Regioselective Catalytic Transformations Involving β-Silyl-Substituted (η³-Allyl)palladium Complexes: An Efficient Route to Functionalized Allylsilanes

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Various alkyl derivatives of 1-(trimethylsilanyl)but-3-en-2-ol acetate (**1a**−**e**) undergo regioselective palladium-catalyzed nucleophilic substitution via β-silyl-substituted (η³-allyl)palladium intermediates. With external nucleophiles, such as malonates and enolates, the nucleophilic substitution occurs with complete allylic rearrangement, providing functionalized allylsilanes as building blocks of high synthetic potential. Internal nucleophiles, such as disilanes and $NaBPh_4$, afford bisallylic disilanes and (allylsilyl)benzene derivatives with good regioselectivity. For both types of nucleophiles, the double bond geometry of the resulting allylsilane is selectively *trans*. The β-silyl-substituted (η³-allyl)palladium intermediates of the reaction were also isolated. The ^{1}H NMR studies indicate selective formation of the *syn*-isomer of the key (η³-allyl)palladium intermediates, which explains the high *trans*-selectivity of the double bond formation in the allylsilane products. According to the ^{13}C NMR studies, the β-silyl functionality exerts deshielding effects on the nearest allylic terminal carbon (C3), which can be ascribed to hyperconjugative interactions between the silyl functionality and the allylpalladium moiety. It was concluded that, together with the steric effects of the silyl group, these electronic interactions are responsible for the high regioselectivity of the nucleophilic attack in the catalytic process.

Introduction

Functionalized allylsilanes have proven to be an exceedingly useful class of organometallic reagents, and they continue to show enormous potential in regio- and stereocontrolled C−C bond formation reactions.[1,2] Accordingly, allylsilanes provide building blocks of unprecedented synthetic potential, which are also frequently used precursors in natural product synthesis.[3−8] Although many excellent ways of making allylsilanes are already known,[9−11] the great importance of allylsilane chemistry for organic synthesis urged a continuing search for new methods for efficient regio- and stereocontrolled preparation of functionalized allylsilanes.

Allylpalladium chemistry has been successfully used for the preparation of allylsilanes.[11−14] Usually the key step in the palladium-catalyzed synthesis of allylsilanes is the nucleophilic attack of the silylating reagent on the (η³-allyl)palladium intermediate of the reaction.[12−14] Alternatively, the catalytic process can be started from an appropriate silyl precursor, which undergoes oxidative addition to Pd(0), providing a β-silyl-substituted (η³-allyl)-palladium intermediate (Scheme 1). Subsequently, this intermediate is attacked by the nucleophile, to give a functionalized allylic silane. The main advantage of this latter method is the employment of the electronic and steric effects of the β-silyl functionality to control the regiochemistry of the nucleophilic attack on the (η³-allyl)-palladium intermediate.

However, there are few methods available on catalytic allylations proceeding through β-silyl-substituted (η³-allyl)palladium intermediates. Apart from our studies[15] on the alkylation of 2-acetoxy-5-(dimethylphenylsilanyl)-cyclohexene, we have only found one example in the literature of this type of catalytic procedure involving a single reaction of 1-(trimethylsilanyl)but-3-en-2-ol acetate (**1a**) with the sodium malonate nucleophile.[16] Besides, in these previously conducted studies only malonate nucleophiles were employed with just two different silyl substrates, and therefore, the synthetic scope of the palladium-catalyzed procedures proceeding through β-silyl-substituted (η³-allyl)palladium intermediates remained largely unexplored. Our recent results[15] on the structure, properties, and reactivity of β-silyl-substituted (η³-allyl)-palladium complexes indicated that the steric and electronic effects of the silyl group enhance the regio- and stereoselectivity of the nucleophilic attack, which prompted

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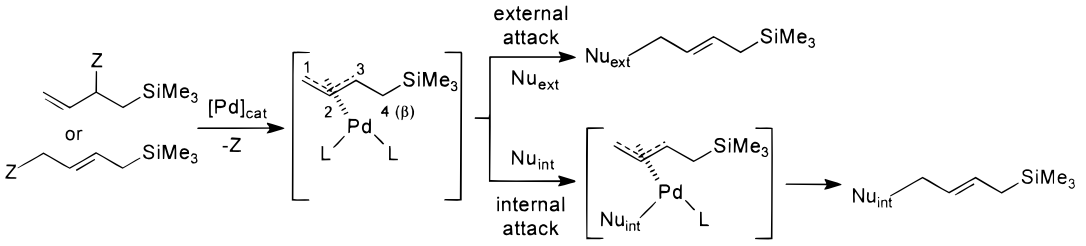
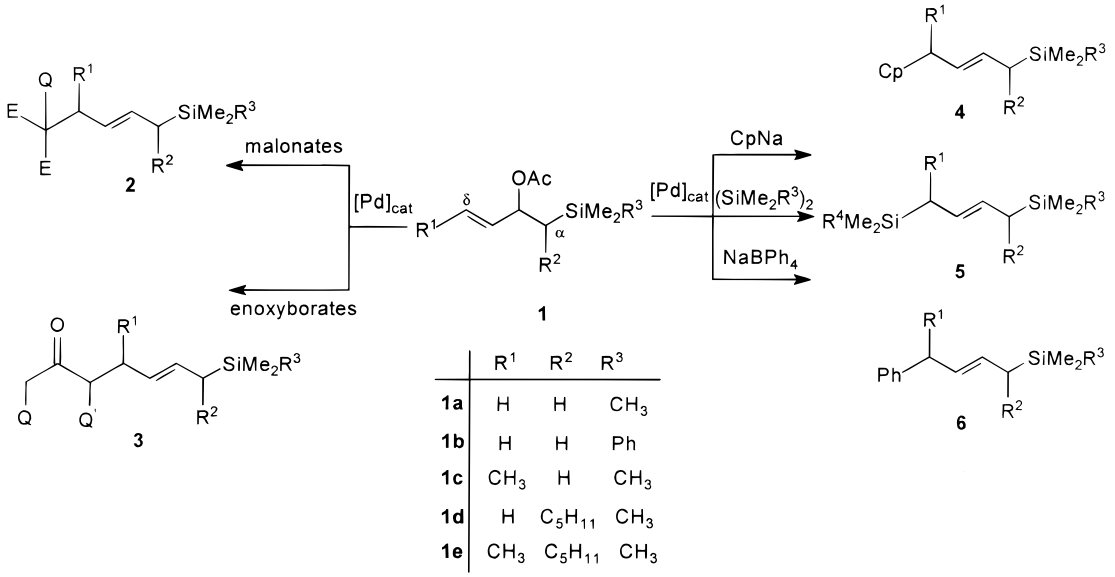
Scheme 1



Scheme 2



	R^1	R^2	R^3
1a	H	H	CH_3
1b	H	H	Ph
1c	CH_3	H	CH_3
1d	H	C_5H_{11}	CH_3
1e	CH_3	C_5H_{11}	CH_3

us to further explore the synthetic utility of the palladium-catalyzed allylic substitution reactions proceeding through this intermediate.

In this study we present our results on the reactivity of several different types of nucleophiles with **1a**−**e** in palladium-catalyzed allylic substitution reactions. In particular, we discuss the level of regioselectivity as a function of the direction of the nucleophilic attack (Scheme 1), as well as the influence of the substitution pattern of **1** on the rate of the catalytic substitution reaction. To gain greater insight into the mechanistic details, we prepared the β-silyl-substituted (η^3-allyl)-palladium key intermediates of the reaction and studied their properties and their reactivities.

Results and Discussion

The substrates of silylallylation reactions, **1a**−**e** (Scheme 2), could be easily obtained by simple literature procedures.[17,18] The precursors of **1a**−**e** (1-(trimethylsilanyl)-but-3-en-2-ol derivatives) are often used for the preparation of conjugated dienes since these silylbutenol derivatives easily undergo Peterson elimination[19] by loss of R_3SiOH. Indeed, when we attempted to replace the hydroxy group of the silylbutenol derivatives by better leaving groups, such as Cl, OCOOR, or $OCOCF_3$ functionalities, the Peterson type of elimination reactions were dominating. On the other hand, the silylbutenol derivatives could be acylated under mild conditions, giving **1a**−**e**, which are stable compounds under nonacidic conditions.

Usually palladium-catalyzed allylic substitution reactions of allylic acetates require a high reaction temperature or a relatively long reaction time[20] since the oxidative addition of allylic acetates to Pd(0) is relatively slow. However, **1a**−**e** undergo unusually facile oxidative addition to Pd(0) (vide supra), which enables one to employ mild reaction conditions in the silylallylation reactions. Using the literature procedures,[17,18] acetates **1d** and **1e** are obtained as 1:1 diastereomeric mixtures. When these compounds undergo allylic substitution reactions leading to diastereomeric allylsilanes, the ratio of the diastereomers in the products is usually the same as in the starting acetates.

Catalytic Allylic Substitution Reactions by External Nucleophiles. Palladium-catalyzed allylic substitution reactions of **1** (Scheme 2 and Table 1) by malonates, enoxyborates, and cyclopentadienyl-sodium proceed smoothly under mild reaction conditions, providing δ-functionalized allylsilanes in good yield. All reactions proceed with complete allylic rearrangement, and the double bond produced has exclusively a *trans* geometry.

