Exploratory Studies on the Synthesis of Unsymmetrically Substituted Diacetylenes Bearing Trialkoxysilyl Groups and Development of a Method for the Preparation of 1-Lithio-4-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecanyl)-1,3-butadiyne: Synthetic and Mechanistic Aspects

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(*Z*)-$CH_3OCH{=}CHC{\equiv}CSi(OCH_3)_3$ (**2**), ((*Z*)-$CH_3OCH{=}CHC{\equiv}C)_2Si(OCH_3)_2$ (**5**), and (*Z*)-CH_3-$OCH{=}CHC{\equiv}CSi(OCH(CH_3)_2)_3$ (**16**) have been synthesized from (*Z*)-$CH_3OCH{=}CHC{\equiv}CH$ (**1**). Enynes **2** and **16** were subjected to a deprotonation−elimination−deprotonation sequence with 2 equiv of lithium diisopropylamide (LDA) in THF and the expected intermediates $(RO)_3SiC{\equiv}CC{\equiv}CLi$ (R = CH_3, $CH(CH_3)_2$) allowed to react with R'_3SiCl (R′ = CH_3, C_6H_5) to produce the unsymmetrical butadiynes $(RO)_3SiC{\equiv}CC{\equiv}CSiR'_3$. Symmetrical butadiynes of the type $R'_3SiC{\equiv}CC{\equiv}CSiR'_3$ were obtained instead of the expected unsymmetrical ones due to cleavage of the $C_{sp}-Si(OR)_3$ bond by CH_3OLi formed in situ. Cleavage of the latter bond can be avoided by using a silatrane moiety in place of the trialkoxysilyl group. Thus, $(CH_3)_3$-$SiC{\equiv}CC{\equiv}CSi(OCH_2CH_2)_3N$ (**26a**) and $(C_6H_5)_3SiC{\equiv}CC{\equiv}CSi(OCH_2CH_2)_3N$ (**26b**) were obtained in 61% and 45% yield, respectively, upon subjecting (*Z*)-$CH_3OCH{=}CHC{\equiv}CSi(OCH_2$-$CH_2)_3N$ (**20**) to a deprotonation−elimination−metalation sequence with 2 equiv of LDA followed by quenching of the intermediate lithium compound $LiC{\equiv}CC{\equiv}CSi(OCH_2CH_2)_3N$ (**25**) with $(CH_3)_3SiCl$ and $(C_6H_5)_3SiCl$. The deprotonation−elimination−metalation sequence applied to **20** is best carried out in pyridine, and the role of pyridine in this reaction is discussed.

Introduction

There have been numerous reports in recent years concerning the synthesis and the study of molecules and polymers containing the diacetylenic fragment A. This

$$-C{\equiv}C-C{\equiv}C-$$
A

intense research is driven by the fact that such molecules or polymers have a very rich chemistry and show interesting prospects in materials science and related fields.[1−12]

The knowledge of diacetylenic species and materials derived from them is well-developed, but one limitation is that this knowledge mainly concerns symmetrically

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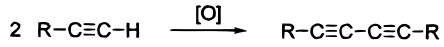
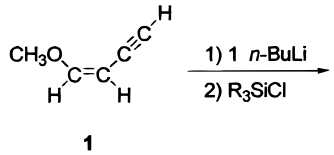
Scheme 1



Scheme 2



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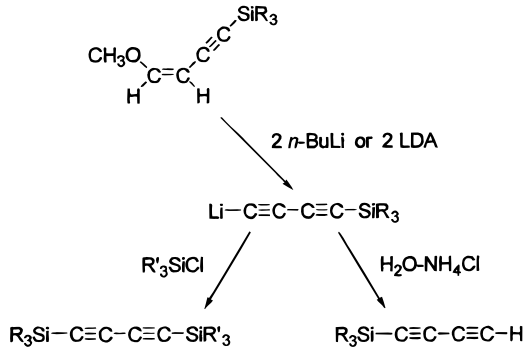


substituted molecules. This is because the method of choice used primarily to prepare such compounds is the oxidative coupling (Glaser, Eglinton, Hay)[13] of terminal alkynes (Scheme 1).

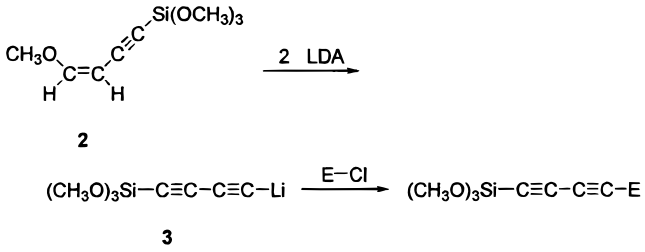
One method developed a few years ago by Zweifel and co-workers[14] to circumvent this problem is based on the utilization of (*Z*)-1-methoxybut-1-en-3-yne (**1**) as starting material (Scheme 2). This method was further developed recently by our group[15] to prepare the unsymmetrically substituted (diphenylphosphino)diacetylene derivatives $Ph_2PC{\equiv}CC{\equiv}CE$.

We describe herein the results of our efforts to apply the methodology developed by Zweifel to (*Z*)-methoxyenynes bearing trialkoxysilyl and silatranyl substituents in order to prepare novel unsymmetrically substituted diacetylenes of the types $(RO)_3SiC{\equiv}CC{\equiv}CE$ and $N(CH_2CH_2O)_3SiC{\equiv}CC{\equiv}CE$. It was especially important to establish whether the corresponding 1-lithio-4-(trialkoxysilyl)-1,3-butadiynes and 1-lithio-4-silatranyl-1,3-butadiynes could be generated and what conditions were suitable to do so (nature of R, nature of the base, solvent, temperature). Also, we wanted to gain some mechanistic insights into the deprotonation−elimination−deprotonation sequence and, in particular, determine the stability of the various intermediates with respect to isomerization, elimination of CH_3OLi, and involvement in side reactions such as nucleophilic attack by CH_3OLi generated in situ and polymerization.

Results and Discussion

Initial Studies. We originally sought to prepare compounds of the type $(CH_3O)_3SiC{\equiv}CC{\equiv}CE$ by subjecting (*Z*)-$CH_3OCH{=}CHC{\equiv}CSi(OCH_3)_3$ (**2**) to a deprotonation−elimination−deprotonation sequence with 2 equiv of lithium diisopropylamide (LDA) followed by condensation of the intermediate anion $(CH_3O)_3SiC{\equiv}CC{\equiv}CLi$ (**3**) with the electrophile E^+ (Scheme 3).[14b] The $(CH_3O)_3Si$ substituent was chosen, as it may be hydrolyzed under mild conditions without the risk of breaking the C_{sp}−Si bond.[9e,f]

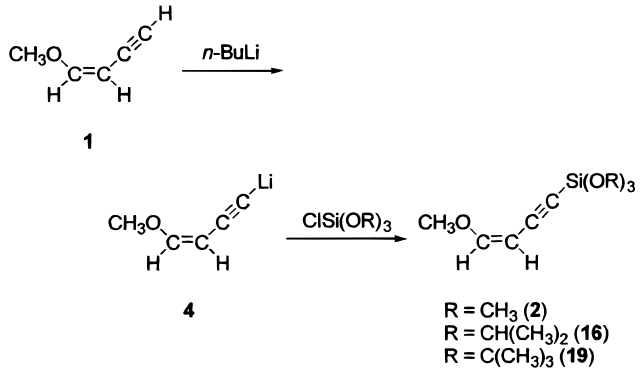
Scheme 3



2

3

Scheme 4



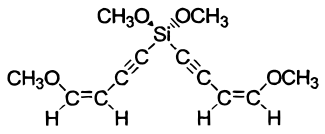
1

4

R = CH_3 (**2**)
R = $CH(CH_3)_2$ (**16**)
R = $C(CH_3)_3$ (**19**)

Enyne **2** is most readily prepared by deprotonation of (*Z*)-1-methoxybut-1-en-3-yne (**1**) with 1 equiv of *n*-BuLi in THF followed by condensation, at −78 °C, of the acetylenic anion with chlorotrimethoxysilane (Scheme 4).[14]

In the case where R = CH_3, a competing reaction also takes place that leads to **5**.



5

We have found that when anion **4** is added to a cold (−78 °C) THF solution of $(CH_3O)_3SiCl$, 49% of **2** and about 17% of **5** are obtained after distillation. When the reverse order of addition is used, only 12% of **2** and 47% of **5** are obtained after distillation.

Enyne **2** was subjected to the reaction sequence outlined in Scheme 3 with ECl being Me_3SiCl and Ph_3SiCl (see the Supporting Information for experimental details).[14b,15] In neither case did we isolate the desired products $Me_3SiC{\equiv}CC{\equiv}CSi(OMe)_3$ (**6**) and $Ph_3SiC{\equiv}CC{\equiv}CSi(OMe)_3$ (**7**) but, instead, the symmetrically substituted diynes **10** and **11** were obtained (Scheme 5).

