# Regioselective 1,4-Silylcupration of 1,3-Dienes − Characterization and Electrophilic Trapping of the Intermediate (σ-Allyl)copper Complex

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**Keywords:** Copper / Dienes / Allylic compounds

Silylcupration reactions of 1,3-dienes with a cyanocuprate reagent $PhMe_2SiCuCNLi$ produce a (4-silyl-2-alken-1-yl)-copper complex, which was trapped by electrophiles. The use of allylic phosphates as electrophiles resulted in highly regioselective reactions with overall 1,4-addition of the silyl and allyl moieties across the diene. Water ($H_3O^+$) or acetyl chloride as the electrophile afforded a mixture of 1,2- and 1,4-addition products, whereas carbon dioxide gave a highly regioselective 1,2-addition. The intermediate (4-silyl-2-alken-1-yl)copper complexes were characterized by NMR spectroscopy. The mechanism of the silylcupration reaction of 1,3-dienes and subsequent electrophilic trapping is discussed.



## Introduction

The silylcupration reaction of acetylenes and allenes has been studied by Fleming and co-workers,[1,2] and by ourselves.[3,4] However, literature data on silyl-metallations of alkenes are scarce. Silylcupration of a double bond in oxabicyclic compounds has been reported.[5] Silylmanganation of acetylenes and 1,3-dienes,[6] silyltitanation[7] of 1,3-dienes, and catalytic silicon-silicon bond addition across double bonds,[8] triple bonds[9] and 1,3-dienes[10] involving silylpalladation have also been reported. Recently, we reported on a silylcupration reaction of styrene[11] and a tandem silylcupration-electrophilic trapping reaction of 1,3-dienes.[12] To the best of our knowledge, there are no other publications in the literature on silylcupration of dienes. At the time of our preliminary communication it was not clear whether the regioisomers arise from a mixture of isomeric (σ-allyl)copper complexes (1,2- and 1,4-isomers) or from one (σ-allyl)copper complex (1,2- or 1,4-isomer) via $S_E2$ and $S_E2'$ cleavage reactions. We have now characterized the (σ-allyl)copper intermediate and found it to be only one regioisomer, namely a [(*Z*)-4-silyl-2-alken-1-yl]copper complex obtained from an overall 1,4-silylcupration across the 1,3-diene system. The mechanism and silylcupration of 1,3-dienes and subsequent electrophilic trapping is discussed.

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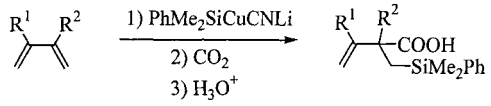
## Results and Discussion

Most of the silylcupration reactions previously studied were carried out with the silylcuprate reagent $(PhMe_2Si)_2CuLi{\cdot}LiCN$ (**1**) or more bulky silylcuprate reagents.[2d] Recently, the cyanocuprate reagent $PhMe_2SiCuCNLi$[13] (**2**) was used by Pulido[14] and ourselves[3] in allene silylcupration reactions. We also employed this reagent in the silylcupration reaction of styrenes[11] and acetylenes.[4] The advantage of the silylcopper reagent $PhMe_2SiCuCNLi$ over the disilyl cuprate reagent $(PhMe_2Si)_2CuLi{\cdot}LiCN$ is that all the silyl species in the reagent are used in the reaction. With the latter reagent only one of the two silyl groups is transferred and the remaining silylcopper reagent leads to side products upon reaction with the electrophile employed. These side-products are formed in equimolar amounts with the desired product, and are difficult to separate from it. Therefore we focussed on the use of the monosilylcopper reagent $PhMe_2SiCuCNLi$ in the silylcupration reaction of 1,3-dienes.

The silylcupration of 1,3-dienes with **2** proceeded smoothly at temperatures ranging from −78 °C to 0 °C. The organocopper intermediates thus obtained were efficiently trapped by different electrophiles, including allylic phosphates,[15] which are viable and readily accessible allylic substrates for metal-catalyzed reactions.[3,11,12,15a,16] Previously we successfully used allylic phosphates as reactive allylic electrophiles in the silylcupration reaction of allenes,[3] styrenes,[11] and acetylenes.[4]

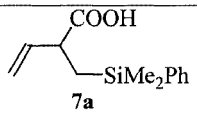
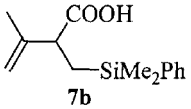
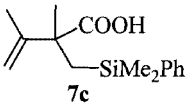
The regioselectivity of the trapping reaction of the copper intermediate obtained from the silylcupration of the diene depends strongly on the electrophile. With carbon dioxide

as electrophile, the 1,2-addition product was formed exclusively (Scheme 1, Table 1).




Scheme 1

Table 1. Silylcupration of 1,3-dienes followed by reaction with $CO_2$ as electrophile

| Entry | Diene | Product | Yield (%)[a] |
|---|---|---|---|
| 1 |  **3** |  **7a** | 82 |
| 2 |  **4** |  **7b** | 76 |
| 3 |  **5** |  **7c** | 73 |

[a] Isolated yields.

With water ($H_3O^+$) and acetyl chloride as electrophiles, mixtures of 1,2- and 1,4-addition products were obtained (Scheme 2, Table 2). The ratio of 1,2- and 1,4-addition products was found to be independent of the reaction temperature. Thus, silylcupration of isoprene at temperatures ranging from −78 °C to 0 °C followed by quenching with a proton source afforded an 85:15 mixture of the 1,2- and 1,4-addition products in all cases (Table 2, entries 2−4).

However, with allylic phosphates, allylic phosphinates or MeI as quenching electrophiles only the 1,4-adducts were formed (Scheme 3, Table 3), except for two cases where a mixture of 1,2- and 1,4-adducts was obtained (Table 3, entries 5, 7). Unfortunately, allylic phosphates from 3,3-disubstituted allylic alcohols were unstable and decomposed upon purification.[17] Therefore, allylic phosphinates[18] were used as a more stable, but still highly reactive,[19] alternative. Allylic phosphinate **19** was prepared from 3,3-dimethyl allyl alcohol, and proved to be sufficiently reactive to give the desired 1,5-diene product (Table 3, entry 8).

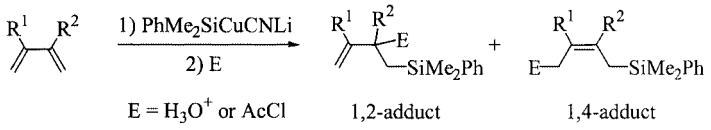
**Mechanism, Scope and Limitations**

The regioselectivity of the tandem silylcupration-electrophilic trapping reaction is interesting from both a synthetic and a mechanistic point of view. A priori a mixture of 1,2- and 1,4-silylcopper intermediates, **33** and **34** respectively, can form in the silylcupration step of the diene (Scheme 4, see Table 2). The electrophilic cleavage may occur in an $S_E2$ and/or $S_E2'$ fashion depending on the electrophile.

