*- and *trans*-dilithioethylene the ease of lithium hydride elimination through independent synthesis of these reactive intermediates;[14] 1,2-dilithioethane can be trapped in a small amount at −120°C.[15]

Scheme 2



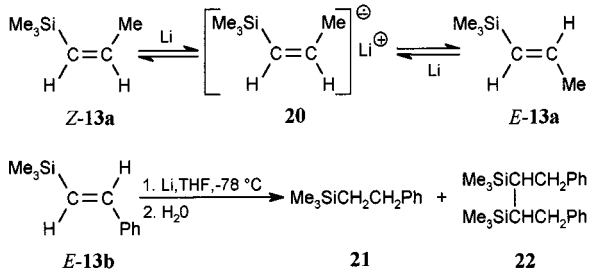
So we propose a general mechanism for the reaction of vinylsilanes with lithium metal, which should also allow a general access to vicinal and geminal dilithiovinylsilanes by repetitive addition of lithium metal to the C−C double bond and subsequent elimination of lithium hydride. In order to explore this synthetic approach the reduction of a series of either α- or β-substituted vinylsilanes with lithium was examined, here the substituent R (≠ H) in **13** and **17** is introduced to prevent the last lithium hydride elimination.

Scheme 3



It has to be mentioned that 2,2-diphenylvinyllithium, which corresponds to structure **18**, does not afford 1,1-dilithio-2,2-diphenylethene upon treatment with lithium.[16] Furthermore two additional results are of interest when discussing the introduction of substituents into the β-position of the vinylsilane: Seyferth et al. reported that (*Z*)-propenyltrimethylsilane [(*Z*)-**13a**] was isomerized quantitatively to the corresponding (*E*) isomer through the intermediate radical anion **20** when brought into contact with a catalytic amount of lithium metal in THF,[17] the alkyl substituent deactivates the double bond, no further reduction was observed. Eisch and Gupta on the other hand showed that (*E*)-styryltrimethylsilane [(*E*)-**13b**] afforded the expected products of reduction and of reductive dimerization, **21** and **22** (*meso* compound), respectively.[18]

Scheme 4



Results and Discussion

Starting Materials

The following compounds were synthesized according to reported procedures: (*Z*)-**13b**,[19] **31**,[20][21] **36** was formed upon Pd-catalyzed coupling of trimethylvinylsilane to *o*-bromoiodobenzene.[22] **17b**,[23][24] **17c**,[25][26] **42b**, **c**,[27][28] **44**, and **51** were synthesized by Peterson olefination from either 2,2-diphenylpropionic aldehyde[29] or 2-methyl-2-phenylpropionic aldehyde[30] with tris(trimethylsilyl)methyllithium.[27]

Reaction of β-Substituted Vinylsilanes with Lithium Metal

(*Z*)-Styryltrimethylsilane [(*Z*)-**13b**] is treated with an excess of lithium metal in diethyl ether, and affords after work-up with dimethyl sulfate 2-phenyl-3-trimethylsilylbutane (**24**) (entry 1 in Table 1) as a mixture of diastereoisomers in 87% yield. Similar results are obtained when diethoxymethane (DEM) is used as the reaction medium [see entries 3 and 4 in Table 1, which summarizes all the various reaction conditions and starting materials employed in the elucidation of the pathways of the reaction of (*Z*)-**13b** with lithium metal].

Scheme 5

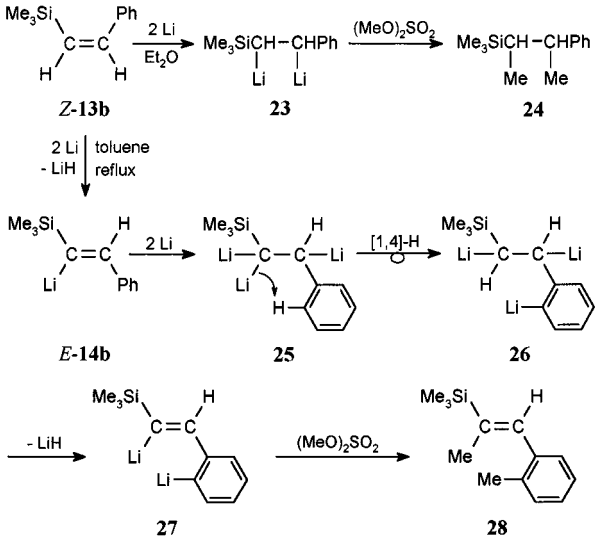
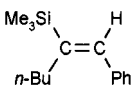


Table 1. Compounds obtained in the elucidation of the reaction mechanism of (*Z*)-**13b** with lithium metal starting from various precursors

Entry	Starting comp.	Reaction conditions	Yields of products after work-up with dimethyl sulfate in%							
			(*E*)-**13b**	**24**[a]	**28**	**32**	**33**	**34**	(*Z*)-**35**	Other[b]
1	(*Z*)-**13b**	3 Li, Et_2O, r.t., 3 h		87						
2	(*Z*)-**13b**	5 Li, toluene, reflux, 10 h			91					
3	(*Z*)-**13b**	6 Li, DEM, r.t., 4 h		80						(*Z*)-**13b**: 3
4	(*Z*)-**13b**	6 Li, LiBr, DEM, r.t., 4 h		83						
5	**36**	1. 2 *t*BuLi, DEM −50°C, 0.5 h 2. 3 Li, −50°C, 2 h	9[c]	7[c]	66					
6	**31**	3 *t*BuLi, 2 eq. TMEDA, THF, −78°C	48				35			
7	**31**	2 *t*BuLi, *n*BuLi, THF, −78°C → 0°C, 2 h	40				48			
8	**31**	3 *n*BuLi, Et_2O, r.t., 24 h					52			**29**: 22, 3[b]
9	**31**	2 *t*BuLi, toluene, −30°C, 1 h				11	78			1[b]
10	**31**	1. 2 *t*BuLi, toluene, −30°C 2. 3 Li, r.t., 2 h	9		63	17				2[b]
11	**31**	1. 2 *t*BuLi, THF, −90°C, 2 h 2. 3 Li, −78°C, 3 h		63			22	3		1[b]
12	**31**	1. 2 *t*BuLi, [D_8]THF, −90°C 2. 3 Li, −90°C, 4 h		44			14	22	1	1[b]
13	**31**	1. 2 *t*BuLi, Et_2O, −90°C, 2 h 2. 3 Li, −90°C, 4 h		18	7		57	7	2	1[b]
14	**31**	1. 2 *t*BuLi, hexane, 2 eq. THF, −78°C, 2 h 2. 3 Li, 2 eq. THF, −78°C, 4 h			86					**31**: 1
15	**31**	1. 2 *t*BuLi, DEM, −40°C, 1 h 2. 3 Li, −40°C, 3 h		30	52		10			
16	**23**+**27**	DEM, r.t., 4 h		86[d]	82[e]					(*Z*)-**13b**: 6
17	**33**	2 Li, Et_2O, r.t., 4 h		27			2	19		**30**: 35, 3[b]
18	(*E*)-**13b**[c]	2 Li, Et_2O, r.t., 4 h	5[c]	78[c]						3[b]
19	**32**	6 Li, DEM, −40°C, 4 h [f], −40°C, 14 h							18[g]	66[h]

[a] Mixture of diastereoisomers. – [b] Volatile, not identified compounds, remainder non-volatile, probably of polymeric nature. – [c] *o*-Tolyl instead of phenyl. – [d] Upon quenching of **23** 98% of **24** and 2% of (*Z*)-**13b** were obtained. – [e] Upon quenching of **27** 95% of **28** and 5% of (*Z*)-**13b** were obtained. – [f] Slow addition of **32** over a period of 4 h. – [g] (*Z*/*E*) Mixture in a ratio of 4:1. – [h] Mixture of dimeric products.



