Nature of the Interactions between the β-Silyl Substituent and Allyl Moiety in (η³-Allyl)palladium Complexes. A Combined Experimental and Theoretical Study

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Three new β-silyl-substituted (η³-allyl)palladium complexes were prepared (**3**−**5**) in order to study the substituent effects of the silyl functionality on the allyl−metal system. Complexes **3**−**5** show a downfield ^{13}C NMR shift for the more substituted allylic terminus (C3). The deshielding effect of the silyl group on C3 is strongest when PPh_3 ligands are coordinated to palladium. Both internal and external nucleophiles attack the less substituted allylic terminus (C1) with high selectivity. A theoretical analysis of the structure and stability of slightly simplified model compounds **7**−**10** was performed by applying density functional theory at the B3PW91 level. The theoretical results indicate hyperconjugative interactions between the π-allyl−metal system and the C−Si σ-bond. The intensity of these interactions depends on the conformation of the silyl substituent and on the σ-donor/π-acceptor character of the ancillary ligand on palladium. The β-substituent effects increase the thermodynamic stability of the complexes, weaken the Pd−C3 bond, and facilitate the heterolytic fission of the C−Si bond. It was also concluded that regioselection of the nucleophilic attack is enhanced in the presence of strong β-silyl effects.

1. Introduction

Catalytic transformations involving (η³-allyl)palladium intermediates have been widely applied in a number of important chemical processes,[1−5] including allylic substitution and the oxidation of alkenes and conjugated dienes. One of the most important aspects of allylpalladium chemistry is the possibility of controlling the regio- and stereoselectivity of the nucleophilic attack on the allyl moiety through the choice of the reaction conditions and the ancillary ligands on palladium.[6−14]

Regioselective catalytic procedures providing unsymmetrically substituted bis-allylic compounds are particularly interesting from a synthetic and mechanistic point of view. Unsymmetrical bis-allylic compounds are useful building blocks in organic synthesis, since they can be selectively functionalized at either allylic position. The key step in the palladium-catalyzed preparation of bis-allylic compounds is the nucleophilic attack on a β-substituted (η³-allyl)palladium complex (Scheme 1). For electron-withdrawing β-substituents, the nucleophilic attack proceeds with remarkably high 1,4-regioselectivity.[15−20] In some recent studies we have discussed the effects of electronegative β-substituents on the structure and properties of (η³-allyl)palladium complexes.[12−14] It was concluded that polar β-substituents are involved in conjugative electronic interactions with the allyl−palladium system, inducing asymmetric electron distribution on the allylic fragment, which makes the less substituted allylic terminus more reactive to nucleophilic attack.

Theoretical and experimental results on the β-effects of electron-withdrawing substituents (OAc, OMe, and Cl) urged us to investigate the electronic effects of

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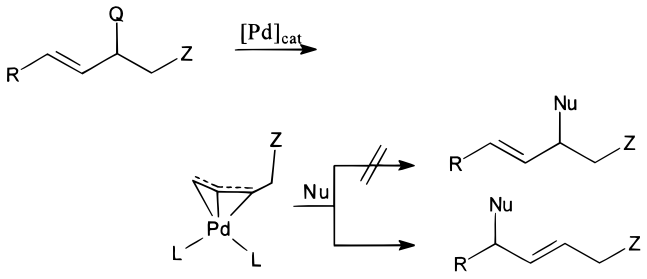
Scheme 1



conjugating *nonpolar* β-substituents in (η^3-allyl)palladium complexes. In the present study we report our results on the substituent effects of the β-silyl functionality. Investigation of the β-*silyl*-substituted (η^3-allyl)-palladium complexes is of both synthetic and mechanistic interest since (a) it can help to design new catalytic procedures providing stereo- and regiodefined allyl−silanes and (b) important information can be acquired on the nature of the electronic interactions between the C−Si bond and allyl−metal π-systems.

In particular, we will address the following questions.

(1) How do the interactions between the C−Si bond and the allyl−palladium fragment influence the geometry, magnetic properties, and stability of the complexes?

(2) What conformational and stereoelectronic requirements have to be fulfilled to obtain the most effective conjugative interactions?

(3) How does the π-acceptor/σ-donor character of the ancillary ligands modify the interactions between C−Si and the allyl−palladium fragment?

(4) How is the regiochemistry of the nucleophilic attack governed by the β-silyl substituent?

To answer these questions, we prepared three new β-silyl-substituted allyl−palladium complexes (Figure 1) and investigated their reactivity with internal and external nucleophiles. The experimental results are interpreted by means of theoretical calculations for the corresponding model systems (Figure 2) and simplified β-substituted allyl complexes (Figures 3−5).

2. Experimental Results

Our previous results[13] clearly indicated that the β-substituent effects are particularly strong in [(η^3-1,2,3)-cyclohexenyl]palladium complexes because the six-membered-ring framework provides a substituent conformation, which is optimal for the conjugative interactions. Accordingly, the target compound for the preparative studies was a β-silyl-substituted [(η^3-1,2,3)-cyclohexenyl]palladium complex.