In order to obtain information concerning the ratio of (σ-allyl)copper intermediates **33** and **34** formed in the reaction, attempts to characterize the silylcupration adduct were made. Silylcupration of 1,3-butadiene by $PhMe_2SiCuCNLi$ in [$D_8$]THF was monitored by $^1H$ NMR spectroscopy at 0 °C. After 10 min, complete conversion into the silylcupration adduct had occurred and only the 1,4-addition product **34a** was observed, as indicated by the appearance of two new doublets for $CH_2Cu$ ($J$ = 9.3 Hz) and $CH_2Si$ ($J$ = 7.7 Hz) at δ = 0.83 ppm and 1.56 ppm, respectively. The corresponding reactions of isoprene (**4**) and 2,3-dimethyl-1,3-butadiene (**5**) with $PhMe_2SiCuCNLi$ in [$D_8$]THF showed that only 1,4-silylcupration to give **34b** and **34c**, respectively, had occurred also for these dienes according to $^1H$ NMR spectroscopy. From the NMR spectra we conclude that there is only 1,4-addition and the 1,2-adduct was not observed.

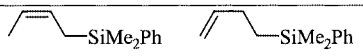
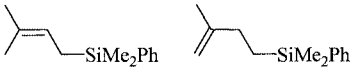
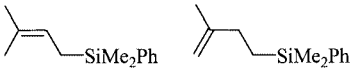
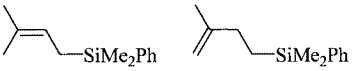
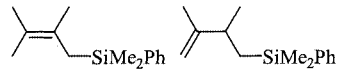
The spectra of the silylcupration products **34a**, **34b**, and **34c** from dienes **3**, **4**, and **5**, respectively, did not change when left at 0 °C for 30 min, indicating either that the 1,4-adduct is the thermodynamically stable (σ-allyl)copper species or that there is no equilibrium between the 1,4- and 1,2-adduct. In the case of 1,3-butadiene NOESY experiments indicate that the 1,4-silylcupration adduct **34a** is of *Z*-stereochemistry, and this stereochemical assignment was supported by a $J_{H,H}$ coupling of 10 Hz between the olefin protons.

It has been recently proposed that silylcupration of styrenes and acetylenes proceeds via a mechanism involving nucleophilic attack by the silylcopper reagent **2** at the terminal carbon of the double and triple bonds respectively.[4,11] A similar mechanism has been proposed for the carbocupration of acetylenes.[20] With an analogous mechanism for 1,3-dienes, attack by copper at the terminal carbon of the diene would give intermediate **35**, with the indicated *cis* configuration. It is known that crotyl anions are more stable in the *cis* form than in the *trans* form.[21,22] Reductive elimination and trapping of the anion by copper(I) would give **34a** and this mechanism explains the *Z*-stereochemistry (Scheme 5).

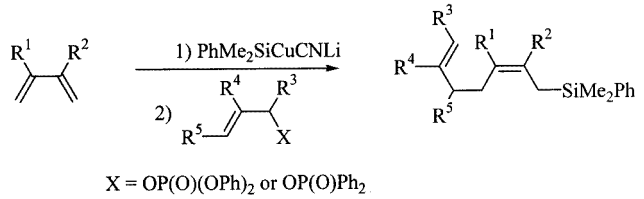



Scheme 2

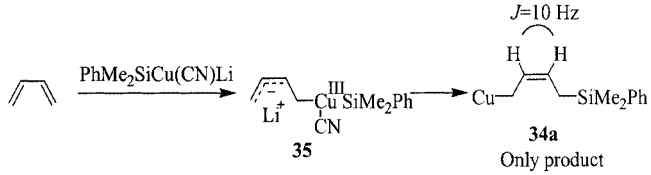
Table 2. Silylcupration of 1,3-dienes followed by reaction with $H_3O^+$ or AcCl as electrophile

| Entry | Diene | Electrophile[a] | T, °C | Products | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | **3** | $H_2O$ | –40 |  40 : 60 **8a** : **8b** | 72 |
| 2 | **4** | $H_2O$ | –40 |  15 : 85 **9a** : **9b** | 76 |
| 3 | **4** | $H_2O$ | –78 |  15 : 85 **9a** : **9b** | 62 |
| 4 | **4** | $H_2O$ | 0 |  15 : 85 **9a** : **9b** | 50 |
| 5 | **4** |  | –40 |  37 : 63 **10b** : **10a** | 75 |
| 6 | **5** | $H_2O$ | –40 |  40 : 60 **11b** : **11a** | 53 |
| 7 | **6** | $H_2O$ | –40 |  30 : 70 **12b** : **12a** | 41 |

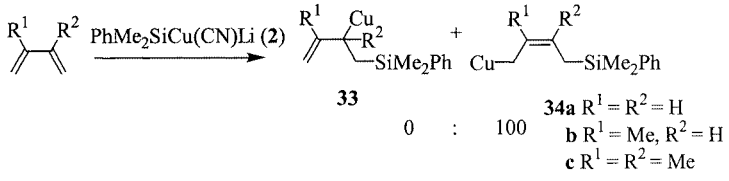
[a] With water as electrophile a saturated aqueous $NH_4Cl$ solution was used. [b] Isolated yields.




Scheme 3

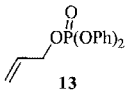
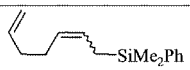
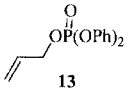
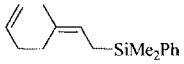
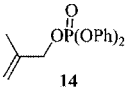
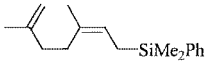
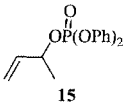
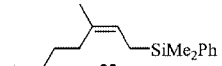
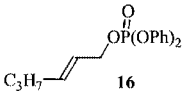
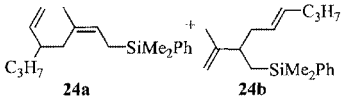
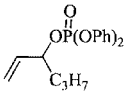
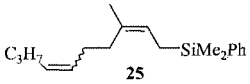
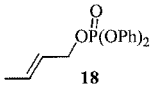
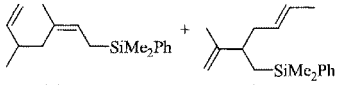
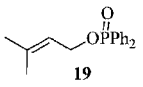
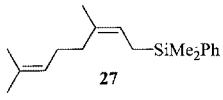
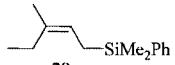
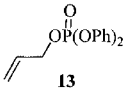
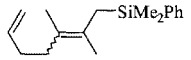
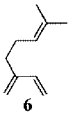
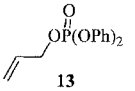
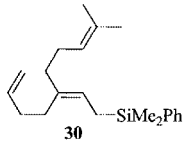
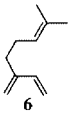
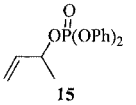
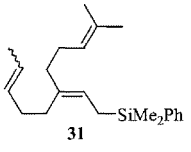
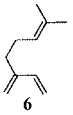
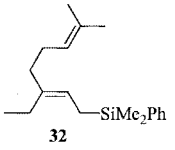



