Allylic Phosphates and Allylic Phosphinates as Electrophiles in Efficient Silylcupration Reactions of Acetylenes

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Received October 23, 2001

Atom-efficient stoichiometric silylcupration reactions of acetylenes followed by electrophilic trapping of the intermediate vinylcopper species with allylic phosphates have been developed. The reaction sequence was also carried out with the use of a catalytic amount of CuCN employing of both allylic phosphates and allylic phosphinates as electrophiles. The methods developed provide an easy access to silylated 1,4-diene systems.

Introduction

Allylic electrophiles are attractive reagents in organic synthesis, because an allylic fragment in the molecule provides possibilities for further functionalization after its introduction. The copper-mediated coupling reaction of allylic electrophiles with organometallic reagents has been studied by us[1,2] and others,[3] and recently experimental evidence for a copper(III) intermediate was provided.[2] We have previously reported on the coupling reaction between allylic electrophiles and a vinylcopper species derived from silylcupration of allenes, as a method for the synthesis of allylsilyl-functionalized 1,4-dienes.[4] We have now investigated the silylcupration reaction of acetylenes and used it in combination with an allylic substitution reaction, which provides easy access to silyl-functionalized 1,4-dienes.

The silylcupration reaction of acetylenes has been studied to some extent by Fleming's group[5] and others.[6] The focus in the previous work was on the utilization of the disilylcuprate reagent $(PhMe_2Si)_2CuLi{\cdot}LiCN$ (**1**). Usually, 1 equiv of disilylcuprate **1** and 1 equiv of acetylene is used, which means that only one silyl group is transferred to the acetylene and the other group remains on copper in the silylcupration reaction. Upon electrophilic trapping of the resulting vinylcopper species, the electrophile can react with either the vinyl group or the remaining silyl group on copper or with both. To ensure complete cleavage of the vinyl-copper bond, an excess of electrophile (≥2 equiv) has to be used, which results in mixtures of products and hence separation problems and bad atom economy.

Here we wish to report on an efficient stoichiometric and catalytic silylcupration reaction of acetylenes followed by an electrophilic trapping reaction of the resulting vinylcopper species with allylic phosphates or allylic phosphinates.[7]

Results and Discussion

A. Stoichiometric Reaction. Preliminary experiments utilizing the silylcupration protocol of Fleming for the addition of **1** to 1-hexyne followed by reaction with an allylic phosphate revealed that the allylic substrate reacts faster with the unreacted silyl group on copper than with the vinylcopper moiety obtained from the silylcupration of the acetylene. The use of an excess of allylic phosphate led to a mixture of several products, which were difficult to separate.

1. Use of Silylcyanocuprate. To overcome the disadvantages of the available methods for silylcupration of acetylenes, we intended to use the monosilylcopper reagent $PhMe_2SiCuCNLi$ (**2**) (later referred to as method A). This would lead to virtually no byproducts after the electrophilic trapping of the vinylcopper species, since the only silyl group on copper in **2** is transferred to the

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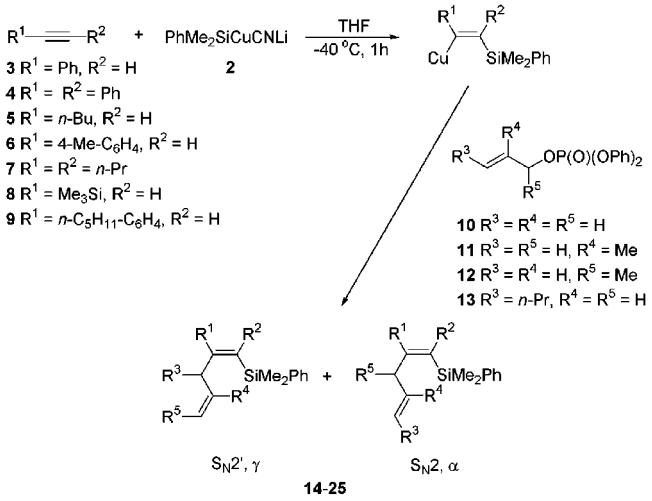
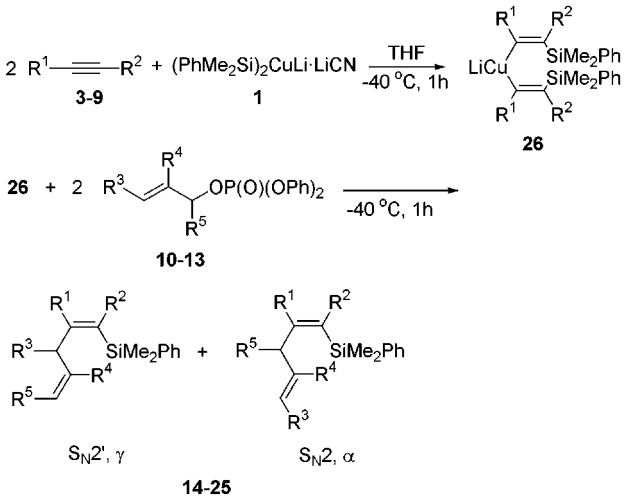
10.1021/jo016229u CCC: $22.00
Published on Web 03/01/2002

Scheme 1



Scheme 2



acetylene (Scheme 1). Reagent **2** has been successfully used in the silylcupration reaction of allenes by Pulido[8] and by us[4] and in the silylcupration reaction of styrenes,[9] but only in one case has **2** been used with acetylenes.[5a]

Silylcupration of different acetylenes (**3**−**9**) with **2** (THF, −40 °C, 1 h) followed by electrophilic trapping with allylic phosphates (**10**−**13**) afforded 1,4-dienes (**14**−**25**) in good yields (Table 1, method A). The silylcupration reaction proceeded with a high degree of regioselectivity to give product where the silyl group had added to the less substituted end of the acetylene.