As the key precursor for the preparation of the target complexes, we employed the *cis*-1,4-disilylcyclohexene **1a** (Figure 1). Although several methods have been published for the preparation of disilylcyclohexenes,[21−23] the procedures in the literature result in mixtures of the *cis* and *trans* 1,2- and 1,4-isomers. Therefore, we devised a new procedure for preparation of **1a**, which

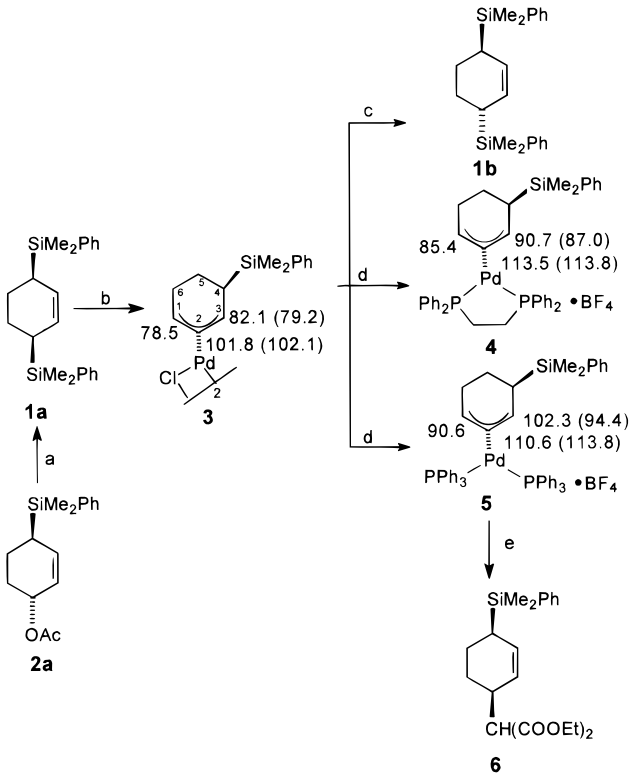


Figure 1. Preparation and reactivity of the β-silyl-substituted (η^3-allyl)palladium complexes: (a) $PhMe_2SiLi$, CuCN, ether, 0 °C; (b) $Li_2[PdCl_4]$, MeOH, 0 °C; (c) AgOAc, $(PhMe_2Si)_2$, $CHCl_3$, 0 °C; (d) $AgBF_4$, dppe, or PPh_3, $CHCl_3$ or $CDCl_3$, 0 °C; (e) THF, $NaCH(COOEt)_2$. The ^{13}C NMR shifts of the allylic carbons are given in ppm. The figures in parentheses are the ^{13}C NMR shifts for the unsubstituted C_s-symmetrical analogues.

is based on silacupration of the *trans*-silylacetatocyclohexene **2a**. Fleming and co-workers[24] have shown that tertiary allylic acetates mainly react with the silyl−cuprate reagent with *anti* stereoselectivity. In accordance with this, silacupration of **2a** afforded **1a** and **1b** in a ratio of 9:1. The 1,4-regioselectivity of the reaction was very high, since the corresponding 1,2-adduct[23] could not be detected in the reaction mixture.

Palladadesilylation[25] of **1a** afforded the β-silyl-substituted (η^3-allyl)palladium complex **3** (Figure 1). Hayashi and co-workers[26] have shown that palladadesilylation of allylsilanes proceeds with clean *anti* stereochemistry. The ancillary chloride ligand could be exchanged with dppe (**4**) and PPh_3 (**5**) by $AgBF_4$ in the presence of the corresponding phosphine. The dppe complex **4** is air-stable and can be purified by chromatography; however, the PPh_3 complex **5** decomposes on evaporation of the solvent. The NOESY spectrum of **4** displays a cross-peak between H4 and the phenyl protons of the dppe ligand, verifiying the *trans* configuration of the 4-$SiMe_2Ph$ functionality. It is interesting to note that **5** was formed as a single *trans* isomer, which did not show any tendency for isomerization. Allylpalladium complexes with PPh_3 ligands usually undergo facile *cis*−*trans* equilibration;[16,27] however, the

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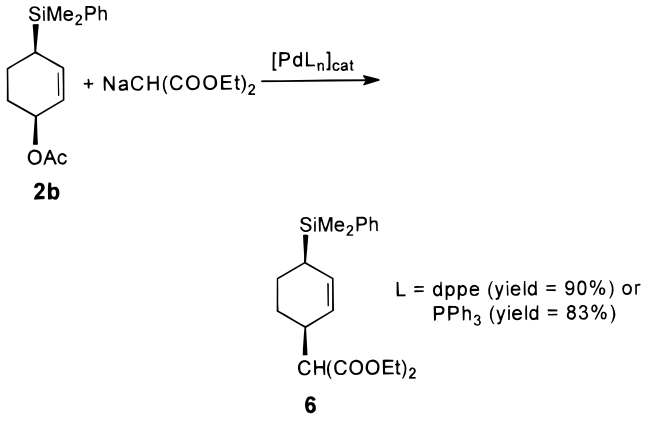
steric strain between the bulky $SiMe_2Ph$ group and the PPh_3 ligand certainly does not allow formation of the *cis* isomer of **5**.

The ^{13}C NMR spectra of **3**−**5** showed some interesting features: the chemical shift of the allylic terminus (C_t) closer to the $SiMe_2Ph$ functionality (C3) was observed at a lower field than that of the remote allylic terminus (C1). Comparison of δ(C1) and δ(C3) in **3**−**5** with the allylic shift (δ(C1)) in the corresponding unsubstituted complex reveals that the 4-silyl substitution generates deshielding effects at the closer allylic terminus (C3). The differences in the chemical shift between C1 and C3 are also dependent on the ligand effects: the difference is rather small (3.6 ppm) for the σ-donor Cl^- ligand (**3**), somewhat larger (5.3 ppm) in the dppe complex (**4**), and a quite large 11.8 ppm for **5**. It is well-documented that an increase in the π-acceptor character of the ancillary ligands shifts the $\delta(^{13}C)$ NMR values of the allylic termini downfield.[28,29] However, as one goes from **4** to **5**, the increasing π-acceptor character of the phosphine ligands also increases the difference between the NMR shifts of C1 and C3. As the palladium atom has a considerable shielding effect on the allylic carbons,[30] partial deshielding of C3 arising from the presence of the β-silyl substituent is indicative of weakening of the Pd−C3 interactions.