Reactions with Malonate Nucleophiles (Entries 1−7). Diethyl malonate can be easily allylsilylated under mild conditions in THF at 45 °C. This reaction proceeds with very high selectivity and with a good yield for all alkyl-substituted derivatives of **1**. The reaction times depend on the substitution pattern of **1**, as well as on

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(18) Wilson, S. R.; Price, M. F. *J. Am. Chem. Soc.* **1982**, *104*, 1124.
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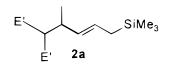
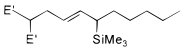
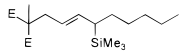
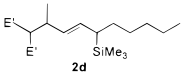
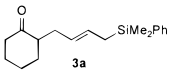
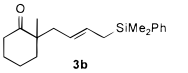
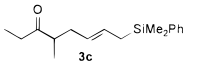
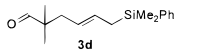
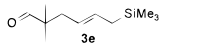
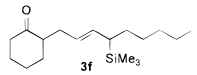
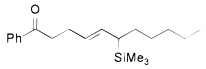
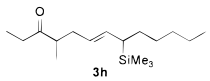
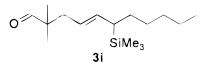
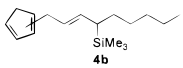
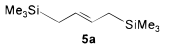
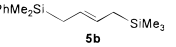
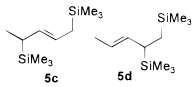
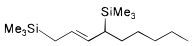
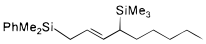
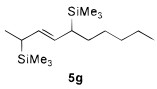
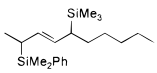
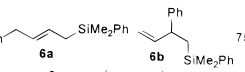
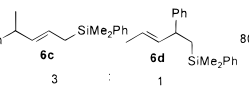
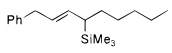
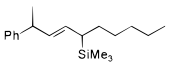
Table 1. Palladium-Catalyzed Allylic Substitution of 1a−e

Entry	Electrophile	Method[a]	Nucleophile	Conditions, °C/h	Product	Yield,[b] %
1	**1c**	A	 **7**	45/7	 **2a**	66
2	**1c**	B	**7**	45/1.1	**2a**	67
3	**1d**	A	**7**	45/2	 **2b**	58
4	**1d**	C	**7**	45/1	**2b**	57
5	**1d**	B	 **8**	45/1.5	 **2c**	68
6	**1e**	A	**7**	45/10	 **2d**	62
7	**1e**	C	**7**	45/2	**2d**	58
8	**1b**	A	 **9a**	25/0.5	 **3a**	75
9	**1b**	A	 **9b**	25/0.5	 **3b**	80
10	**1b**	A	 **10a**	0/0.5	 **3c**	61
11	**1b**	A	 **11**	0/0.5	 **3d**	75
12	**1a**	A	**11**	0/0.5	 **3e**	89
13	**1d**	A	**9a**	0/0.5	 **3f**	58
14	**1d**	A	 **10b**	0/0.5	 **3g**	77
15	**1d**	A	**10a**	0/0.5	 **3h**	62
16	**1d**	A	**11**	0/0.5	 **3i**	88
17	**1b**	C	 **12**	25/2	**4a**	60[c]
18	**1d**	C	**12**	25/2	 **4b**	63[c]
19	**1a**	E	$Me_3SiSiMe_3$ **13a**	30/17	 **5a**	70
20	**1a**	E	$PhMe_2SiSiMe_2Ph$ **13b**	30/17	 **5b**	75
21	**1a**	D	**13b**	30/17	**5b**	88
22	**1c**	D	**13a**	30/17	 **5c** **5d** 4 : 1	78
23	**1d**	E	**13a**	30/17	 **5e**	75
24	**1d**	E	**13b**	30/17	 **5f**	73
25	**1e**	D	**13a**	30/17	 **5g**	62
26	**1e**	D	**13b**	30/17	 **5h**	37
27	**1b**	F	$NaBPh_4$ **14**	60/3	 **6a** **6b** 6 : 1	75
28	**1c**	F	**14**	60/3	 **6c** **6d** 3 : 1	80
29	**1d**	F	**14**	60/3	 **6e**	81
30	**1e**	F	**14**	60/3	 **6f**	53

[a] Unless otherwise stated 5 mol % palladium catalyst was used in THF. Method A, $Pd(PPh_3)_4$; B, $Pd(dba)_2$, dppe, 1:1; C, $Pd(dba)_2$, $P(OMe)_3$, 1:1; D, **17**, MAH, 1:3 in CH_2Cl_2; E, $Pd(OAc)_2$, MAH, 1:3 in CH_2Cl_2; F, 2 mol % $Pd(dba)_2$, $Pd(PPh_3)_4$, 1:2. For details see the Experimental Section. [b] Isolated yield. [c] 1- and 2-cyclopentadienyl isomers form in a ratio of 1:1.

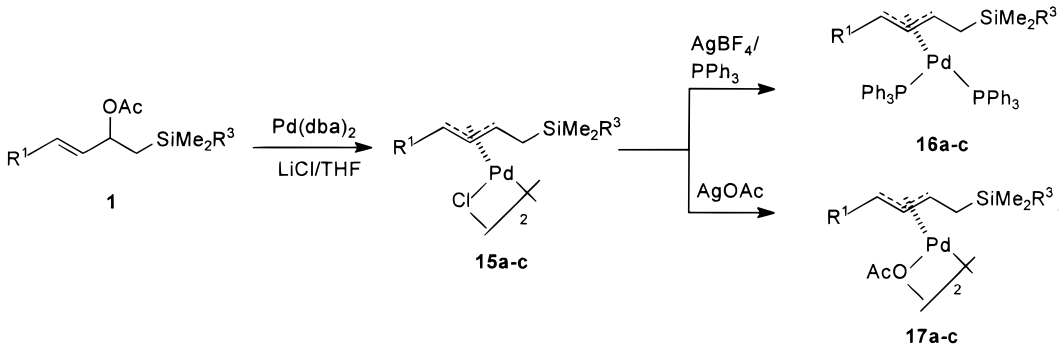
the applied ancillary ligand. The catalytic reactions are complete in 1−2 h for **1c** and **1e**; however, a longer reaction time is required when the attacked carbon bears an alkyl substituent ($R^1 = CH_3$). It was also found that the alkylation reaction proceeds faster in the presence of $P(OCH_3)_3$ and dppe ligands than with a PPh_3 ligand.

Enoxyborates as Nucleophiles (Entries 8−16). Enoxyborates were introduced by Negishi and coworkers[21−23] as versatile enolate type nucleophiles in allylpalladium chemistry. Enoxyborate reagents are easily obtained by treating potassium enolates with trialkylboranes, such as triethylborane. These reagents are particularly useful for the preparation of keto- and formyl-functionalized allylsilanes from **1**. The silylallylation process is remarkably fast for substrates that are unsubstituted at the δ-carbon ($R^1 = H$). The presence of an alkyl group at the α-position ($R^2 = C_5H_{11}$) does not influence the rate of alkylation. Allylic substitution of **1a**, **1b**, and **1d** with enoxyborates is usually complete in 30 min at 0 °C. It is interesting to note that the typical reaction conditions for palladium-catalyzed alkylation of enoxyborates usually involve stirring for 12 h at ambient temperature.[22] The alkylation of enoxyborates failed for allylic acetates **1c** and **1e** bearing an alkyl substituent at the δ-position ($R^1 = CH_3$). Under the applied alkylation conditions, **1c** and **1e** undergo AcOH elimination, giving silyl-substituted 1,3-pentadienes.

Silylallylation of Cyclopentadiene (Entries 17 and 18). We have briefly investigated the application of cyclopentadienyl-sodium as a nucleophile[24] in palladium-

(21) Negishi, E.-i.; Matsushita, H.; Chatterjee, S.; John, R. A. *J. Org. Chem.* **1982**, *47*, 3188.
(22) Negishi, E.-i.; Luo, F.-T. *J. Org. Chem.* **1983**, *48*, 2427.
(23) Negishi, E.-i.; John, R. A. *J. Org. Chem.* **1983**, *48*, 4098.
(24) Fiaud, J. C.; Malleron, J. L. *Tetrahedron Lett.* **1980**, *21*, 4437.

Scheme 3



catalyzed allylic substitution of **1b** and **1d**. The rate of alkylation is rather high at rt, and a good yield of the cyclopentadienyl products **4a** and **4b** is obtained when the δ-carbon is unsubstituted. However, the yield is poor when **1c** is used as a substrate due to the extensive formation of trimethylpenta-1,3-dienylsilane. Although the regioselectivity and *trans*-selectivity of the catalytic reaction are excellent, the 1- and 2-cyclopentadienyl isomers form in a ratio of 1:1.

Catalytic Allylic Substitution Reactions by Internal Nucleophiles. Palladium-catalyzed allylic substitution reactions of allylic acetates with disilanes **13a,b** and $NaBPh_4$ (**14**) involve coordination of the nucleophile to palladium followed by *cis* attack on the allyl moiety (see Scheme 1).[12,25] Reagents **13** and **14** react with **1** in a relatively good yield, leading to the *E*-isomers of **5** and **6**; however, the regioselectivity is usually lower than with external nucleophiles.