The most probable explanation for these results is that lithium methoxide, formed in situ during the deprotonation of **2**, attacks the starting compound and/or the intermediate anion. This process leads to the

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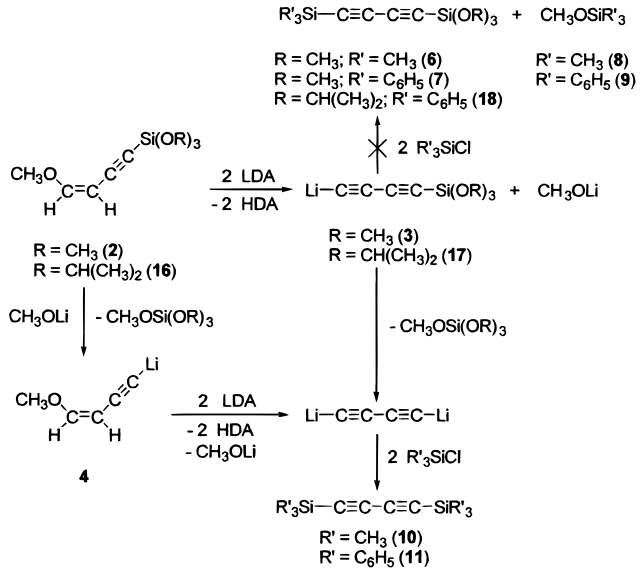
Scheme 5



cleavage of the C_{sp}—Si bond with formation of 1,4-dilithiobuta-1,3-diyne that subsequently undergoes condensation with 2 equiv of chlorosilane (Scheme 5). Some test experiments have been carried out that support the attack of CH_3OLi on **2** and **3**, and the results of these experiments are described in the Supporting Information.

We thought of increasing the steric demand of the substituents around silicon so as to prevent the attack by CH_3OLi generated during the elimination step, and to this end, methoxyenyne **16** was prepared (Scheme 4).

Compound **16** was subjected to a deprotonation—elimination—deprotonation sequence with 2 equiv of LDA followed by quenching of the expected anion **17** with 2 equiv of Ph_3SiCl (Scheme 5). The desired product **18** was not obtained, and instead, **11** was isolated in 43% yield, once again suggesting that the C_{sp}—$Si(OR)_3$ bond had been cleaved by CH_3OLi formed during the reaction (see the Supporting Information for experimental details).

Finally, several attempts have been made to prepare enyne **19** by the reaction of anion **4** with $ClSi(OC(CH_3)_3)_3$ and $HSi(OC(CH_3)_3)_3$ but, whatever the experimental conditions used, only marginal results were obtained (see the Supporting Information).

Silatrane Chemistry: Synthesis of (*Z*)-1-Methoxy-4-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecanyl)but-1-en-3-yne (20). Results from this laboratory[16] and elsewhere[17] have shown that the Si—X bond in halosilatranes shows enhanced stability with respect to solvolysis and nucleophilic attack, even though photoelectron spectroscopy (PES) data and X-ray fluorescence studies indicate a higher positive charge on silicon as compared to alkyltrialkoxysilanes,[18] similar to what is known for regular anionic pentacoordinate silicon species.[19] This is due to the bridgehead nature of the silicon

Scheme 6

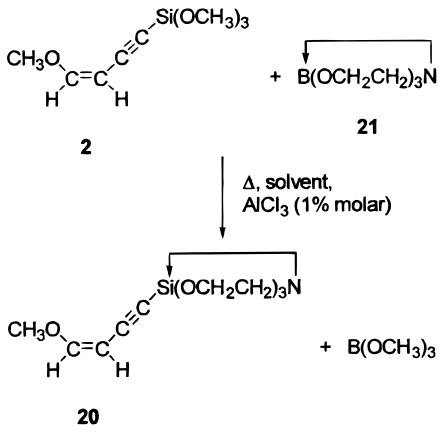
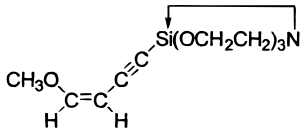


Table 1. Preparation of 20 via Boron—Silicon Exchange as a Function of Solvent and Reflux Time

	solvent				
	$CHCl_3$	toluene		*o*-xylene	
reflux time (h)	20	20	63	20	63
enyne **2** (%)	100	21.0	3.3	3.3	0
boratrane **21** (%)	100	31.4	8.7	7.2	6.1
silatrane **20** (%)	0	45.8	85.3	85.8	86.1
trans compd (%)	0	1.7	2.7	3.6	7.8

atom in the silatrane, which precludes backside attack. With this in mind, we set out to synthesize (*Z*)-1-methoxy-4-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]-undecanyl)but-1-en-3-yne (**20**). Owing to the robustness of the C_{sp}-silatrane bond, it should be possible to prepare the diacetylenic anion analogous to **3** and **17**.



20

Two methods of preparation of **20** were tested. In the first method, the boron—silicon exchange reaction reported by Cradock *et al.*[20] and Bellama and co-workers[21] was used (Scheme 6).

The results are summarized in Table 1.

No reaction was observed upon refluxing **2** and **21** for 20 h in chloroform. The desired reaction (Scheme 6) does take place when higher boiling solvents are employed. Thus, 45.8% of **20** is achieved upon refluxing **2** and **21** in toluene for 20 h, and this percentage reaches 85.8% in *o*-xylene for the same amount of time. Longer periods of reflux increase the amount of **20** that is produced. Also, it is noteworthy that the amount of remaining boratrane in the final solid is always greater than that of remaining **2**. Presumably, this is due to partial decomposition of the starting enyne upon refluxing. Another interesting point is that increasing amounts of a *trans* compound ($^3J_{HH} = 12.8$ Hz) are produced upon

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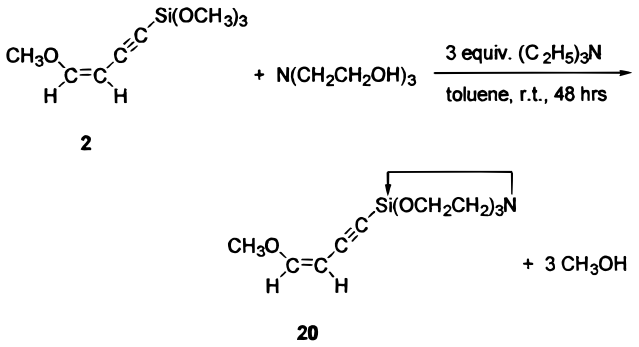
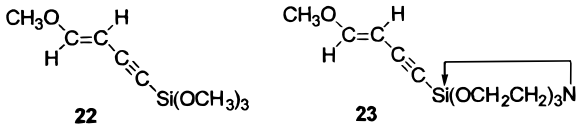
Scheme 7



increasing the boiling point of the solvent or the duration of reflux. The *trans* compound is believed to be either **22** or **23**. These compounds would arise from *cis* → *trans* isomerization of **2** and **20**.



To test this hypothesis, we have attempted to isomerize **2** and **20**. In the first series of experiments, **2** was refluxed for 65 h in anhydrous toluene and **20** for 60 h in toluene and *o*-xylene. No *trans* compound was detected in these experiments by infrared, ^{1}H NMR, and ^{29}Si NMR spectroscopy. These attempts were repeated in the presence of 2.6 mol % of $AlCl_3$, and the formation of a *trans* compound was indeed observed in the case of **20**. The chemical shifts of the olefinic protons, 6.92 and 4.90 ppm, and the $^{3}J_{HH}$ coupling constant, 12.8 Hz, found for **23** are in good agreement with those previously measured for the *trans* compound observed in the boron−silicon exchange reactions.[22]

Although the boron−silicon exchange reaction described above leads to the desired product, there are several drawbacks associated with it: first, it requires refluxing enyne **2** for long periods of time in high-boiling solvents. This leads to partial decomposition of **2** and to $AlCl_3$-catalyzed isomerization of **20** into **23**. Second, because of the partial decomposition of **2**, a small amount of boratrane **21** always remains in the final solid. Attempts to separate boratrane **21** from enyne **20** by fractional crystallization and column chromatography (SiO_2, Al_2O_3, Florisil) have not been successful.

In the second method, enyne **2** is allowed to react with 1 equiv of triethanolamine, in toluene, at room temperature, in the presence of 3 equiv of triethylamine (Scheme 7).[23−25]

Silatrane **20** is insoluble in toluene and precipitates from the solution during the reaction. The product is easily recovered by filtration and, after recrystallization from a chloroform−pentane mixture, it is isolated with a 79% yield.

(22) Interestingly, the Lewis-acid-catalyzed *Z* to *E* isomerization of 1,2-bis(diphenylphosphino)ethene has recently been reported. See: Sigl, M.; Schier, A.; Schmidbaur, H. *Z. Naturforsch., B* **1998**, *53*, 1301.

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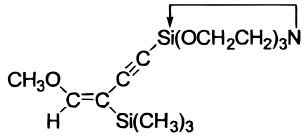
Silatrane Chemistry: Deprotonation of (*Z*)-1-Methoxy-4-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]-undecanyl)but-1-en-3-yne (20), Characterization of the Intermediate Anion 25, and Preparation of Unsymmetrical, Silicon-Containing, Diacetylenic Molecules. With **20** in hand, we set out to look at its deprotonation chemistry as outlined in Scheme 8.

Initial studies were carried out in THF using *n*-BuLi as a base, as previously described by Zweifel and collaborators.[14] These attempts met with failure, and compound **26a** was not isolated. *n*-BuLi was anticipated to participate in a sequence of metalation−elimination−metalation reactions leading to **25**, but clearly, a side reaction occurs that might be the attack of *n*-BuLi at the silicon atom of the silatrane moiety.[16] Thus, subsequent attempts to prepare **26a** and **26b** were carried out with LDA, a strong nonnucleophilic base.