Scheme 5



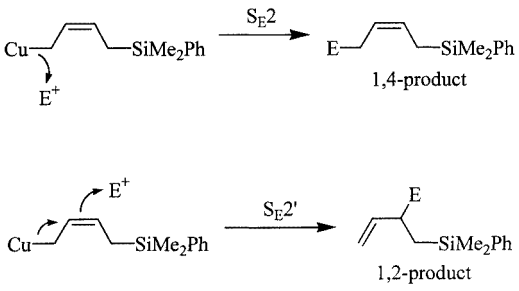

Scheme 4

Table 3. Selective 1,4-Silylcupration-electrophilic trapping reaction of 1,3-dienes

| Entry | Diene | Electrophile | Products | Yield (%)[a] |
|---|---|---|---|---|
| 1 |  **3** |  **13** |  **20** *E*/*Z* = 25:75 | 72 |
| 2 |  **4** |  **13** |  **21** | 72 |
| 3 |  **4** |  **14** |  **22** | 71 |
| 4 |  **4** |  **15** |  **23** *E*/*Z* = 70:30 | 68 |
| 5 |  **4** |  **16** |  **24a** 65 : **24b** 35 | 71 |
| 6 |  **4** |  **17** |  **25** *E*/*Z* = 60:40 | 53 |
| 7 |  **4** |  **18** |  **26a** 70 **26b** 30 | 55 |
| 8 |  **4** |  **19** |  **27** | 52 |
| 9 |  **4** | MeI |  **28** | 69 |
| 10 |  **5** |  **13** |  **29** *E*/*Z* = 55:45 | 57 |
| 11 |  **6** |  **13** |  **30** | 53 |
| 12 |  **6** |  **15** |  **31** *E*/*Z* = 70:30 | 70 |
| 13 |  **6** | MeI |  **32** | 67 |

[a] Isolated yields.

The selectivity of the electrophilic trapping step is very dependent on the electrophile employed, and the electrophilic cleavage can occur in either an $S_E2$ or an $S_E2'$ manner (Scheme 6).




Scheme 6. Electrophilic trapping step of the copper intermediate

Carbon dioxide reacts exclusively via an $S_E2'$ pathway, whereas allylic phosphates give mainly $S_E2$ reaction products. A similar selectivity was observed by Normant in the electrophilic trapping of an allylcopper intermediate resulting from addition of *t*BuCu to 1,3-butadiene.[23] However, no mechanistic discussion or explanation was given.

We believe that the reaction leading to the 1,4-product is not a normal $S_E2$ cleavage but that it occurs in two steps: first the allylic phosphate oxidatively adds to copper in intermediate **34** to give a copper(III) intermediate[20] (**36**). Subsequent reductive elimination then gives the observed product (Scheme 7). The same two-step mechanism via oxidative addition would also apply to allylic phosphinates and MeI. We have recently obtained experimental evidence that the reaction between allylic esters and diallyl cuprates proceeds via $Cu^{III}$.[24]

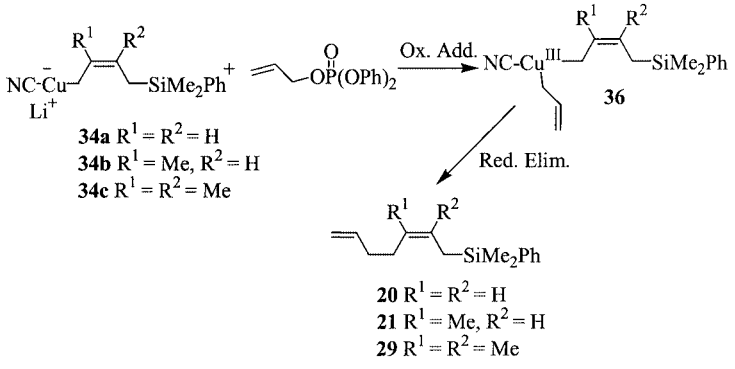
In the case of selective γ-cleavage by $CO_2$ the mechanism most likely involves a classical $S_E2'$ electrophilic cleavage (Scheme 8). Many allylmetal species, such as allylboranes,[25] allyltin[26] and allylsilanes,[27] are known to react with electrophiles in an $S_E2'$ manner.

When mixtures of 1,2- and 1,4-products are obtained, both mechanisms (oxidative addition/reductive elimination and $S_E2'$ electrophilic cleavage) are likely to operate. Alternatively the 1,4-product may be formed via a classical $S_E2$ cleavage and this is a likely pathway for the protonolysis (three-center mechanism).

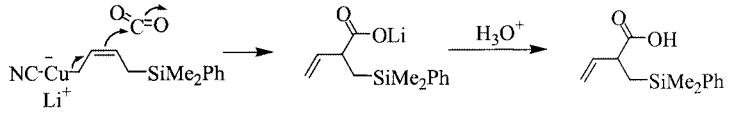
In two particular cases the reaction of the silylcuprated diene with allylic phosphates gave a mixture of 1,4- and 1,2-addition products. Allylic phosphates can react in the α- or γ-position. The regioselectivity for the 1,4-γ- and 1,2-α-product is surprisingly high; no 1,4-α- or 1,2-γ-product was observed. Thus, as can be seen from Table 3 (entries 5 and 7) the 1,4-product is a result of a selective γ-substitution reaction of the allylic phosphate, whereas the 1,2-product gives only the α-substituted allylic chain. It is proposed that the initial product of these reactions, similar to all other reactions involving allylic phosphates as electrophiles, is the $Cu^{III}$ intermediate **37** formed by γ-selective oxidative addition.[28] In this case the formation of 1,2-α-product via a cyclic transition state (3,3′-coupling) would compete with the normal reductive elimination (1,1′-coupling) due to steric hindrance in the latter pathway (Scheme 9).

Another explanation for the formation of the 1,2-α-product would be the [3,3]-sigmatropic rearrangement of the initially formed 1,4-γ-product. However, when compound **24a** (1,4-γ-product) was heated for one hour at 280 °C, no rearranged product was detected and only starting material could be recovered. A control experiment was carried out to see whether copper can catalyze this Cope rearrangement under the reaction conditions. Thus, compound **24a** was added to a silylcupration-electrophilic trapping reaction mixture, but no rearranged product **24b** could be detected. A [3,3]-sigmatropic rearrangement of an initially formed 1,4-γ-product to the 1,2-α-product can therefore be ruled out.