2. Use of Disilylcuprate. Another approach that could be used to avoid formation of byproducts is to employ 1 equiv of disilylcuprate **1** and 2 equiv of the acetylene in the reaction (referred to as method B). This would lead to the formation of divinylcuprate **26**, which in the electrophilic trapping reaction with 2 equiv of allylic electrophile should give only the desired product (Scheme 2). In this case both silyl groups on copper in **1** (and also both vinyl groups in **26**) are utilized. This approach has previously been used for silylcupration of *N*,*N*-bis(trimethylsilyl)propargylamine by Reginato and Ricci to give, after trapping with different electrophiles, functionalized allylamines.[6c]

We applied this method to the silylcupration of a variety of different acetylenes with subsequent electrophilic trapping by allylic phosphates, which gave the desired 1,4-dienes in good yields (Table 1, method B). As can be seen from Table 1, in most of the cases studied, method B resulted in better yields than method A. This means that both vinyl groups on copper in **26** are efficiently transferred to the allylic electrophile. Thus, the amount of copper salt used in the silylcupration reaction is reduced to half, which makes method B a more attractive alternative for large-scale applications.

The regioselectivity of the allylic substitution step (S_N2, α vs S_N2', γ) was briefly examined (Table 1, entries 3−5). Mixtures of S_N2 and S_N2' products were obtained with preference for the S_N2' product (γ-substitution product). Method A was more regioselective (for γ-product) than method B for the cases studied. In method B, a divinylcuprate is the reagent in the beginning of the reaction, which explains the lower relative amount of γ-product.[10]

B. Catalytic Reaction. To further reduce the amount of copper salt employed in the silylcupration reaction of acetylenes, it was desirable to develop a reaction that is catalytic in copper. For a catalytic reaction, a change of cation in the silyl reagent $PhMe_2SiLi$ from lithium to, for example, magnesium, zinc, or aluminum was desirable.[11,12] Oshima and co-workers[11] have reported a catalytic silylmetalation of acetylenes and allenes using $PhMe_2SiMgMe$ (**27**) in the presence of a catalytic amount of a copper(I) salt (Scheme 3).

We have further studied this methodology with a number of different acetylenes and trapped the resulting vinylmetal species with different allylic substrates (Scheme 4).

The results of this catalytic tandem silylcupration−allylic substitution reaction leading to 1-silyl-1,4-dienes are presented in Table 2. Thus, $PhMe_2SiLi$ was transmetalated with MeMgI to give $PhMe_2SiMgMe$ (**27**), which was reacted with an acetylene in the presence of 5 mol % of CuCN, followed by trapping with the allylic electrophiles. Use of CuI instead of CuCN resulted in comparable yields, and since CuI is more difficult to purify and dry, we decided to use CuCN. As in the stoichiometric reaction (Table 1), allylic phosphates (**10**, **11**, **13**) were successfully employed as electrophiles also in the catalytic version of the silylcupration−allylic substitution reaction (Table 2, entries 1−6). The yields obtained were slightly lower than or comparable to the yields of the stoichiometric reactions (Table 2, entries 1−4, and Table 1, entries 1, 6, 8, 11). However, some allylic phosphates could not be employed as substrates, since they proved to be unstable and decomposed upon purification.[13] We previously demonstrated that allylic

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(10) It is known that dicarbocuprates favor α-substitution (see ref 1a).

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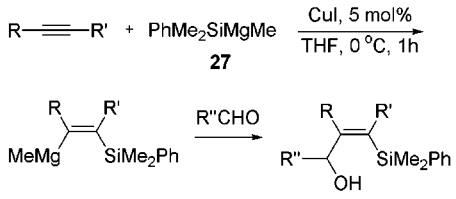
Table 1. Stoichiometric Tandem Silylcupration–Allylic Substitution Reaction

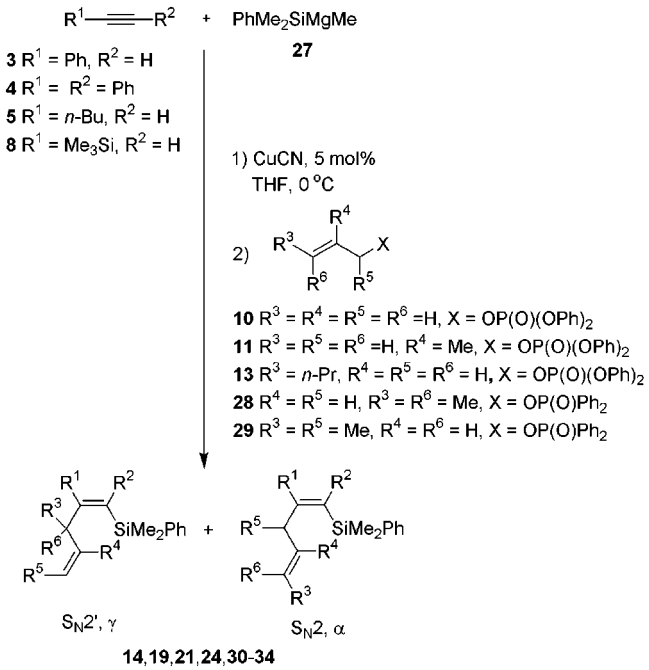
Entry	Acetylene	Electrophile	Product	Yield (%)[a]	
		X=OP(O)(OPh)$_2$		Method A	Method B
1	Ph—≡ **3**	X **10**	SiMe$_2$Ph, Ph **14**	90	85
2	**3**	X **11**	SiMe$_2$Ph, Ph **15**	69	84
3	**3**	X **12**	R, R', SiMe$_2$Ph, Ph **16a** (α) R = H, R' = Me **16b** (γ) R = Me, R' = H	67[b]	83[c]
4	**3**	*n*-Pr, X **13**	R, R', SiMe$_2$Ph, Ph **17a** (α) R = *n*-Pr, R'=H **17b** (γ) R = H, R' = *n*-Pr	68[d]	83[e]
5	Ph—≡—Ph **4**	**13**	R, R', SiMe$_2$Ph, Ph, Ph **18a** (α) R = *n*-Pr R' = H **18b** (γ) R = H, R' = *n*-Pr	83[f]	94[g]
6	*n*-Bu—≡ **5**	**10**	SiMe$_2$Ph, *n*-Bu **19**	68	80
7	**5**	**11**	SiMe$_2$Ph, *n*-Bu **20**	67	61
8	**4**	**10**	SiMe$_2$Ph, Ph, Ph **21**	77	79
9	Me **6**	**10**	SiMe$_2$Ph, Me **22**	62	81
10	*n*-Pr—≡—*n*-Pr **7**	**10**	SiMe$_2$Ph, *n*-Pr, *n*-Pr **23**	60	53
11	TMS—≡ **8**	**10**	SiMe$_2$Ph, TMS **24**	63	75
12	*n*-C$_5$H$_{11}$ **9**	**10**	SiMe$_2$Ph, *n*-C$_5$H$_{11}$ **25**	73	84