In THF, in the presence of 2 equiv of LDA, the desired metalation−elimination−metalation sequence does take place but, whatever the temperature scheme chosen, complete disappearance of **20** is not observed (Table 2). Beside the desired product **26a**, the final solid contains various amounts of **20** and **10**. Also, in several cases, the presence of a fourth compound was detected, namely (*E*)-1-methoxy-2-(trimethylsilyl)-4-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecanyl)but-1-en-3-yne (**27**). The stereochemistry of the double bond in **27** was elucidated by ^{29}Si NMR spectroscopy (vide infra).



Silatrane **20** is only sparingly soluble in THF, and so this is probably why, in the above experiments, complete consumption of this compound was not observed. To circumvent this problem, the metalation−elimination−metalation reaction sequence was carried out in pyridine and, after the intermediate anion was quenched with Me_3SiCl, compound **26a** was isolated in 61% yield. The chemical structure of **26a** was established by spectroscopic means, mass spectrometry, and elemental analysis. Similarly, 4-(triphenylsilyl)-1-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecanyl)buta-1,3-diyne (**26b**) was prepared in 45% yield using Ph_3SiCl as the electrophile.

Preparation of Enyne 27 and NMR Spectroscopic Elucidation of the Stereochemistry of the Double Bond. We have attempted to prepare large amounts of **27**, as the vinylsilane functionality present in this compound conjugated with the ethynylsilatrane fragment make it an interesting synthon for further reactions. The best results were obtained by carrying out the deprotonation of **20** with 1 equiv of LDA, in THF, without allowing the reaction mixture to come to room temperature before the addition of Me_3SiCl (see Table 3, experiment 1). In this case, purification of the 0.6 g of impure material gave 0.12 g of a solid that contained 90 mol % of **27** and 10 mol % of **20**.

With a fairly pure sample of **27** in hand, we carried out a complete spectroscopic characterization of this

Scheme 8

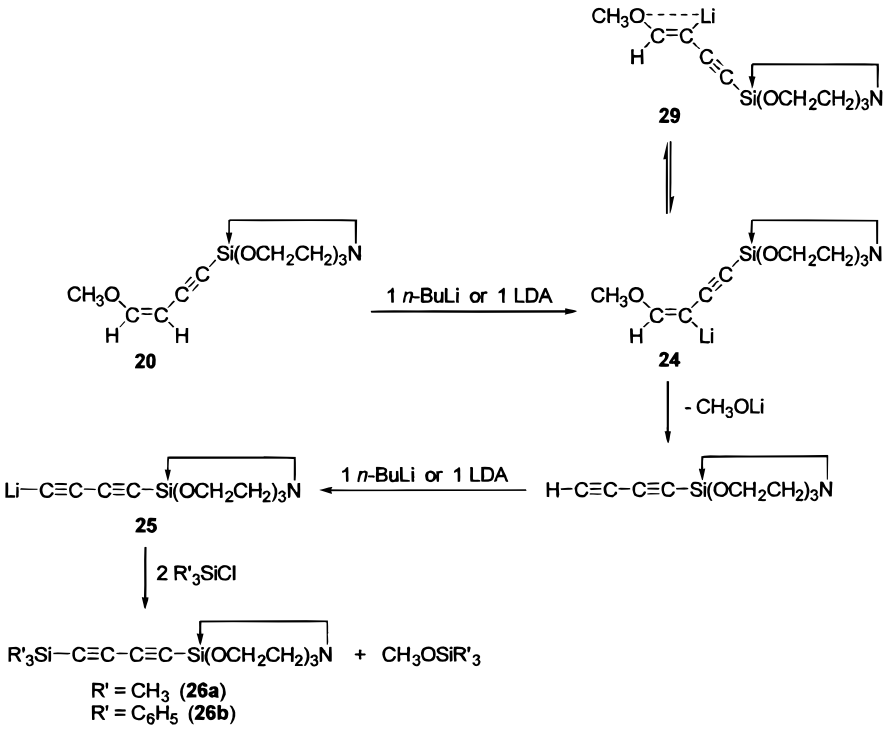


Table 2. Results from the Metalation−Elimination−Metalation Experiments Carried out on 20 with LDA in THF[a]

	expt no.			
	1	2	3	4
temp scheme after the addition of LDA	−70 °C, 2 h; room temp, 1.5 h	−50 °C, 2 h; room temp, 1.5 h	−70 °C, 7 h; room temp, 1.5 h	−50 °C, 7 h; room temp, 21 h
temp scheme after the addition of Me_3SiCl	−70 °C, 2 h; room temp, overnight	−50 °C, 2 h; room temp, overnight	−70 °C, 2 h; room temp, overnight	−50 °C, 2 h; room temp, overnight
mol % of the final solid	7.1% **10** 64.8% **20** 23.4% **26a** 4.7% **27**	14.7% **10** 49.8% **20** 23.6% **26a** 11.8% **27**	9.3% **10** 53.6% **20** 27.1% **26a** 10.0% **27**	20.7% **10** 63.0% **20** 16.3% **26a**

[a] General conditions: 1.02 g of **20** suspended in 120 mL of THF, 4 mL of 2 M solution of LDA, 1.1 mL of Me_3SiCl.

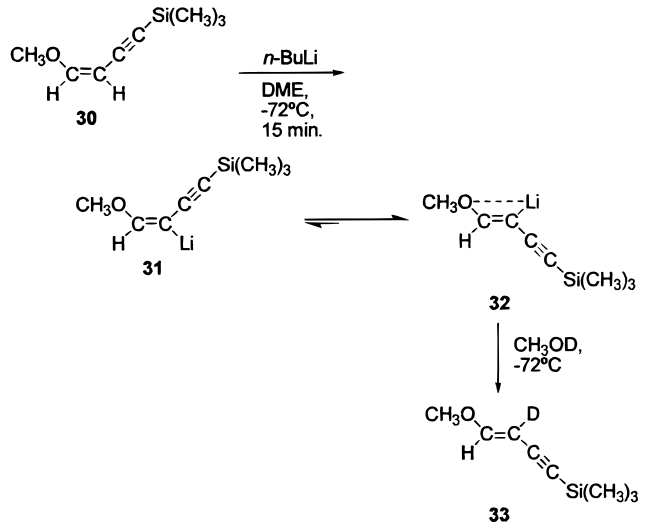
Table 3. Results from the Monodeprotonation Experiments Carried out on 20 as a Function of Solvent and Temperature Scheme

	expt no.				
	1	2	3	4	5
amt of **20** used (g)	1.96	1.36	1.8	1.61	1.61
solvent (mL)	THF (150)	pyridine (120)	pyridine (150)	THF (150), TMEDA (20)	THF (150), TMEDA (20)
amt of 2 M soln of LDA used (mL)	3.85	2.67	3.53	3.15	3.16
temp scheme after the addition of LDA	−80/−85 °C, 5 h	−40 °C, 2.17 h; room temp, 1.58 h	−35/−40 °C, 2.75 h	−75 °C, 2 h	≤−70 °C, 2 h; room temp, 1.5 h
quantity of Me_3SiCl added (mL) and temp of addition	0.97, −80 °C	0.7, −40 °C	0.9, −40 °C	0.8, −75 °C	0.8, −85 °C
temp scheme after the addition of Me_3SiCl	−80 °C, 2.5 h; room temp, overnight	−40 °C, 15 min; room temp, overnight	−40 °C, 2 h	−75 °C, 1.5 h; room temp, overnight	≤−68 °C, 2 h; room temp, overnight
results	1.42 g of unreacted **20** + 0.6 g of a solid containing 21 mol % of **20** and 79 mol % of **27**	69% **20**, 31% **26a**	78% **20,** 6% **23**, 16% **26a**	86% **20**, 14% **27**	79% **20**, 21% **26a**

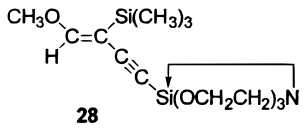
material. In particular, it was important to establish the stereochemistry of the double bond. On the basis of the results previously obtained by Zweifel and Rajagopalan (Scheme 9),[14a] it was anticipated that the monodeprotonation of **20** with LDA, in THF, followed by quenching of the intermediate anion with Me_3SiCl, would lead predominantly to **28**.