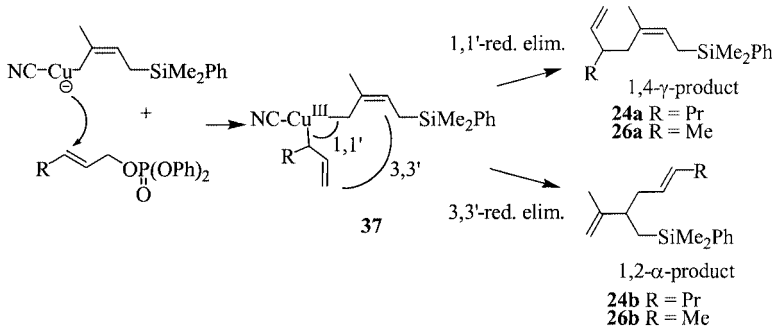
As can be seen from the data above, only 1,3-dienes with unsubstituted terminal carbons are used, as, unfortunately,




Scheme 7. Allylic substitution mechanism




Scheme 8. A plausible mechanism of a γ-selective electrophilic trapping by $CO_2$




Scheme 9

cyclic and terminally substituted 1,3-dienes are not reactive enough in this reaction. A similar observation has been reported in the carbocupration reaction of 1,3-dienes.[23] Thus, under standard silylcupration reaction conditions used for silylcupration of dienes **3**, **4**, **5** and **6** neither 1,3-pentadiene nor 1,3-cyclohexadiene gave any reaction product. The diene was left intact under these conditions. Upon addition of electron-releasing ligands such as $PPh_3$ or P*n*$Bu_3$ to the reaction mixture, however, small amounts of the desired products could be isolated. Unfortunately, the yields of these reactions could not be brought up to useful levels. In the case of 1,3-cyclohexadiene we isolated 6% of the product, whereas 1,3-pentadiene gave 34% isolated yield of the addition-protonolysis product.

## Conclusion

An efficient 1,4-silylcupration reaction of terminal 1,3-dienes followed by electrophilic trapping with various electrophiles has been developed. This method provides an easy access to substituted 1,5-diene systems containing the silyl group, which are useful intermediates in organic synthesis. Mechanistic studies indicate a highly selective 1,4-silylcupration step leading to (σ-allyl)copper complexes which were characterized by NMR spectroscopy. Different electrophiles used in the trapping reaction of the copper intermediate can give different regiochemistry, i.e. $S_E2$ or $S_E2'$ substitution products. This method broadens the scope of the silylcupration reaction and gives an insight into the mechanism of the reaction.

## Experimental Section

**General:** $^1H$ 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 $CDCl_3$ ($\delta$ = 7.26 ppm for $^1H$ and $\delta$ = 77.17 ppm for $^{13}C$) or in [$D_8$]THF ($\delta$ = 3.58 ppm for $^1H$) as internal standard; chemical shifts are reported in ppm. Millipore Matrex 60 Å (35−70 μm) silica gel was used for flash chromatography. TLC analysis was performed on Merck 60 $F_{254}$ precoated plates. Some isomeric products were separated using $AgNO_3$/silica gel column chromatography technique,[29] since they were inseparable even by HPLC. The stereochemistry of the products was confirmed by NOE or NOESY experiments.

Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Allylic phosphates,[15] phosphinates[18] and $PhMe_2SiLi$[13a] were prepared according to published procedures. Elemental analysis was performed by Analytische Laboratorien, Lindlar, Germany. Tetrahydrofuran (THF) and diethyl ether ($Et_2O$) were freshly distilled from sodium benzophenone ketyl under an argon atmosphere prior to use. All reactions were performed under an argon atmosphere using flame-dried glassware.

**General Procedure for Silylcupration of 1,3-Dienes Followed by Electrophilic Trapping with Water or Acetyl Chloride:** $PhMe_2SiLi$ (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 20 min. The mixture was then cooled to the temperature indicated in Table 1 and the diene (1.05 mmol, 1.5 equiv.) was added dropwise (butadiene was added from a cylinder in excess). After stirring for 0.5 h at this temperature the reaction mixture was quenched with saturated aqueous $NH_4Cl$ (4 mL) and the aqueous phase was extracted with pentane (5 × 3 mL). If acetyl chloride was used as electrophile, 1.5 equiv. of it was added dropwise to the reaction mixture (instead of $NH_4Cl$ aq.) and the reaction mixture was stirred at the same temperature for 1 h followed by quenching with saturated aqueous $NH_4Cl$ (4 mL) and extraction as indicated before. Evaporation of the solvent and subsequent column chromatography on silica with pentane (pentane/diethyl ether in the case of acetates) as eluent afforded the products indicated in Table 1 as colorless oils.

**General Procedure for Silylcupration of 1,3-Dienes Followed by Electrophilic Trapping with Carbon Dioxide:** $PhMe_2SiLi$ (1.0 mmol, ≈1 M solution in THF) was added to a stirred suspension of CuCN (1.0 mmol, 1 equiv.) in dry THF (1 mL) at 0 °C. After stirring at this temperature for 20 min the mixture was cooled to −30 °C and the diene (1.5 mmol, 1.5 equiv.) was added dropwise (butadiene was added from a cylinder in excess). The reaction mixture was stirred for 0.5 h at this temperature, and then $CO_2$ gas was passed through the reaction mixture for about 10 min. The reaction mixture was quenched with 4 mL of aqueous 1 M HCl solution followed by extraction with diethyl ether. After evaporation of the solvent, column chromatography on silica with pentane/ethyl acetate as eluent afforded the products indicated in Table 2 as colorless oils.

**General Procedure for Silylcupration of 1,3-Dienes Followed by Electrophilic Trapping with Allylic Phosphates, Phosphinates or MeI:** $PhMe_2SiLi$ (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. After stirring at this temperature for 20 min the reaction mixture was cooled to −40 °C and the diene (1.05 mmol, 1.5 equiv.) was added dropwise (butadiene was added from a cylinder in excess). The reaction mixture was stirred for 0.5 h at this temperature and then the temperature was lowered to −78 °C and allylic phosphate or allylic phosphinate (1.2 equiv.) in 0.6 mL THF was added slowly over 30 min with a syringe pump. After the reaction mixture had been stirred for 1 h at −78 °C, 4 mL of saturated aqueous $NH_4Cl$ was added and the aqueous phase was extracted with pentane (5 × 3 mL).

When MeI was used in the electrophilic trapping step, 3 equiv. of it was added to the silylcupration mixture at −40 °C, and the reaction mixture was stirred at this temperature for 1 h. The workup procedure was identical to that described above. Evaporation of the solvent and subsequent column chromatography on silica with pentane as eluent afforded the products indicated in Table 3 as colorless oils.

The identity of some products was proven by comparison with published spectroscopic data: **8a**,[30] **8b**,[31] **9a**,[32] **9b**,[33] **10a**[2c], **11a**[33], **11b**[2c], **27**.[34]

**2-[(Dimethylphenylsilyl)methyl]-3-butenoic Acid (7a):** Mol. wt. = 234.37; yield = 192 mg, 82%. $^1$H NMR (300 MHz): δ = 9.44 (br. s, 1 H), 7.51 (m, 2 H), 7.36 (m, 3 H), 5.81 (ddd, *J* = 17.0, 10.0, 8.5 Hz, 1 H), 5.12 (dt, *J* = 17.0, 1.2 Hz, 1 H), 5.10 (dt, *J* = 10.0, 1.2 Hz, 1 H), 3.11 (app. q, *J* = 8.5 Hz, 1 H), 1.36 (dd, *J* = 14.8, 7.1 Hz, 1 H), 1.12 (dd, *J* = 14.8, 8.5 Hz, 1 H), 0.33 (s, 3 H), 0.32 (s, 3 H) ppm. $^{13}$C NMR (75.4 MHz): δ = 181.4, 138.4, 137.6, 133.8, 129.3, 128.0, 117.0, 46.0, 19.1, −2.2, −2.5 ppm. MS (EI): *m*/*z* (%) = 219 (30), 175 (78), 137 (73), 135 (100), 113 (28), 97 (35), 75 (29).