Reactions with Disilanes 13a,b (Entries 19−26). Bisallylic disilanes could be obtained from **1a**−**e** under mild conditions using a modified version of the palladium-catalyzed silylation procedure by Tsuji and coworkers.[12] According to the original procedure[12] allylic acetates are reacted with disilanes **13a,b** in the presence of CF_3COOH at ambient temperature or in the presence of LiCl at 100 °C. However, these harsh reaction conditions are not suitable for the preparation of **5**. A further problem is that phosphine ligands cannot be used in the silylation reaction (vide supra), and in the absence of PPh_3 or other π-acceptor ligands, amorphous Pd(0) is precipitated after a couple of catalytic cycles. However, we have found that the catalytic activity of Pd(0) can be maintained when the reaction is conducted under neutral conditions at 30 °C in CH_2Cl_2 in the presence of maleic anhydride (MAH).[26] Relatively good yields can be obtained with $Pd(OAc)_2$ as the catalyst; however, the yields are improved when $Pd(OAc)_2$ is replaced by a catalytic amount of the allylpalladium intermediates of the reaction. A complete control of the regioselectivity can be achieved for substrates **1a**, **1d**, and **1e**; however, a considerable amount (20%) of 1,2-isomer is formed when **1c** is applied as substrate.

Phenylation with $NaBPh_4$ (Entries 27−30). Allylic acetates undergo a substitution reaction with $NaBPh_4$ (**14**) in the presence of a catalytic amount of $Pd(PPh_3)_4$, providing allylbenzene derivatives with rather poor regioselectivity.[27] However, for certain substrates, when a β-silyl functionality is present in the intermediary (η^3-allyl)palladium complex, useful levels of the regioselectivity can be achieved. Thus, palladium-catalyzed phenylation of **1d** and **1e** with $NaBPh_4$ gives only δ-substituted products **6e** and **6f**. The level of the regioselectivity is still acceptable for phenylation of **1b** (**6a**:**6b** = 6:1); however, the regioselectivity is poor when **1c** is employed as a substrate. The phenylation reaction required a higher temperature (60 °C) than the other allylic substitution reactions of **1** because of the sluggish phenyl transfer in the presence of the PPh_3 ligand (vide supra).

Structure and Properties of the (η^3-Allyl)palladium Intermediates. Compounds **1a**, **1b**, and **1c** react smoothly with $Pd(dba)_2$ in the presence of LiCl at room temperature, giving allylpalladium complexes **15a**−**c** (Scheme 3). A complete conversion could be achieved in 2 h without desilylation of the allylic acetates or the products. At room temperature the rate of addition is much faster than the oxidative addition of other allylic acetates without a silyl functionality.[20] Since the oxidative addition could be carried out without desilylation, the driving force of the reaction is apparently the formation of an exceptionally stable (η^3-allyl)palladium complex.

Air-stable complexes **15a**−**c** could easily be purified by chromatography. The chloride ligand of **15a**−**c** could be exchanged to PPh_3 (**16a**−**c**) and OAc (**17a**−**c**) ligands, generating the active intermediates of the external (entries 1−18) and the internal (entries 19−30) nucleophilic attacks, respectively. The phosphine and acetate complexes are fairly stable at room temperature or at a slightly elevated temperature (up to 40−50 °C), but decompose when the solvent is evaporated.

The ^1H NMR spectrum of **15a**−**c** shows that only a single isomer is formed in the oxidative addition process. The relatively large $^3J_{H2-H3}$ coupling constant (11.2 Hz) indicates the selective formation of the *syn*-isomers. Exchange of the chloride ligand to phosphine does not change the configuration of the complex. The high configurational stability of **15a**−**c** and **16a**−**c** explains the excellent *trans*-selectivity of the double bond formation. The ^{13}C NMR spectra of **15** and **16** show some interesting features. Comparison of the ^{13}C NMR shifts of the allylic terminal carbons in **18**[28] and **15a,b** reveals the perturbation effects of the $SiMe_2R^3$ group on the electronic structure of the allylic moiety (Figure 1). The chemical shift difference between the terminal carbons ($\Delta\delta_t$) increases in the presence of the silyl substituent.

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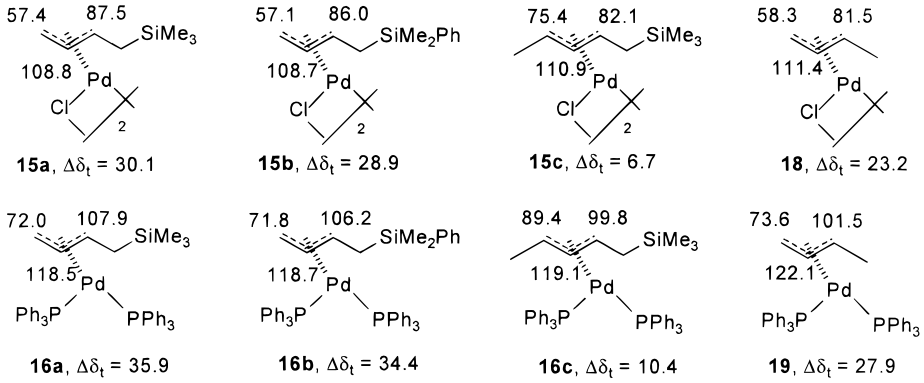


Figure 1. ^{13}C NMR shifts (ppm) in $CDCl_3$ of the allylic carbons. $\Delta\delta_t$ denotes the chemical shift differences between C3 and C1 ($\Delta\delta_t = \delta C3 - \delta C1$).

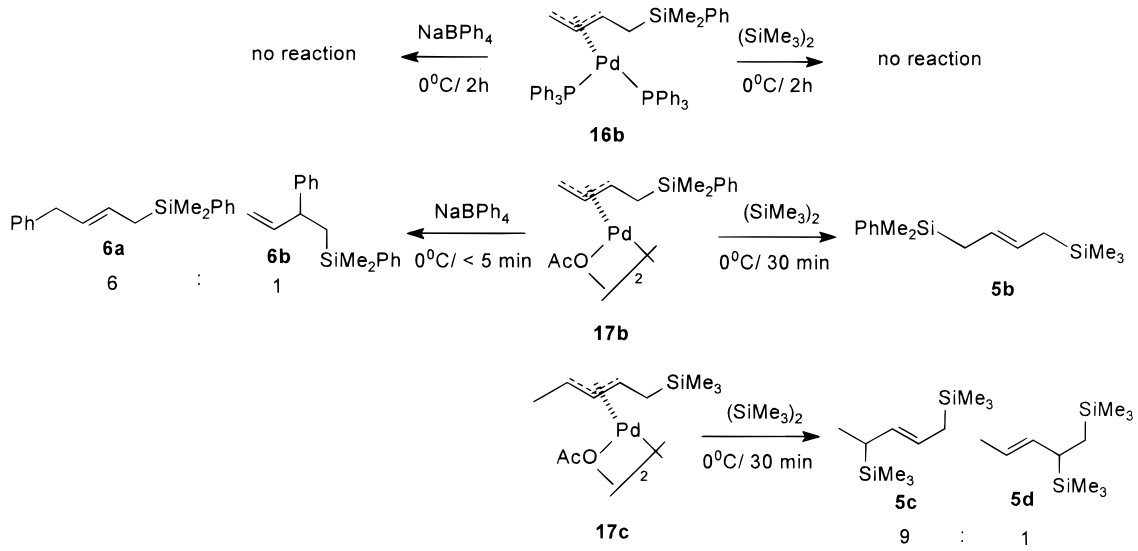
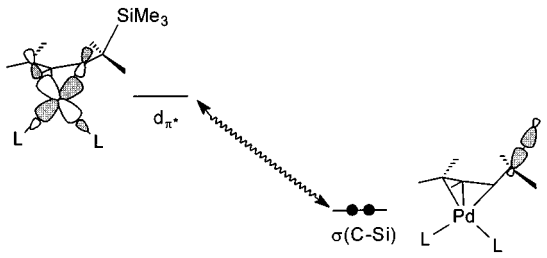


Figure 2. Reactivity of (η^3-allyl)palladium complexes **16b** and **17b,c** toward nucleophiles **13a** and **14**.