The ^{29}Si NMR data indicate that the correct structure is in fact **27**. In the $^{29}Si\{^1H\}$ NMR spectrum, the signal corresponding to the $Si(CH_3)_3$ group is observed at

Scheme 9



−3.5 ppm. This value is close to the ^{29}Si chemical shifts found for $(CH_3)_3SiCH{=}CH_2$ (−6.80 ppm ≤ δ ≤ −7.60 ppm) and $(CH_3)_3SiCH{=}CHC_6H_5$ (−6.49 ppm).[26] A slight



upfield shift (up to 10 ppm) might have been expected if structure **28** were present as a result of the interaction, due to geometrical constraints, between the oxygen lone pairs of the methoxy group and the silicon atom.[27,28] More convincing evidence for the existence of structure **27** was obtained by measuring the magnitude of the $^3J_{^{29}Si^1H}$ coupling constant: 3.7 Hz. This value is close to that measured for ^{29}SiC=CH (*cis*) in *gem*-$(CH_3)_3SiClC{=}CH_2$, i.e., 4.36 Hz, and to those reported for other vinylsilanes.[29,30] $^3J_{^{29}Si^1H}$(*trans*) coupling constants are typically in the range 9−21 Hz.[29,30]

This assignment is in apparent contradiction with Zweifel's work[14a] and with the results we have obtained concerning the monodeprotonation of (*Z*)-$CH_3OCH{=}CHC{\equiv}CSi(CH_3)_3$ (**30**) in THF (vide infra). We believe that the presence of the silatrane moiety in **20** influences the course of the deprotonation in that it coordinates to the lithium ions present in solution and prevents intramolecular chelation leading to **29** from occurring (Scheme 8).[31] However, the difference in electronic effects that exists between a $SiMe_3$ substituent and a silatrane group may also be important in that it might affect the stability of the resulting vinyllithium and, thus, modify its reactivity.[32]

Effects of Temperature and Nature of the Solvent on the Elimination of CH_3OLi (Table 3). The monodeprotonation of **20** with LDA was carried out in pyridine, at −40 °C, for 2.17 h, and warming of the reaction mixture to room temperature was effected over a period of 1 h 35 min (experiment 2). The mixture was cooled again to −40 °C, 1 equiv of Me_3SiCl was added, and stirring was continued, first at −40 °C for 15 min and then at room temperature overnight. After workup, only 0.15 g of solid was recovered (1.74 g was expected) and spectroscopic characterization (IR and ^{1}H NMR) indicated the presence of starting enyne **20** (69% molar) and diacetylene **26a** (31% molar). Compound **27** was not observed. The same experiment was repeated without allowing the mixture to come to room temperature at any time during the deprotonation step (experiment 3). A 10 mL aliquot of the final mixture was withdrawn and concentrated to dryness, and the residue was analyzed by ^{1}H NMR spectroscopy. The NMR analysis showed the presence of three main compounds, starting enyne **20** (78 mol %), its *trans* isomer **23** (6 mol %), and diacetylenic silatrane **26a** (16 mol %).[33] Once again, compound **27** was not detected.

The preparation of **27** was carried out in THF, in the presence of 20 equiv of TMEDA, without allowing the mixture to come to room temperature at any time during the deprotonation step (experiment 4); it was found that enyne **27** accounted for about 14 mol % of the residual solid and that the major constituent was starting silatrane **20** (86 mol %). Diacetylenic silatrane **26a** was not detected. The same experiment was repeated except that the reaction mixture was allowed to come to room temperature during the deprotonation step (experiment 5). Spectroscopic characterization of the final solid indicated that starting enyne **20** and diyne **26a** were the only two compounds present; the mole fractions of these compounds were, respectively, 79% and 21%.

It is clear from these experiments that monodeprotonation of **20** with LDA yields the organolithium compound **24** (Scheme 8). In the case where weakly coordinating solvents such as THF and THF−TMEDA are used, intermolecular chelation of lithium by a nearby silatrane moiety occurs and stabilizes **24** and prevents isomerization of the latter anion to its intramolecularly coordinated isomer **29**. This stabilization is quite significant, as the reaction mixture must be warmed to room temperature for some time during the deprotonation step to allow the favorable *anti* elimination of CH_3OLi leading to the production of $HC{\equiv}CC{\equiv}CSi(OCH_2CH_2)_3N$.[34] On the other hand, the temperature scheme chosen appears to have little impact on the elimination of CH_3OLi when the solvent used is strongly coordinating (neat pyridine). Coordination of Li^+ by

(26) Marsmann, H. In *NMR, Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1981; Vol. 17, p 65.

(27) It is worth pointing out that no compound has been reported to date in which an interaction between an oxygen-containing group and a tetraalkylsilane has been established.

(28) The shift in the position of the ^{29}Si NMR signal that is given has been estimated from data obtained on fluorosilanes. See: Mix, A.; Berlekamp, U. H.; Stammler, H.-G.; Neumann, B.; Jutzi, P. *J. Organomet. Chem.* **1996**, *521*, 177.

(29) Danyluk, S. S. *J. Am. Chem. Soc.* **1965**, *87*, 2300.

(30) Bratovanov, S.; Kozminski, W.; Fässler, J.; Molnar, Z.; Nanz, D.; Bienz, S. *Organometallics* **1997**, *16*, 3128.

(31) (a) Corriu, R. J. P.; Guérin, C.; Henner, B. J. L.; Wang, Q. *Organometallics* **1991**, *10*, 3574. (b) Corriu, R.; Guérin, C.; Henner, B.; Wang, Q. *Inorg. Chim. Acta* **1992**, *198−200*, 705.

(32) Miller, J. A.; Leong, W.; Zweifel, G. *J. Org. Chem.* **1988**, *53*, 1839.

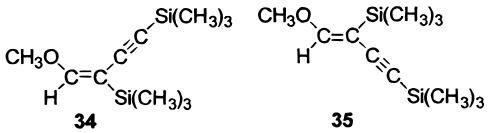
(33) *cis* → *trans* isomerization of the starting enyne presumably involves the formation of the (*Z*)-enynyllithium derivative, isomerization of this intermediate to its *E* isomer, and protonation. A similar type of isomerization has been observed by Zweifel and Rajagopalan.[14a] Furthermore, the configurational lability of (α-alkynylvinyl)lithiums at low temperature has been commented upon.[32]

(34) (a) Ficini, J.; Depezay, J.-C. *Tetrahedron Lett.* **1968**, 937. (b) Lau, K. S. Y.; Schlosser, M. *J. Org. Chem.* **1978**, *43*, 1595. (c) Gschwend, H. W.; Rodriguez, H. R. *Org. React. (N.Y.)* **1979**, *26*, 1.

pyridine[35] overpowers intermolecular chelation by a nearby silatrane goup, destabilizes anion **24**, and facilitates the elimination of CH_3OLi, even at low temperature. Furthermore, complexation of Li^+ by pyridine is expected to increase the kinetic basicity of LDA[34c,36] and favor elimination-type processes.[37]

Influence of the Solvent on the Position of the Equilibrium Between the (*Z*)- and (*E*)-Enynyllithium Intermediates. Zweifel and Rajagopalan carried out the monodeprotonation of **30** in DME, at −72 °C, and quenched the intermediate $CH_3OCH{=}C(Li)C{\equiv}CSi(CH_3)_3$ with various electrophiles[14a] (Scheme 9 in the case where the electrophile is deuterium). In these experiments, the recovered products predominantly had the same geometry as **33**; i.e., the methoxy group was *cis* to the entering electrophile (isomeric purities ≥93%). These results were ascribed to the fact that anion **32** was the predominant species in solution.

We have repeated these experiments with 1 equiv of LDA, using pyridine and THF as solvents. The intermediate anion was quenched with 1 equiv of Me_3SiCl. In pyridine, a mixture of **34**, **35**, and **10** was obtained in the molar ratio 0.48:0.07:0.45. In THF, a mixture of **34** (24 mol %), **35** (70 mol %) and **10** (6 mol %) was isolated. These results agree fully with Zweifel's observations and with those in our silatrane chemistry (vide supra): in THF, in the absence of a competing silatrane moiety, internal chelation of lithium by the methoxy group present in the substrate takes over and anion **32** is formed predominantly. This anion is quite stable and does not eliminate CH_3OLi as long as it is kept at low temperature. As a result, only small amounts of **10** are produced beside **35**. In neat pyridine, coordination of lithium by pyridine overpowers internal chelation by the methoxy group, making anion **31** the predominant species in solution. Consequently, **34** is the major enyne in the final mixture. However, anion **31** possesses favorable stereochemistry for an *anti* elimination, and so fairly large amounts of **10** are also produced.



Finally, some comments concerning the NMR data for **34** and **35** need to be made. The chemical shift value for the ethylenic proton of **34** is very similar to that of the ethylenic proton of **27**. The same is true for the ethylenic carbon bearing the methoxy group and for the silicon atom bound to the double bond. The $^3J_{SiH}$ values are also very close together. The similarity between the NMR data of the two compounds is a strong indication that the assignment of the geometry of **27** is correct. The NMR data of **35** are noticeably different from those of **27** and **34**: the chemical shift value for the ethylenic proton of **35** is 7.04 ppm, whereas it is 6.14 ppm in the case of **34**. A significant downfield shift is also observed for the ethylenic carbon bearing the methoxy group: 165.6 ppm for **35** vs 159.5 ppm for **34**. On the other hand, the chemical shift value for the silicon atom bound to the double bond is upfield by 2.6 ppm. It is not clear whether these differences are merely the result of steric repulsion in **35** between the methoxy group and the $Si(CH_3)_3$ moiety borne by the double bond or if they arise from weak intramolecular interactions between the methoxy group and the silicon atom. We are currently attempting to elucidate this point.

Conclusion

The present work shows that it is not possible to prepare the diacetylenic lithium derivatives $LiC{\equiv}CC{\equiv}CSi(OR)_3$ ($R = CH_3$, $CH(CH_3)_2$) by subjecting (*Z*)-$CH_3OCH{=}CHC{\equiv}CSi(OR)_3$ to a deprotonation−elimination−metalation sequence. This is because the $C_{sp}-Si(OR)_3$ bond is cleaved by CH_3OLi formed during the reaction. However, $LiC{\equiv}CC{\equiv}CSi(OCH_2CH_2)_3N$ (**25**) can be obtained from (*Z*)-$CH_3OCH{=}CHC{\equiv}CSi(OCH_2CH_2)_3N$ (**20**). The use of the silatrane moiety is essential, in that the C_{sp}−silatrane bond is resistant to nucleophilic attack by CH_3OLi. Thus, the easy access to **25** has allowed us to prepare unsymmetrical diacetylenic molecules bearing a functionalized silicon atom.