**2-[(Dimethylphenylsilyl)methyl]-3-methyl-3-butenoic Acid (7b):** Mol. wt. = 248.39; yield = 189 mg, 76%. $^1$H NMR (300 MHz): δ = 10.16 (br. s, 1 H), 7.51 (m, 2 H), 7.36 (m, 3 H), 4.91 (m, 1 H), 4.89 (quintet, *J* = 1.5 Hz, 1 H), 3.15 (app. t, *J* = 7.5 Hz, 1 H), 1.74 (dd, *J* = 1.5, 1.0 Hz, 3 H), 1.41 (dd, *J* = 14.9, 8.2 Hz, 1 H), 1.12 (dd, *J* = 14.9, 7.2 Hz, 1 H), 0.32 (s, 6 H) ppm. $^{13}$C NMR (75.4 MHz): δ = 180.8, 144.0, 138.4, 133.8, 129.2, 127.9, 114.2, 48.8, 19.8, 17.1, −2.66, −2.71 ppm. MS (EI): *m*/*z* (%) = 189 (45), 157 (29), 137 (36), 135 (100), 111 (34), 75 (28), 73 (52).

**2-[(Dimethylphenylsilyl)methyl]-2,3-dimethyl-3-butenoic Acid (7c):** Mol. wt. = 262.42; yield = 192 mg, 73%. $^1$H NMR (300 MHz): δ = 11.13 (br. s, 1 H), 7.53 (m, 2 H), 7.35 (m, 3 H), 4.98 (m, 1 H), 4.92 (dt, *J* = 2.5, 1.3 Hz, 1 H), 1.77 (d, *J* = 1.4 Hz, 3 H), 1.55 (d, *J* = 14.6 Hz, 1 H), 1.35 (d, *J* = 14.6 Hz, 1 H), 1.32 (s, 3 H), 0.36 (s, 3 H), 0.34 (s, 3 H) ppm. $^{13}$C NMR (75.4 MHz): δ = 183.3, 148.1, 139.8, 133.7, 129.0, 127.9, 111.7, 50.1, 25.1, 24.1, 20.2, −1.3, −1.4 ppm. MS (EI): *m*/*z* (%) = 203 (19), 171 (27), 137 (23), 135 (100), 125 (57), 75 (24), 73 (18).

**(*Z*)-6-(Dimethylphenylsilyl)-4-methyl-4-hexen-2-one (10b):** Mol. wt. = 246.42; yield = 129 mg, 75% (mixture of **10a** and **10b**). $^1$H NMR ($CDCl_3$ 300 MHz): δ = 7.51 (m, 2 H), 7.37 (m, 3 H), 5.41 (tq, *J* = 8.3, 1.1 Hz, 1 H), 2.97 (s, 2 H), 2.05 (s, 3 H), 1.71 (q, *J* = 1.1 Hz, 3 H), 1.66 (d, *J* = 8.3 Hz, 2 H), 0.29 (s, 6 H) ppm. $^{13}$C NMR ($CDCl_3$ 75 MHz): δ = 207.3, 138.7, 133.7, 129.2, 127.9, 126.9, 124.3, 47.2, 29.2, 24.2, 18.3, −3.1 ppm. MS (EI): *m*/*z* (%) = 231 (8), 153 (7), 137 (23), 136 (14), 135 (100), 107 (7), 75 (46).

**Dimethyl(7-methyl-3-methylene-6-octenyl)phenylsilane (12a):** Mol. wt. = 272.50; yield = 78 mg, 41% (mixture of **12a** and **12b**). $^1$H NMR ($CDCl_3$ 400 MHz): δ = 7.51 (m, 2 H), 7.35 (m, 3 H), 5.10 (m, 1 H), 4.75 (s, 1 H), 4.69 (s, 1 H), 2.03 (m, 6 H), 1.68 (s, 3 H), 1.59 (s, 3 H), 0.89 (ddd, *J* = 8.1, 5.0, 4.0 Hz, 2 H), 0.28 (s, 6 H) ppm. $^{13}$C NMR ($CDCl_3$ 100 MHz): δ = 152.3, 139.4, 133.7, 131.7, 129.0, 127.9, 124.4, 107.8, 36.0, 30.4, 26.6, 25.8, 17.8, 14.0, −3.0 ppm.

**[(2*E*)-3,7-Dimethyl-2,6-octadienyl]dimethyl(phenyl)silane (12b):** Although this compound is known, only the $^{13}$C NMR spectrum has been reported,[35] therefore we give the $^1$H NMR spectrum of this compound here. Mol. wt. = 272.50; yield = 78 mg, 41% (mixture of **12a** and **12b**). $^1$H NMR ($CDCl_3$ 400 MHz): δ = 7.51 (m, 2 H), 7.35 (m, 3 H), 5.17 (tq, *J* = 8.5, 1.2 Hz, 1 H), 5.09 (tt, *J* = 6.7, 1.3 Hz, 1 H), 2.02 (m, 4 H), 1.68 (s, 3 H), 1.64 (d, *J* = 8.5 Hz, 2 H), 1.60 (s, 3 H), 1.49 (s, 3 H), 0.26 (s, 6 H) ppm.

**(2*Z*)-2,6-Heptadienyldimethyl(phenyl)silane [(*Z*)-20]:** Mol. wt. = 230.42; yield = 116 mg, 72% (mixture of **(*Z*)-20** and **(*E*)-20**). $^1$H NMR ($CDCl_3$ 400 MHz): δ = 7.56 (m, 2 H), 7.39 (m, 3 H), 5.83 (m, 1 H), 5.45 (m, 1 H), 5.32 (m, 1 H), 5.03 (ddt, *J* = 17.1, 2.1, 0.9 Hz, 1 H), 4.98 (ddt, *J* = 10.1, 2.1, 1.0 Hz, 1 H), 2.07 (m, 4 H), 1.76 (dd, *J* = 8.5, 1.3 Hz, 2 H), 0.33 (s, 6 H) ppm. $^{13}$C NMR ($CDCl_3$ 100 MHz): δ = 138.9, 133.8, 129.23, 129.15, 129.11, 128.0, 127.7, 114.7, 34.0, 26.8, 17.9, −3.01 ppm.