Furthermore, the chemical shift of the allylic terminus closer to the silyl functionality (C3) in **15a,b** is observed at a lower field than the corresponding ^{13}C shift in **18**, indicating a deshielding effect of the β-$SiMe_2R^3$ group on the C3 allylic position. The asymmetrizing effect of the silyl substituent on the electronic structure of the allylic moiety is also reflected by the ^{13}C shifts of **15c**. The presence of the silyl functionality leads to a difference of 6.7 ppm in the C_t shift values, and the closer allylic terminus (C3) is less shielded than the remote one. The same trend applies to the phosphine complexes. The $\Delta\delta_t$ values of **16a,b** and **19**[28] differ even more than the corresponding values in the chloro complexes **15a,b** and **18**. Similarly, the perturbation effects of the silyl functionality on the allylic terminal carbons are stronger in the phosphine complex **16c** ($\Delta\delta_t = 10.4$ ppm) than in the chloro complex **15c** ($\Delta\delta_t = 6.7$ ppm). There is a small but significant difference between the electronic effects of the $SiMe_3$ and $SiMe_2Ph$ functionalities. Since the Ph group is more electron withdrawing than the methyl group, replacement of a $SiMe_3$ with a $SiMe_2Ph$ functionality is expected to lead to some deshielding effect at C3. On the contrary, in the presence of the $SiMe_3$ (**15a** and **16a**) group, δ(C3) is larger by 1.5−1.7 ppm than for the $SiMe_2$-Ph functionality, indicating that the electronic interactions between the silyl functionality and allylpalladium moiety cannot simply be explained on the basis of inductive effects. The above differences in the ^{13}C chemical shift values are also in line with our recent observations[15] on the β-effects of the silyl group occurring in stereodefined cyclic (η^3-allyl)palladium complexes.

Nucleophilic Attack on β-Silyl Substituted (η^3-Allyl)palladium Complexes. The reactivity of **16a−c** and **17a−c** was studied with both external and internal nucleophiles. The outcome of the reaction of **16a−c** with malonates is the same as in the corresponding catalytic processes. However, the reaction of the allylpalladium complexes with **13** and **14** revealed some interesting mechanistic features. When **1b** is reacted with **14**, Pd-$(PPh_3)_4$ is used as the catalyst, suggesting that the key intermediate of the reaction would be the phosphine complex **16b**. However, complex **16b** does not react with $NaBPh_4$ at 0 °C or ambient temperature. On the other hand, the acetate complex **17b** reacts immediately with $NaBPh_4$ at 0 °C, giving **6a** and **6b** (Figure 2). Since, **17b** is supposed to be the primary product of the oxidative addition of **1b** to palladium, it is assumed that the key intermediate of the phenylation process is the acetate complex, while formation of **16b** inhibits the catalytic cycle. The most probable explanation for the inhibitory effect of PPh_3 is that phosphine ligands coordinate too strongly to Pd, and accordingly, the phenyl transfer from BPh_4^- to palladium is hindered. The high reaction temperature (60 °C) employed in the catalytic reactions is required because of this inhibitory effect of the PPh_3 ligand. On the other hand, the PPh_3 ligand is required

Scheme 4



to maintain the catalytic cycle by complexing Pd(0) formed in the reductive elimination step.

Phosphine ligands also inhibit the nucleophilic attack by disilanes **13**. Phosphine complexes **16a**−**c** do not undergo silylation with **13a,b**, probably because the silyl coordination is also hindered in the presence of a PPh_3 ligand (Figure 2). On the other hand, disilanes **13** react readily with the acetate complexes **17a**−**c**. However, a complete conversion of **17a**−**c** with **13** requires at least 0.5 h at 0 °C. This indicates that acetate complexes react considerably more slowly with disilanes than with the $NaBPh_4$ reagent. The regioisomer ratio in the stoichiometric reaction of **17c** with hexamethyldisilane (**13a**) is 9:1 (**5c**:**5d**), which is better than the isomer ratio (4:1) in the corresponding catalytic process (entry 22). It seems that the low reaction temperature (0 °C) considerably improves the isomer ratio of the internal attack with preference to the C1 attack of the (η^3-allyl)palladium intermediate. On the other hand, the catalytic silylation and phenylation reactions proceed slowly at 0 °C, and at low temperature, the starting material **1** cannot be completely converted to the corresponding products. The chloro complexes **15a**−**c** also react with **13a**; however, the reaction is very slow at ambient or slightly elevated temperatures. For example, the reaction of **15c** with **13a** could not be completed within 24 h at 30 °C. Chloride is also a strongly coordinating ligand, and probably, the silyl coordination is hindered in the presence of chloride ligands.

Regioselectivity of the Nucleophilic Attack. Apparently, the steric effects of the silyl functionality are important factors for the regiochemical outcome of the external nucleophilic attack. However, the ^{13}C NMR studies (Figure 1) and the previous theoretical studies[15] have shown that the silyl functionality has considerable electronic effects on the allylic moiety. It is well established that σ(C−Si) orbitals readily conjugate with low-lying unfilled π-levels.[29,30] The interactions between σ(C−Si) and the p_π-orbital of carbocations form the basis of the well-known β-silicon effect.[29,30] The effects of β-silicon substituents in (η^3-allyl)palladium complexes can also be ascribed to the electronic interactions between the unfilled LUMO of the allylpalladium fragment (d_{π^*}) and the high-lying σ(C−Si) orbital (Scheme 4). Delocalization of electrons from the bonding σ(C−Si) orbital leads to weakening of the C−Si bond. Since the d_{π^*} is Pd−C_t antibonding, the allylpalladium bonding is also weakened. The σ(C−Si) orbital directly overlaps with the π-lobe of C3, and accordingly, the Pd−C3 bonding is weakened to a larger extent than the Pd−C1 bonding (see also ref 15). Systematic changes in the $\delta(C_t)$ values (Figure 1) can also be ascribed to this effect. As the palladium atom has a considerable shielding effect on the allylic carbons,[31] partial deshielding of C3 arising from the presence of the β-silyl substituent is indicative of weakening of the Pd−C3 interactions. Accordingly, variation of the ^{13}C NMR shifts in **15** and **16** indicates significant hyperconjugative interactions between the C−Si bond and the allylmetal π-system.

The regioselectivity of the nucleophilic attack is influenced by three important effects arising from the hyperconjugative interactions:

(1) The hyperconjugation is extended to the C1−C4 fragment and the silicon atom (Scheme 4). A nucleophilic attack at the C3 position would interrupt this conjugation, so the C1 terminus is preferentially attacked. Besides, the π-lobe in the LUMO at C3 is partially occupied because of the interaction with the filled σ(C−Si) MO, which effectively hinders the charge transfer from the lone pair of an attacking nucleophile.

(2) For an external attack (entries 1−18), the steric effects of the bulky silyl group also facilitate the nucleophilic attack at the C1 position of the allyl. Previously conducted theoretical studies have shown[15] that the hyperconjugative interactions stabilize such conformations where the silyl group is *trans* to palladium and the C−Si bond is perpendicular to the plane of the allyl moiety (Scheme 4). Accordingly, the electronic interactions restrict the conformation of the silyl functionality so that the steric effects of $SiMe_2R$[3] can direct the external nucleophiles to the less substituted allylic position most effectively.

(3) The nucleophilic attack on the allyl moiety involves Pd−C bond breaking,[32] which is easier for the Pd−C3 bond weakened by the hyperconjugative interactions. However, this interaction would facilitate the 1,2-attack of the nucleophile to a greater extent.

The electronic (1) and the steric (2) effects work in the same direction for an external nucleophilic attack on the (η^3-allyl)palladium intermediates. However, for an internal attack, the steric effect of the β-silyl substituent does not influence the regioselectivity, and the subtle balance between the opposing effects (1 and 3) determines the level of the regioselectivity. Apart from entry 22, the silylation reactions provide useful levels of regioselectivity. However, phenylation by $NaBPh_4$ requires the presence of a bulky alkyl group at the α-position to proceed with high regioselectivity (entries 29 and 30). The stoichiometric reaction (Figure 2) between **17b** and $NaBPh_4$ suggests that the internal attack is very fast and the coordination of Ph to palladium leads to immediate *cis*-migration. However, the silyl migration is considerably slower than the phenyl migration process. Thus, before the *cis*-migration takes place, the various silyl-coordinated (η^3-allyl)palladium complexes can equilibrate to a greater extent than the phenyl coordinated ones, inducing a more selective nucleophilic attack in the silylation process. Furthermore, the stoichiometric reaction of **17c** with **13a** (Figure 2) at low temperature (0 °C) proceeds slower but with higher regioselectivity than the corresponding catalytic reactions at 30 °C, which also indicates that a slow *cis*-migration process involves larger dif-

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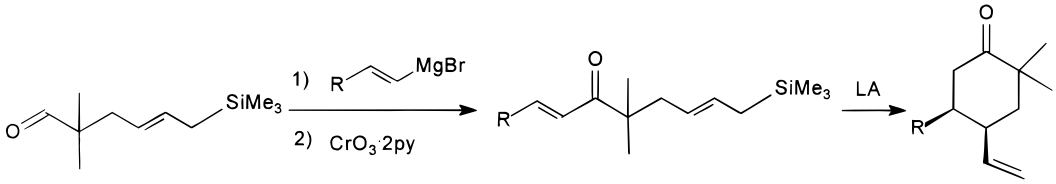
Scheme 5



	R	yield (%)
21a	H	72
21b	CH_3	65

ferentiation between the C1 and C3 carbons of the (η^3-allyl)palladium intermediates.

Synthetic Utility of Functionalized Allylsilanes 2−6. Products of the above silylallylation reactions are useful building blocks of high synthetic potential. Cyclopentadienyl derivatives **4a,b** can be used for the preparation of new types of cyclopentadienyl ligands to modulate the structure and reactivity of different transition metal based metallocenes.[33] Bisallylic disilanes **5a−h** are useful precursors for the preparation of regio- and stereodefined homoallylic silanes.[34] Our method can also be used for the preparation of bisallylic silanes with different silyl groups (entries 20, 24, and 26). Because of the different reactivity[1] of the $SiMe_3$ and $SiMe_2Ph$ functionalities, these silyl groups can be selectively functionalized. (Allylsilyl)benzene derivatives are often used as synthetic intermediates,[9] and the above method offers a simple access to some new derivatives.