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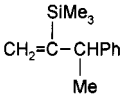
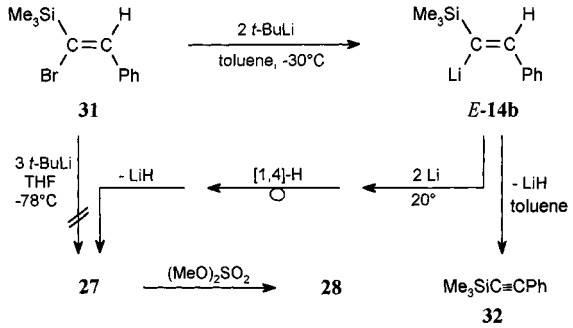


30

The addition of a vinyllithium compound (in this case **27**) to complex the lithium hydride did not induce lithium hydride elimination (entry 16). In order to enforce this elimination we switched to less polar solvents, but in hexane no reaction at all could be observed. This was successfully realized by heating (*Z*)-**13b** for 10 h with lithium metal in toluene under reflux (entry 2). The exclusive formation of (*E*)-1-lithio-2-(*o*-lithiophenyl)-1-trimethylsilylethene (**27**) was evidenced by the isolation of 91% of the corresponding dimethyl derivative **28**. The formation of lithium hydride was proved by X-ray powder diffraction of the remaining solid,[31] which was filtered off in all the reactions performed prior to quenching of the reaction mixture with dimethyl sulfate.

Therefore, not only two consecutive lithium additions and lithium hydride eliminations must have occurred, but also a 1,4-proton shift with lithiation at the *ortho* position of the phenyl moiety, in order to account for the formation of **27**. This type of intramolecular rearrangement has been observed before in the case of 2-, 3-, 4-, and 5-phenyl-1-lithioalkanes and 1,1-dilithio-2,2-diphenylethene.[32]

Scheme 6



The three intermediates (*E*)-**14b**, **25**, and **26** are each accessible by different and independent routes:

(i) Bromine-lithium exchange of α-bromostyryltrimethylsilane (**31**) with *t*BuLi affords the vinyllithium compound (*E*)-**14b**; which is prone to lithium hydride elimination under the reaction conditions in toluene, as evidenced by the formation of trimethylsilylphenylacetylene (**32**) (entry 9).

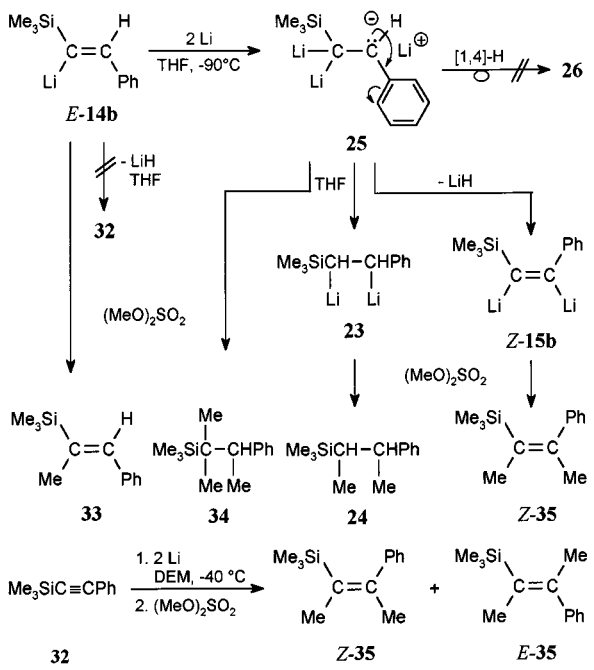
(ii) The trilithium compound **25** can be accessed by reaction of (*E*)-**14b** with lithium metal in toluene at −30°C;

from this intermediate 63% of **28** is isolated (entry 10). The addition of lithium to the vinyllithium compound (*E*)-**14b** works even better when hexane containing four equivalents of THF is used as the solvent system (entry 14, 86% yield of **28**) and the reaction is performed at −78°C, thereby suppressing lithium hydride elimination from (*E*)-**14b**. A second metallation of (*E*)-**14b** with *t*BuLi did not occur, although this reaction is reported to work well with *n*BuLi at room temperature in diethyl ether.[33] In our hands, the reaction of **31** with either *n*- or *t*BuLi did not afford **27** (entries 6−8), probably because it is absolutely essential to work at room temperature. Quite remarkable is the observation of 22% of **29**, the product of substitution (entry 8).

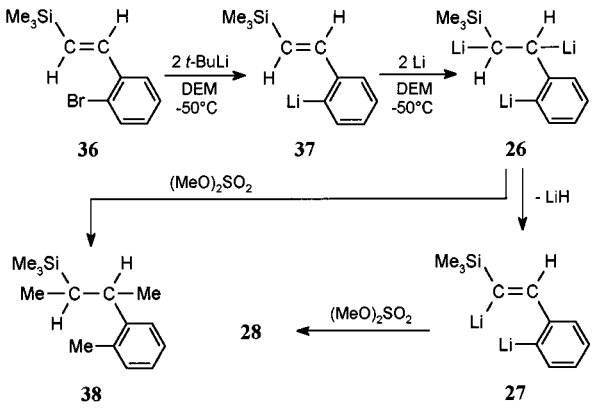
(iii) When the synthesis of (*E*)-**14b** and the addition of lithium metal is carried out in the more polar solvent THF (entry 11), a completely different product mixture is obtained. The intermediate trilithium organic compound **25** does not eliminate lithium hydride, and a 1,4-proton shift is not observed. This might be due to the formation of a solvent-separated ion pair for the lithium in the benzylic position diminishing the acidity of the *ortho* proton by resonance. Derivatization of **25** should lead to **34**, which is indeed one of the products, although it is only formed to a small extent (3%, entry 11). Clearly, solvent decomposition of **25** to the stable vicinal dilithioalkane **23** (affording 63% of **24** after work-up) is the favoured reaction. In perdeuterated THF, which is known to be less acidic and more stable towards cleavage by lithiumorganic compounds,[34] and by keeping the reaction temperature as low as −90°C throughout the whole synthetic sequence, 22% of **34** is found (entry 12). Another interesting feature of the aforementioned reactions in [D_8]THF and in diethyl ether is the detection of another side product, (*Z*)-2-phenyl-3-trimethylsilyl-2-butene [(*Z*)-**35**] (1 and 2%, respectively). Very slow addition of phenyltrimethylsilylacetylene (**32**) to a suspension of lithium in DEM affords 14% of (*Z*)-**35**, together with 4% of the corresponding (*E*) isomer (entry 19). The main product was composed of a mixture of products of dimerization. Here again, a similarity to the reaction of tolane with lithium metal in diethyl ether is apparent.[35]

(iv) Diethoxymethane (DEM) exhibits a remarkable stability towards lithiumorganic compounds,[36] and is the solvent of choice not only for the latter reaction, but also in the approach to the second trilithium intermediate **26**. Bromine-lithium exchange of (*E*)-(*o*-bromophenyl)trimethylsilylethene (**36**) with *t*BuLi furnished the corresponding monolithium compound (entry 5), which was then treated with lithium metal at −50°C. The main product after work-up with dimethyl sulfate was **28**. Intermediate **26** is very unstable and prone to lithium hydride elimination. Thus, the product of derivatization, **24** (*o*-tolyl instead of phenyl) was found in a yield of just 7%, as a mixture of diastereomers. The structural assignment of the two trimethyl derivatives originating from either **25** and **26** was established through independent syntheses of these compounds by addition of lithium to (*E*)-**13b** (*o*-tolyl instead of phenyl) or to **33**, with subsequent work-up with dimethyl sulfate (entries 17 and 18).