The conditions required to carry out the metalation−elimination−metalation sequence on **20** have been studied. The nature of the solvent is a determining factor, as it governs the stability of the (*Z*)-enynyllithium intermediate with respect to elimination and isomerization. Also, the presence of the silatrane moiety appears to have some influence on the stereochemistry of this intermediate.

Further work is currently in progress to investigate the polymerization of these molecules and prepare other functionalized diacetylenic compounds bearing a silatrane substituent. Also, studies are being conducted to transform the silatrane moiety into other silicon-containing groups with potential applications in materials science.

Experimental Section

General Considerations. All manipulations were carried out under an inert atmosphere of dinitrogen or argon using standard Schlenk-line techniques. Solvents were refluxed on and distilled from appropriate drying agents prior to use: THF, Et_2O (Na/benzophenone); toluene, hexanes (Na); *o*-xylene, TMEDA, Et_3N, pyridine, CH_2Cl_2 (CaH_2); pentane ($LiAlH_4$); $CHCl_3$, CCl_4 (P_2O_5).

^1H, ^{11}B, ^{13}C, and ^{29}Si NMR spectra were recorded on Bruker spectrometers of the following types: AVANCE DRX 400, AC 250, WP 200 SY, and AVANCE DPX 200. Chemical shifts were referenced as follows: ^1H (protio impurities of the NMR solvents), ^{13}C (NMR solvents), ^{29}Si (tetramethylsilane), ^{11}B ($BF_3{\cdot}Et_2O$). Solid-state NMR spectra were recorded with magic-angle spinning (MAS) of the sample on a Bruker AM 300 spectrometer using the TOSS (^{13}C) and CP (^{29}Si) pulse sequences. Samples were spun at 5 kHz in zirconia rotors. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer with a 4 cm^{-1} resolution. Mass spectra were obtained on JEOL instruments of the types JMS-DX300 and JMS-SX102A. Melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. Elemental anal-

(35) (a) Clegg, W.; Dunbar, L.; Horsburgh, L.; Mulvey, R. E. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 753. (b) Müller, A.; Marsch, M.; Harms, K.; Lohrenz, J. C. W.; Boche, G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1518.

(36) Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon Press: Oxford, U.K., 1974.

(37) (a) Ficini, J.; Barbara, C.; Colodny, S.; Duréault, A. *Tetrahedron Lett.* **1968**, 943. (b) Normant, H. *Bull. Soc. Chim. Fr.* **1968**, 791.

yses were carried out at the Laboratoire de Microanalyse of the Ecole Nationale Supérieure de Chimie de Montpellier (ENSCM) or at the Service Central de Microanalyse of the Centre National de la Recherche Scientifique (CNRS), Vernaison, France.

Materials. The following chemicals were used as supplied: 2.5 M solution of *n*-BuLi in hexanes (Acros Organics), 2 M solution of LDA in THF/*n*-heptane (Acros Organics), 1.5 M solution of MeLi−LiBr in diethyl ether (Aldrich), boric acid (Prolabo), and triethanolamine (Labosi).

Chlorotrimethylsilane was purchased from Acros Organics and distilled from magnesium powder prior to use. Chlorotriphenylsilane was prepared via chlorination of triphenylsilane with chlorine gas in CCl_4 at 0 °C.[38] (*Z*)-1-Methoxybut-1-en-3-yne (**1**) was purchased from Aldrich, purified as described in the literature,[39] and distilled from CaH_2. Chlorotrimethoxysilane was synthesized by following a reported method.[9e] Chlorotriisopropoxysilane and chlorotri-*tert*-butoxysilane were prepared via a slight modification of a literature procedure,[40] and the ^{29}Si NMR data were identical with those reported elsewhere.[41] (*Z*)-$CH_3OCH{=}CHC{\equiv}CLi$ (**4**) was obtained by treatment of **1** with 1 equiv of *n*-BuLi in THF.[14] The syntheses of diyne **10**,[14a] boratrane **21**,[21] and enyne **30**[14a] have been described previously.

Syntheses. (*Z*)-$CH_3OCH{=}CHC{\equiv}CSi(OCH_3)_3$ (2) and ((*Z*)-$CH_3OCH{=}CHC{\equiv}C)_2Si(OCH_3)_2$ (5). A suspension of **4** (0.11 mol) was added dropwise, via a cannula, to a solution of 81.6% pure chlorotrimethoxysilane (19 mL, 0.135 mol) in THF (50 mL) cooled to −70 °C. The resulting solution was stirred at −70 °C for 10 min; then the cooling bath was removed. The reaction mixture was warmed to room temperature overnight while stirring. The suspension was filtered through a glass frit to remove LiCl, and the volatiles were eliminated in vacuo. A 60 mL portion of dry chloroform was added to the residue to precipitate the remaining LiCl, and the suspension was filtered through a glass frit. The filtrate was concentrated under reduced pressure and the residue distilled under approximately 2×10^{-2} Torr. A 10.8 g (53.4 mmol) portion of enyne **2** was collected in the range 70−75 °C (49% yield). Compound **5** was distilled at 135 °C and was obtained in 17% yield (2.37 g, 9.4 mmol). A 12% yield of **2** and 47% yield of **5** were recovered after distillation when the reverse order of addition was used.

Characterization data for **2** are as follows. ^{1}H NMR ($CDCl_3$, 200.1 MHz): δ (ppm) 3.60 (s, 9H, $Si(OCH_3)_3$), 3.80 (s, 3H, $CH_3OCH{=}$), 4.57 (d, $^3J_{HH}$ = 6.6 Hz, 1H, $CHC{\equiv}C$), 6.40 (d, $^3J_{HH}$ = 6.6 Hz, 1H, $CH_3OCH{=}$). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ (ppm) 50.8 ($Si(OCH_3)_3$), 60.8 ($CH_3OCH{=}$), 84.2 ($CHC{\equiv}C$), 86.9 ($C{\equiv}CSi$), 100.2 ($C{\equiv}CSi$), 159.5 ($CH_3OCH{=}$). ^{29}Si NMR ($CDCl_3$, 39.8 MHz): δ (ppm) −68.3. IR (CCl_4): 2942 s, 2843 s ($\nu_{C(sp^3)H}$), 2157 s ($\nu_{C\equiv C}$), 1633 s ($\nu_{C=C}$), 1456 m (δ_{OCH_3}), 1273 s ($\nu_{C(sp^2)O}$), 1194 s ($SiOCH_3$ rocking), 1118 vs (ν_{CO}), 1094 vs (ν(as)$_{Si-OC}$) cm^{-1}. MS (EI, 30 eV): *m*/*z* (assignment, relative intensity) 202 (M^+, 52), 187 ([M − CH_3]$^+$, 63), 171 ([M − OCH_3]$^+$, 88), 157 ([M − CH_3 − CH_2O]$^+$, 45), 141 ([M − OCH_3 − CH_2O]$^+$, 43), 127 ([M − CH_3 − $2CH_2O$]$^+$, 100), 121 ([$Si(OCH_3)_3$]$^+$, 86), 91 ([$Si(OCH_3)_3$ − CH_2O]$^+$, 67), 81 ([$CH_3OCH{=}CHC{\equiv}C$]$^+$, 29), 59 ([$SiOCH_3$]$^+$, 85). Anal. Calcd for $C_8H_{14}O_4Si$: C, 47.50; H, 6.98. Found: C, 48.62; H, 7.41.

Characterization data for **5** are as follows. ^{1}H NMR ($CDCl_3$, 200.1 MHz): δ (ppm) 3.59 (s, 6H, $Si(OCH_3)_2$), 3.79 (s, 6H, $CH_3OCH{=}$), 4.54 (d, $^3J_{HH}$ = 6.7 Hz, 2H, $CHC{\equiv}C$), 6.39 (d, $^3J_{HH}$ = 6.6 Hz, 2H, $CH_3OCH{=}$). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ (ppm) 50.9 ($Si(OCH_3)_2$), 60.7 ($CH_3OCH{=}$), 84.4 ($CHC{\equiv}C$), 90.0 ($C{\equiv}CSi$), 100.2 ($C{\equiv}CSi$), 159.3 ($CH_3OCH{=}$). ^{29}Si NMR ($CDCl_3$, 39.8 MHz): δ (ppm) −63.5. IR (CCl_4): 2953 m, 2937 s, 2852 m, 2841 m ($\nu_{C(sp^3)H}$), 2155 s ($\nu_{C\equiv C}$), 1630 s ($\nu_{C=C}$), 1456 m (δ_{OCH_3}), 1272 s ($\nu_{C(sp^2)O}$), 1192 m ($SiOCH_3$ rocking), 1119 vs (ν_{CO}), 1093 vs (ν(as)$_{Si-OC}$) cm^{-1}. MS (FAB+, no matrix used): *m*/*z* (assignment, relative intensity) 253 ([M + H]$^+$, 17), 221 ([M − OCH_3]$^+$, 62), 171 ([$CH_3OCH{=}CHC{\equiv}CSi(OCH_3)_2$]$^+$, 100), 141 ([$CH_3OCH{=}CHC{\equiv}CSi(OCH_3)_2$ − CH_2O]$^+$, 57), 59 ([$SiOCH_3$]$^+$, 96). Anal. Calcd for $C_{12}H_{16}O_4Si$: C, 57.12; H, 6.39. Found: C, 57.94; H, 7.01.