[a] Isolated yield after column chromatography. [b] **16a**:**16b** = 2:98, *E*/*Z* of **16b** = 82:18. The *E*-and *Z*- isomers could not be separated. [c] **16a**:**16b** = 3:97, *E*/*Z* of **16b** = 75:25. The *E*-and *Z*- isomers could not be separated. [d] **17a**:**17b** = 16:84, *E*-isomer only. [e] **17a**:**17b** = 36:64, *E*-isomer only. [f] **18a**:**18b** = 24:76, *E*-isomer only. [g] **18a**:**18b** = 42:58, *E*-isomer only.

Scheme 3



Scheme 4



acetates are not reactive enough as electrophiles in the trapping reaction of vinylcopper species.[4] Therefore, allylic phosphinates[14] were investigated as a more stable alternative to phosphates, hoping that they would retain the high reactivity of allylic phosphates. We managed to prepare allylic phosphinates **28** and **29** from alcohols that failed to give the corresponding phosphates. Indeed, allylic phosphinates **28** and **29** proved to be reactive enough to give the desired 1,4-diene products under catalytic conditions (Table 2, entries 7−10).

The phosphinates studied are, however, less reactive substrates than allylic phosphates. We were unable to react them with a vinylcopper species at low temperatures (−40 °C and below), but since the catalytic reaction is carried out at 0 °C, the reaction of the vinylcopper species with the corresponding allylic phosphinate proceeded smoothly within 1−2 h.

In the catalytic reaction between **4** and **13**, the allylic substitution step predominately gave the α-product **18a**, whereas in the stoichiometric reaction, in particular with method A, the γ-product was the major isomer (for comparison, see Table 1, entry 5 and Table 2, entry 6). This can be explained by the fact that in the stoichiometric reaction via method A the vinylcopper species present in the reaction mixture is the less reactive *monovinylcopper complex*, whereas in the catalytic reaction it is the more reactive *divinylcuprate*.[10] Selectivity for the γ-product was also observed in the stoichiometric reaction between **3** and **12** and between **3** and **13** (Table 1, entries 3 and 4). It is interesting to note that the reaction with the γ-disubstituted phosphinate **28** under catalytic conditions was completely α-selective. This can be explained by the steric hindrance of the γ-position of the allylic phosphinate. In some cases *E*- and *Z*-isomers were formed (Table 1, entry 3 and Table 2, entry 10).

Mechanistic Considerations. The mechanism of the silylcupration of acetylenes has to our knowledge not been discussed in the literature. We would like to propose a mechanism for the catalytic silylmetalation allylic substitution reaction presented in this paper. The silylcupration of acetylenes shows close analogies to the carbocupration reaction.[15] Both reactions proceed with syn-selectivity to yield an intermediate vinylcopper species that can be trapped with electrophiles. The carbocupration of acetylenes was previously thought to proceed via a direct 1,2-addition of R−Cu across the triple bond.[16] More recently it has been suggested that the mechanism involves an oxidative addition to yield a Cu(III) species followed by reductive elimination to yield the vinylmetal intermediate.[17] On the basis of our experimental results, the catalytic cycle in Scheme 5 can be proposed for the silylcupration step. Cyanosilylcuprate **35** is formed, which gives a π-complex with the triple bond of the acetylene.[18] Nucleophilic addition of copper to the acetylene produces a vinylic anion that is captured by the magnesium cation to give a copper(III) intermediate. The latter undergoes reductive elimination to give a silylcopper species and a vinylmagnesium intermediate. The vinylmagnesium intermediate then undergoes copper-catalyzed allylic substitution with the available allylic phosphate, involving divinylcuprate **36**.

The mechanism of the allylic substitution reaction is also thought to involve a Cu(III) intermediate.[1a,1e,2,19] The distribution of the possible S_N2 and S_N2'-substitution products at different reaction conditions can be explained if the reaction proceeds via regioisomeric σ-allyl Cu(III) species.[1,19] We also recently obtained experimental evidence that the reaction between allylic esters and diallyl cuprates proceeds via Cu(III).[2]

The second possible mechanism for the catalytic silylcupration−electrophilic trapping reaction is given in Scheme 6. Oxidative addition of allylic phosphate or phosphinate to the divinylcuprate **36** obtained in the silylcupration reaction of acetylene produces a copper(III) intermediate, which rapidly undergoes a selective reductive elimination to the allylic substitution product and the corresponding vinylcopper species. The latter vinylcopper intermediate is transformed back into the active divinyl cuprate **36** via silylcupration of the acetylene by **38**. This mechanism does not involve the formation of a vinylmagnesium intermediate. In a control experiment involving simultaneous addition of the acetylene **4** and the allylic phosphate **10** to **27** and a catalytic amount of **38**, a mixture of the desired product, unreacted

(14) McCallum, J. S.; Liebeskind, L. S. *Synthesis* **1993**, 819.

(15) Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841.

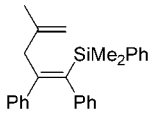
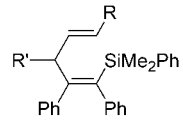
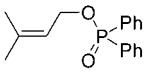
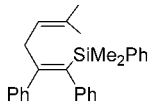
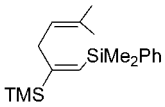
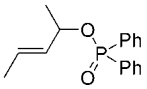
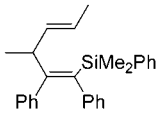
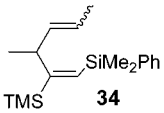
(16) Berlan, J.; Battioni, J. P.; Koosha, K. *Bull. Chim. Soc. Fr.* **1979**, II-183.