Reactions of β-Silyl-Substituted (η^3-Allyl)palladium Complexes. The regiochemistry of the nucleophilic attack was studied in two stoichiometric reactions. Complex **5** was reacted with sodium diethyl malonate, providing the 1,4-substituted product **6** with very high regio- and stereoselectivity. The *cis* position of the ring substituents was established on the basis of the NOESY spectrum of **6**, which displayed a cross-peak between the C*H*(COOEt) proton of malonate and the methyl protons of the $SiMe_2Ph$ functionality. These protons also showed a dNOE effect of 7% (see Experimental Section). Since the external attack by the malonate proceeds by a *trans* mechanism,[16] it also involves steric influence of the 4-$SiMe_2Ph$ group. To investigate the effects of purely electronic factors on the regiochemistry of the nucleophilic attack, the Cl^- ligands of **3** were exchanged to OAc^- and the acetate complex was reacted with $(PhMe_2Si)_2$. Tsuji and co-workers[10] have shown that allyl−palladium complexes with acetate ligands react with alkyl- and aryldisilanes through *cis* migration of the silyl nucleophile from palladium to allyl. Transformation of **3** afforded *trans*-1,4-disilyl compound **1b**, which was also the minor component in silacupration of **2a**.

Palladium-Catalyzed Alkylation Proceeding Through Complexes 4 and 5. To explore the synthetic potential of allylic substitution reactions proceeding through β-silyl-substituted allyl−palladium complexes, the *cis* analogue of **2a** was reacted with sodium diethyl malonate (Scheme 2) in the presence of catalytic amounts of $Pd(dba)_2$/dppe and $Pd(PPh_3)_4$. This catalytic procedure provided **6** as a single stereo- and regioisomer in good yield. The catalytic reaction required milder

Scheme 2



reaction conditions and shorter reaction times than the alkylation of analogous cyclohexenylallyl acetates.[31] For example, when $Pd(dba)_2$/dppe was used as the catalyst source, the reaction was complete in 3 h at 40 °C.

3. Theoretical Studies

Computational Details. The geometries were fully optimized by employing a Becke-type[32] three-parameter density functional model (B3PW91). This so-called hybrid functional includes the exact (Hartree−Fock) exchange, the gradient-corrected exchange functional of Becke,[32] and the more recent correlation functional of Perdew and Wang.[33] All calculations were carried out using a double-ζ(DZ)+P basis constructed from the LANL2DZ basis[34−36] by adding one set of d-polarization functions to the heavy atoms (exponents: C, 0.63; P, 0.34; Cl, 0.514; Si, 0.262) and one set of diffuse d-functions on palladium (exponent: 0.0628). The charges were calculated by the natural bond orbital (NBO) method of Weinhold and co-workers.[37] All calculations were carried out by employing the Gaussian 94 program package.[38]

Structures **7** and **8** are derived from the corresponding experimentally investigated complexes **3**−**5**. The $SiMe_2Ph$ substituent was approximated by the computationally less demanding $SiMe_3$ group. Furthermore, the calculations were performed for monomeric **7** instead of the dimeric chloro complex **3**. However, this is not a serious simplification, since it has been shown that the structures and properties of monomeric and chloro-bridged (η^3-allyl)palladium complexes are very similar.[39,40] The di- and triphenylphosphine complexes **4** and

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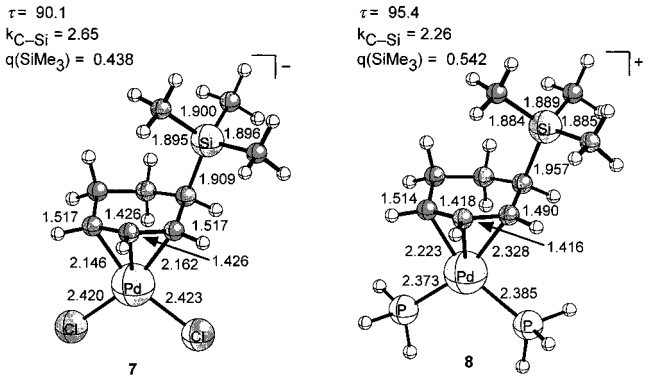

Figure 2. B3PW91/LANL2DZ+P geometries, C−Si force constants, and NBO charges of slightly simplified model compounds **7** and **8** (bond lengths in Å, angles in deg, force constants in mdyn/Å, charges in electron units).

5 were approximated by the phosphine complex **8**. Since phosphine is a fairly strong π-acceptor but a less effective σ-donor than the usual alkyl- or arylphosphines,[41,42] approximation of PPh_3 and dppe with PH_3 may lead to underestimation of the σ-donor properties of the ancillary ligand in **4** and **5**. Consequences of the approximation of phenyl substituents by hydrogens in PPh_3 are briefly discussed for the simplified model complexes **9a**−**d** (*vide infra*).

Structure of the β-Silyl-Substituted [(η^3-1,2,3)-Cyclohexenyl]palladium Complexes. In complexes **7** and **8** (Figure 2) the C−Si bond is perpendicular to the allyl moiety (τ, defined as C2C3C4Si, is 90.1 and 95.4°, respectively). The calculated Pd−C bond lengths indicate asymmetrical allyl−palladium bonding that is more pronounced in the case of the π-acceptor ligand (**8**), where the Pd−C3 bond is 0.11 Å longer than the Pd−C1 bond. Involvement of the silyl group in the intensive electronic interactions in **8** is indicated by the unusually long (1.957 Å) and weak (k_{C-Si} = 2.26 mdyn/Å) C4−Si bond, as well as by shortening of the C3−C4 bond. Shortening of C3−C4 can be ascribed to the increased π-character of the C3−C4 bond, suggesting a conformational dependence for the β-silyl functionality.