**(2*E*)-2,6-Heptadienyldimethyl(phenyl)silane [(*E*)-20]:** Mol. wt. = 230.42; yield = 116 mg, 72% [mixture of **(*Z*)-20** and **(*E*)-20**]. $^1$H NMR ($CDCl_3$ 400 MHz): δ = 7.56 (m, 2 H), 7.39 (m, 3 H), 5.83 (m, 1 H), 5.45 (m, 1 H), 5.32 (m, 1 H), 5.03 (ddt, *J* = 17.1, 2.1, 0.9 Hz, 1 H), 4.98 (ddt, *J* = 10.1, 2.1, 1.0 Hz, 1 H), 2.11 (m, 4 H), 1.70 (dq, *J* = 7.7, 0.9 Hz, 2 H), 0.31 (s, 6 H) ppm. $^{13}$C NMR ($CDCl_3$ 100 MHz): δ = 139.1, 133.9, 129.2, 129.15, 129.11, 127.9, 127.7, 114.7, 34.4, 32.5, 21.9, −3.14 ppm. $C_{15}H_{22}Si$ [mixture of **(*Z*)-20** and **(*E*)-20**]: calcd. C 78.19, H 9.62; found C 77.92, H 9.46.

**Dimethyl[(2*Z*)-3-methyl-2,6-heptadienyl]phenylsilane (21):** Mol. wt. = 244.45; yield = 123 mg, 72%. $^1$H NMR ($CDCl_3$ 400 MHz): δ = 7.54 (m, 2 H), 7.38 (m, 3 H), 5.82 (m, 1 H), 5.21 (app. t, *J* = 8.3 Hz, 1 H), 5.02 (dq, *J* = 17.1, 1.5 Hz, 1 H), 4.95 (ddt, *J* = 10.2, 2.1, 1.0 Hz, 1 H), 2.06 (m, 4 H), 1.71 (app. q, *J* = 1.2 Hz, 3 H), 1.68 (dq, *J* = 8.3, 1.1 Hz, 2 H), 0.30 (s, 6 H) ppm. $^{13}$C NMR ($CDCl_3$ 100 MHz): δ = 139.3, 139.1, 133.7, 133.1, 129.0, 127.8, 120.2, 114.3, 32.2, 31.1, 23.5, 17.6, −3.0 ppm. $C_{16}H_{24}Si$: calcd. C 78.62, H 9.90; found C 78.46, H 9.83.

**[(2*Z*)-3,6-Dimethyl-2,6-heptadienyl]dimethyl(phenyl)silane (22):** Mol. wt. = 258.47; yield = 128 mg, 71%. $^1$H NMR ($CDCl_3$ 400 MHz): δ = 7.54 (m, 2 H), 7.38 (m, 3 H), 5.20 (t, *J* = 8.5 Hz, 1 H), 4.71 (s, 1 H), 4.69 (s, 1 H), 2.10 (m, 2 H), 2.00 (m, 2 H), 1.75 (s, 3 H), 1.72 (m, 3 H), 1.68 (d, *J* = 8.5 Hz, 2 H), 0.31 (s, 6 H) ppm. $^{13}$C NMR ($CDCl_3$ 75.4 MHz): δ = 146.4, 139.3, 133.8, 133.6, 129.0, 127.8, 120.0, 109.6, 36.0, 30.2, 23.5, 22.7, 17.6, −3.0 ppm. $C_{17}H_{26}Si$: calcd. C 79.00, H 10.14; found C 79.02, H 10.05.

**Dimethyl[(2*Z*,6*E*)-3-methyl-2,6-octadienyl]phenylsilane [(*E*)-23]:** Mol. wt. = 258.47; yield = 123 mg, 68% [mixture of **(*Z*)-23** and **(*E*)-23**]. $^1$H NMR ($CDCl_3$ 400 MHz): δ = 7.56 (m, 2 H), 7.39 (m, 3 H), 5.45 (m, 2 H), 5.21 (m, 1 H), 2.05 (m, 2 H), 2.01 (s, 3 H), 1.75−1.63 (m, 7 H), 0.299 (s, 6 H) ppm. $^{13}$C NMR ($CDCl_3$ 100 MHz): δ = 139.42, 133.74, 131.56, 130.64, 129.02, 127.84, 124.77, 119.97, 31.81, 31.01, 23.53, 18.08, 17.50, −3.02.

**Dimethyl[(2*Z*,6*Z*)-3-methyl-2,6-octadienyl]phenylsilane [(*Z*)-23]:** Mol. wt. = 258.47; yield = 123 mg, 68% [mixture of **(*Z*)-23** and **(*E*)-23**]. $^1$H NMR ($CDCl_3$ 400 MHz): δ = 7.56 (m, 2 H), 7.39 (m, 3 H), 5.45 (m, 2 H), 5.21 (m, 1 H), 2.05 (m, 2 H), 2.01 (s, 3 H), 1.75−1.63 (m, 7 H), 0.302 (s, 6 H) ppm. $^{13}$C NMR ($CDCl_3$

100 MHz): δ = 139.42, 133.49, 131.56, 130.64, 129.02, 127.84, 123.94, 120.11, 31.51, 25.35, 23.46, 17.56, 12.90, −3.02 ppm. $C_{17}H_{26}Si$ [mixture of **(*E*)-23** and **(*Z*)-23**]: calcd. C 79.00, H 10.14; found C 78.91, H 9.99.

**Dimethyl[(2*Z*)-3-methyl-5-propyl-2,6-heptadienyl]phenylsilane (24a):** Mol. wt. = 286.53; yield = 142 mg, 71% (mixture of **24a** and **24b**). $^1$H NMR ($CDCl_3$ 400 MHz): δ = 7.52 (m, 2 H), 7.36 (m, 3 H), 5.54 (m, 1 H), 5.21 (t, *J* = 8.1 Hz, 1 H), 4.92 (ddd, *J* = 17.0, 2.0, 0.8 Hz, 1 H), 4.91 (dd, *J* = 10.3, 2.0 Hz, 1 H), 2.15 (m, 1 H), 1.98 (dd, *J* = 13.5, 6.7 Hz, 1 H), 1.92 (dd, *J* = 13.5, 8.2 Hz, 1 H), 1.66 (s, 3 H), 1.64 (d, *J* = 8.1 Hz, 2 H), 1.24 (m, 4 H), 0.87 (t, *J* = 7.0 Hz, 3 H), 0.27 (s, 6 H) ppm. $^{13}$C NMR ($CDCl_3$ 100 MHz): δ = 143.4, 139.5, 133.8, 132.4, 129.0, 127.8, 121.0, 113.7, 42.2, 37.5, 36.8, 24.0, 20.5, 17.6, 14.3, −3.0 ppm. $C_{19}H_{30}Si$ (mixture of **24a** and **24b**): calcd. C 79.65, H 10.55; found C 79.46, H 10.36.

**[(*E*)-2-Isopropenyl-4-octenyl]dimethyl(phenyl)silane (24b):** Mol. wt. = 286.53; yield = 142 mg, 71% (mixture of **24a** and **24b**). $^1$H NMR ($CDCl_3$ 300 MHz): δ = 7.50 (m, 2 H), 7.34 (m, 3 H), 5.32 (dt, *J* = 15.4, 6.2 Hz, 1 H), 5.25 (dt, *J* = 15.4, 6.5 Hz, 1 H), 4.65 (m, 2 H), 2.24 (m, 1 H), 2.00 (m, 2 H), 1.93 (app. q, *J* = 7.1 Hz, 2 H), 1.57 (t, *J* = 1.1 Hz, 3 H), 1.34 (sextet, *J* = 7.3 Hz, 2 H), 0.92 (d, *J* = 6.0 Hz, 1 H), 0.90 (d, *J* = 8.6 Hz, 1 H), 0.87 (t, *J* = 7.3 Hz, 3 H), 0.29 (s, 3 H), 0.27 (s, 3 H) ppm. $^{13}$C NMR ($CDCl_3$ 75 MHz): δ = 149.2, 140.1, 133.7, 133.5, 128.9, 128.8, 127.8, 111.0, 43.8, 40.3, 34.8, 22.9, 20.3, 18.3, 13.8, −1.9, −2.5 ppm.