Allylsilanes functionalized by keto, formyl, and carboxy groups are particularly important synthetic intermediates,[18,35−39] which are frequently used as precursors in natural product synthesis. Accordingly, among the difunctional allylsilanes obtained using the above technology (Scheme 2), **2** and **3** are certainly the most useful synthetic precursors. These compounds possess a carbonyl functionality, which can be converted by both nucleophilic and reductive reagents without affecting the silyl functionality. On the other hand, the allylsilyl functionality can be transformed by electrophiles without affecting the carbonyl group. Furthermore, these compounds can also be valuable precursors for the preparation of stereodefined isocyclic compounds and sesquiterpene analogues.[18,39] This can be illustrated by the synthesis sequence shown in Scheme 5. Aldehyde **3e** is converted to **20a,b** by a Grignard reaction followed by oxidation. When **20a,b** are treated with Lewis acids, an intramolecular Hosomi−Sakurai reaction[40] takes place, affording isocyclic compounds **21a,b**. When R = CH_3, the intramolecular cyclization of **20** provides selectively the *cis*-derivative **21b**. The mechanism of this stereoselective Hosomi−Sakurai cyclization of **20b** is currently under investigation.

Conclusions

In this study we have shown that palladium-catalyzed allylic substitution involving β-substituted (η^3-allyl)-palladium intermediates is a versatile method for the preparation of functionalized allylsilanes. An excellent regioselectivity was obtained when external nucleophiles, such as malonates and enoxyborates, were employed. Still useful levels of regiochemistry can be achieved using internal nucleophiles such as disilanes and $NaBPh_4$. For both types of nucleophiles, the double bond geometry in the resulting allylsilane is selectively *trans*. NMR studies of the key intermediates **15** and **16** revealed that hyperconjugative interactions occur between the β-silyl substituent and the allylpalladium moiety, and that these interactions are also dependent on the electronic effects of the ancillary ligand employed. It was concluded that these electronic effects enhance the regioselectivity of the nucleophilic attack on the (η^3-allyl)palladium intermediates of the catalytic reactions.

Experimental Section

The starting materials were purchased from Aldrich or Lancaster. All solvents were freshly distilled prior to use. All the reactions were conducted under an argon atmosphere by employing standard manifold techniques. All ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions at 300 and 75 MHz, respectively. The chemicals shifts (ppm) are obtained using $CDCl_3$ as internal standard (7.26 ppm, ^1H; 77.0 ppm, ^{13}C). For chromatography Merck silica gel 60 (230−400 mesh) was used.

General Procedure for Catalytic Alkylation with Sodium Malonates (Entries 1−7). Method A. Dialkyl malonate (1.92 mmol) in THF (2.6 mL) was slowly added to a slurry of NaH (1.47 mmol, 0.059 g, 60% suspension in mineral oil) in THF (2.6 mL). After the resulting clear solution was transferred via cannula to a mixture of acetate **1** (0.37 mmol) and $Pd(PPh_3)_4$ (0.018 mmol, 5 mol %, 0.021 g) in THF (0.9 mL), the combined mixture was stirred for the temperatures and times listed in Table 1. After the reaction was complete, the reaction mixture was diluted by ether (30 mL), filtered through Celite, followed by extraction with saturated NH_4Cl solution and brine, and dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo and purification of the residual yellow oil by chromatography (pentane−ether, 9:1) gave the product as a colorless oil.

Method B. $Pd(dba)_2$ (0.018 mmol, 5 mol %, 0.011 g) and dppe (0.018 mmol, 0.007 g) were used as the catalyst.

Method C. $Pd(dba)_2$ (0.018 mmol, 5 mol %, 0.011 g) and $P(OMe)_3$ (0.04 mmol, 0.005 g) were employed as the catalysts. Otherwise the method was the same as method A.

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(*E*)-2-(5-(Trimethylsilanyl)pent-3-en-2-yl)malonic Acid Diethyl Ester (2a). ^{1}H NMR: δ 5.48 (m, 1H), 5.17 (m, 1H), 4.15 (m, 4H), 3.20 (d, J = 9.1 Hz, 1H), 2.88 (m, 1H), 1.39 (dd, J = 8.1 and 1.1 Hz, 2H), 1.23 (m, 6H), 1.05 (d, J = 6.7 Hz, 3H), −0.04 (s, 9H). ^{13}C NMR: δ 168.7, 168.6, 130.1, 128.0, 61.5, 61.4, 58.9, 37.9, 23.1, 19.4, 14.6, −1.6. Anal. Calcd for $C_{15}H_{28}O_4Si$: C, 59.96; H, 9.39. Found: C, 59.96; H, 9.50.

(*E*)-2-(4-(Trimethylsilanyl)non-2-enyl)malonic Acid Diethyl Ester (2b). ^{1}H NMR: δ 5.33 (m, 1H), 5.15 (m, 1H), 4.18 (m, 4H), 3.35 (t, J = 7.6 Hz, 1H), 2.60 (dt, J = 7.7 and 0.9 Hz, 2H), 1.39 (m, 1H), 1.26 (t, J = 6.9 Hz, 6H), 1.22 (br m, 8H), 0.87 (t, J = 6.6 Hz, 3H), −0.07 (s, 9H). ^{13}C NMR: δ 169.5, 135.8, 123.2, 61.6, 53.2, 33.5, 32.5, 32.1, 29.3, 29.0, 23.3, 14.5, 14.4, −2.9. Anal. Calcd for $C_{19}H_{36}O_4Si$: C, 64.00; H, 10.17. Found: C, 64.04; H, 10.26.

(*E*)-2-Methyl-2-(4-(trimethylsilanyl)non-2-enyl)malonic Acid Dimethyl Ester (2c). ^{1}H NMR: δ 5.31 (m, 1H), 5.07 (m, 1H), 3.71 (s, 6H), 2.59 (dd, J=7.5 and 0.8 Hz, 2H), 1.39 (s, 3H), 1.25 (br m, 9H), 0.87 (m, 3H), −0.05 (s, 9H). ^{13}C NMR: δ 173.0, 137.6, 121.3, 54.3, 52.8, 39.7, 33.7, 32.0, 29.4, 29.0, 22.9, 20.1, 14.5, −2.9. Anal. Calcd for $C_{18}H_{34}O_4Si$: C, 63.11; H, 10.00. Found: C, 63.20; H, 10.14.

(*E*)-2-(5-(Trimethylsilanyl)dec-3-en-2-yl)malonic Acid Diethyl Ester (2d). Formed as a 1:1 mixture of diastereomers from a 1:1 diastereomeric mixture of **1e**. ^{1}H NMR: δ 5.26 (m, 1H), 5.07 (m, 1H), 4.16 (m, 4H), 3.23 (t, J = 7.5 Hz, 1H), 2.90 (m, 1H), 1.4−1.1 (br m, 15H), 1.06 (dd, J = 6.6 and 1.8 Hz, 3H), 0.87 (t, J = 6.6 Hz, 3H), −0.06 (s, 9H). ^{13}C NMR: δ 168.9, 168.7, 133.7, 133.4, 129.5, 129.4, 61.5, 61.4, 59.0, 58.8, 38.0, 37.8, 33.5, 33.2, 32.1, 32.0, 29.4, 29.2, 29.1, 28.9, 22.9, 19.6, 19.4, 14.5, −2.9. Anal. Calcd for $C_{20}H_{38}O_4Si$: C, 64.82; H, 10.33. Found: C, 64.76; H, 10.46.

General Procedure for Catalytic Alkylation with Enoxyborates (Entries 8−16). The corresponding ketone (1.84 mmol) in THF (0.9 mL) was slowly added to a slurry of KH (1.68 mmol, 0.225 g, 30% suspension in mineral oil) in THF (0.8 mL) at 0 °C and stirred at rt until the gas evaluation had finished. Triethylborane (1.84 mmol, 1.84 mL, 1 M solution in THF) was slowly added to the suspension of potassium enolate formed, and the mixture was stirred for a further 5 min. The resulting clear, pale yellow solution was transferred via cannula to the THF (1.5 mL) solution of acetate **1** (0.51 mmol) and $Pd(PPh_3)_4$ (0.026 mmol, 5 mol %, 0.031 g) and then stirred for the temperatures and times given in Table 1. After the reaction mixture was diluted by ether (30 mL), it was extracted with saturated NH_4Cl solution and brine, followed by drying over anhydrous $MgSO_4$. Subsequently, the solvent was removed, and the residual yellow oil was purified by chromatography.