($CH_3)_3SiC{\equiv}C-C{\equiv}CSi(OCH_3)_3$ (6). A 1.5 M solution of MeLi−LiBr (7.34 mL, 11.01 mmol) was added very slowly, at room temperature, to a solution of **10** (2.14 g, 11.01 mmol) in diethyl ether (40 mL). An emerald green suspension was obtained after stirring at room temperature for 6 h. A solution of chlorotrimethoxysilane (2.24 g, 14.31 mmol) in diethyl ether (10 mL) was added to the suspension, and stirring was continued overnight. The reaction mixture was filtered and the filtrate concentrated to dryness under reduced pressure. The residue was washed with pentane, and the resulting suspension was filtered. After elimination of the solvent under reduced pressure, the residue was heated to 40 °C under 0.1 Torr to remove some of the unreacted **10**. Distillation under 6×10^{-3} Torr allowed the elimination of the small amount of $(CH_3O)_3SiC{\equiv}CC{\equiv}CSi(OCH_3)_3$ that had also formed during the reaction, but the rest of remaining **10** could not be removed. The following analyses have been carried out on a mixture (molar ratio 95.5:4.5) of **6** and **10**.

^{1}H NMR ($CDCl_3$, 250.1 MHz): δ (ppm) 0.21 (s, 9H, $Si(CH_3)_3$), 3.59 (s, 9H, $Si(OCH_3)_3$). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm) −0.4 ($Si(CH_3)_3$), 51.2 ($Si(OCH_3)_3$), 75.0 ($C{\equiv}CSi(OCH_3)_3$), 87.66, 87.72, 87.85 ($(CH_3)_3SiC{\equiv}C-C{\equiv}C$). ^{29}Si NMR ($CDCl_3$, 49.7 MHz): δ (ppm) −15.3 ($Si(CH_3)_3$), −71.4 ($Si(OCH_3)_3$). IR (neat): 2962 s, 2945 s, 2845 s ($\nu_{C(sp^3)H}$), 2075 s ($\nu_{C\equiv C}$), 1458 m (δ_{OCH_3}), 1410 m (δ_{as} $SiCH_3$), 1252 s (δ_s $SiCH_3$), 1194 s ($SiOCH_3$ rocking), 1091 s (ν(as)$_{Si-OC}$) cm^{-1}.

(*Z*)-$CH_3OCH{=}CHC{\equiv}CSi(C_6H_5)_3$. A similar procedure to that leading to **30** was followed.[14a] After hydrolysis with a saturated solution of NH_4Cl and extraction with pentane, the organic layer was dried over $MgSO_4$. The volatiles were removed under reduced pressure. The residual oily paste was solubilized in hot dichloromethane and the solution cooled to −18 °C. (*Z*)-$CH_3OCH{=}CHC{\equiv}C-Si(C_6H_5)_3$ was obtained as a beige microcrystalline powder with a 74% yield (14.19 g, 41.66 mmol). Mp: 100.0−102.7 °C.

^{1}H NMR ($CDCl_3$, 250.1 MHz): δ (ppm) 3.67 (s, 3H, CH_3O), 4.57 (d, $^3J_{HH}$ = 6.6 Hz, 1H, $CHC{\equiv}C$), 6.23 (d, $^3J_{HH}$ = 6.6 Hz, 1H, $CH_3OCH{=}$), 7.22−7.61 (m, 15H, C_6H_5). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm) 60.6 ($CH_3OCH{=}$), 85.2 ($CHC{\equiv}C$), 92.2 ($C{\equiv}CSi$), 104.7 ($C{\equiv}CSi$), 127.8 ($C_{2,6}$), 129.6 (C_4), 134.0 (C_1), 135.6 ($C_{3,5}$), 158.4 ($CH_3OCH{=}$). ^{29}Si NMR ($CDCl_3$, 49.7 MHz): δ (ppm) −29.4. IR (CCl_4): 3070 s, 3053 s ($\nu_{CH\ arom}$), 2935 m, 2856 m ($\nu_{C(sp^3)H}$), 2150 s ($\nu_{C\equiv C}$), 1633 s, 1619 s ($\nu_{C=C\ aliph}$), 1590 w, 1485 m, 1430 s (phenyls), 1453 m (δ_{OCH_3}), 1272 s ($\nu_{C(sp^2)O}$), 1115 vs (SiC_6H_5) cm^{-1}. Anal. Calcd for $C_{23}H_{20}OSi$: C, 81.13; H, 5.92; Si, 8.25. Found: C, 80.52; H, 5.71; Si, 8.85.

($C_6H_5)_3SiC{\equiv}CC{\equiv}CH$ (14). Diyne **14** was prepared from (*Z*)-$CH_3OCH{=}CHC{\equiv}CSi(C_6H_5)_3$ by following a reported method.[14b] After extraction with pentane and drying of the organic layer over $MgSO_4$, the volatiles were removed under reduced pressure. The residual solid was recrystallized from a CH_2Cl_2−pentane mixture (40:60 v/v); orange crystals of **14** were obtained in 67% yield (2.39 g, 7.75 mmol). Mp: 119.7−121.5 °C.

^{1}H NMR ($CDCl_3$, 250.1 MHz): δ (ppm) 2.26 (s, 1H, $HC{\equiv}C$), 7.40−7.70 (m, 15H, C_6H_5). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm) 68.5 ($HC{\equiv}C$), 68.8 ($HC{\equiv}C$), 80.1 ($C{\equiv}CSi$), 91.7 ($C{\equiv}CSi$), 128.6 ($C_{2,6}$), 130.7 (C_4), 132.6 (C_1), 136.0 ($C_{3,5}$). ^{29}Si NMR ($CDCl_3$, 49.7 MHz): δ (ppm) −28.3. IR (CCl_4): 3310 vs ($\nu_{C(sp)H}$), 3072 s, 3054 s, 3026 m ($\nu_{CH\ arom}$), 2191 s, 2038 s ($\nu_{C\equiv C}$), 1590 w, 1486 m, 1430 vs (phenyls), 1114 vs (SiC_6H_5) cm^{-1}. MS (EI, 70 eV): *m*/*z* (assignment, relative intensity) 308 (M^+, 18), 307 ([M − H]$^+$, 59), 231 ([M − C_6H_5]$^+$, 81), 181 ([$(C_6H_5)_2Si$ − H]$^+$,

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65), 153 ([M − $2C_6H_5$ − H]$^+$, 22), 105 ([C_6H_5Si]$^+$, 46), 77 ($C_6H_5^+$, 28). Anal. Calcd for $C_{22}H_{16}Si$: C, 85.67; H, 5.23; Si, 9.11. Found: C, 85.51; H, 5.36; Si, 8.60.

$(C_6H_5)_3SiC{\equiv}CC{\equiv}CSi(OCH_3)_3$ (7). A 2.46 M solution of *n*-BuLi (5.77 mL, 14.19 mmol) was added dropwise to a solution of **14** (4.37 g, 14.19 mmol) in diethyl ether (100 mL) cooled to −78 °C. The mixture containing $LiC{\equiv}CC{\equiv}CSi(C_6H_5)_3$ became orange-red after stirring at −78 °C for 15 min. A solution of chlorotrimethoxysilane (2.89 g, 18.44 mmol) in diethyl ether (10 mL) was added dropwise to the previous solution. The cooling bath was removed and the mixture stirred for 3.5 h. The suspension was filtered through a glass frit, and the volatiles were removed under reduced pressure. **7** is a very viscous oil that solidifies upon standing in a freezer. It was obtained in 98% yield (5.96 g, 13.91 mmol). Mp: 55.5−57.8 °C.

^{1}H NMR ($CDCl_3$, 250.1 MHz): δ (ppm) 3.61 (s, 9H, Si(OCH_3)$_3$), 7.36−7.65 (m, 15H, C_6H_5). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm) 51.1 (Si(OCH_3)$_3$), 76.6 (C≡*C*Si(OCH_3)$_3$), 82.5 ((C_6H_5)$_3$Si*C*≡C), 87.5 (*C*≡CSi(OCH_3)$_3$), 91.4 ((C_6H_5)$_3$SiC≡*C*), 128.3 ($C_{2,6}$), 130.5 (C_4), 132.1 (C_1), 135.7 ($C_{3,5}$). ^{29}Si NMR ($CDCl_3$, 49.7 MHz): δ (ppm) −28.1 (Si(C_6H_5)$_3$), −71.7 (Si(OCH_3)$_3$). IR (neat): 3070 m, 3050 m ($\nu_{CH\ arom}$), 2944 s, 2844 s ($\nu_{C(sp^3)H}$), 2075 s ($\nu_{C\equiv C}$), 1588 w, 1484 m, 1429 s (phenyls), 1456 w (δ_{OCH_3}), 1193 s ($SiOCH_3$ rocking), 1116 vs (SiC_6H_5), 1090 vs (ν(as)$_{Si-OC}$) cm^{-1}. MS (EI, 30 eV): *m*/*z* (assignment, relative intensity) 428 (M$^+$, 39), 413 ([M − CH_3]$^+$, 100), 383 ([M − $3CH_3$]$^+$, 22), 351 ([M − CH_3 − $2CH_3O$]$^+$, 16), 307 ([M − Si(C_6H_5)$_3$]$^+$, 11), 181 ([(C_6H_5)$_2$Si − H]$^+$, 17), 139 ([M − $2CH_3$ − Si(C_6H_5)$_3$]$^+$, 62), 105 ([C_6H_5Si]$^+$, 10), 91 ([Si(OCH_3)$_2$ + H]$^+$, 20), 59 ([$SiOCH_3$]$^+$, 7). Anal. Calcd for $C_{25}H_{24}O_3Si_2$: C, 70.05; H, 5.64; Si, 13.11. Found: C, 70.14; H, 5.78; Si, 14.35.