(17) For a thorough discussion, see: Nakamura, E.; Mori, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 3751.

(18) Although we cannot rule out that a disilylcuprate operates in the cycle in Scheme 5, we believe that after an initial cycle with the disilylcuprate, a silylcyanocuprate is formed, which reacts faster with the acetylene and becomes the active intermediate.

(19) (a) Goering, H. L.; Singleton, V. D., Jr. *J. Org. Chem.* **1983**, *48*, 1531. (b) Goering, H. L.; Kantner, S. S.; Seitz, E. P., Jr. *J. Org. Chem.* **1985**, *50*, 5495. (c) Goering, H. L.; Kantner, S. S. *J. Org. Chem.* **1984**, *49*, 422.

Table 2. Catalytic Tandem Silylcupration−Allylic Substitution Reaction

entry	acetylene	electrophile	product	yield (%)[a]
1	**5**	**10**	**19**	62
2	**3**	**10**	**14**	61
3	**8**	**10**	**24**	61
4	**4**	**10**	**21**	74
5	**4**	**11**	 **30**	73
6	**4**	**13**	 **18a** (α) R = *n*-Pr, R' = H **18b** (γ) R = H, R' = *n*-Pr	67[b]
7	**4**	 **28**	 **31**	68
8	**8**	**28**	 **32**	51
9	**4**	 **29**	 **33**	61
10	**8**	**29**	 **34**	63[c]

[a] Isolated yields after column chromatography. [b] **18a**:**18b** = 85:15, *E*-isomer only. [c] *E*/*Z* = 3:1. The *E*- and *Z*- isomers could not be separated.

acetylene, and the addition product between a silyl copper species **37** and the allylic phosphate is obtained. This result indicates that the reaction between an allylic phosphate and **37** is equally fast or faster than the reaction between **38** and the acetylene. This speaks against the mechanism depicted in Scheme 6, and the mechanism in Scheme 5 seems to be favored. The relative rates of the two competing reactions, however, can be highly substrate dependent, and therefore, a clear distinction between the two mechanisms presented cannot be made.

Conclusion

In conclusion, an efficient stoichiometric and catalytic silylcupration reaction of a wide variety of acetylenes followed by electrophilic trapping with allylic phosphates and phosphinates has been developed. This method provides an easy access to substituted 1,4-diene systems containing the silyl group, which are useful intermediates in organic synthesis.

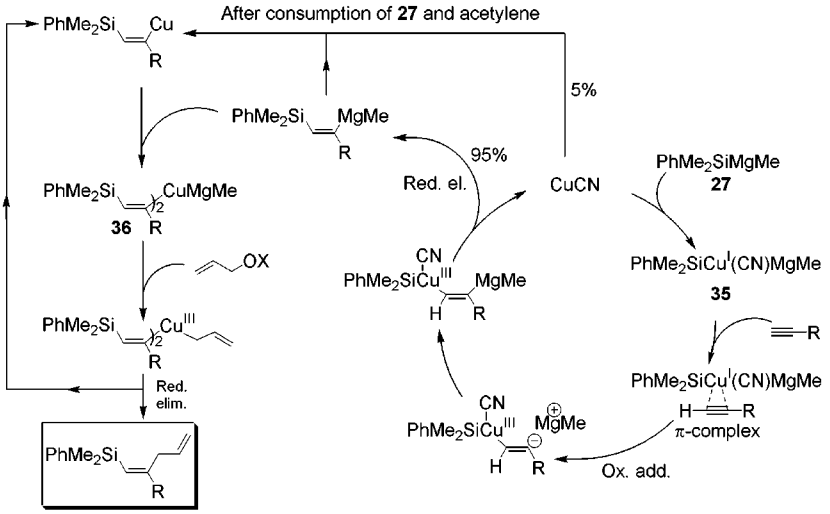
Experimental Section.

^{1}H NMR (400 or 300 MHz) and ^{13}C NMR (100 or 75 MHz) spectra were recorded on Varian Mercury spectrometers using the residual solvent peak in $CDCl_3$ (7.26 ppm for ^{1}H and 77.17 ppm for ^{13}C) as internal standard. Chemical shifts are reported in ppm. Matrex 60 Å (35−70 μm) silica gel from Amicon Europe was used for flash chromatography. TLC analysis was performed on Merck 60 F_{254} precoated plates.

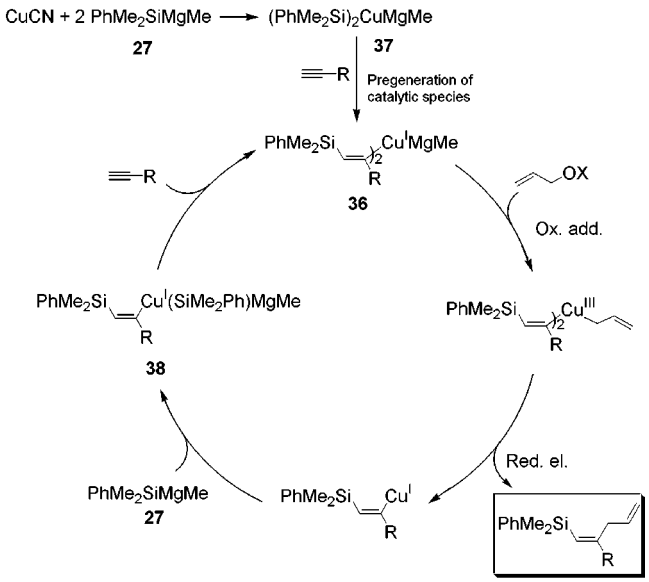
Unless otherwise noted, all material were obtained from commercial suppliers and used without further purification. Allylic phosphates,[20] phosphinates,[14] and $PhMe_2SiLi$[21] were prepared according to published procedures. Elemental analy-

(20) (a) Yamamoto, H.; Nomura, N.; Yanagisawa, A. *Tetrahedron* **1994**, *50*, 6017. (b) Knochel, P.; Jubert, C.; Tucker, E. C.; Nowotny, S. *J. Org. Chem.* **1995**, *60*, 2762.