Effects of the Substituent Conformation. To analyze the stereoelectronic aspects of the interactions between the silyl functionality and the allyl−metal complex, we calculated the rotation potential for acyclic model systems **9a** and **10a** (Figures 3 and 4a). The rotation potential was calculated in the region of 60° < τ <180°, where steric interactions between the $SiMe_3$ functionality and ancillary ligands are negligible. The absolute minima were encountered close to τ = 90° (91.1°, **9a**; 92.7°, **10a**) representing the conjugated conformation, which is also very close to the τ value calculated for the cyclic complexes **7** and **8**. Similar to **8**, in **9a** the Pd−C1 and Pd−C3 bond lengths differ strongly, by 0.12 Å. In contrast to **9a**, the allyl−palladium bonding is less asymmetrical in **10a**, where the Pd−C1 and Pd−C3 bond lengths differ by only 0.01 Å.

The deeper potential clearly indicates more intense interactions for the phosphine ligand. In **9b** and **10b** τ is constrained at 180°, where the π-orbitals of the allyl system and the σ(C−Si) orbitals are orthogonal and the conjugative interactions are shut off. Accordingly, the electronic interactions in **9a** provide a stabilization energy of 6.1 kcal/mol, while the corresponding stabilization energy in **10a** is much lower, only 0.9 kcal/mol. The structural changes are also more pronounced for the **9a** → **9b** process than for the corresponding **10a** → **10b** conformational change. As one goes from **9a** to **9b**, (a) the difference between Pd−C3 and Pd−C1 decreases by 0.04 Å, (b) the C3−C4 bond is elongated by 0.03 Å, and (c) the C−Si bond is shortened by 0.03 Å.

The C−Si bond strength is also a function of τ (Figure 5a). Dependence of the k_{C-Si} values on the substituent conformation is more pronounced for the phosphine complex than for the chloride complex. In the phosphine complex the C−Si force constant is at its smallest in **9a** (2.26 mdyn/Å) and at its largest when τ = 180° (2.60 mdyn/Å). Interestingly, the C−Si bond is the weakest in the equilibrium conformation; hence, the electronic interactions thermodynamically stabilize the kinetically least stable conformation.

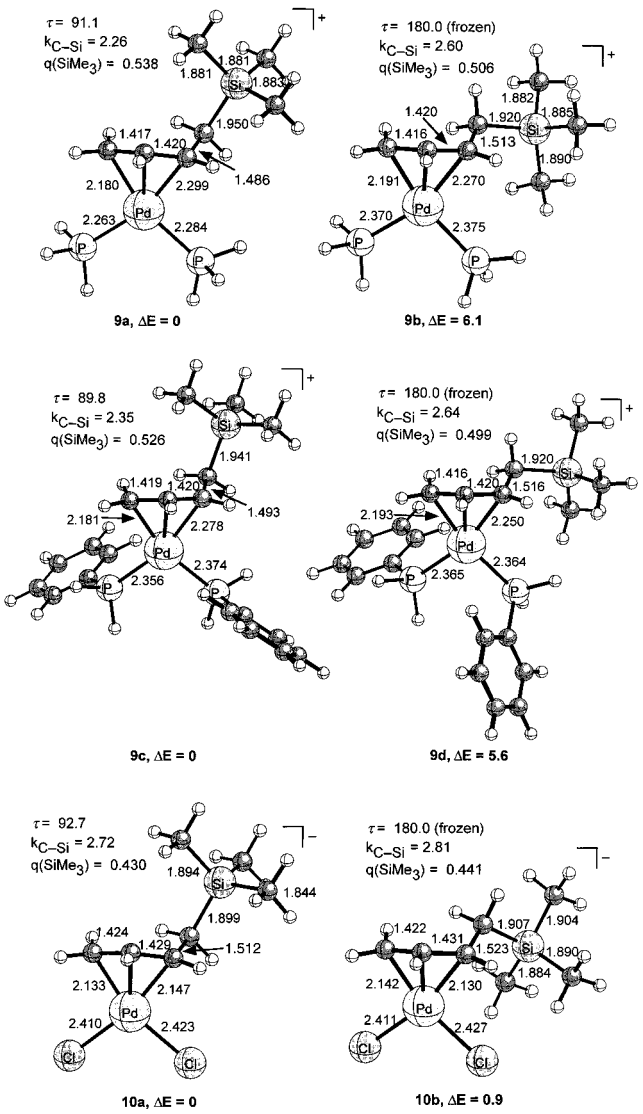

Figure 3. B3PW91/LANL2DZ+P geometries, C−Si force constants, and NBO charges of acyclic model systems (for computational details, see the caption for Figure 2).

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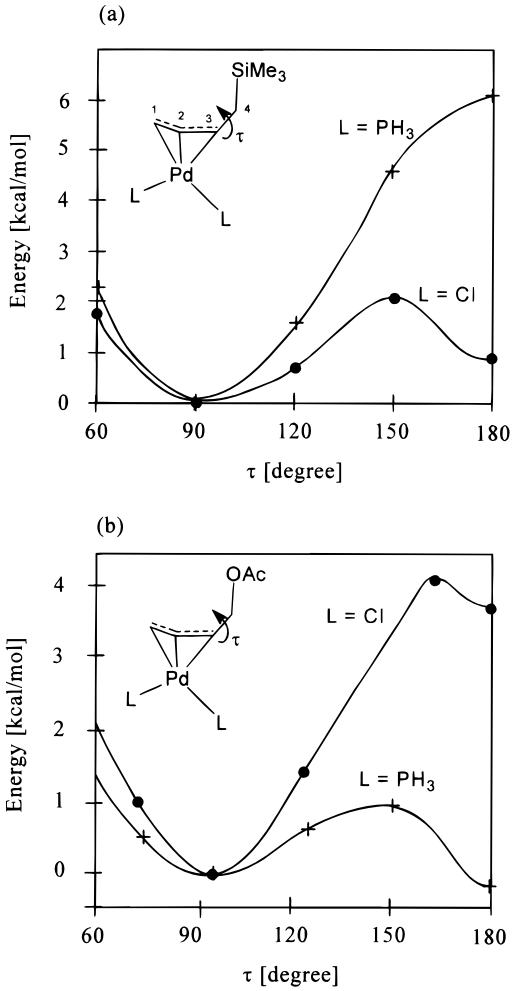


Figure 4. Rotation potentials of (a) **9** and **10** and (b) their β-acetoxy analogues. Energy values are obtained by freezing the C2−C3−C4−Si dihedral angle (τ) at different values and reoptimizing all the other geometrical parameters at the B3PW91/LANL2DZ+P level.