***(Z)*-$CH_3OCH{=}CHC{\equiv}CSi(OCH(CH_3)_2)_3$ (16).** A solution of chlorotriisopropoxysilane (13.31 g, 55.25 mmol) in THF (50 mL) was added dropwise to a suspension of **4** (55.01 mmol) cooled to −78 °C. The reaction mixture was stirred at −78 °C for 2 h and then at room temperature overnight. The volatiles were removed in vacuo. A 100 mL portion of dry CCl_4 was added to the residue to precipitate LiCl. The suspension was filtered through a fine glass frit. A 50 mL amount of dry hexanes was added to the filtrate, and the resulting suspension was filtered. The solvents were removed in vacuo. Two distillations of the residual liquid under reduced pressure (93−97 °C, 6×10^{-2} Torr) were necessary to obtain a clean sample of enyne **16**. Yield: 3.31 g, 11.56 mmol (21%).

^{1}H NMR ($CDCl_3$, 250.1 MHz): δ (ppm) 1.24 (d, $^3J_{HH}$ = 6.1 Hz, 18H, CH(CH_3)$_2$), 3.78 (s, 3H, CH_3O), 4.33 (septet, $^3J_{HH}$ = 6.1 Hz, 3H, C*H*(CH_3)$_2$), 4.55 (d, $^3J_{HH}$ = 6.5 Hz, 1H, C*H*C≡C), 6.36 (d, $^3J_{HH}$ = 6.6 Hz, 1H, CH_3OCH=). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm) 25.6 ((CH_3)$_2$CHO), 60.9 (*C*H_3OCH=), 66.1 ((CH_3)$_2$*C*HO), 85.0 (*C*HC≡C), 90.4 (C≡*C*Si), 99.1 (*C*≡CSi), 159.3 (CH_3OCH=). ^{29}Si NMR ($CDCl_3$, 49.7 MHz): δ (ppm) −75.7. IR (neat): 2973 s, 2940 s, 2898 s ($\nu_{C(sp^3)H}$), 2154 s ($\nu_{C\equiv C}$), 1631 s ($\nu_{C=C}$), 1466 m (isopropyl groups), 1455 m (δ_{OCH_3}), 1382 s, 1370 s (isopropyl groups), 1274 s ($\nu_{C(sp^2)O}$), 1174 s, 1133 s (isopropyl groups), 1117 vs (ν_{CO}), 1044 vs (ν(as)$_{Si-OC}$) cm^{-1}. MS (EI, 30 eV): *m*/*z* (assignment, relative intensity) 271 ([M − CH_3]$^+$, 15), 243 ([M − CH(CH_3)$_2$]$^+$, 3), 228 ([M − $(CH_3)_2CO$]$^+$, 14), 213 ([M − CH_3 − $(CH_3)_2CO$]$^+$, 25), 171 ([M − CH_3 − CH_2CHCH_3 − $(CH_3)_2CO$]$^+$, 13), 143 ([M − CH(CH_3)$_2$ − CH_2CHCH_3 − $(CH_3)_2CO$]$^+$, 36). Anal. Calcd for $C_{14}H_{26}O_4Si$: C, 58.70; H, 9.15; Si, 9.81. Found: C, 58.41; H, 9.03; Si, 10.00.

Preparation of *(Z)*-$CH_3OCH{=}CHC{\equiv}CSi(OCH_2CH_2)_3N$ (20) via Boron−Silicon Exchange. A 100 mL round-bottomed flask was charged with 1.57 g (1.6 mL, 7.76 mmol) of **2**, 20 mg (0.15 mmol) of $AlCl_3$, 1.22 g (7.77 mmol) of **21**, and 40 mL of dry solvent (chloroform, toluene, *o*-xylene). The mixture was heated under an inert atmosphere for a given amount of time (20 or 63 h). The volatiles were removed in vacuo, and the residue was analyzed by infrared and ^{1}H, ^{29}Si, and ^{11}B NMR spectroscopy.

Preparation of 20 by Transesterification. A 7 mL (57.4 mmol) portion of triethanolamine and 23 mL (165.5 mmol) of triethylamine were added to a solution of **2** (11.27 g, 55.7 mmol) in toluene (90 mL). The mixture was stirred at room temperature for 48 h, during which time a precipitate formed. The precipitate was collected by filtration and recrystallized from a mixture of chloroform (100 mL) and pentane (80 mL). An 11.18 g (43.8 mmol) amount of a white powder was obtained (79% yield). Mp: 220.0−223.5 °C.

^{1}H NMR ($CDCl_3$, 200.1 MHz): δ (ppm) 2.91 (t, $^3J_{HH}$ = 5.9 Hz, 6H, CH_2N), 3.74 (s, 3H, CH_3OCH=), 3.89 (t, $^3J_{HH}$ = 5.9 Hz, 6H, OCH_2), 4.57 (d, $^3J_{HH}$ = 6.5 Hz, 1H, C*H*C≡C), 6.18 (d, $^3J_{HH}$ = 6.5 Hz, 1H, CH_3OCH=). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ (ppm) 51.0 (*C*H_2N), 57.5 (O*C*H_2), 60.2 (*C*H_3OCH=), 86.5 (*C*HC≡C), 91.7 (*C*≡CSi), 98.9 (C≡*C*Si), 156.0 (CH_3OCH=). ^{29}Si NMR ($CDCl_3$, 39.8 MHz): δ (ppm) −94.2. IR (KBr): 3058 w ($\nu_{C(sp^2)H}$), 2972 m, 2936 m, 2886 m, 2828 w ($\nu_{C(sp^3)H}$), 2150 m ($\nu_{C\equiv C}$), 1634 s ($\nu_{C=C}$), 1486 m (δ_{CH_2}), 1457 m (δ_{OCH_3}), 1275 s ($\nu_{C(sp^2)O}$ and CH_2 wag), 1116 vs (ν_{CO}), 1089 vs (ν(as)$_{Si-OC}$) cm^{-1}. MS (EI, 30 eV): *m*/*z* (assignment, relative intensity) 255 (M$^+$, 63), 240 ([M − CH_3]$^+$, 23), 224 ([M − OCH_3]$^+$, 61), 174 ([Si(OCH_2CH_2)$_3$N]$^+$, 26), 162 ([($CH_3OCH{=}CHC{\equiv}C)_2$]$^+$, 100). Anal. Calcd for $C_{11}H_{17}NO_4Si$: C, 51.74; H, 6.71; N, 5.48. Found: C, 51.94; H, 6.89; N, 5.34.

$(CH_3)_3SiC{\equiv}CC{\equiv}CSi(OCH_2CH_2)_3N$ (26a). A 2 M solution of LDA (6 mL, 12 mmol) was added dropwise, over a 15-min period, to a solution of **20** (1.45 g, 5.7 mmol) in pyridine (180 mL) cooled to −40 °C. Stirring was continued at this temperature for 2.5 h and then at room temperature for 1.5 h. The mixture was cooled again to −40 °C, and Me_3SiCl (1.5 mL, 11.9 mmol) was added with a syringe over a 15-min period. Stirring was continued at this temperature for 15 min and then at room temperature overnight. A brown solid was obtained upon removal of the solvent in vacuo at room temperature. Chloroform (150 mL) was added to the residue, and the resulting suspension was filtered. The filtrate was washed with three 200 mL portions of water, and the organic layer was dried over $MgSO_4$. After removal of the drying agent by filtration, the solution was concentrated to one-fourth of its initial volume, and pentane (150 mL) was added. The precipitate that formed was collected, washed with 10 mL of pentane, and dried under vacuum. A 1.03 g (3.5 mmol) amount of a pale rosy powder was obtained (61% yield). Mp: 300 °C dec.

^{1}H NMR ($CDCl_3$, 200.1 MHz): δ (ppm) 0.12 (s, 9H, Si(CH_3)$_3$), 2.92 (t, $^3J_{HH}$ = 5.9 Hz, 6H, CH_2N), 3.87 (t, $^3J_{HH}$ = 5.9 Hz, 6H, OCH_2). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ (ppm) −0.3 (Si(*C*H_3)$_3$), 51.2 (*C*H_2N), 57.4 (O*C*H_2), 80.3, 82.8, 88.2, 89.7 (Si*C*≡*CC*≡*C*Si). ^{29}Si NMR ($CDCl_3$, 39.8 MHz): δ (ppm) −16.7 (Si(CH_3)$_3$), −96.4 (Si(OCH_2CH_2)$_3$N). IR (KBr): 2932 s, 2884 s ($\nu_{C(sp^3)H}$), 2065 s ($\nu_{C\equiv C}$), 1488 w, 1451 m (δ_{CH_2}), 1272 s (CH_2 wag), 1253 s ($\delta_s SiCH_3$), 1117 vs (ν_{CO}), 1087 vs (ν(as)$_{Si-OC}$) cm^{-1}. MS (EI, 30 eV): *m*/*z* (assignment, relative intensity) 295 (M$^+$, 90), 280 ([M − CH_3]$^+$, 100), 265 ([M − $2CH_3$]$^+$, 30), 222 ([M − Si(CH_3)$_3$]$^+$, 25), 174 ([Si(OCH_2CH_2)$_3$N]$^+$, 16), 73 ([Si(CH_3)$_3$]$^+$, 29). Anal. Calcd for $C_{13}H_{21}NO_3Si_2$: C, 52.85; H, 7.16; N, 4.74. Found: C, 52.61; H, 7.22; N, 4.87.