Scheme 7



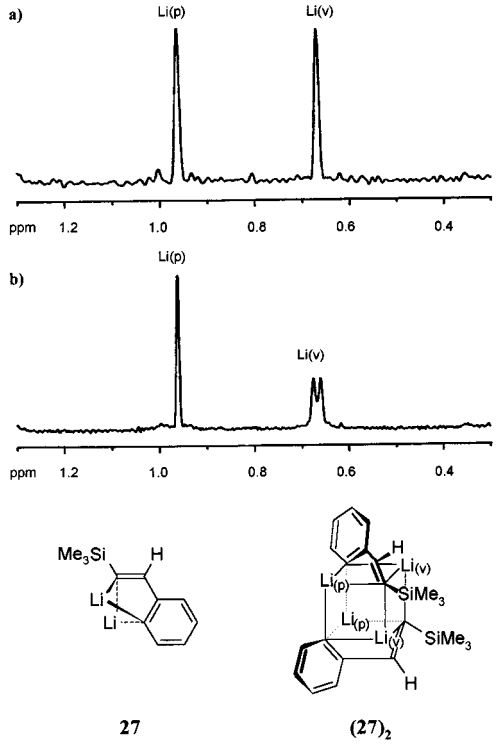
Scheme 8



The formation of the substituted *ortho*-lithiated styryllithium **27** is only surprising on first sight. *o*-Lithiostyryllithium can be obtained by lithium-tellurium exchange.[37] We have shown that a number of substituted methylenecyclopropanes and -butanes are cleaved with lithium metal and form, in these cases by an intermolecular rearrangement, substituted *o*-lithiated styryllithiums.[38] The *ortho* position of the aromatic ring is activated by agostic interactions with the lithium atom in the vinylic position. The high stability of these dilithiumorganic compounds can be understood by assuming a doubly bridged structure, as illustrated in Figure 2. Calculations by Schleyer et al. on the monomeric species confirm this structure.[39] In solution, a dimeric species is present, which was demonstrated by detailed NMR investigations.[40] The NMR data of **27** prepared with ^{6}Li in [D_8]THF are very similar to those reported for other *o*-lithiostyryllithiums. In particular, the complex splitting of the ^{6}Li-coupled ^{13}C signals shows that

a dimeric structure is present at 220 K.[41] Figure 2 depicts the ^{6}Li-NMR spectra (proton-coupled and proton-decoupled) of **27** at 220 K; the signals of the two lithium atoms in the vinylic position Li(v) and the phenylic position Li(p) coalesce to form one signal at $\delta = 0.89$ at room temperature. The small splitting of 0.9 Hz for Li(v) arises from the $^3J_{LiH}$ coupling with the proton *trans* to the lithium atom.

Figure 2. 59-MHz ^{6}Li-spectra of **27** in [D_8]THF at 220 K a) with proton decoupling b) without decoupling[41]



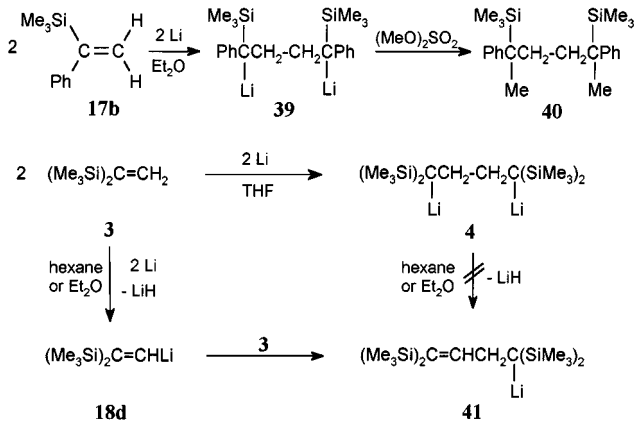
27 **$(27)_2$**

Reaction of α-Substituted and α,β-Disubstituted Vinylsilanes with Lithium Metal

In terms of changing the position of the activating phenyl group in the trimethylvinylsilane, the isomeric α-trimethylsilylstyrene (**17b**) would be the compound of choice to allow comparisons to be made with the reaction pathways of (*Z*)-**13b**. However, no reaction could be observed either in refluxing hexane or in refluxing toluene. In diethyl ether at room temperature, **17b** forms smoothly and exclusively the stable product of reductive dimerization **39**. Upon derivatization with dimethyl sulfate, 92% of a mixture of *meso*- and *d,l*-2,5-bis(trimethylsilyl)-2,5-diphenylhexane (**40**) is isolated (entry 1 in Table 2). To promote lithium hydride elimination, a *tert*-butyl group was introduced in place of the phenyl group at the α-position. However, 3,3-dimethyl-2-trimethylsilyl-1-butene (**17c**) did not react with lithium in any of the solvents employed in this investigation (entry 2). Even attempted reaction with lithium di-*tert*-butylbiphenyl[42] was unsuccessful, although this reagent has proved to be a valuable alternative to lithium metal in the synthesis of lithium- and polylithiumorganic compounds, having the advantage that the reductions can be performed in homogeneous solutions.[43]

We reinvestigated the reactivity of 1,1-bis(trimethylsilyl) ethene (**3**) towards lithium metal. In THF, the exclusive formation of the product of reductive dimerization was reported by Sakurai et al.,[4] and we obtained the same result (entry 3 in Table 2). In hexane a very slow reaction took place. After 3 days at room temperature, besides mainly starting material, **4** was still the only product (entry 4). The reaction could be enhanced by the use of ultrasonic activation; not only did the turnover increase, but also a second dimerization product was found. Quenching with deuterium oxide showed that the monolithiumorganic compound **41** had been formed (entry 5).

Scheme 9



The reaction worked even better when diethyl ether was used as solvent; an almost quantitative yield of a 1:1 mixture of the two dimers **4** and **41** was isolated (entry 6). Lithium hydride elimination from the 1,4-dilithioalkane **4** would appear to be a reasonable explanation for the formation of **41**. However, this can be ruled out since mixtures of **4** and **41**, once synthesized, were found to be stable for prolonged periods under ultrasonication and showed no elimination of lithium hydride. Clearly, **18d** adds to **3** with formation of **41** in the less polar solvents.

Thus, introduction of a second substituent at the β-position of the vinylsilane would appear to prevent the addition of the vinyllithium intermediate to the starting vinylsilane. This is the case for **42c**. 1,1-Bis(trimethylsilyl)-3,3-dimethyl-1-butene (**42c**) reacted only sluggishly with lithium metal and no Schlenk dimerization was observed; the 1,1-bis(trimethylsilyl)-1,2-dilithioalkane **43c** was the sole product (entry 7). The only follow-up reaction was slow decomposition of the solvent. The general reaction pathway was the same when the *tert*-butyl group at the β-position was replaced with a phenyl group (**42b**). Although no reaction was observed in hexane, the addition of two equivalents of diethyl ether was sufficient to drive the reaction to an almost quantitative yield of **43b** (entry 9). With these results at hand, the following conclusions can be drawn: (i) If R = H, either reductive dimerization or addition of the intermediate **18** to the starting vinylsilane is possible. (ii) If the substituent R is a bulky alkyl group, a polar solvent such as THF is required to bring about the reaction, although lithium hydride elimination usually requires much less polar solvents.

Table 2. Lithiumorganic compounds obtained in the reaction of vinylsilanes **3**, **17b**, **c**, **42b**, **c**, **44**, and **51** with lithium metal