(*E*)-2-(4′-(Dimethylphenylsilyl)but-2′-enyl)cyclohexanone (3a). ^{1}H NMR: δ 7.49 (m, 2H), 7.34 (m, 3H), 5.39 (m, 1H), 5.20 (m, 1H), 2.52−2.14 (br m, 4H), 2.08−1.96 (m, 3H), 1.90 (m, 1H), 1.82 (m, 1H), 1.66 (d, J = 7.7 Hz, 2H), 1.74−1.52 (br m, 2H), 1.37−1.22 (m, 1H), 0.27 (s, 6H). ^{13}C NMR: δ 213.3, 139.2, 133.9, 129.2, 128.0, 127.8, 127.1, 51.4, 42.3, 33.5, 33.1, 28.3, 25.2, 22.2, −2.9. Anal. Calcd for $C_{18}H_{26}OSi$: C, 75.46; H, 9.15. Found: C, 75.29; H, 9.40.

(*E*)-2-Methyl-2-(4′-(dimethylphenylsilyl)but-2′-enyl)-cyclohexanone (3b). ^{1}H NMR: δ 7.49 (m, 2H), 7.34 (m, 3H), 5.39 (m, 1H), 5.14 (m, 1H), 2.47−2.01 (br m, 4H), 1.90−1.56 (m, 1H), 1.67 (d, J = 7.8 Hz, 2H), 1.54−1.38 (br m, 2H, H5), 1.37−1.22 (m, 1H), 0.99 (s, 3H), 0.26 (s, 6H). ^{13}C NMR: δ 216.0, 133.9, 129.3, 128.1, 129.6, 124.2, 41.1, 39.2, 38.8, 27.7, 23.0, 22.3, 21.4, −3.0. Anal. Calcd for $C_{19}H_{28}OSi$: C, 75.94; H, 9.39. Found: C, 75.71; H, 9.56.

(*E*)-4-Methyl-8-(dimethylphenylsilyl)oct-6-en-3-one (3c). ^{1}H NMR: δ 7.49 (m, 2H), 7.34 (m, 3H), 5.40 (m, 1H), 5.15 (m, 1H), 2.49 (m, 1H), 2.40 (dq, J = 7.5 and 3.3 Hz, 2H), 2.29 (m, 3H,), 2.01 (m, 1H), 1.65 (d, J = 7.8 Hz, 2H), 1.02 (t, J = 7.1 Hz, 3H), 1.01 (d, J = 6.9 Hz, 3H), 0.26 (s, 6H). ^{13}C NMR: δ 215.1, 139.1, 133.9, 129.3, 128.1, 128.5, 126.6, 46.2, 36.7, 34.7, 22.1, 16.4, 8.0, −3.1. Anal. Calcd for $C_{17}H_{26}OSi$: C, 74.39; H, 9.55. Found: C, 74.06; H, 9.68.

(*E*)-2,2-Dimethyl-6-(dimethylphenylsilyl)hex-4-enal (3d). ^{1}H NMR: δ 9.42 (s, 1H), 7.49 (m, 2H), 7.35 (m, 3H), 5.42 (m, 1H), 5.16 (m, 1H), 2.12 (d, J = 7.5 Hz, 2H), 1.68 (d, J = 7.8 Hz, 2H), 0.98 (s, 6H), 0.27 (s, 6H). ^{13}C NMR: δ 206.8, 139.0, 133.9, 129.3, 128.1, 130.3, 123.7, 46.4, 41.0, 22.3, 21.5, −3.0. Anal. Calcd for $C_{16}H_{24}OSi$: C, 73.79; H, 9.29. Found: C, 73.65; H, 9.47.

(*E*)-2,2-Dimethyl-6-(trimethylsilanyl)hex-4-enal (3e). ^{1}H NMR: δ 9.48 (s, 1H), 5.43 (m, 1H), 5.13 (m, 1H), 2.14 (d, J = 7.2 Hz, 2H), 1.43 (d, J = 7.8 Hz, 2H), 1.03 (s, 6H), −0.02 (s, 9H). ^{13}C NMR: δ 206.5, 130.8, 122.7, 46.6, 41.1, 23.4, 21.6, −1.4. Anal. Calcd for $C_{11}H_{21}OSi$: C, 66.94; H, 10.72. Found: C, 66.74; H, 10.91.

(*E*)-2-(4′-(Trimethylsilanyl)non-2′-enyl)cyclohexanone (3f). ^{1}H NMR: δ 5.18 (m, 2H), 2.54−2.20 (br m, 3H), 2.18−1.91 (br m, 4H), 1.89−1.78 (m, 1H), 1.76−1.54 (br m, 2H, H5), 1.48−1.06 (br m, 10H), 0.87 (t, J = 7.0 Hz, 3H), −0.06 (s, 9H). ^{13}C NMR: δ 213.3, 134.2, 125.5, 51.5, 42.3, 33.5, 33.4, 33.2, 28.3, 25.1, 23.0, 14.5, −2.8. HRMS (EI): *m*/*z* calcd for $C_{18}H_{34}OSi$ (M^+) 294.2379, found 294.2378.

(*E*)-6-(Trimethylsilanyl)-1-phenylundec-4-en-1-one (3g). ^{1}H NMR: δ 7.95 (m, 2H) 7.49 (m, 3H), 5.27 (m, 2H, H4), 3.01 (t, J = 7.8 Hz, 2H), 2.45 (m, 2H), 1.38 (m, 1H), 1.33−1.11 (m, 8H), 0.86 (t, J = 6.8 Hz, 3H), −0.07 (s, 9H). ^{13}C NMR: δ 200.3, 137.5, 133.2, 128.9, 128.4, 133.4, 126.4, 39.5, 33.4, 32.1, 29.4, 29.1, 28.1, 22.9, 14.5, −2.8. Anal. Calcd for $C_{20}H_{32}OSi$: C, 75.89; H, 10.19. Found: C, 75.74; H, 10.36.

(*E*)-4-Methyl-6-(trimethylsilanyl)tridec-6-en-3-one (3h). Formed as a 1:1 mixture of diastereomers from a diastereomeric mixture of **1d**. ^{1}H NMR: δ 5.21 (m, 1H), 5.10 (m, 1H), 2.54 (m, 1H), 2.44 (dq, J = 7.2 and 1.5 Hz, 2H), 2.32 (m, 3H), 2.03 (m, 1H), 1.42−1.32 (m, 1H), 1.30−1.08 (m, 8H), 1.04 (d, J = 7.0 Hz, 3H), 1.02 (t, J = 7.2 Hz, 3H), 0.86 (t, J = 6.8 Hz, 3H), −0.07 (s, 9H). ^{13}C NMR: δ 215.1, 134.7, 124.9, 47.0, 46.9, 37.0, 36.8, 34.8, 34.7, 33.5, 33.4, 32.1, 32.0, 29.4, 29.1, 22.9, 16.5, 16.4, 14.5, 8.0, −3.1. Anal. Calcd for $C_{17}H_{34}OSi$: C, 72.27; H, 12.13. Found: C, 72.10; H, 12.31.

(*E*)-2,2-Dimethyl-6-(trimethylsilanyl)undec-4-enal (3i). ^{1}H NMR: δ 9.47 (s, 1H), 5.25 (m, 1H), 5.11 (m, 1H), 2.17 (d, J = 7.4 Hz, 2H), 1.40 (m, 1H), 1.34−1.14 (m, 8H), 1.03 (s, 6H), 0.87 (t, J = 6.0 Hz, 3H), −0.05 (s, 9H). ^{13}C NMR: δ 206.8, 136.6, 122.1, 46.5, 41.2, 33.7, 32.0, 29.4, 29.0, 23.0, 21.6, 21.5, 14.5, −2.8. Anal. Calcd for $C_{16}H_{32}OSi$: C, 71.56; H, 12.01. Found: C, 71.34; H, 12.09.

General Procedure for Catalytic Allylic Substitution with Cyclopentadienyl-sodium (Entries 17 and 18). A mixture of acetate **1** (0.37 mmol), $Pd(dba)_2$ (0.018 mmol, 5 mol %, 0.011 g), and dppe (0.018 mmol, 0.007 g) in THF (0.9 mL) was treated with cyclopentadienyl-sodium in THF (4 mL), prepared from freshly distilled cyclopentadiene (1.1 mmol, 0.073 g) and NaH (0.74 mmol, 0.03 g). After this reaction mixture was stirred at rt for 2 h, it was diluted with ether (20 mL) and then washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over Na_2SO_4, concentrated, and chromatographed (pentane) to afford the air-sensitive product as a colorless oil.

(*E*)-1- and 2-(4′-(Dimethylphenylsilyl)but-2′-enyl)-cyclopenta-1,3-diene (4a). Formed as a 1:1 mixture. ^{1}H NMR: δ 7.53 (m, 2H), 7.37 (m, 3H), 6.42, 6.26, 6.11, 5.97 (m, 3H), 5.54−5.34 (br m, 2H), 3.08 (dd, J = 15.0 and 6.7 Hz, 2H), 2.97 (s, 1H), 2.90 (s, 1H), 1.72 (dd, J = 7.8 and 2.8 Hz, 2H), 0.30 (s, 6H). ^{13}C NMR: δ 149.2, 146.4, 134.9, 133.9, 132.7, 131.1, 126.8, 126.4, 139.1, 133.9, 129.1, 128.0, 133.9, 127.9, 127.3, 127.2, 43.7, 41.7, 34.8, 33.9, 22.2, 22.1, −2.7, −2.8. MS (EI): *m*/*z* (rel intens) 254 (M^+, 46), 150 (6), 135 (100), 119 (3), 91 (9), 75 (23).