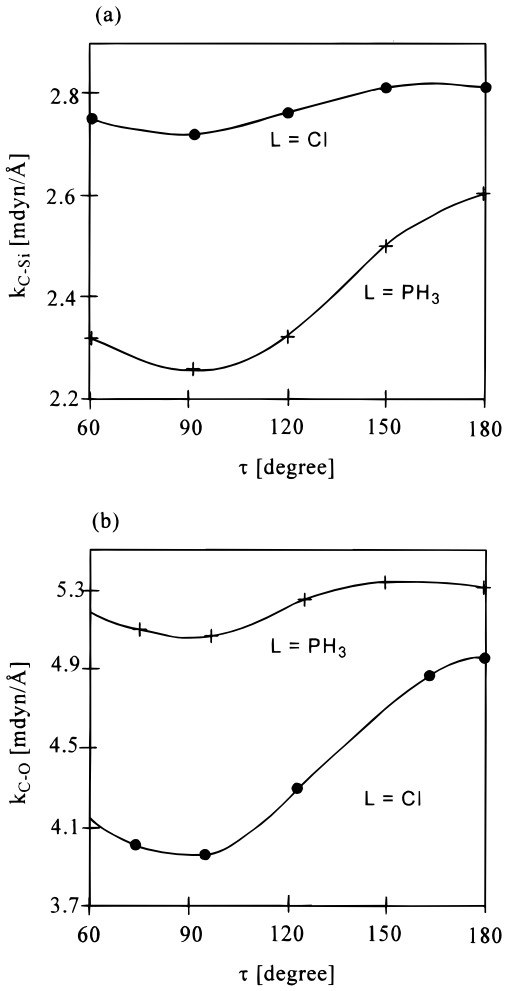


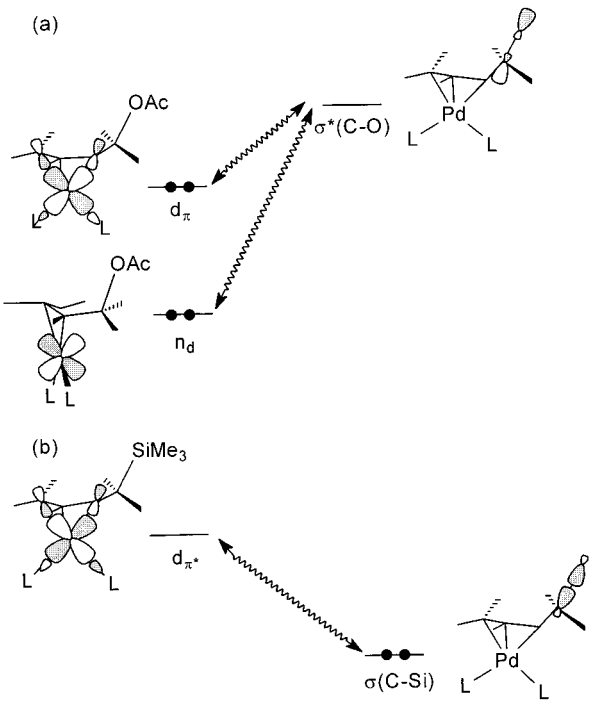
Figure 5. Stretching force constants of (a) **9** and **10** and (b) their β-acetoxy analogues as a function of τ.

The phosphine ligands of **4** and **5** were approximated with PH_3 in the theoretical studies. Since the arylphosphines are usually better σ-donors than PH_3, we have also investigated the influence of the phenyl substitution of the PH_3 ligand. Replacement of the PH_3 ligands of **9a** with the $PPhH_2$ ligands (**9c**) leads to a slight decrease in the intensity of the β-substituent effects. The structural effects indicate an increase of the σ-donor character of the ligand. As one goes from **9a** to **9c,** (a) the difference between Pd−C3 and Pd−C1 decreases, (b) the C3−C4 bond is slightly elongated, and (c) the C−Si bond is somewhat shortened. Increase of the σ-donor character could also be confirmed by rotation of the $SiMe_3$ functionality. When τ is changed from 90° (**9c**) to 180° (**9d**), the energy is increased by 5.6 kcal/mol, while the corresponding **9a** → **9b** process involves an energy change of 6.1 kcal/mol. On the basis of these calculations it can be estimated that replacement of the other two hydrogens of the $PPhH_2$ ligands by phenyls in **9c** would decrease the conformational energy change of the $SiMe_3$ rotation (τ = 90° → 180°) by a further 1 kcal/mol to about 4.6 kcal/mol. Altough phenyl substitution of PH_3 decreases somewhat the intensity of the electronic interactions in **9a**, the stabilization energy estimated for the PPh_3 ligands (4.6 kcal/mol) is still considerably higher than the corresponding stabilization energy in the chloro complex **10a** (0.9 kcal/mol).

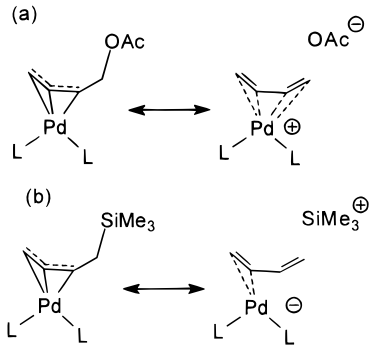
Increases in both the conformational energy and the C−Si bond strength as a function of τ clearly indicate that the intensity of the electronic interactions between the C−Si bond and the allyl−metal system is determined by stereoelectronic effects. These electronic interactions are also dependent on the σ-donor/π-acceptor character of the ancillary ligands. Systematic changes in the conformational energy, geometrical parameters, and C−Si bond strength clearly indicate that the electronic effects are stronger for π-acceptor phosphine ligands than for σ-donor chloride ligands. The influence of the ancillary ligands on the β-silyl−allyl interactions is the reverse of the ligand effects observed[12−14] for the electron-withdrawing β-substituents, such as OAc, OMe, and Cl.