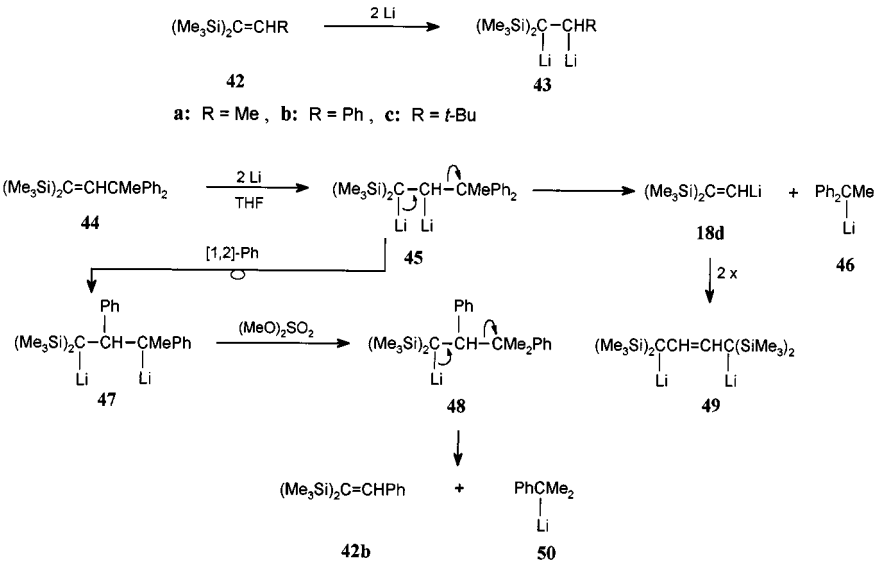
Entry	Starting comp.	Reaction conditions	Yield of products corresponding to lithiumorganic compound in%							
			Electrophile	**18d**	**39/4**	**41**	**43**	**49**	Frag[a]	Other[b]
1	**17b**	6 Li, Et_2O, r.t., 3 h	Me_2SO_4		92					
2	**17c**	Li, hexane, Et_2O, THF, LiDBB	no reaction							
3	**3**	1.3 Li, THF, r.t., 2 h, ultrasonication	D_2O	–	91					
4	**3**	5 Li, hexane, r.t., 3 d	H_2O	–	48					**3**: 40, polym.: 8
5	**3**	1.2 Li, hexane, r.t., 2 h, ultrasonication	D_2O	–	35	25				**3**: 21
6	**3**	1.3 Li, Et_2O, r.t., 2 h, ultrasonication	H_2O	–	45	43				
7	**42c**	3 Li, THF, r.t., 2 h	Me_2SO_4				60			**42c**: 24, hydrolysis[c]: 9
8	**42b**	3 Li, Et_2O, r.t., 4 h	Me_2SO_4				87			**42b**: 3, hydrolysis: 2, n.i.[d]: 2
9	**42b**	2 Li, hexane, 2 eq. Et_2O, r.t., 4 h	Me_2SO_4				91			
10	**42b**	3 Li, THF, r.t., 2 h	Me_2SO_4				79			**42b**: 2, hydrolysis: 7
11	**44**	3 Li, THF, r.t., 2.5 h	Me_2SO_4	–				32	**46**: 34 **50**: 42	**42b**: 40, n.i.: 2
12	**44**	3 Li, THF, r.t., 2.5 h	H_2O	–				28	**46**: 29	**47**: 56
13	**51**	2 Li, THF, r.t., 1.5 h	Me_2SO_4	11				46	**50**: 61	**51**: 20, n.i.: 2
14	**51**	2 Li, THF, r.t., 4 h	Me_2SO_4	–				82	**50**: 84	
15	**51**	5 Li, THF, r.t., 5 h slow addition, 1 h	Me_2SO_4	2				77	**50**: 72	n.i.: 2

[a] Fragments, cleavage products. – [b] Remainder non-volatile, probably of polymeric nature. – [c] Mixture of compounds, for details see Experimental Section. – [d] n.i.: not identified, volatile compounds.

(iii) If the substituent is sufficiently bulky to prevent dimerization and is also able to stabilize the resulting dilithioalkane, a less polar solvent can be employed. Due to this enhanced stabilization, the 1,1-bis(trimethylsilyl)-1,2-dilithioalkane **43** shows no tendency to eliminate lithium hydride.

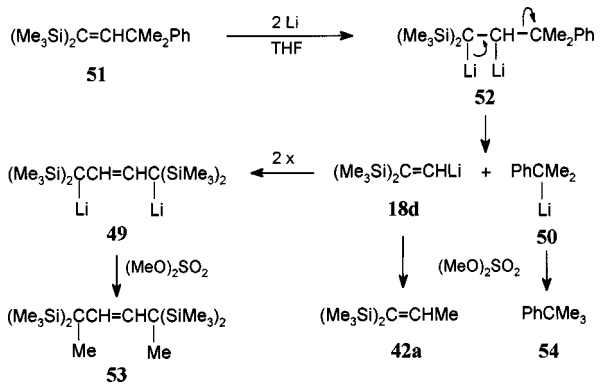
In order to verify the assumptions outlined above, **44** and **51** were synthesized and subjected to reaction with lithium metal in THF. Less polar solvents were found to be unsuitable for this purpose. The reaction cascades observed for **44**, which could be deduced from the product mixtures obtained after derivatization, were more complex: Firstly, the substituent was found to act as a leaving group in the vicinal dilithioalkane **45**. No derivatization product of **18d** was found; instead, comparable amounts of the 1,4-dilithio-2-butene derivative **49** were isolated (entry 11), pointing to another type of dimerization, which is discussed below. A second reaction cascade of **45** could be delineated by comparison with the product mixture obtained after hydrolysis (entry 12). **45** was found to rearrange by a 1,2-phenyl shift, i.e. a Grovenstein-Zimmerman rearrangement,[44] to the more stable 1,3-dilithioalkane **47**. This underwent further fragmentation during the work-up with dimethyl sulfate with formation of **42b** and the corresponding lithium derivative of the nucleofuge **50**. This cleavage did not occur during the work-up with water; in this case **47** was trapped

Scheme 10



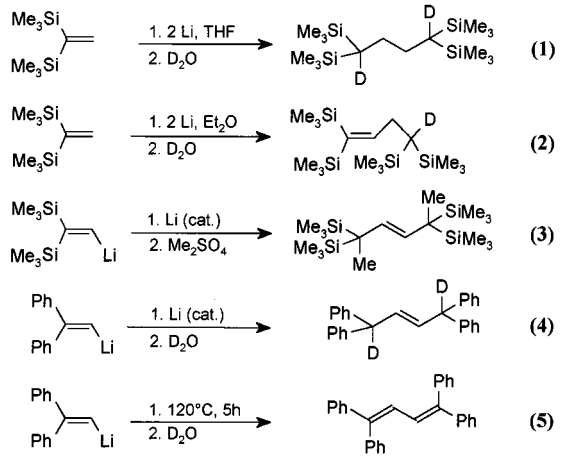
and a mixture of diastereomers (**47**, H instead of Li) was isolated in 56% yield. In **51** (entries 13−15), the cumyl group inhibits the Grovenstein-Zimmerman rearrangement since an anion at a tertiary center would be formed. Hence, only cleavage to **18d** is observed.

Scheme 11



Upon derivatization of the reaction mixture before completion, e.g. after 1.5 h, the existence of this vinyllithium compound as a stable intermediate in the reaction cascade can be proved; 11% of 1,1-bis(trimethylsilyl)-1-propene (**42a**) is obtained after derivatization with dimethyl sulfate. After a prolonged reaction time of 4 h, exclusive formation of comparable amounts of the dimer **49** and the lithium derivative of the nucleofuge **50** is observed. This unusual dimerization has not previously been reported. Recently, we observed and analyzed the dimerization of 2,2-diphenylvinyllithium. This dimerization is catalyzed by electron transfer (Equation 4), and thus requires only catalytic amounts of lithium metal.[16] It is very probable that a similar dimerization takes place for **18d**. In Figure 3, the different types of dimerization are summarized. Additionally, the dimerization observed by Ludvig and Lagow in the thermolysis of 2,2-diphenylvinyllithium[45] is shown in Equation 5. However, the product obtained after quenching with deuterium oxide did not show any deuterium incorporation. The paramagnetic properties reported for 2,2-diphenylvinyllithium[45] might also be responsible for the unusual dimerization of **18d**. Probably, only detailed theoretical calculations of the electronic properties of trimethylsilylvinyllithium compounds in the various solvents can aid in the understanding and the predictability of the reaction pathways which have been found and examined.