(*E*)-1- and 2-(4′-(Trimethylsilanyl)non-2′-enyl)cyclopenta-1,3-diene (4b). Formed as a 1:1 mixture. ^{1}H NMR: δ 6.43, 6.27, 6.15, 6.01 (m, 3H), 5.29 (m, 2H), 3.10 (dd, J = 18.0 and 5.7 Hz, 2H), 2.96 (m, 1H), 2.88 (m, 1H), 1.43 (m, 1H), 1.35−1.13 (br m, 8H), 0.88 (t, J = 7.1 Hz, 3H), −0.03 (s, 9H). ^{13}C NMR: δ 149.6, 146.7, 135.0, 133.4, 132.7, 131.0, 126.7, 126.3, 133.8, 133.1, 126.3, 125.6, 43.7, 41.7, 34.9, 34.0, 33.5, 32.2, 29.5, 29.3, 23.1, 14.6, −2.5, −2.6. MS (EI): *m*/*z* (rel intens) 262 (M^+, 24), 247 (2), 191 (23), 189 (22), 131 (16), 117 (100), 91 (21), 73 (84).

General Procedure for Catalytic Allylic Substitution with Disilanes (Entries 19−26). Method D (See Table 1). A mixture of the chloride complex **15** (0.025 mmol) and AgOAc (0.1 mmol, 0.017 g) in CH_2Cl_2 (0.7 mL) was stirred for 1 h at 0 °C. After the white AgCl precipitate was removed, the yellow solution was added to the mixture of the corresponding acetate **1** (0.5 mmol) and maleic anhydride (0.075 mmol, 0.0074 g) in CH_2Cl_2 solution (4 mL). To this reaction mixture was added disilane **13** (1.0 mmol) in CH_2Cl_2 (4 mL) by syringe pump for 3 h at 30 °C; this was followed by stirring for an additional 14 h. After the solvent was removed, the residue was purified by column chromatography (pentane) to yield the disilylated product as a colorless oil.

Method E is identical to **method D**, with one exception, that $Pd(OAc)_2$ (0.025 mmol, 5 mol %, 0.0056 g) was used as the catalyst.

(*E*)-1,4-Bis(trimethylsilanyl)non-2-ene (5e). ^{1}H NMR: δ 5.06 (br m, 2H), 1.43−1.26 (m, 14H), −0.04 (s, 18H). ^{13}C NMR: δ 130.3, 124.0, 33.4, 32.1, 29.4, 29.3, 23.2, 23.0, 14.5, −1.5, −2.7. MS (EI): *m*/*z* (rel intens) 270 ($M^+ - 1$, 29), 196 (26), 154 (13), 126 (11), 122 (28), 73 (100).

(*E*)-1-(Dimethylphenylsilyl)-4-(trimethylsilanyl)non-2-ene (5f). ^{1}H NMR: δ 7.53−7.33 (m, 5H), 1.68 (d, J = 6.6 Hz, 2H), 1.35−1.25 (m, 9H), 0.89 (t, J = 6.9 Hz, 3H), 0.27 (s, 6H), −0.08 (s, 9H). ^{13}C NMR: δ 134.0, 132.6, 129.1, 128.0, 131.2, 123.2, 23.0, 22.2, 14.5, 33.5, 32.1, 29.3, −2.8, −2.9. Anal. Calcd for $C_{20}H_{36}Si_2$: C, 72.21; H, 10.91. Found: C, 72.03; H, 10.99.

(*E*)-2,5-Bis(trimethylsilanyl)dec-3-ene (5g). Formed as a 1:1 mixture of diastereoisomers from a 1:1 diastereomeric mixture of **1e**. ^{1}H NMR: δ 5.22 (dd, J = 15.1 and 8.1 Hz, 1H), 4.96 (dd, J = 15.1 and 9.0 Hz, 1H), 1.55−1.16 (m, 10H) 1.02 (d, J = 7.2 Hz, 3H), 0.88 (m, 3H), −0.04 (s, 18H). ^{13}C NMR: δ 131.0, 127.8, 127.6, 33.6, 33.5, 32.1, 29.5, 29.4, 29.3, 26.8, 26.7, 23.1, 14.8, 14.7, 14.6, −2.5, −2.8. MS (EI): *m*/*z* (rel intens) 284 ($M^+ - 1$, 25), 211 (12), 210 (40), 137 (61), 93 (13), 73(100).

(*E*)-2-(Dimethylphenylsilyl)-5-(trimethylsilanyl)dec-3-ene (5h). Formed as a 1:1 mixture of diastereoisomers from a 1:1 diastereomeric mixture of **1e**. ^{1}H NMR: δ 5.22 (m, 1H), 4.98 (m, 1H), 1.77 (m, 1H), 1.40−1.16 (m, 9H) 1.04 (d, J = 7.1 Hz, 3H), 0.90 (m, 3H), 0.25 (s, 6H), −0.07 (s, 9H). ^{13}C NMR: δ 134.2, 130.5, 128.9, 127.8, 131.4, 128.6, 26.3, 23.2, 15.0, 14.7, 33.6, 32.1, 29.4, 29.3, −2.6, −4.0. HRMS (EI): *m*/*z* calcd for $C_{21}H_{38}Si_2$ (M^+) 346.2512, found 346.2507.

Phenylation with Sodium Tetraphenylborate (Entries 27−30). A mixture of $Pd(dba)_2$ (0.01 mmol, 2 mol %, 0.006 g), PPh_3 (0.02 mmol, 0.005 g), and the acetate **1** (0.5 mmol) in THF (0.5 mL) was stirred for 15 min at 25 °C. This mixture was transferred via cannula to the THF solution (0.5 mL) of $NaBPh_4$ (0.27 mmol, 0.094 g), and the resulting reaction mixture was stirred for 3 h at 60 °C. The final product was obtained by chromatography (pentane) as a colorless oil.

(*E*)-4-(Trimethylsilanyl)-1-phenylnon-2-ene (6e). ^{1}H NMR: δ 7.33−7.17 (m, 5H), 5.42−5.20 (m, 2H), 3.35 (d, J = 5.4 Hz, 2H), 1.53−1.20 (m, 9H), 0.88 (t, J = 6.6 Hz, 3H), −0.04 (s, 9H). ^{13}C NMR: δ 141.9, 133.7, 128.7, 128.5, 126.6, 125.9, 39.8, 33.5, 32.2, 29.6, 29.3, 23.1, 14.6, −2.5. Anal. Calcd for $C_{18}H_{30}Si$: C, 78.75; H, 11.02. Found: C, 78.57; H, 11.25.

(*E*)-5-(Trimethylsilanyl)-2-phenyldec-3-ene (6f). Formed as a 1:1 mixture of diastereomers from a 1:1 diastereomeric mixture of **1e**. ^{1}H NMR: δ 7.32−7.15 (m, 5H), 5.44−5.23 (m, 2H), 3.44 (m, 1H), 1.45−1.19 (m, 12H), 0.86 (t, J = 6.6 Hz, 3H), −0.06 (s, 9H). ^{13}C NMR: δ 147.3, 133.2, 128.6, 126.1, 131.0, 127.5, 42.8, 33.3, 32.0, 29.4, 29.1, 23.0, 22.1, 14.5, −2.7. Anal. Calcd for $C_{19}H_{32}Si$: C, 79.09; H, 11.18. Found: C, 78.93; H, 11.35.

Preparation of (η^3-Allyl)palladium Chlorides. A mixture of the corresponding acetate (2.68 mmol), $Pd(dba)_2$ (2.40 mmol, 1.38 g), and LiCl (10.72 mmol, 0.45 g) was stirred in THF (15 mL) for 2 h at room temperature. After the solvent was removed in vacuo, the residue was purified by chromatography (CH_2Cl_2), affording the allylpalladium complexes as yellow crystals.

Bis(μ-chloro)bis[(1,2,3-η)-3-methyltrimethylsilyl]palladium (15a). ^{1}H NMR δ 5.12 (dt, J = 11.2 and 6.4 Hz, 1H), 4.08 (dt, J = 11.2 and 4.8 Hz, 1H), 3.82 (d, J = 6.4 Hz, 1H), 2.74 (d, J = 11.6 Hz, 1H), 1.29 (dd, J = 13.2 and 4.0 Hz, 1H), 1.16 (m, 1H), 0.05 (s, 9H). ^{13}C NMR: δ 108.8, 87.5, 57.4, 24.5, −1.4. MS (CI): *m*/*z* (rel intens) 539 (M^+, 7), 466 (63), 393 (35), 237 (26), 149 (36), 111 (88), 73 (100).

Bis(μ-chloro)bis[(1,2,3-η)-3-methyldimethylphenylsilyl]-palladium (15b). ^{1}H NMR: δ 7.48−7.32 (m, 5H), 4.99 (m, 1H), 3.99 (m, 1H), 3.75 (d, J = 6.6 Hz, 1H), 2.66 (d, J = 11.7 Hz, 1H), 1.52 (dd, J = 13.2 and 4.2 Hz, 1H), 1.34 (m, 1H), 0.31 (s, 6H). ^{13}C NMR: δ 137.6, 133.7, 129.6, 128.1, 108.9, 86.3, 57.4, 23.6, −3.0. MS (CI): *m*/*z* (rel intens) 661 ($M^+ - 1$, 7), 189 (85), 167 (31), 151 (37), 149 (100), 135 (18), 77 (14), 75 (64).