Comparison of the β-Effects of $SiMe_3$ and OAc Groups. Replacement of the $SiMe_3$ group in **9** with an OAc functionality leads to flattening of the rotation potential (Figure 4b) and to a rather weak dependence of the C−O bond strength on τ (Figure 5b). When the $SiMe_3$ group is exchanged to OAc in the chloro complex **10**, the rotational potential becomes deeper and k_{C-O} increases strongly when τ increases from 90° to 180°. We have reported earlier[14] that the β-OAc group also generates asymmetric bonding in allyl−palladium complexes. In contrast to the geometrical effects described

Scheme 3



Scheme 4



for **7**−**10**, the conjugative interactions between a β-OAc substituent and (η^3-allyl)palladium leads to *shortening* of the Pd−C3 and Pd−C4 bonds.[14]

The structural effects induced by OAc and other electron-withdrawing substituents were rationalized[12−14] by the electronic interactions shown in Schemes 3a and 4a using the MO formalism and resonance structures, respectively. Accordingly, partial coordination of C4 to palladium lends C1−C4 similarity to a butadiene moiety. Charge transfer from the high-lying HOMO orbital (d_π) of the complex and a properly positioned lone-pair orbital of palladium (n_d) into the σ^*(C−O) leads to weakening and elongation of the C−O single bond. The interaction between n_d and σ^*(C−O) leads to partial coordination of C4 to palladium (*cf*. MO interactions in (η^4-butadiene)palladium complexes[43]) and therefore *shortening* of the Pd−C4 distance and the Pd−C3 bond length.

The nature of the electronic interactions is somewhat different for the electron-supplying $SiMe_3$ group. It is well-established that σ(C−Si) orbitals readily conjugate with low-lying unfilled π-levels.[44,45] The interactions between σ(C−Si) and the p_π-orbital of carbocations is the basis of the well-known β-silicon effect.[44,45] 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 allyl−palladium fragment (d_{π^*}) and the high-lying σ(C−Si) orbital (Scheme 3b). 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 allyl−palladium bonding is also weakened. The σ(C−Si) orbital directly overlaps with the π-lobe of C3, and therefore, the Pd−C3 bond is weakened to a much greater extent than the Pd−C1 bond. On the other hand, in-phase overlap between σ(C−Si) and d_{π^*} increases the C3−C4 bonding, leading to shortening of the C3−C4 bond. Coordination of π-acceptor ligands involves charge transfer from the metal to the ligand through back-donation, leading to orbital contraction and therefore lowering of the d_{π^*} level. Decreasing the energy of d_{π^*} causes the energy gap between d_{π^*} and σ(C−Si) to decrease, which leads to increased orbital interactions.

The conjugative interactions can be shut off upon rotation of the $SiMe_3$ functionality by 90° (**9b** and **10b**). The positive charge in the interacting form (**9a**) is larger by 0.03 electron unit than in **9b**, indicating that the electronic interactions involve charge transfer from the $SiMe_3$ functionality to the allyl−palladium system. The structural, energy, and charge-transfer effects clearly indicate significant hyperconjugative interactions between the C−Si bond and the allyl−metal π-system in **9a**. The stereoelectronic and structural aspects of this interaction are related to the β-silicon effects in carbocations; however, there are two important differences: (1) the intensity of the hyperconjugative interactions in (η^3-allyl)palladium complexes can be fine-tuned by making an appropriate choice of the ancillary ligand, and (2) the desilylation induced by weakening the C−Si bond can be avoided in (η^3-allyl)palladium systems, and therefore the silyl functionality can be kept in reactions proceeding through β-silyl-substituted allyl−palladium intermediates.

4. Relevance of the Hyperconjugative Interactions in the Chemistry of β-Substituted Allyl−Palladium Complexes

Structure and Stability of the Complexes. The hyperconjugative interactions weaken the Pd−C3 and C−Si bonds and strengthen the C3−C4 bond of the complexes, in particular when π-acceptor ligands are coordinated to palladium, as in **4** and **5**. Weakening of the Pd−C3 bonding is reflected by the downfield ^{13}C NMR shift observed for C3, which is most pronounced for the strong π-acceptor ligand PPh_3 (**5**). It is interesting to note that in the β-OAc analogue of **3**, this effect is reversed and C3 is shifted upfield[46] (δ(C1) 82 ppm, δ(C3) 74.6 ppm), indicating strengthening of the Pd−C3 bond.

Transformation of allylsilanes often involves desilylation of the substrate. Desilylation is usually the

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consequence of hyperconjugative interactions between the C−Si bond and the low-lying π-type MOs, since these interactions weaken the C−Si bond. However, in the case of the palladium-mediated transformations of allylsilanes, the strength of the hyperconjugative interactions can be fine-tuned through the proper choice of the ancillary ligands. Desilylation can be avoided through a decrease of the π-acceptor ability of the ancillary ligand, which attenuates the hyperconjugation and leads to strengthening of the C−Si bond.

The hyperconjugation thermodynamically stabilizes the phosphine complexes by about 5−6 kcal/mol. This extra stabilization can also facilitate the formation of the (η^3-allyl)palladium intermediates in the catalytic procedures. The relatively mild reaction conditions required in the catalytic alkylation (Scheme 2) indicate an easy formation of the allyl−palladium intermediate of the reaction.

Implications for the Regiochemistry of the Nucleophilic Attack. The regioselectivity of the nucleophilic attack is influenced by three important effects from the hyperconjugative interactions.