Figure 3. Various types of dimerization of vinyllithium compounds, equation 5: ref.[45]



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Experimental Section

General: All reactions involving air- or moisture-sensitive compounds were performed under dry argon (99.996%) using standard Schlenk techniques. Ethereal solvents were purified by adsorptive filtration through basic aluminium oxide (activity grade I) and were freshly distilled under argon from sodium/benzophenone ketyl. Toluene and hexane were freshly distilled from sodium prior to use. Dimethyl sulfate employed in the derivatization of lithiumorganic compounds was distilled and stored over molecular sieves (3 A). − GC/MS analyses were performed with an HP 5988A mass spectrometer, using an HP5 capillary column and an ionization energy of 70 eV in each case. High-resolution mass spectra were recorded with a Varian MAT 311 A instrument. − NMR spectra (^{1}H at 200 MHz and ^{13}C at 50 MHz) were recorded with a Bruker AC 200 NMR spectrometer, unless stated otherwise. − Separations were performed by preparative gas chromatography (Wilken 1520, 3 m OV 101 column with helium as the carrier gas). For analytical gas chromatography an HP 5980a with an HP3396 integrator and a 25-m 5% phenylmethylsilicon capillary column were employed. − Melting points and boiling points are not corrected. Elemental analyses were performed by the Mikroanalytisches Labor Beller (Göttingen). − For all reactions, lithium dust containing 2% sodium was used.[46]

General Procedure for the Derivatization of Lithiumorganic Compounds with Dimethyl Sulfate: The reaction mixtures were filtered through a G3 glass sinter frit, then an excess of dimethyl sulfate, dissolved in the requisite solvent, was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for several hours. By adding concentrated ammonia solution and stirring again for several hours, the excess dimethyl sulfate was destroyed. Water was then added until the initially formed solid had dissolved. The aqueous layer was discarded and the organic layer was washed with 0.1 M hydrochloric acid until neutral, then thrice with water, dried with $MgSO_4$, and the solvent was evaporated in vacuo.

Starting Materials: (E)-1-(o-Bromophenyl)-2-trimethylsilylethene (**36**): A mixture of 0.07 g (0.3 mmol) of $Pd(OAc)_2$, 0.16 g (0.6 mmol) of PPh_3, 1.70 g (10 mmol) of $AgNO_3$, 2.83 g (10 mmol) of *o*-bromoiodobenzene (Fluka), 1.21 g (12 mmol) of triethylamine and 2.00 g (20.0 mmol) of vinyltrimethylsilane was heated for 16 h at 50°C in 150 ml of CH_3CN. After cooling, the mixture was filtered, 100 ml of water was added and the mixture was extracted with Et_2O (4 × 50 ml). The combined organic layers were washed with water, dried with $MgSO_4$, and the solvent was evaporated in vacuo. The residue was subjected to chromatography on silica gel with pentane to afford 1.73 g (6.8 mmol, 68%) of **36**. − GC/MS analysis revealed a mixture of (*E*/*Z*) isomers in the ratio of 49:1. − ^{1}H NMR ($CDCl_3$): δ = 0.30 (s, 9 H, $SiMe_3$), 6.55 (d, *J* = 19 Hz, 1 H, =CH), 6.90−7.50 (m, 4 H, aromatic H), 7.34 (d, *J* = 19 Hz, =CH). − ^{13}C NMR ($CDCl_3$): δ = −1.3, 123.7, 126.9, 127.4, 129.0,

132.9, 133.3, 138.0, 142.1. − MS; *m/z* (%): 254/256 (9) [M^+/(M^+ + 2)], 241 (60), 239 (60), 160 (37), 159 (100), 145 (45), 139 (62), 137 (61), 131 (44), 59 (80), 43 (38). − $C_{11}H_{15}BrSi$ (255.2): calcd. C 51.77, H 5.92; found C 51.93, H 6.04.

1,1-Bis(trimethylsilyl)-3,3-diphenyl-1-butene (**44**): The reaction was performed as described for **51** (see below), starting from 12.76 g (55 mmol) of tris(trimethylsilyl)methane in 110 ml of THF and 42 ml (67.2 mmol) of a 1.6 M solution of MeLi in Et_2O. To this mixture was added 14.11 g (67.2 mmol) of 2,2-diphenylpropionic aldehyde[29]. After distillation, **44** solidified upon standing at 0°C: 7.50 g (21.3 mmol, 39%), b.p. 120−124°C (0.01 Torr), m.p. 42−45°C. − ^{1}H NMR ($CDCl_3$): δ = −0.08 (s, 9 H, $SiMe_3$), 0.21 (s, 9 H, $SiMe_3$), 1.94 (s, 3 H, Me), 7.10−7.47 (m, 10 H, aromatic H), 7.49 (s, 1 H, =CH). − ^{13}C NMR ($CDCl_3$): δ = 1.6, 2.7, 29.5, 52.6, 125.9, 127.9, 129.1, 142.5, 150.0, 161.1. − MS; *m/z* (%): 352 (1) [M^+], 207 (5), 171 (28), 135 (8), 103 (3), 83 (4), 75 (4), 74 (8), 73 (100), 45 (7). − $C_{22}H_{32}Si_2$ (352.7): calcd. C 74.93, H 9.15; found C 75.08, H 9.32.

1,1-Bis(trimethylsilyl)-3-methyl-3-phenyl-1-butene (**51**): To a solution of 20.00 g (86.2 mmol) of tris(trimethylsilyl)methane in 172 ml of THF, 70 ml (112 mmol) of a 1.6 M solution of MeLi in Et_2O was added, and the mixture was stirred for 3 d at room temperature. The solution was then cooled to −78°C and a solution of 16.60 g (112 mmol) of 2-methyl-2-phenylpropionic aldehyde[30] in 5 ml of THF was added dropwise. The mixture was allowed to warm to room temperature and stirred for a further hour. Then, 50 ml of water and 100 ml of pentane were added, the organic layer was washed five times with water, and dried with $MgSO_4$. The remaining solution was filtered through aluminium oxide (activity grade I) with pentane to remove the unreacted aldehyde. After evaporation of tris(trimethylsilyl)methane at 20 Torr, the residue was distilled to afford 14.56 g (50.2 mmol, 58%) of **51**, b.p. 78−80°C (0.01 Torr). − ^{1}H NMR ($CDCl_3$): δ = −0.14 (s, 9 H, $SiMe_3$), 0.20 (s, 9 H, $SiMe_3$), 1.47 (s, 6 H, Me), 7.12 (s, 1 H, =CH), 7.20−7.40 (m, 5 H, Ph). − ^{13}C NMR ($CDCl_3$): δ = 1.5, 2.6, 32.5, 43.6, 120.0, 125.6, 126.8, 142.1, 150.5, 166.7. − MS; *m/z* (%): 290 (1) [M^+], 172 (7), 171 (36), 135 (10), 97 (5), 91 (7), 83 (7), 75 (5), 74 (12), 73 (100), 45 (8). − $C_{17}H_{30}Si_2$ (290.6): calcd. C 70.26, H 10.41; found C 70.09, H 10.51.

Reaction of (*Z*)-**13b** *with Lithium in Et_2O: erythro- and threo-2-Phenyl-3-trimethylsilylbutane* (**24**): To a suspension of 0.29 g (41.7 mmol) of lithium in 20 ml of Et_2O at room temperature, was added a solution of 2.00 g (11.3 mmol) of (*Z*)-**13b** in 10 ml of Et_2O. The reaction mixture was stirred for 3 h at room temperature and then quenched with dimethyl sulfate according to the general procedure to afford 2.02 g (9.8 mmol, 87%) of **24**, b.p. 137−140°C (20 Torr), in an *erythro/threo* ratio of 1:3, as determined from the integrals of the ^{1}H-NMR signals of the mixture. − *erythro*-**24**: ^{1}H NMR ($CDCl_3$): δ = 0.08 (s, 9 H, $SiMe_3$), 0.75−1.08 (m, 4 H, CH, Me), 1.36 (d, *J* = 7.14 Hz, 3 H, Me), 2.70 (dq, *J* = 7.14, 8.86 Hz, 1 H, CH), 7.23−7.35 (m, 5 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = −1.6, 13.8, 22.9, 27.6, 43.1, 125.7, 127.5, 128.0, 148.0. − *threo*-**24**: ^{1}H NMR ($CDCl_3$): δ = −0.01 (s, 9 H, $SiMe_3$), 0.75−1.08 (m, 4 H, CH, Me), 1.31 (d, *J* = 6.89 Hz, 3 H, Me), 2.95 (dq, *J* = 6.89, 7.14 Hz, 1 H, CH), 7.23−7.35 (m, 5 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = −2.2, 10.2, 17.9, 27.8, 40.4, 125.6, 127.4, 128.1, 148.3. − MS; *m/z* (%): 206 (4) [M^+], 191 (15), 135 (27), 132 (17), 117 (7), 105 (21), 91 (6), 74 (8), 73 (100), 59 (10), 45 (9). − $C_{13}H_{22}Si$ (206.4): calcd. C 75.65, H 10.74; found C 75.78, H 10.57.