Scheme 5. Catalytic Cycle for the Formation of a Vinylmagnesium Intermediate Leading to Silylcupration



Scheme 6. Catalytic Cycle That Does Not Involve the Formation of the Vinylmagnesium Intermediate



sis was performed by Analytische Laboratorien, Lindlar, Germany. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were freshly distilled from sodium benzophenone ketyl under argon atmosphere prior to use. All reactions were performed under an argon atmosphere using flame-dried glassware.

General Procedure for Stoichiometric Silylcupration−Electrophilic Trapping of Acetylenes. Method A. $PhMe_2SiLi$ (0.7 mmol, ~1 M solution in THF) was added to a stirred suspension of CuCN (0.7 mmol, 1 equiv) in dry THF (0.7 mL) at 0 °C and stirred at this temperature for 30 min. The mixture was cooled to −40 °C, the alkyne (0.84 mmol, 1.2 equiv) in THF (0.5 mL) was added dropwise over 2 min, and the reaction mixture was stirred for 1 h at this temperature. Then the allylic phosphate (0.91 mmol, 1.3 equiv) in THF (0.6 mL) was added over 15 min with a syringe pump. After the reaction mixture had been stirred for 1 h at −40 °C and 10 min at 0 °C, saturated aqueous NH_4Cl (4 mL) was added and the aqueous phase was extracted with pentane (5 × 3 mL). Column chromatography on silica with pentane as eluent afforded the products indicated in Table 1 as colorless oils.

(21) Fleming, I. In *Organocopper reagents. A practical approach*; Taylor, R. J. K., Ed.; Oxford University press: New York, 1994; Vol. 12, p 257.

General Procedure for Stoichiometric Silylcupration−Electrophilic Trapping of Acetylenes. Method B. $PhMe_2SiLi$ (0.7 mmol, ~1 M solution in THF) was added to a stirred suspension of CuCN (0.35 mmol, 0.5 equiv) in dry THF (0.7 mL) at 0 °C and stirred at this temperature for 30 min. The mixture was cooled to −40 °C, the alkyne (0.84 mmol, 1.2 equiv) in THF (0.5 mL) was added dropwise over 2 min, and the reaction mixture was stirred for 1 h at this temperature. Then the allylic phosphate (0.91 mmol, 1.3 equiv) in THF (0.6 mL) was added over 15 min. with a syringe pump. After the reaction mixture had been stirred for 1 h at −40 °C and 10 min at 0 °C, the workup was done as described for method A.

General Procedure for Catalytic Silylcupration−Electrophilic Trapping of Acetylenes. MeMgI (0.7 mmol, ~1 M solution in Et_2O) was added to a stirred solution of $PhMe_2SiLi$ (0.7 mmol, ~1 M solution in THF) at 0 °C. After the reaction had been stirred for 10 min at this temperature, it was transferred via a cannula to a stirred suspension of CuCN (0.035 mmol, 5 mol %) in dry THF (0.7 mL) at 0 °C and stirred at this temperature for 15 min. Then alkyne (0.84 mmol, 1.2 equiv) in THF (0.5 mL) was added dropwise over 2 min, and the reaction mixture was stirred for 20 min at this temperature. The allylic phosphate (0.91 mmol, 1.3 equiv) in THF (0.6 mL) was subsequently added over 15 min. After the reaction mixture had been stirred for 1 h at 0 °C, saturated aqueous NH_4Cl (4 mL) was added and the aqueous phase was extracted with pentane (5 × 3 mL). Column chromatography on silica with pentane as eluent afforded the products indicated in Table 2 as colorless oils.

Analytical data for compounds **14**−**25** and **30**−**34**:

Dimethyl(phenyl)[(1*E*)-2-phenyl-1,4-pentadienyl]silane (14). ^{1}H NMR (300 MHz): δ 7.47 (m, 10H), 6.14 (s, 1H), 5.73 (m, 1H), 4.98 (m, 1H), 4.94 (m, 1H), 3.37 (dt, J = 6.0, 1.7 Hz, 2H), 0.51 (s, 6H).^{13}C NMR (75.4 MHz): δ 155.8, 143.2, 139.5, 136.2, 133.9, 129.0, 128.2, 127.9, 127.6, 127.1, 126.4, 116.3, 39.2, −0.5. MS (EI) *m*/*z* (rel): 278 (29, M^+), 263 (23), 250 (48), 237 (20), 205 (27), 197 (31), 187 (30), 185 (66), 183 (22), 177 (29), 174 (40), 159 (35), 149 (21), 148 (38), 136 (43), 135 (100).

Dimethyl[(1*E*)-4-methyl-2-phenyl-1,4-pentadienyl]phenylsilane (15). ^{1}H NMR (400 MHz): δ 7.50 (m, 10H), 6.24 (s, 1H), 4.79 (m, 1H), 4.72 (m, 1H), 3.30 (s, 2H), 1.65 (s, 3H), 0.52 (s, 6H).^{13}C NMR (100 MHz): δ 155.5, 143.6, 143.5, 139.6, 134.0, 129.1, 128.4, 128.2, 128.0, 127.6, 126.4, 112.5, 42.8, 23.0, −0.8. MS (EI) *m*/*z* (rel): 292 (2.7, M^+), 263 (23), 250 (49), 235 (13), 214 (14), 199 (19), 188 (22), 156 (21), 148 (21), 138 (17), 136 (44), 135 (100).

Dimethyl[(1*E*)-3-methyl-2-phenyl-1,4-pentadienyl]phenylsilane (16a). ^{1}H NMR (400 MHz): δ 7.37 (m, 5H), 7.27 (m, 5H), 5.85 (ddd, J = 17.2, 10.4, 5.5 Hz, 1H), 5.70 (s, 1H), 4.98 (dt, J = 10.4, 1.6 Hz, 1H), 4.90 (dt, J = 17.2, 1.6 Hz, 1H),

3.48 (m, 1H), 1.02 (d, J = 6.8 Hz, 3H), 0.46 (s, 3H), 0.45 (s, 3H).^{13}C NMR (100 MHz): δ 163.2, 143.7, 142.1, 139.8, 134.0, 129.1, 128.1, 128.0, 127.9, 127.7, 127.0, 114.0, 44.1, 18.2, −0.4, −0.6.