(1) The hyperconjugation is extended to the C1−C4 fragment and the silicon atom (Schemes 3b and 4b). A nucleophilic attack at the C3 position would interrupt this conjugation; therefore, the C1 terminus is preferentially attacked. Besides, the π-lobe in the LUMO at C3 is partially occupied due to the interaction with the filled σ(C−Si) MO, effectively hindering the charge transfer from the lone pair of a nucleophile.

(2) For an external attack (**5** → **6**), the steric effects of the bulky silyl group also facilitate the nucleophilic attack at the C1 position of the allyl. Since 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 (e.g., **9a**), the steric effects will also improve the 1,4-selectivity of the external nucleophilic attack even for acyclic systems.

(3) The nucleophilic attack on the allyl moiety involves Pd−C bond breaking,[47] which is easier for the Pd−C3 bond weakened by the hyperconjugative interactions. However, this interaction would probably facilitate the 1,2-attack of the nucleophile.

Because of (1) and (2), the external nucleophilic attack on cyclic and acyclic complexes is expected to occur with a high 1,4-regioselectivity, in particular when strong π-acceptor ligands are applied. However, for an internal attack the steric effect of the β-substituent does not influence the regioselectivity and the opposing effects (1) and (3) may lead to decrease of the regioselectivity. On the other hand, the **3** → **1b** process occurs with high 1,4-regioselectivity, indicating that conservation of the hyperconjugation (1) prevails, which can be the case for other types of internal nucleophilic attacks as well.

5. Conclusions

We have prepared three new β-silyl-substituted allylpalladium complexes. These complexes are stable species, which do not undergo spontaneous desilylation under ambient conditions. The β-silyl-substituted allyl−palladium complexes show a downfield ^{13}C NMR shift for the more substituted allylic terminus (C3), indicating weakening of the Pd−C3 interactions. Both internal (**3** → **1b**) and external (**5** → **6**) nucleophiles attack the less substituted allylic terminus selectively.

Calculations show that the weakening of the Pd−C3 bond can be ascribed to hyperconjugative interactions between the C4−Si bond and the allyl−palladium moiety. These interactions influence (a) the structure of (η^3-allyl)palladium complexes, (b) the kinetic (Figure 5) and thermodynamic (Figure 4) stability of these species, and (c) the regioselectivity of the nucleophilic attack.

The structural changes can be summarized as follows: (1) the C−Si bond is perpendicular to the allyl moiety; (2) the C−Si bond is elongated; (3) the C3−C4 bond is shortened; (4) the Pd−C3 bond is elongated; (5) electron density is transferred from the β-substituent to the allyl moiety. It should be noted that (4) and (5) are the reverse of the structural effects reported for electron-withdrawing substituents.[12−14]

The hyperconjugation thermodynamically stabilizes the phosphine complexes (e.g. **8**, **9a**, and **9c**) by about 5−6 kcal/mol. Weakening of the C−Si bond, as shown by the C−Si stretching constants, facilitates its heterolytic fission, and therefore strong β-substituent effects may lead to desilylation of this complex. The theoretical results predict high 1,4-regioselectivity, in particular for the external nucleophilic attack of the allyl moiety. The β-silicon effects in allyl−palladium complexes can be enhanced by (1) employing π-acceptor ligands on palladium and (2) enforcing the C−Si bond perpendicular to the allyl moiety (*e.g.*, **7** and **8**).

In summary, our results imply that the β-silyl-substituted allyl−palladium complexes are stable species attacked with very high regioselectivity by nucleophiles. These results will certainly inspire further palladium-catalyzed transformations suitable for synthesis of regio- and stereodefined allylsilanes.

6. Experimental Section

The starting materials were purchased from Aldrich or Lancaster. All solvents were freshly distilled prior to use. Unless otherwise stated, the reactions were conducted under a nitrogen atmosphere at 0 °C by employing standard manifold techniques.

***cis*-1,4-Bis(dimethylphenylsilyl)-2-cyclohexene (1a).** (For alternative procedures see refs 21−23.) $PhMe_2SiLi$ (8 mmol) was added to a stirred ethereal solution of CuCN (2.67 mmol, 0.24 g) and PPh_3 (8 mmol, 2.1 g) from a syringe over a period of 30 min. Then silyl−acetate **2a**[48,49] (1.82 mmol, 0.5 g) was added and the reaction mixture was stirred for an additional 5 h. The reaction mixture was quenched with saturated NH_4-Cl solution, and the aqueous layer was extracted with petroleum ether (3 × 100 mL). The organic layers were combined, concentrated under vacuum, and subjected to chromatography on silica gel with petroleum ether as eluent to produce 0.35 g (55%) and 0.04 g (6%) of the colorless oils **1a** and **1b**, respectively.

Bis[*trans*-4-(dimethylphenylsilyl)((1−3-η)-cyclohexenyl]-palladium Chloride (3). Disilyl compound **1a** (0.13 mmol, 0.05 g) was added to the stirred solution of $Li_2[PdCl_4]$ (0.13 mmol, 0.03 g) in methanol. After about 3 h yellow crystals

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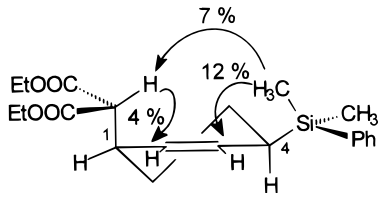
precipitated, which were filtered out and recrystallized from petroleum ether/ether (4:1), yielding 0.03 g of **3** (58%). Complex **3** decomposes slowly at room temperature; however, it can be stored at −18 °C for several months without decomposition. ^{1}H NMR (5 °C): δ 7.52−7.34 (m, 5H, Ar), 5.45 (t, 1H, H2), 5.21 (d, 1H, H3), 5.07 (t, 1H, H1), 1.88 (m, 2H, H5 + H6), 1.56 (m, 2H, H4 + H6′), 0.98 (m, 1H, H5′), 0.33−0.31 (ss, 6H, Si(CH_3)$_2$). ^{13}C NMR (5 °C): δ 136.3, 134.2, 129.7, 128.3 (Ph), 101.8 (C2), 82.1 (C3), 78.5 (C1), 30.8 (C4), 30.3 (C6), 21.1 (C5), −4.5, −4.7 (Si(*C*H$_3$)$_2$).