Reaction of (*Z*)-**13b** *with Lithium Metal in Toluene: (E)-1-(o-Tolyl)-2-trimethylsilylpropene* (**28**): The reaction was carried out as described above, starting from 0.36 g (51.4 mmol) of lithium in 50 ml toluene and 2.00 g (11.3 mmol) of (*Z*)-**13b** in 5 ml of toluene. The mixture was heated to reflux for 10 h. Derivatization with dimethyl sulfate was performed according to the general procedure to afford 2.11 g (10.3 mmol, 91%) of **28**, b.p. 140−142°C (20 Torr). − ^{1}H NMR ($CDCl_3$): δ = 0.20 (s, 9 H, $SiMe_3$), 1.80 (d, *J* = 1.72 Hz, 3 H, Me), 2.27 (s, 3 H, Me), 6.78 (q, *J* = 1.72 Hz, 1 H, =CH), 7.10−7.30 (m, 4 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = −1.2, 16.0, 19.7, 125.2, 126.6, 129.0, 129.8, 136.3, 137.8, 140.0. − MS; *m/z* (%): 204 (17) [M^+], 189 (21), 149 (33), 130 (8), 129 (7), 74 (9), 73 (100), 59 (49), 45 (16), 43 (8). − $C_{13}H_{20}Si$ (204.4): calcd. C 76.40, H 9.86; found C 76.58, H 9.99.

Reaction of **36** *with tBuLi and Lithium Metal in DEM:* A solution of 1.73 g (6.8 mmol) of **36** in 20 ml of DEM was cooled to −50°C. Then, 8.5 ml (13.6 mmol) of a 1.6 M solution of *t*BuLi in pentane was added dropwise. The reaction mixture was stirred for 0.5 h, 0.16 g (22.9 mmol) of lithium metal was added, and stirring was continued for a further 0.5 h at −50°C. After filtration and the usual derivatization with dimethyl sulfate, 0.92 g (4.5 mmol, 66%) of **28**, 0.11 g (0.6 mol, 9%) of (*E*)-**13b** (*o*-tolyl instead of Ph), and 0.11 g (0.5 mmol, 7%) of **24** (*o*-tolyl instead of Ph) were obtained. For characterization of the minor components, (*E*)-**13b** (*o*-tolyl instead of Ph) was prepared according to ref.[29]

24 *(o-Tolyl Instead of Ph):* To a suspension of 0.18 g (25.7 mmol) of lithium in 30 ml of Et_2O at room temperature, was added 2.00 g (10.5 mmol) of (*E*)-**13b** (*o*-tolyl instead of Ph) and the mixture was stirred for 4 h. After the usual derivatization with dimethyl sulfate and work-up, the main product was purified by preparative GC: 1.80 g (8.2 mmol, 78%) as a mixture of *erythro*- and *threo*-2-(*o*-tolyl)-3-trimethylsilylbutane in a ratio of 4:1. − *erythro*-**24** (*o*-tolyl instead of Ph): − ^{1}H NMR ($CDCl_3$): δ = 0.11 (s, 9 H, $SiMe_3$), 0.69−1.15 (m, 4 H, CH and Me), 1.25 (d, *J* = 6.90 Hz, 3 H, Me), 2.33 (s, 3 H, Me), 2.70 (dq, *J* = 6.90, 10.58 Hz, 1 H, CH), 7.05−7.30 (m, 4 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = −1.3, 14.5, 19.8, 22.9, 27.2, 37.7, 125.1, 125.5, 126.2, 129.9, 134.4, 146.8. − *threo*-**24** (*o*-tolyl instead of Ph): ^{1}H NMR ($CDCl_3$): δ = −0.02 (s, 9 H, $SiMe_3$), 0.69−1.15 (m, 4 H, CH and Me), 1.22 (d, *J* = 7.14 Hz, 3 H, Me), 2.35 (s, 3 H, Me), 3.25 (dq, *J* = 7.14, 4.43 Hz, 1 H, CH), 7.05−7.30 (m, 4 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = −2.1, 9.5, 17.2, 19.5, 25.0, 34.8, 125.3, 125.4, 126.6, 130.4, 134.6, 146.0. − MS; *m/z* (%): 220 (9) [M^+], 149 (23), 119 (37), 117 (6), 115 (5), 74 (10), 73 (100), 59 (10), 45 (11), 43 (5). − $C_{14}H_{24}Si$ (220.4): calcd. C 76.28, H 10.97; found C 76.39, H 11.05.

Reaction of **31** *with 2 Equivalents of tBuLi in Toluene:* To a solution of 3.00 g (11.8 mmol) of **31** in 30 ml of toluene at −30°C, 15 ml (24 mmol) of a 1.6 M solution of *t*BuLi in pentane was added dropwise. After 0.5 h at −30°C, a solid was formed. After a further 0.5 h, derivatization with dimethyl sulfate was performed as described above to afford after preparative GC 1.75 g (9.2 mmol, 78%) of (*E*)-1-phenyl-2-trimethylsilylpropene (**33**): − ^{1}H-NMR data in $CDCl_3$ were in accordance with those reported in ref.[27] − ^{13}C NMR ($CDCl_3$): δ = −2.1, 16.3, 126.4, 128.0, 129.0, 136.8, 138.4, 140.3. Additionally, 0.23 g (1.3 mmol, 11%) of phenyltrimethylsilylacetylene (**32**) was found.[19]

Reaction of **31** *with nBuLi in Et_2O:* To a stirred solution of 2.00 g (7.8 mmol) of **31** in 30 ml of Et_2O at room temperature, was added 15 ml (24 mmol) of a 1.6 M solution of *n*BuLi in hexane. The reaction mixture was stirred for 24 h and then quenched with dimethyl sulfate as described in the general procedure. Preparative GC afforded 0.72 g (4.1 mmol, 52%) of **33** and 0.39 g (1.7 mmol, 22%) of (*E*)-1-phenyl-2-trimethylsilyl-1-hexene (**29**): ^{1}H-NMR data in $CDCl_3$ were in accordance with those reported in ref.[47a] − ^{13}C

NMR ($CDCl_3$): δ = 0.3, 14.0, 22.8, 31.6, 34.8, 126.1, 128.1, 131.9, 143.6, 144.8.

Reaction of **31** *with tBuLi and Lithium in [D_8]THF:* 2.00 g (7.9 mmol) of **31** was dissolved in 18 ml of [D_8]THF and the solution was cooled to −90°C. 10 ml (16 mmol) of a 1.6 M solution of *t*BuLi in pentane was added dropwise and the yellow solution was stirred for 2 h at −90°C. Then, 0.17 g (24.3 mmol) of lithium was added and stirring was continued for a further 4 h at −90°C. After filtration and derivatization with dimethyl sulfate, the product mixture was subjected to preparative GC to afford 0.20 g (1.1 mmol, 14%) of **33**, 0.71 g (3.5 mmol, 44%) of **24**, 0.02 g (0.1 mmol, 1%) of (*Z*)-**35** and 0.37 g (1.7 mmol, 22%) of **34**. Characterization of **34**: ^{1}H NMR ($CDCl_3$): δ = −0.01 (s, 9 H, $SiMe_3$), 0.76/0.88 (2 s, 2 × 3 H, 2 Me), 1.30 (d, *J* = 7.14 Hz, 3 H, Me), 2.78 (q, *J* = 7.14 Hz, 1 H, CH), 7.10−7.30 (m, 5 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = −2.5, 17.6, 19.0, 22.9, 23.8, 45.9, 125.7, 127.4, 129.2, 144.7. − MS; *m/z* (%): 220 (1) [M^+], 146 (10), 135 (13), 131 (11), 106 (11), 105 (21), 91 (6), 74 (8), 73 (100), 70 (25), 45 (6). − $C_{14}H_{24}Si$ (220.4): calcd. C 76.28, H 10.97; found C 76.41, H 11.08.