**Dimethyl[(2*Z*,6*E*)-3-methyl-2,6-decadienyl]phenylsilane [(*E*)-25]:** Mol. wt. = 286.53; yield = 106 mg, 53% [mixture of **(*Z*)-25** and **(*E*)-25**]. $^1$H NMR ($CDCl_3$ 400 MHz): δ = 7.54 (m, 2 H), 7.37 (m, 3 H), 5.41 (m, 2 H), 5.18 (t, *J* = 8.4 Hz, 1 H), 2.01 (m, 4 H), 1.97 (m, 2 H), 1.69 (s, 3 H), 1.66 (d, *J* = 8.4 Hz, 2 H), 1.39 (q, *J* = 7.2 Hz, 2 H), 0.91 (t, *J* = 7.2 Hz, 3 H), 0.29 (s, 6 H) ppm. $^{13}$C NMR ($CDCl_3$ 100 MHz): δ = 139.44, 133.75, 133.53, 130.45, 130.32, 129.0, 127.84, 119.94, 34.86, 31.89, 31.05, 23.56, 22.86, 17.52, 13.83, −3.01 ppm.

**Dimethyl[(2*Z*,6*Z*)-3-methyl-2,6-decadienyl]phenylsilane [(*Z*)-25]:** Mol. wt. = 286.53; yield = 106 mg, 53% [mixture of **(*Z*)-25** and **(*E*)-25**]. $^1$H NMR ($CDCl_3$ 400 MHz): δ = 7.51 (m, 2 H), 7.35 (m, 3 H), 5.35 (app. t., *J* = 4.5 Hz, 2 H), 5.16 (t, *J* = 8.5 Hz, 1 H), 2.01 (m, 6 H), 1.69 (s, 3 H), 1.65 (d, *J* = 8.5 Hz, 2 H), 1.37 (q, *J* = 7.6 Hz, 2 H), 0.90 (t, *J* = 7.6 Hz, 3 H), 0.26 (s, 6 H) ppm. $^{13}$C NMR ($CDCl_3$ 100 MHz): δ = 139.40, 133.75, 133.52, 129.97, 129.86, 129.03, 127.83, 120.09, 31.82, 29.46, 25.74, 23.50, 23.05, 17.58, 13.97, −3.03 ppm.

**[(2*Z*)-3,5-Dimethyl-2,6-heptadienyl]dimethyl(phenyl)silane (26a):** Mol. wt. = 258.47; yield = 100 mg, 55% (mixture of **26a** and **26b**). $^1$H NMR ($CDCl_3$ 400 MHz): δ = 7.52 (m, 2 H), 7.36 (m, 3 H), 5.74 (ddd, *J* = 17.3, 10.4, 7.0 Hz, 1 H), 5.22 (t, *J* = 8.1 Hz, 1 H), 4.95 (dt, *J* = 17.3, 1.6 Hz, 1 H), 4.88 (ddd, *J* = 10.4, 1.7, 1.1 Hz, 1 H), 2.31 (m, 1 H), 1.94 (d, *J* = 7.1 Hz, 1 H), 1.93 (d, *J* = 7.8 Hz, 1 H), 1.66 (s, 3 H), 1.64 (d, *J* = 8.9 Hz, 2 H), 0.93 (d, *J* = 6.8 Hz, 3 H), 0.26 (s, 6 H) ppm. $^{13}$C NMR ($CDCl_3$ 100 MHz): δ = 144.8, 139.4, 133.7, 132.3, 129.0, 127.8, 121.2, 112.1, 38.7, 35.9, 23.9, 19.6, 17.6, −3.01, −3.02 ppm.

**[(*E*)-2-Isopropenyl-4-hexenyl]dimethyl(phenyl)silane (26b):** Mol. wt. = 258.47; yield = 100 mg, 55% (mixture of **26a** and **26b**). $^1$H NMR ($CDCl_3$ 400 MHz): δ = 7.51 (m, 2 H), 7.35 (m, 3 H), 5.34 (m, 1 H), 5.27 (m, 1 H), 4.65 (m, 2 H), 2.24 (m, 1 H), 1.99 (m, 2 H), 1.62 (dq, *J* = 6.0, 1.4 Hz, 3 H), 1.57 (s, 3 H), 0.90 (d, *J* = 6.0 Hz, 1 H), 0.89 (d, *J* = 8.7 Hz, 1 H), 0.29 (s, 3 H), 0.27 (s, 3 H) ppm. $^{13}$C NMR ($CDCl_3$ 100 MHz): δ = 149.2, 140.1, 133.7, 129.9, 128.8, 127.8, 125.9, 111.0, 43.7, 40.2, 20.3, 18.2, 18.1, −1.9, −2.6 ppm.

**Dimethyl[(*Z*)-3-methyl-2-pentenyl]phenylsilane (28):** Mol. wt. = 218.41; yield = 105 mg, 69%. $^1$H NMR ($CDCl_3$ 400 MHz): δ = 7.52 (m, 2 H), 7.35 (m, 3 H), 5.12 (tq, *J* = 8.3, 1.2 Hz, 1 H), 1.97 (q, *J* = 7.5 Hz, 2 H), 1.70 (app. q, *J* = 1.2 Hz, 3 H), 1.67 (dq, *J* = 8.3, 1.2 Hz, 2 H), 0.92 (t, *J* = 7.5 Hz, 3 H), 0.29 (s, 6 H) ppm. $^{13}$C NMR ($CDCl_3$ 100 MHz): δ = 139.5, 135.4, 133.8, 129.0, 127.8, 118.9, 24.5, 23.0, 17.4, 12.5, −3.1 ppm. $C_{14}H_{22}Si$: calcd. C 76.99, H 10.15; found C 76.60, H 9.99.

**(5*Z*)-5,6,8-Trimethyl-8-phenyl-1,5-nonadiene [(*Z*)-29]:** Mol. wt. = 258.47; yield = 103 mg, 57% [mixture of **(*Z*)-29** and **(*E*)-29**]. $^1$H NMR ($CDCl_3$ 300 MHz): δ = 7.52 (m, 2 H), 7.35 (m, 3 H), 5.79 (ddt, *J* = 17.0, 10.3, 6.3 Hz, 1 H), 4.97 (dq, *J* = 17.0, 1.6 Hz, 1 H), 4.91 (ddt, *J* = 10.3, 2.1, 1.1 Hz, 1 H), 2.00 (m, 4 H), 1.78 (s, 2 H), 1.62 (s, 3 H), 1.56 (s, 3 H), 0.29 (s, 6 H) ppm. $^{13}$C NMR ($CDCl_3$ 75 MHz): δ = 140.0, 139.3, 133.7, 129.0, 127.8, 125.29, 125.26, 114.1, 34.3, 32.4, 24.7, 21.5, 18.1, −2.1 ppm. MS (EI): *m*/*z* (%) = 217 (21), 181 (5), 161 (11), 137 (6), 136 (15), 135 (100), 107 (4).