[*trans*-4-(Dimethylphenylsilyl)-(1−3)-η-cyclohexenyl]-palladium Phosphine Complexes (4 and 5). The chloroform ($CHCl_3$ or $CDCl_3$) solution of the chloride complex **3** (0.03 mmol, 0.02 g) was mixed with $AgBF_4$ (0.06 mmol, 0.012 g) in the presence of the corresponding phosphine ligand. The AgCl precipitate was removed, and **4** was purified by silica gel chromatography using CH_2Cl_2/MeOH (9:1) as the eluent. The PPh_3 complex (**5**) decomposes on evaporation of solvent; therefore, this compound was used without purification. **4**: ^{1}H NMR (5 °C) δ 7.57−7.21 (m, 25H, Ar), 5.89 (m, 1H, H3), 5.83 (m, 1H, H1), 5.71 (t, 1H, H2), 2.89−2.30 (m, 4H, (CH_2)$_2$ dppe), 2.11 (m, 1H, H6), 1.28 (m, 2H, H5 + H6′), 1.02 (m, 1H, H4), 0.88 (m, 1H, H5′), 0.18, 0.17 (ss, 6H, Si(CH_3)$_2$); ^{13}C NMR (5 °C) δ 135.9−128.7 (5Ph), 113.5 (C2), 90.7 (C3), 85.4 (C1), 31.0 (C4), 30.0 (C6), 28.1, 27.1 (*C*H$_2$)$_2$ dppe), 20.5 (C5), −4.8, −5.3 (Si(*C*H$_3$)$_2$). **5**: ^{1}H NMR (5 °C) δ 7.44−7.15 (m, 35H, Ar), 5.97 (t, 1H, H2), 5.23 (bm, 1H, H3), 4.85 (bm, 1H, H1), 1.88 (m, 1H, H5), 1.11 (m, 2H, H5′ + H6), 0.74 (bm, 1H, H4), 0.62 (bm, 1H, H6′) 0.12, 0.05 (ss, 6H, Si(CH_3)$_2$; ^{13}C NMR (5 °C) δ 135.7−128.2 (7Ph), 110.7 (C2), 102.2 (C3), 90.4 (C1), 30.0 (C4), 25.0 (C6), 22.6 (C5), −3.9, −4.9 (Si(*C*H$_3$)$_2$).

Reaction of Complex 3 with $(PhMe_2Si)_2$. The chloroform solution of chloride complex **3** (0.028 mmol, 0.02 g) was mixed with AgOAc (0.06 mmol, 0.01 g). The AgCl precipitate was removed, and $(PhMe_2Si)_2$ (0.17 mmol, 0.05 g) was added in $CHCl_3$. The black Pd(0) precipitate was filtered out, and the solvent was evaporated. According to GC and NMR analysis, **3** was quantitatively converted to **1b**.

Reaction of Complex 5 with Sodium Diethyl Malonate. Complex **5** (0.06 mmol) in CH_2Cl_2 was added by syringe to the THF solution of freshly prepared sodium diethyl malonate (0.22 mmol) and stirred for 30 min. According to GC and NMR analysis, complex **5** was quantitatively converted to **6**.

Catalytic Alkylation of 2b with Dietyl Malonate. Acetate **2b**[48] (0.37 mmol, 0.1 g), $Pd(dba)_2$ (0.018 mmol, 5 mol %, 0.011 g), and dppe (0.018 mmol, 0.007 g) were stirred in THF (0.9 mL) for 10 min under an argon atmosphere. In a separate flask, diethyl malonate (1.92 mmol, 0.31 g) in THF (2.6 mL) was slowly added to a slurry of NaH (1.47 mmol, 0.59 g, 60% suspension in mineral oil) in THF (2.6 mL) and stirred for 10 min. The resulting clear solution was transferred via cannula to the former and the combined mixture stirred at 40 °C for 3 h. The reaction mixture was diluted by ether (30 mL) and filtered on 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 column chromatography (SiO_2, pentane−ether 7:3) gave 0.13 g (90%) of **6** as a colorless oil. Alkylation of **2b** using of $Pd(PPh_3)_4$ as a catalytic source (0.018 mmol, 5 mol %, 0.021 g) was performed as above, except that the reaction mixture was refluxed in THF for 3 h, yielding 0.11 g (83%) of product. Anal. Calcd for $C_{21}H_{30}O_4Si$: C, 67.34; H, 8.07. Found: C, 67.43; H, 8.15. ^{1}H NMR: δ 7.44−7.15 (m, 5H, Ar), 5.74 (dq, 1H, H3), 5.72 (dq, 1H, H2), 4.18 (q, 4H, −OCH_2−CH$_3$), 3.04 (d, 1H, −C*H*(COOEt)$_2$), 2.90 (bm, 1H, H1), 1.78 (bm, 1H, H4), 1.71 (bm, 1H, H5), 1.59 (bm, 1H, H6), 1.36−1.21 (bm, 8H, H5′, H6′, −OCH$_2$−CH_3), 0.30, 0.29 (ss, 6H, Si(CH_3)$_2$. ^{13}C NMR: δ 168.8 (C=O), 138.0, 134.2, 129.4, 128.1 (Ph), 130.7 (C3), 125.9 (C2), 61.7 (−O*C*H$_2$−CH$_3$), 57.4 (−*C*H(COOEt)$_2$), 34.7 (C1), 26.2 (C4), 25.8 (C6), 14.5 (−OCH$_2$−*C*H$_3$) −4.1, −4.2 (Si(*C*H$_3$)$_2$). DNOE observed for **6**:



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