Reaction of **32** *with Lithium:* To a suspension of 0.50 g (71.4 mmol) of lithium in 30 ml of DEM at −40°C, a solution of 2.00 g (11.5 mmol) of **32** in 15 ml of DEM was added dropwise over a period of 4 h. The reaction mixture was stirred for 14 h at −40°C to afford after the usual work-up with dimethyl sulfate 0.43 g (2.1 mmol, 18%) of a mixture of (*Z*/*E*)-**35** in a ratio of 4:1. Additionally, 1.45 g (3.8 mmol, 66%) of a mixture of dimers was found. ^{1}H-NMR and ^{13}C-NMR data of (*E*)-**35** in $CDCl_3$ were in accordance with those reported in ref.[47b] − (*Z*)-**35**: ^{1}H NMR ($CDCl_3$): δ = −0.24 (s, 9 H, $SiMe_3$), 1.82/2.02 (2 q, *J* = 0.98 Hz, 2 × 3 H, 2 Me), 7.10−7.35 (m, 5 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = −0.24, 18.3, 22.6, 127.2, 128.2, 128.6, 129.1, 132.8, 148.3. − MS; *m/z* (%): 204 (10) [M^+], 190 (13), 189 (11), 136 (11), 135 (21), 74 (6), 73 (8), 59 (100), 45 (25), 43 (6).

Reaction of **33** *with Lithium:* To a suspension of 0.15 g (21.4 mmol) of lithium in 30 ml of Et_2O at room temperature, was added 2.00 g (10.5 mmol) of **33** in 10 ml of Et_2O. The reaction mixture was stirred for 4 h, and then quenching with dimethyl sulfate and work-up was performed as described in the general procedure to afford 0.58 g (2.8 mmol, 27%) of **24**, 0.44 g (2.0 mmol, 19%) of **34**, and 0.75 g (3.7 mmol, 35%) of 3-phenyl-2-trimethylsilyl-1-butene (**30**): ^{1}H NMR ($CDCl_3$): δ = 0.07 (s, 9 H, $SiMe_3$), 1.50 (d, *J* = 6.9 Hz, 3 H, Me), 3.78 (br. q, *J* = 6.9 Hz, 1 H, CH), 5.64 (dd, *J* = 2.4, 1.0 Hz, 1 H, =CH), 5.84 (dd, *J* = 2.4, 1.0 Hz, =CH), 7.20−7.70 (m, 5 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 1.0, 21.5, 44.4, 123.3, 125.9, 128.1, 128.2, 145.7, 155.9. − MS; *m/z* (%): 204 (7) [M^+], 189 (16), 136 (7), 135 (48), 130 (8), 105 (11), 74 (10), 73 (100), 59 (14), 45 (7). − $C_{13}H_{20}Si$ (204.4): calcd. C 76.40, H 9.86; found C 76.39, H 9.75.

Reaction of **17b** *with Lithium:* To a suspension of 0.55 g (78.6 mmol) of lithium metal in 50 ml of Et_2O, a solution of 2.00 g (11.3 mmol) of α-trimethylsilylstyrene[23] (**17b**) in 5 ml of Et_2O was added at room temperature and the mixture was stirred for 3 h. After filtration and the usual derivatization with dimethyl sulfate, 1.98 g (5.2 mmol, 92%) of a 2:1 mixture of *meso*- and *d,l*-2,5-bis(trimethylsilyl)-2,5-diphenylhexane (**40**) was obtained. The two diastereomers were separated by fractional crystallization from ethanol. The physical and spectroscopic data of the two diastereomers were in accordance with those reported in ref.[7]

Reaction of **42b** *with Lithium Metal in THF:* To a suspension of 0.17 g (24.3 mmol) of lithium in 20 ml of THF, a solution of 1.70 g (6.8 mmol) of 1,1-bis(trimethylsilyl)-2-phenylethene (**42b**)[27] in 10 ml of THF was added dropwise and the reaction mixture was stirred for 2 h at room temperature. After derivatization with dimethyl sulfate and the usual work-up, 1.49 g (5.37 mmol, 79%) of 2,2-bis(trimethylsilyl)-3-phenylbutane, 0.04 g (0.14 mmol, 2%) of 1,1-bis(trimethylsilyl)-2-phenylpropane and 0.09 g (0.34 mmol, 5%) of 1,1-bis(trimethylsilyl)-2-phenylethane were obtained. − *Characterization of 2,2-bis(trimethylsilyl)-3-phenylbutane:* ^{1}H NMR ($CDCl_3$): δ = 0.06/0.13 (2 s, 2× 9 H, 2 $SiMe_3$), 1.06 (s, 3 H, Me), 1.51 (d, *J* = 8.0 Hz, 3 H, Me), 2.86 (q, *J* = 8.0 Hz, 1 H, CH), 7.10−7.30 (m, 5 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 0.3, 1.2, 3.8, 18.8, 20.6, 46.2, 126.0, 127.5, 129.6, 145.5. − MS; *m/z* (%): 278 (1) [M^+], 205 (6), 175 (18), 135 (19), 113 (10), 105 (12), 74 (8), 73 (100), 59 (11), 45 (15), 43 (6). − $C_{16}H_{30}Si_2$ (278.6): calcd. C 68.98, H 10.95; found C 69.09, H 10.81. − *1,1-Bis(trimethylsilyl)-2-phenylpropane:* MS; *m/z* (%): 264 (2) [M^+], 176 (11), 175 (8), 161 (27), 135 (31), 105 (9), 99 (16), 74 (9), 73 (100), 59 (10), 45 (11). − *1,1-Bis(trimethylsilyl)-2-phenylethane:* MS; *m/z* (%): 250 (3) [M^+], 235 (10), 162 (24), 161 (38), 147 (24), 135 (14), 74 (9), 73 (100), 59 (12), 45 (13), 43 (9).

Reaction of **3** *with Lithium Metal:* To a suspension of 0.08 g (11.4 mmol) of lithium in 50 ml of Et_2O, a solution of 1.50 g (8.7 mmol) of 1,1-bis(trimethylsilyl)ethene in 50 ml of Et_2O was added dropwise. During the addition, the reaction mixture was ultrasonicated, and the temperature was kept below 25°C. After stirring for a further hour, the solution was filtered and derivatization was performed with water to afford after distillation (50−60°C, 0.005 Torr) a mixture of 0.68 g (1.96 mmol, 45%) of **4** (H instead of Li)[4] and 0.65 g (1.89 mmol, 43%) of 1,1,4,4-tetrakis(trimethylsilyl)-1-butene **41** (H instead of Li). Since no satisfactory separation could be achieved, the mixture was characterized as such.

41 *(H Instead of Li):* − ^{1}H NMR (80 MHz, $CDCl_3$): δ = −0.33 (m, 1 H, CH), 0.04 (s, 18 H, $SiMe_3$), 0.09/0.11 [2 s, 2× 9 H, =C($SiMe_3$)$_2$], 2.43 (t, *J* = 6.5 Hz, CH_2), 6.58 (t, *J* = 6.5 Hz, 1 H, =CH). − MS; *m/z* (%): [M^+ peak not observed], 241 (5), 183 (4), 169 (6), 168 (29), 167 (8), 153 (8), 74 (8), 73 (100), 59 (9), 45 (32).

Upon derivatization with deuterium oxide, **41** (D instead of Li) was obtained: − ^{1}H NMR (80 MHz, $CDCl_3$): δ = 0.04 (s, 18 H, $SiMe_3$), 0.09/0.18 [2 s, 2 × 9 H, =C($SiMe_3$)$_2$], 2.43 (t, *J* = 6.5 Hz, CH_2), 6.58 (t, *J* = 6.5 Hz, 1 H, =CH). − MS; *m/z* (%): [M^+ not observed], 242 (4), 184 (4), 170 (5), 169 (27), 168 (16), 154 (6), 74 (8), 73 (100), 59 (6), 45 (25).