Dimethyl(phenyl)[(1*E*,4*E*)-2-phenyl-1,4-hexadienyl]silane ((*E*)-16b). ^{1}H NMR (400 MHz): δ 7.63 (m, 2H), 7.49 (m, 2H), 7.39 (m, 3H), 7.31 (m, 3H), 6.07 (s, 1H), 5.32 (m, 2H), 3.28 (m, 2H), 1.55 (m, 3H), 0.49 (s, 6H).^{13}C NMR (100 MHz): δ 156.7, 143.4, 139.8, 134.04, 129.0, 128.6, 128.2, 127.9, 127.56, 126.7, 126.5, 126.4, 38.1, 18.1, −0.6.

Dimethyl(phenyl)[(1*E*,4*Z*)-2-phenyl-1,4-hexadienyl]silane ((*Z*)-16b). ^{1}H NMR (400 MHz): δ 7.63 (m, 2H), 7.49 (m, 2H), 7.39 (m, 3H), 7.31 (m, 3H), 6.06 (s, 1H), 5.32 (m, 2H), 3.34 (m, 2H), 1.57 (m, 3H), 0.50 (s, 6H).^{13}C NMR (100 MHz): δ 157.4, 143.4, 139.7, 134.0, 129.1, 128.8, 128.0, 127.6, 126.5, 126.4, 126.3, 124.8, 33.3, 13.2, −0.6. Anal. Calcd for $C_{20}H_{24}Si$ (mixture of **16a** and (*E*)- and (*Z*)-**16b**): C, 82.13; H, 8.27. Found: C, 81.94; H, 8.42.

Dimethyl(phenyl)[(1*E*,4*E*)-2-phenyl-1,4-octadienyl]silane (17a). ^{1}H NMR (400 MHz): δ 7.42 (m, 10H), 6.04 (s, 1H), 5.27 (m, 2H), 3.26 (dt, J = 4.5, 1.3 Hz, 2H), 1.84 (m, 2H), 1.25 (sextet, J = 7.0 Hz, 2H), 0.77 (t, J = 7.3 Hz, 3H), 0.46 (s, 6H).^{13}C NMR (100 MHz): δ 156.8, 143.5, 139.8, 134.0, 132.3, 129.0, 128.2, 128.0, 127.6, 127.5, 126.6, 126.4, 38.2, 34.8, 22.6, 13.6, −0.6.

Dimethyl(phenyl)[(1*E*)-2-phenyl-3-propyl-1,4-pentadienyl]silane (17b). ^{1}H NMR (400 MHz): δ 7.63 (m, 2H), 7.38 (m, 3H), 7.27 (m, 5H), 5.76 (m, 1H), 5.72 (s, 1H), 5.01 (dt, J = 10.5, 1.5 Hz, 1H), 4.90 (dt, J = 17.3, 1.5 Hz, 1H), 3.28 (m, 1H), 1.37 (m, 2H), 1.07 (m, 2H), 0.73 (t, J = 7.3 Hz, 3H), 0.49 (s, 3H), 0.48 (s, 3H).^{13}C NMR (100 MHz): δ 162.5, 144.1, 141.1, 140.0, 134.1, 129.1, 128.8, 128.2, 127.9, 127.6, 126.9, 114.9, 50.3, 35.1, 20.7, 14.2, −0.3, −0.6. Anal. Calcd for $C_{22}H_{28}Si$ (mixture of **17a** and **17b**): C, 82.43; H, 8.80. Found: C, 82.28; H, 8.85.

[(1*E*,4*E*)-1,2-Diphenyl-1,4-octadienyl](dimethyl)phenylsilane (18a). ^{1}H NMR (400 MHz): δ 7.27 (m, 11H), 7.11 (m, 2H), 7.02 (m, 2H), 5.14 (dtt, J = 15.2, 6.6, 1.2 Hz, 1H), 5.05 (dtt, J = 15.2, 6.6, 1.0 Hz, 1H), 2.86 (d, J = 6.6 Hz, 2H), 1.84 (m, 2H), 1.26 (sextet, J = 7.3 Hz, 2H), 0.80 (t, J = 7.3 Hz, 3H), −0.10 (s, 6H).^{13}C NMR (100 MHz): δ 153.8, 144.1, 143.6, 140.2, 140.1, 134.0, 132.1, 129.3, 128.8, 128.4, 128.0, 127.6, 127.4, 126.9, 126.8, 125.4, 41.2, 34.7, 22.7, 13.7, −1.06.

[(1*E*)-1,2-Diphenyl-3-propyl-1,4-pentadienyl](dimethyl)phenylsilane (18b). ^{1}H NMR (400 MHz): δ 7.74 (m, 2H), 7.42 (m, 3H), 7.02 (m, 5H), 6.85 (m, 5H), 5.40 (ddd, J = 17.2, 10.5, 8.1 Hz, 1H), 4.87 (ddd, J = 10.5, 1.8, 0.7 Hz, 1H), 4.55 (ddd, J = 17.2, 1.8, 0.7 Hz, 1H), 3.32 (q, J = 8.1 Hz, 1H), 1.26 (m, 2H), 1.08 (m, 1H), 0.87 (m, 1H), 0.71 (t, J = 7.4 Hz, 3H), 0.313 (s, 3H), 0.308 (s, 3H).^{13}C NMR (100 MHz): δ 158.4, 144.4, 140.4, 140.3, 139.8, 139.5, 134.1, 130.1, 129.1, 129.0, 128.1, 127.3, 126.7, 125.7, 124.5, 115.1, 51.0, 35.5, 20.5, 14.2, −0.00, −0.05. Anal. Calcd for $C_{28}H_{32}Si$ (mixture of **18a** and **18b**): C, 84.79; H, 8.13. Found: C, 84.61; H, 7.99.