**(5*E*)-5,6,8-Trimethyl-8-phenyl-1,5-nonadiene [(*E*)-29]:** Mol. wt. = 258.47; yield = 103 mg, 57% [mixture of **(*Z*)-29** and **(*E*)-29**]. $^1$H NMR ($CDCl_3$ 300 MHz): δ = 7.52 (m, 2 H), 7.35 (m, 3 H), 5.82 (m, 1 H), 5.02 (dm, *J* = 17.1 Hz, 1 H), 4.94 (dm, *J* = 10.1 Hz, 1 H), 2.09 (m, 4 H), 1.76 (s, 2 H), 1.56 (m, 3 H), 1.51 (m, 3 H), 0.30 (s, 6 H) ppm. $^{13}$C NMR ($CDCl_3$ 75 MHz): δ = 140.0, 139.3, 133.7, 129.0, 127.8, 125.7, 125.5, 114.3, 34.3, 32.9, 25.2, 20.9, 19.1, −2.1 ppm. MS (EI): *m*/*z* (%) = 217 (19), 181 (4), 161 (10), 137 (7), 136 (13), 135 (100), 107 (4).

**{(2*E*)-3-[(3-Butenyl)]-7-methyl-2,6-octadienyl}dimethyl(phenyl)silane (30):** Mol. wt. = 312.56; yield = 116 mg, 53%. $^1$H NMR ($CDCl_3$ 400 MHz): δ = 7.54 (m, 2 H), 7.37 (m, 3 H), 5.82 (m, 1 H), 5.21 (app. t, *J* = 8.3 Hz, 1 H), 5.12 (t pent., *J* = 6.8, 1.5 Hz, 1 H), 5.01 (ddt, *J* = 17.0, 2.1, 1.5 Hz, 1 H), 4.95 (ddt, *J* = 10.1, 2.1, 1.0 Hz, 1 H), 2.05 (m, 8 H), 1.71 (s, 3 H), 1.69 (d, *J* = 8.3 Hz, 2 H), 1.63 (s, 3 H), 0.30 (s, 6 H) ppm. $^{13}$C NMR ($CDCl_3$ 100 MHz): δ = 139.3, 139.1, 136.9, 133.8, 131.4, 129.0, 127.8, 124.8, 120.3, 114.3, 37.0, 32.4, 29.2, 27.2, 25.9, 17.9, 17.6, −3.1 ppm. $C_{21}H_{32}Si$: calcd. C 80.70, H 10.32; found C 80.40, H 10.08.

**Dimethyl{(2*E*)-7-methyl-3-[(*E*)-3-pentenyl]-2,6-octadienyl}phenylsilane [(*E*)-31]:** Mol. wt. = 326.59; yield = 160 mg, 70% (mixture of **(*Z*)-31** and **(*E*)-31**). $^1$H NMR ($CDCl_3$ 400 MHz): δ = 7.52 (m, 2 H), 7.35 (m, 3 H), 5.41 (m, 2 H), 5.17 (m, 1 H), 5.10 (m, 1 H), 2.02 (m, 6 H), 1.98 (s, 3 H), 1.70−1.56 (m, 10 H), 0.272 (s, 6 H) ppm. $^{13}$C NMR ($CDCl_3$ 100 MHz): δ = 139.42, 137.25, 133.77, 131.61, 131.33, 130.68, 129.03, 127.83, 124.77, 120.07, 37.09, 31.29, 29.89, 27.22, 25.90, 18.08, 17.87, 17.54, −3.11.

**Dimethyl{(2*E*)-7-methyl-3-[(*Z*)-3-pentenyl]-2,6-octadienyl}phenylsilane [(*Z*)-31]:** Mol. wt. = 326.59; yield = 160 mg, 70% (mixture of **(*Z*)-31** and **(*E*)-31**). $^1$H NMR ($CDCl_3$ 400 MHz): δ = 7.52 (m, 2 H), 7.35 (m, 3 H), 5.41 (m, 2 H), 5.17 (m, 1 H), 5.10 (m, 1 H), 2.02 (m, 6 H), 1.98 (s, 3 H), 1.70−1.56 (m, 10 H), 0.275 (s, 6 H) ppm. $^{13}$C NMR ($CDCl_3$ 100 MHz): δ = 139.42, 137.25, 133.77, 131.61, 131.33, 130.68, 129.03, 127.83, 124.82, 120.21, 37.05, 31.29, 29.58, 27.27, 25.66, 18.08, 17.61, 12.91, −3.11 ppm. $C_{22}H_{34}Si$ (mixture of **(*E*)-31** and **(*Z*)-31**): calcd. C 80.91, H 10.49; found C 81.05, H 10.47.

**[(2*E*)-3-Ethyl-7-methyl-2,6-octadienyl]dimethyl(phenyl)silane (32):** Mol. wt. = 286.53; yield = 134 mg, 67%. $^1$H NMR ($CDCl_3$ 400 MHz): δ = 7.52 (m, 2 H), 7.35 (m, 3 H), 5.10 (m, 2 H), 2.01

(m, 4 H), 1.94 (q, $J$ = 7.5 Hz, 2 H), 1.68 (s, 3 H), 1.65 (d, $J$ = 8.5 Hz, 2 H), 1.60 (s, 3 H), 0.89 (t, $J$ = 7.5 Hz, 3 H), 0.26 (s, 6 H) ppm. $^{13}$C NMR ($CDCl_3$ 100 MHz): δ = 139.5, 139.2, 133.8, 131.3, 129.0, 127.8, 124.9, 119.1, 36.6, 27.2, 25.9, 22.6, 17.9, 17.4, 12.8, −3.1 ppm. $C_{19}H_{30}Si$: calcd. C 79.65, H 10.55; found C 79.61, H 10.38.

**{(*Z*)-4-[Dimethyl(phenyl)silyl]-2-butenyl}copper (34a):** $^1$H NMR ([D$_8$]THF 400 MHz): δ = 7.49 (m, 2 H), 7.25 (m, 3 H), 5.71 (dt, $J$ = 10.0, 9.3 Hz, 1 H), 4.33 (dt, $J$ = 10.0, 7.7 Hz, 1 H), 1.56 (d, $J$ = 7.7 Hz, 2 H), 0.83 (d, $J$ = 9.3 Hz, 2 H), 0.19 (s, 6 H) ppm.

## Acknowledgments

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

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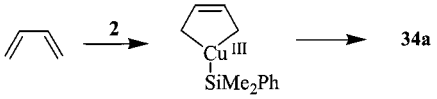


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Received June 13, 2002
[O02318]