Reaction of **42c** *with Lithium:* To a suspension of 0.18 g (25.7 mmol) of lithium in 20 ml of THF a solution of 2.40 g (8.7 mmol) of 1,1-bis(trimethylsilyl)-3,3-dimethyl-1-butene (**42c**) in 10 ml of THF was added at room temperature. The reaction mixture was stirred for 2 h, filtered, and derivatized with dimethyl sulfate. After the usual work-up, 1.34 g (5.2 mmol, 60%) of 2,2-bis(trimethylsilyl)-3,4,4-trimethylpentane, 0.05 g (0.2 mmol, 2%) of 2,2-bis(trimethylsilyl)-4,4-dimethylpentane, and 0.14 g (0.6 mmol, 7%) of 1,1-bis(trimethylsilyl)-3,3-dimethylbutane were obtained, besides 24% of recovered starting material.

2,2-Bis(trimethylsilyl)-3,4,4-trimethylpentane: ^{1}H NMR ($CDCl_3$): δ = 0.13/0.14 (2 s, 2 × 9 H, 2 $SiMe_3$), 1.01 (s, 9 H, CMe_3), 1.02 (d, *J* = 6.6 Hz, 3 H, Me), 1.24 (s, 3 H, Me), 1.48 (q, *J* = 6.6 Hz, 1 H, CH). − ^{13}C NMR ($CDCl_3$): δ = 0.9, 4.1, 17.9, 20.5, 27.6, 31.7, 37.4, 56.1. − MS; *m/z* (%): 258 (0.2) [M^+], 131 (21), 128 (7), 127 (60), 99 (12), 74 (9), 73 (100), 59 (9), 57 (33), 45 (11), 43 (6). − $C_{24}H_{34}Si_2$ (258.2): calcd. 258.2199; found 258.2194.

2,2-Bis(trimethylsilyl)-4,4-dimethylpentane: MS; *m/z* (%): [M^+ peak not found], 229 (1) [M^+ − 15], 187 (10), 155 (7), 131 (10), 100 (8), 99 (76), 74 (9), 73 (100), 59 (7), 57 (6), 45 (10).

1,1-Bis(trimethylsilyl)-3,3-dimethylbutane: This compound was prepared independently according to ref.[48] from vinyltrimethylsilane, chlorotrimethylsilane, and *t*BuLi. ^{1}H-NMR data were in accordance with the reported values. – ^{13}C NMR ($CDCl_3$): δ = 0.9, 7.2, 29.9, 31.5, 37.8. – MS; *m/z* (%): 230 (0.3) [M^+], 173 (11), 141 (20), 127 (5), 99 (6), 86 (6), 85 (64), 74 (8), 73 (100), 59 (11), 45 (10).

Reaction of **44** *with Lithium Metal and Derivatization with Dimethyl Sulfate:* To a suspension of 0.15 g (21.4 mmol) of lithium metal in 20 ml of THF, a solution of 2.20 g (6.3 mmol) of 1,1-bis(trimethylsilyl)-3,3-diphenyl-1-butene in 10 ml of THF was added dropwise and the mixture was stirred for 2.5 h. After filtration, derivatization, and the usual work-up, the low-boiling products were separated by bulb-to-bulb distillation and subjected to preparative gas chromatography. The residue was distilled to afford 0.37 g (1.0 mmol, 32%) of 2,2,5,5-tetrakis(trimethylsilyl)-3-hexene (**53**); b.p. 120–124°C (0.001 Torr). – ^{1}H NMR ($CDCl_3$): δ = −0.01 (s, 36 H, $SiMe_3$), 1.07 (s, 6 H, Me), 5.21 (s, 2 H, =CH). – ^{13}C NMR ($CDCl_3$): δ = −1.7, 14.3, 21.2, 128.9. – MS; *m/z* (%): 372 (5) [M^+], 211 (17), 181 (5), 159 (8), 137 (9), 131 (17), 123 (9), 74 (8), 73 (100), 59 (7), 45 (9). – $C_{18}H_{44}Si_4$ (372.9): calcd. C 57.98, H 11.98; found C 57.88, H 11.89.

In addition, 0.41 g (2.1 mmol, 34%) of 2,2-diphenylpropane (spectroscopic data in accordance with ref.[49a]), 0.35 g (2.6 mmol, 42%) of *tert*-butylbenzene (**54**, spectroscopic data in accordance with ref.[49b]), and 0.62 g (2.5 mmol, 40%) of 1,1-bis(trimethylsilyl)-2-phenylethene (**42b**) were obtained.

Reaction of **44** *with Lithium Metal and Derivatization with Water:* The reaction was performed on the same scale as above and derivatized with water. After the usual work-up, the product mixture was separated by bulb-to-bulb distillation and then subjected to preparative gas chromatography to afford 0.33 g (1.8 mmol, 29%) of 1,1-diphenylethane (spectroscopic data in accordance with those reported in ref.[50]) and 0.31 g (0.9 mmol, 28%) of 1,1,4,4-tetrakis(trimethylsilyl)-2-butene as a mixture of isomers. The main product consisted of 1.24 g (3.5 mmol, 56%) of a mixture of *erythro*- and *threo*-**47** (H instead of Li), b.p. 150–160°C (0.001 Torr). The diastereomers were separated by column chromatography on silica with hexane as eluent. – *erythro*-**47** (H instead of Li) – ^{1}H NMR ([D_6]acetone): δ = −0.10/−0.05 (2 s, 2 × 9 H, 2 $SiMe_3$), 0.39 (d, *J* = 2.22 Hz, 1 H, CH), 0.98 (d, *J* = 6.40 Hz, 3 H, Me), 3.37 (dq, *J* = 11.2, 6.40 Hz, 1 H, CH), 3.48 (dd, *J* = 11.2, 2.22 Hz, 1 H, CH), 7.25–7.50 (m, 10 H, aromatic H). – ^{13}C NMR ([D_6]acetone): δ = 1.6, 3.5, 21.4, 22.7, 45.8, 52.3, 126.8, 127.1, 128.8, 128.9, 129.2, 130.2, 145.0, 147.9. – *threo*-**47** (H instead of Li) – ^{1}H NMR ([D_6]acetone): δ = −0.06/0.22 (2 s, 2 × 9 H, 2 $SiMe_3$), 0.96 (d, *J* = 2.96 Hz, 1 H, CH), 1.40 (d, *J* = 6.40 Hz, 3 H, Me), 3.26 (dq, *J* = 11.1, 6.40 Hz, 1 H, CH), 3.36 (dd, *J* = 11.1, 2.96 Hz, 1 H, CH), 6.90–7.10 (m, 10 H, aromatic H). – ^{13}C NMR ([D_6]acetone): δ = 1.5, 3.7, 20.9, 22.3, 46.7, 53.9, 126.2, 126.5, 128.3, 128.4, 130.1, 130.2, 145.8, 147.9. – MS; *m/z* (%): [M^+ peak not found], 339 (2) [M^+ − 15], 250 (8), 249 (32), 162 (16), 161 (100), 145 (15), 135 (22), 105 (10), 73 (76), 59 (10), 55 (7). – $C_{22}H_{34}Si_2$ (354.7): calcd. C 74.50, H 9.66; found C 74.60, H 9.62. The mass spectrum of **31** (H instead of Li) was in accordance with data given in ref.[51]

Reaction of **51** *with Lithium Metal:* To a suspension of 0.16 g (22.9 mmol) of lithium in 20 ml of THF, a solution of 2.50 g (8.6 mmol) of 1,1-bis(trimethylsilyl)-3-methyl-3-phenyl-1-butene in 10 ml of THF was added at room temperature. The mixture was stirred for 1.5 h, filtered, and derivatization with dimethyl sulfate was performed as described above to afford 0.19 g (1.0 mmol, 11%) of 1,1-bis(trimethylsilyl)-1-propene (**42a** which was prepared independently according to ref.[27]), 0.70 g (5.2 mmol, 61%) of *tert*-butylbenzene (**54**), and 0.74 g (2.0 mmol, 46%) of **53**.

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