[(1*Z*)-2-Butyl-1,4-pentadienyl](dimethyl)phenylsilane (19). ^{1}H NMR (300 MHz): δ 7.59 (m, 2H), 7.39 (m, 3H), 5.69 (m, 1H), 5.49 (s, 1H), 5.02 (m, 1H), 4.98 (m, 1H), 2.86 (dt, J = 6.8; 1.4 Hz, 2H), 2.16 (t, J = 8.2 Hz, 2H), 1.42 (m, 6H), 0.96 (t, J = 7.2 Hz, 3H), 0.42 (s, 6H).^{13}C NMR (75 MHz): δ 159.2, 140.2, 136.5, 133.8, 128.8, 127.8, 121.9, 116.1, 40.9, 38.8, 30.5, 22.8, 14.3, −0.3. Anal. Calcd for $C_{17}H_{26}Si$: C, 79.00; H, 10.14. Found: C, 78.87; H, 10.26.

[(1*Z*)-2-Butyl-4-methyl-1,4-pentadienyl](dimethyl)phenylsilane (20). ^{1}H NMR (300 MHz): δ 7.59 (m, 2H), 7.38 (m, 3H), 5.55 (s, 1H), 4.79 (s, 1H), 4.71 (s, 1H), 2.81 (s, 2H), 2.09 (t, J = 8.0 Hz, 2H), 1.58 (s, 3H), 1.39 (m, 4H), 0.95 (t, J = 7.2 Hz, 3H), 0.40 (s, 6H).^{13}C NMR (75 MHz): δ 158.8, 143.8, 140.3, 133.8, 128.7, 127.8, 123.0, 112.0, 44.5, 38.7, 30.7, 30.0, 22.8, 22.5, 14.3, −0.4. Anal. Calcd for $C_{18}H_{28}Si$: C, 79.34; H, 10.36. Found: C, 79.40; H, 10.37.

[(1*E*)-1,2-Diphenyl-1,4-pentadienyl](dimethyl)phenylsilane (21). ^{1}H NMR (300 MHz): δ 7.75 (m, 2H), 7.45(m, 3H), 7.01 (m, 10H), 5.55 (m, 1H), 4.86 (dq, J = 6.6; 1.5 Hz, 1H), 4.77 (dq, J = 17; 1.5 Hz, 1H), 3.32 (dt, J = 6.6; 1.5 Hz, 2H), 0.37 (s, 6H).^{13}C NMR (75 MHz): δ 152.9, 144.3, 142.5, 139.8, 139.7, 135.3, 133.9, 129.2, 129.0, 128.0, 127.4, 127.2, 125.9, 124.7, 116.4, 42.9, −0.2. Anal. Calcd for $C_{25}H_{26}Si$: C, 84.69; H, 7.39. Found: C, 84.49; H, 7.23.

Dimethyl[(1*E*)-2-(4-methylphenyl)-1,4-pentadienyl]phenylsilane (22). ^{1}H NMR (300 MHz): δ 7.63 (m, 2H), 7.40 (m, 5H), 7.15 (d, J = 7.9 Hz, 2H), 6.10 (s, 1H), 5.73 (m, 1H), 4.97 (dq, J = 5.9; 1.8 Hz, 1H), 4.93 (t, J = 1.8 Hz, 1H), 3.34 (dt, J = 6.1; 1.7 Hz, 2H), 2.37 (s, 3H), 0.49 (s, 6H).^{13}C NMR (75 MHz): δ 155.5, 140.2, 139.6, 137.4, 136.3, 133.9, 129.0, 128.9, 127.9, 126.3, 126.0, 116.2, 39.2, 21.3, −0.5. Anal. Calcd for $C_{20}H_{24}Si$: C, 82.13; H, 8.27. Found: C, 82.02; H, 8.39.

[(1*Z*)-1,2-Dipropyl-1,4-pentadienyl](dimethyl)phenylsilane (23). ^{1}H NMR (400 MHz): δ 7.54 (m, 2H), 7.34(m, 3H), 5.54 (m, 1H), 4.91 (m, 2H), 2.77 (d, J = 6.6 Hz, 2H), 2.16 (m, 4H), 1.40 (m, 4H), 0.95 (t, J = 7.4, Hz, 3H), 0.93 (t, J = 7.4, Hz, 3H) 0.40 (s, 6H).^{13}C NMR (100 MHz): δ 150.8, 141.2, 137.3, 133.9, 132.9, 128.6, 127.8, 115.9, 41.4, 34.5, 33.4, 24.6, 22.2, 14.6, 14.5, 0.1. Anal. Calcd for $C_{19}H_{30}Si$: C, 79.64; H, 10.55. Found: C, 79.50; H, 10.42.

Dimethyl(phenyl)[(1*E*)-2-(1,1,1-trimethylsilyl)-1,4-pentadienyl]silane (24). ^{1}H NMR (400 MHz): δ 7.55 (m, 2H), 7.36 (m, 3H), 6.28 (s, 1H), 5.66 (m, 1H), 3.04 (d, J = 6.2 Hz, 2H), 0.40 (s, 6H), 0.10 (s, 9H).^{13}C NMR (100 MHz): δ 164.8, 140.6, 140.0, 137.6, 133.9, 128.9, 127.9, 115.8, 40.9, −0.4, −0.6. Anal. Calcd for $C_{16}H_{26}Si_2$: C, 70.00; H, 9.55. Found: C, 69.83; H, 9.56.

Dimethyl[(1*E*)-2-(4-pentylphenyl)-1,4-pentadienyl]phenylsilane (25). ^{1}H NMR (400 MHz): δ 7.61 (m, 2H), 7.39 (m, 5H), 7.14 (m, 2H), 6.10 (s, 1H), 5.72 (m, 1H), 4.95 (dq, J = 8.0; 1.8 Hz, 1H), 4.92 (t, J = 1.8 Hz, 1H), 3.32 (dt, J = 6.0; 1.8 Hz, 2H), 2.60 (t, J = 7.7 Hz, 2H), 1.63 (m, 2H), 1.35 (m, 4H), 0.91 (t, J = 7.0 Hz, 3H), 0.47 (s, 6H).^{13}C NMR (100 MHz): δ 155.7, 142.6, 140.4, 139.8, 136.5, 134.0, 129.0, 128.3, 128.0, 126.3, 126.1, 116.2, 39.1, 35.7, 31.7, 31.2, 22.7, 14.2, −0.6. Anal. Calcd for $C_{24}H_{32}Si$: C, 82.69; H, 9.25. Found: C, 82.58; H, 9.28.