$(C_6H_5)_3SiC{\equiv}CC{\equiv}CSi(OCH_2CH_2)_3N$ (26b). A procedure similar to that leading to **26a** was followed using 2.28 g (8.9 mmol) of **20** dissolved in 150 mL of pyridine, 9 mL (18 mmol) of a 2 M solution of LDA, and 5.27 g (17.9 mmol) of Ph_3SiCl dissolved in 25 mL of pyridine. A 2.26 g portion of an off-white solid containing small amounts of Ph_3SiOH and Ph_3SiOMe was obtained after workup of the reaction mixture. The solid was stirred in 40 mL of THF for 1 h, and then the suspension was filtered. The material (**26b**) that was collected on the glass frit was dried in vacuo at 110 °C for 1.5 h. Yield: 1.94 g (45%). Mp: 350 °C dec.

^{1}H NMR ($CDCl_3$, 200.1 MHz): δ (ppm) 2.89 (t, $^3J_{HH}$ = 5.9 Hz, 6H, CH_2N), 3.85 (t, $^3J_{HH}$ = 5.9 Hz, 6H, OCH_2), 7.30−7.67 (m, 15H, C_6H_5). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ (ppm) 51.1

(CH_2N), 57.5 (OCH_2), 77.2, 80.0, 90.4, 94.1 (Si*C*≡*CC*≡*C*Si), 128.0 ($C_{2,6}$), 130.0 (C_4), 133.1 (C_1), 135.6 ($C_{3,5}$). ^{29}Si NMR ($CDCl_3$, 39.8 MHz): δ (ppm) −28.8 ($Si(C_6H_5)_3$), −96.9 ($Si(OCH_2CH_2)_3N$). IR (KBr): 3067 w, 3049 w, 3020 w ($\nu_{CH\ arom}$), 2973 m, 2930 m, 2879 m ($\nu_{C(sp^3)H}$), 2065 s ($\nu_{C\equiv C}$), 1588 m, 1483 s, 1429 s (phenyls), 1455 s (δ_{CH_2}), 1269 s (CH_2 wag), 1115 vs (Si-C_6H_5), 1088 vs (ν(as)$_{Si-OC}$) cm^{-1}. MS (EI, 30 eV): *m*/*z* (assignment, relative intensity) 481 (M^+, 42), 404 ($[M - C_6H_5]^+$, 7), 307 ($[M - Si(OCH_2CH_2)_3N]^+$, 16), 259 ($[Si(C_6H_5)_3]^+$, 24), 174 ($[Si(OCH_2CH_2)_3N]^+$, 100), 105 ($[C_6H_5Si]^+$, 21). Anal. Calcd for $C_{28}H_{27}NO_3Si_2$: C, 69.82; H, 5.65; N, 2.91. Found: C, 69.98; H, 5.72; N, 2.66.

(*E*)-CH_3OCH═$C(Si(CH_3)_3)C$≡$CSi(OCH_2CH_2)_3N$ (27). The reaction was carried out as described in Table 3, experiment 1 (vide supra). A 1.42 g amount of unreacted **20** was recovered by filtration of the final suspension, and 0.6 g of a solid was isolated by concentration of the filtrate to dryness (expected yield 2.51 g). After several washings of the 0.6 g of solid with diethyl ether, chloroform, and toluene, and recrystallization from a toluene−chloroform−pentane mixture, 0.12 g of material was isolated that contained 90 mol % of **27** and 10 mol % of **20**. The following data were obtained on this mixture.

^{1}H NMR ($CDCl_3$, 200.1 MHz): δ (ppm) 0.12 (s, 9H, Si(C*H*$_3$)$_3$), 2.86 (t, $^3J_{HH}$ = 5.9 Hz, 6H, C*H*$_2$N), 3.70 (s, 3H, C*H*$_3$OCH═), 3.83 (t, $^3J_{HH}$ = 5.9 Hz, 6H, OC*H*$_2$), 6.06 (s, 1H, CH_3OCH═). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ (ppm) −0.9 (Si(*C*H$_3$)$_3$), 51.4 (*C*H$_2$N), 57.9 (O*C*H$_2$), 60.4 (*C*H$_3$OCH═), 93.9, 96.2, 100.9 (═*C*(Si(CH$_3$)$_3$)*C*≡*C*Si), 159.9 (CH$_3$O*C*H═). ^{29}Si NMR ($CDCl_3$, 39.8 MHz): δ (ppm) −3.5 ($^3J_{SiH}$ = 3.7 Hz, CH═CSi(CH$_3$)$_3$), −92.8 (C≡CSi(OCH$_2$CH$_2$)$_3$N). IR (CH_2Cl_2): 3051 w ($\nu_{C(sp^2)H}$), 2936 m, 2883 m, 2838 w ($\nu_{C(sp^3)H}$), 2138 m ($\nu_{C\equiv C}$), 1599 s ($\nu_{C=C}$), 1484 w (δ_{CH_2}), 1457 w (δ_{OCH_3}), 1125 vs (ν_{CO}), 1102 vs (ν(as)$_{Si-OC}$) cm^{-1}. MS (FAB+, NBA): *m*/*z* (assignment, relative intensity) 677 ($[2\ M + Na]^+$, 14), 350 ($[M + Na]^+$, 63), 327 (M^+, 23), 296 ($[M - OCH_3]^+$, 3), 174 ($[Si(OCH_2CH_2)_3N]^+$, 100), 73 ($[Si(CH_3)_3]^+$, 34).

Monodeprotonation of 30 and Quenching of the Intermediate Anion with Me_3SiCl. A 2 M solution of LDA (10 mL, 20 mmol) was added dropwise, over a 12-min period, to a solution of **30** (3.088 g, 20 mmol) in pyridine (150 mL) cooled to −40 °C. The mixture containing CH_3OCH═C(Li)C≡$CSi(CH_3)_3$ became dark. The temperature was maintained between −40 and −45 °C for 2.5 h with stirring, and Me_3SiCl (2.55 mL, 20 mmol) was added. The mixture was stirred at −40/−45 °C for another 1 h and then at room temperature overnight. A dark solid was obtained upon removal of the solvent in vacuo at room temperature. The solid was analyzed by infrared and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, and the results indicated the presence of **34**, **35**, and **10** in the molar ratio 0.48:0.07:0.45.

The same experiment was repeated using THF (150 mL) as a solvent. The temperature during the deprotonation step and subsequent reaction of the anion with Me_3SiCl was maintained below −73 °C. A small amount of an ocher suspension was obtained after removal of the solvent in vacuo. The suspension was analyzed by infrared and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, and the results indicated the presence of **34**, **35**, and **10** in the molar ratio 0.24:0.70:0.06.

Characterization data for **34** are as follows. ^{1}H NMR ($CDCl_3$, 200.1 MHz): δ (ppm) 0.140 (s, 9H, Si(C*H*$_3$)$_3$), 0.183 (s, 9H, Si(C*H*$_3$)$_3$), 3.79 (s, 3H, C*H*$_3$OCH═), 6.14 (s, 1H, CH$_3$OC*H*═). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ (ppm) 159.5 (CH$_3$O*C*H═). ^{29}Si NMR ($CDCl_3$, 39.8 MHz): δ (ppm) −3.0 ($^3J_{SiH}$ = 3.8 Hz, CH═CSi(CH$_3$)$_3$), −19.0 (C≡CSi(CH$_3$)$_3$). IR (CCl_4): 2130 s ($\nu_{C\equiv C}$), 1599 vs ($\nu_{C=C}$) cm^{-1}.

Characterization data for **35** are as follows. ^{1}H NMR ($CDCl_3$, 200.1 MHz): δ (ppm) 0.156 (s, 9H, Si(C*H*$_3$)$_3$), 0.164 (s, 9H, Si(C*H*$_3$)$_3$), 3.66 (s, 3H, C*H*$_3$OCH═), 7.04 (s, 1H, CH$_3$OC*H*═). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ (ppm) 165.6 (CH$_3$O*C*H═). ^{29}Si NMR ($CDCl_3$, 39.8 MHz): δ (ppm) −5.6 ($^3J_{SiH}$ = 8.0 Hz, CH═CSi(CH$_3$)$_3$), −19.7 (C≡CSi(CH$_3$)$_3$). IR (CCl_4): 2121 s ($\nu_{C\equiv C}$), 1592 vs ($\nu_{C=C}$) cm^{-1}.

Supporting Information Available: Text giving a description of the test reactions supporting the attack of CH_3OLi on **2** and **3** (Results and Discussion and Experimental Section), experimental details concerning the deprotonation−elimination−metalation chemistry of **2** and **16** with LDA, and experimental details concerning the attempted syntheses of **19**. Ordering information is given on any current masthead page.

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