Bis(μ-chloro)bis[(1,2,3-η)-1-methyl-3-methyltrimethylsilyl]palladium (15c). ^{1}H NMR: δ 5.02 (t, J = 11.3 Hz, 1H), 3.86 (dt, J = 11.3 and 4.2 Hz, 1H), 3.62 (m, 1H), 1.26 (d, J = 6.3 Hz, 3H), 1.20 (d, J = 4.5 Hz, 1H), 1.15 (m, 1H), 0.03 (s, 9H). ^{13}C NMR: δ 110.9, 82.1, 75.4, 23.8, 18.2, −1.5. MS (CI): *m*/*z* (rel intens) 565 (M^+, 4), 491 (20), 418 (8), 265 (32), 213, (44), 125 (49), 73(100).

Preparation of (η^3-Allyl)palladium Phosphine Complexes. Chloride complex **15** (0.05 mmol) was dissolved in $CDCl_3$ (0.2 mL), mixed with $AgBF_4$ (0.11 mmol, 0.022 g) in the presence of PPh_3 (0.22 mmol, 0.058 g) at 0 °C, and then stirred for 10 min. The AgCl precipitate was removed, and the resulting yellow solution was used without further purification.

Bis(triphenylphosphine)[(1,2,3-η)-3-methyltrimethylsilyl]palladium Tetrafluoroborate (16a). ^{1}H NMR: δ 7.41−7.12 (br m, 30H), 5.54 (m, 1H), 4.51 (m, 1H), 3.41 (m, 1H), 3.24 (m, 1H), 0.92 (t, J = 13.1 Hz, 1H), 0.21 (m, 1H), −0.23 (s, 9H). ^{13}C NMR: δ 134.3−129.0 (6 Ph), 118.5, 107.9, 72.0, 23.5, −1.7.

Bis(triphenylphosphine)[(1,2,3-η)-3-methyldimethylphenylsilyl]palladium Tetrafluoroborate (16b). ^{1}H NMR: δ 7.46−7.08 (br m, 35H), 5.44 (m, 1H), 4.46 (m, 1H), 3.37 (m, 1H), 3.24 (m, 1H), 1.09 (tm, J = 12.3 Hz, 1H), 0.46 (m, 1H), 0.01 (s, 6H). ^{13}C NMR: δ 136.6−128 (6 Ph), 118.7, 106.2, 71.8, 22.4, −3.6.

Bis(triphenylphosphine)[(1,2,3-η)-1-methyl-3-methyltrimethylsilyl]palladium Tetrafluoroborate (16c). ^{1}H NMR: δ 7.41−7.12 (br m, 30 H), 5.29 (m, 1H), 4.45 (m, 1H), 4.16 (m, 1H), 0.90 (m, 3H) 0.74 (m, 1H), 0.05 (m, 1H), −0.21 (s, 9H). ^{13}C NMR: δ 134.1−129.0 (6 Ph), 119.1, 99.8, 89.4, 22.5, 16.8, −1.7.

Preparation of 20a,b. The corresponding alkenylmagnesium bromide (4.0 mmol) was added dropwise to **3e** (2.0 mmol) in THF (4 mL) at 0 °C. After the reaction mixture was stirred for 12 h at rt, it was quenched with saturated NH_4Cl solution, diluted with ether (20 mL), and washed with brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated. The residue was oxidized without further purification using the procedure described in the literature by Ratcliffe and Rodehorst.[41] After chromatography with pentane−ether, 20:1, the product was obtained as a colorless oil.

(*E*)-4,4-Dimethyl-8-(trimethylsilanyl)octa-1,6-dien-3-one (20a). ^{1}H NMR: δ 6.79 (dd, J = 17.0 and 10.2 Hz, 1H), 6.31 (dd, J = 17.0 and 2.2 Hz, 1H), 5.62 (dd, J = 10.2 and 2.1 Hz, 1H), 5.41 (m, 1H), 5.09 (m, 1H), 2.18 (d, J = 7.2 Hz, 2H), 1.39 (d, J = 8.0 Hz, 2H), 1.11 (s, 6H), −0.04 (s, 9H). ^{13}C NMR: δ 203.8, 131.3, 130.3, 128.2, 123.6, 47.2, 43.1, 24.1, 23.3, −1.4. MS (EI): *m*/*z* (rel intens) 224 (M^+, 7), 209 (5), 170 (75), 155 (40), 127 (100), 75 (36).

(2*E*,7*E*)-5,5-Dimethyl-9-(trimethylsilanyl)nona-2,7-dien-4-one (20b). ^{1}H NMR: δ 6.79 (m, 1H), 6.5 (dq, J = 15.0 and 1.7 Hz, 1H), 5.41 (m, 1H), 5.09 (m, 1H), 2.20 (dd, J = 7.2 and 0.9 Hz, 2H), 1.87 (dd, J = 6.9 and 1.8 Hz, 3H), 1.39 (dd, J = 8.1 and 0.8 Hz, 2H), 1.09 (s, 6H), −0.04 (s, 9H). ^{13}C NMR: δ 204.0, 142.7, 130.2, 126.5, 123.9, 46.8, 43.2, 24.2, 23.2, 18.6, −1.6. MS (EI): *m*/*z* (rel intens) 238 (M^+, 5), 170 (61), 127 (78), 75 (31), 73 (100).

2,2-Dimethyl-4-vinylcyclohexanone (21a). $BF_3{\cdot}Et_2O$ (0.61 mmol, 0.08 mL) was added to ketone **20** (0.36 mmol) in dry CH_2Cl_2 (2.4 mL) at −78 °C, and this mixture was stirred for

(41) Ratcliffe, R.; Rodehorst, R. *J. Org. Chem.* **1970**, *35*, 400.

20 min. Subsequently, the reaction mixture was allowed to warm to rt, and then it was stirred for an additional 3 h. After the resultant yellow solution was diluted with CH_2Cl_2 (10 mL) and extracted with saturated $NaHCO_3$ solution and brine, it was dried over anhydrous $MgSO_4$ and concentrated. Column chromatography with pentane−ether, 9:1, afforded the product as a colorless oil. ^{1}H NMR: δ 5.75 (m, 1H), 5.05 (dt, J = 17.0 and 1.5 Hz, 1H), 4.97 (dt, J = 10.0 and 1.5 Hz, 1H), 2.62 (m, 2H), 2.28 (ddd, J = 14.8, 4.7 and 2.6 Hz, 1H), 2.05 (m, 1H), 1.78 (dt, J = 13.6 and 4.4 Hz, 1H), 1.52 (ddd, J = 12.8, 4.5 and 1.6 Hz, 1H), 1.46 (q, J = 13 Hz, 1H), 1.21 (s, 3H), 1.05 (s, 3H). ^{13}C NMR: δ 215.9, 142.3, 113.7, 47.1, 45.1, 37.8, 37.0, 33.2, 26.1, 25.8. MS (EI): *m*/*z* (rel intens) 152 (M^+, 17), 123 (6), 110 (17), 97 (50), 79 (59), 67 (100).

2,2,5-Trimethyl-4-vinylcyclohexanone (21b). $TiCl_4$ (0.21 mmol, 0.21 mL, 1.0 M solution in CH_2Cl_2) was added slowly to the CH_2Cl_2 (1.0 mL) solution of ketone **20** (0.18 mmol) at −78 °C, and this mixture was stirred for 30 min. After the red reaction mixture was diluted with ether (15 mL), it was extracted with brine and then dried over anhydrous $MgSO_4$. The product was obtained after chromatography (pentane−ether, 20:1) as a colorless oil. ^{1}H NMR: δ 5.81 (m, 1H), 5.07 (m, 1H), 5.03 (dt, J = 11.2 and 1.3 Hz, 1H), 2.86 (m, 1H), 2.85 (dd, J = 13.9 and 5.8 Hz, 1H), 2.31 (m, 1H), 2.11 (dd, J = 13.9 and 2.7 Hz, 1H), 1.70 (q, J = 13.6 Hz, 1H), 1.62 (ddd, J = 13.6, 4.4 and 1.5 Hz, 1H), 1.21 (s, 3H), 1.06 (s, 3H), 0.79 (d, J = 6.8 Hz, 3H). ^{13}C NMR: δ 216.1, 141.1, 114.8, 45.5, 45.0, 40.4, 39.9, 36.6, 26.6, 25.8, 13.7. MS (EI): *m*/*z* (rel intens) 166 (M^+, 10), 151 (12), 138 (34), 110 (23), 95 (61), 81 (31), 67 (100).

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Supporting Information Available: NMR peak assignment and determination of the stereochemistry for **21b** and ^{13}C NMR spectra for compounds **2a**, **2c,d**, **3c**, **3e,f**, **3i**, **4a**, **5e**, **5g,h**, **6e**, **15a−c**, **20a,b**, and **21a,b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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