Dimethyl[(1*E*)-4-methyl-1,2-diphenyl-1,4-pentadienyl]-phenylsilane (30). ^{1}H NMR (400 MHz): δ 7.16 (m, 15H), 4.58 (m, 1H), 4.45 (m, 1H), 2.96 (s, 2H), 1.50 (s, 3H), −0.10 (s, 6H).^{13}C NMR (100 MHz): δ 152.7, 144.3, 143.3, 142.8, 142.0, 140.1, 134.0, 129.2, 128.7, 128.5, 128.0, 127.6, 127.5, 127.0, 125.5, 112.7, 45.7, 22.9, −1.0. Anal. Calcd for $C_{26}H_{28}Si$: C, 84.72; H, 7.66. Found: C, 84.52; H, 7.77.

Dimethyl[(1*E*)-5-methyl-1,2-diphenyl-1,4-hexadienyl]-phenylsilane (31). ^{1}H NMR (400 MHz): δ 7.24 (m, 11H), 7.08 (m, 2H), 7.00 (m, 2H), 4.86 (t, J = 7.5 Hz, 1H), 2.84 (d, J = 7.5 Hz, 2H), 1.53 (s, 3H), 1.06 (s, 3H), −0.13 (s, 6H).^{13}C NMR (100 MHz): δ 154.2, 144.3, 143.8, 140.1, 139.7, 134.0, 132.3, 129.2, 128.8, 128.4, 128.0, 127.6, 127.4, 126.8, 125.4, 121.0, 36.9, 25.8, 17.5, −1.0. Anal. Calcd for $C_{27}H_{30}Si$: C, 84.76; H, 7.90. Found: C, 84.61; H, 7.72.

1-[(*E*)-1-(1,1-Dimethyl-1-phenylsilyl)methylidene]-4-methyl-3-pentenyl(trimethyl)silane (32). ^{1}H NMR (400 MHz): δ 7.55 (m, 2H), 7.36 (m, 3H), 6.20 (s, 2H), 4.87 (t, J = 6.7 Hz, 1H), 2.98 (d, J = 6.7 Hz, 2H), 1.65 (s, 3H), 1.57 (s, 3H), 0.41 (s, 6H), 0.08 (s, 9H).^{13}C NMR (100 MHz): δ 166.8, 140.2, 139.0, 133.9, 131.5, 128.8, 127.9, 124.1, 35.9, 25.8, 18.2, −0.3, −0.8. MS (EI) m/z (rel) 302 (0.15, M^+), 224 (40), 150 (16), 137 (17), 136 (62), 135 (100), 126 (17), 111 (13), 75 (10), 73 (24).

Dimethyl[(1*E*,4*E*)-3-methyl-1,2-diphenyl-1,4-hexadienyl]-phenylsilane (33). ^{1}H NMR (300 MHz): δ 7.25 (m, 11H), 7.03 (m, 4H), 5.19 (m, 2H), 3.28 (quintet, J = 6.6 Hz, 1H), 1.61 (d, J = 5.8 Hz, 3H), 0.84 (d, J = 6.8 Hz, 3H), −0.14 (s, 3H), −0.16 (s, 3H).^{13}C NMR (75 MHz): δ 158.0, 143.9, 140.2, 139.9, 139.3, 134.2, 134.0, 130.7, 129.0, 128.4, 128.1, 128.0, 127.4, 127.0, 126.7, 125.4, 123.9, 41.4, 19.0, 18.1, −1.0, −1.3. Anal. Calcd for $C_{27}H_{30}Si$: C, 84.76; H, 7.90. Found: C, 84.61; H, 7.87.

Dimethyl[(1*E*,4*E*)-3-methyl-2-(1,1,1-trimethylsilyl)-1,4-hexadienyl]phenylsilane ((*E*)-34). ^{1}H NMR (400 MHz): δ 7.55 (m, 2H), 7.35 (m, 3H), 6.14 (s, 1H), 5.42 (m, 1H), 5.19 (m, 1H), 3.29 (m, 1H), 1.61 (dt, J = 6.4, 1.5 Hz, 3H), 1.03 (d, J = 7.1 Hz, 3H), 0.40 (s, 6H), 0.12 (s, 9H). MS (EI) m/z (rel): 302 (0.07, M^+), 287 (16), 224 (17), 168 (14), 151 (37), 150 (94), 138 (34), 136 (77), 135 (100), 74 (29).

Dimethyl[(1*E*,4*Z*)-3-methyl-2-(1,1,1-trimethylsilyl)-1,4-hexadienyl]phenylsilane ((*Z*)-34). ^{1}H NMR (400 MHz): δ 7.55 (m, 2H), 7.35 (m, 3H), 6.13 (s, 1H), 5.51 (m, 1H), 5.33 (m, 1H), 3.58 (m, 1H), 1.35 (dd, J = 6.8, 1.8 Hz, 3H), 0.99 (d, J = 6.9 Hz, 3H), 0.44 (s, 3H), 0.43 (s, 3H). 0.16 (s, 9H).^{13}C NMR (mixture of ((*E*)-**34** and (*Z*)-**34**), 100 MHz): δ 171.8, 171.6, 140.3, 138.4, 138.2, 135.3, 134.7, 133.95, 133.91, 128.9, 128.8, 127.9, 127.8, 124.0, 123.9, 45.9, 41.6, 22.7, 20.2, 18.1, 13.0, 1.4, 1.3, −0.2, −0.3. MS (EI) *m*/*z* (rel): 302 (0.09, M^+), 223 (12), 151 (14), 150 (56), 137 (13), 136 (41), 135 (100), 7 (21).

Acknowledgment. Financial support from the Swedish Natural Science Research Council and The Swedish Foundation for Strategic Research is gratefully acknowledged.

Supporting Information Available: Copies of ^{13}C and ^{1}H NMR spectra of compounds **14**, **15**, **32**, and **34**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO016229U