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Electrophilic addition to styrylsilanes: sequential carbon–carbon bond forming reactions

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Abstract

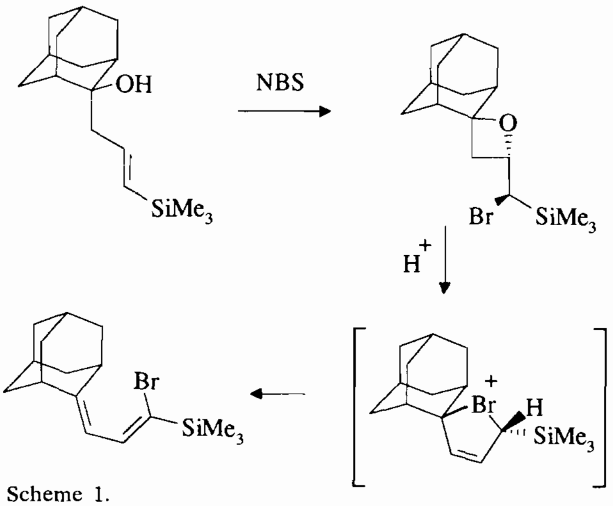
The replacement of the usual electron donating alkyl groups on silicon, with electronegative chloride ligands, changes the mechanism and outcome of the reaction of (*E*)-β-(dichlorobenzylsilyl)styrene with proton and carbon electrophiles. Electrophilic addition rather than the usual substitution occurs, so that the silicon remains intact to mediate further chemical reactions. The experimental results show that Friedel–Crafts reactions of the silylated alkene are subject to the same limitations observed for non-silylated alkenes; the extent of polymerization increases as the stability of the carbenium ion decreases.

Key words: Electrophilic addition; Carbon–carbon bond formation; Silicon compounds; Styryl compounds; Friedel–Crafts reaction; Cyclization; β-effect

Introduction

For the most part, organosilicon π-nucleophiles undergo regio- and stereoselective electrophilic substitution reactions [1]. Regiocontrol in these reactions has been attributed to the electronic steering influence of the β-stabilized (hyperconjugative stabilization, the β-effect) cationic intermediate [2], while stereocontrol (retention versus inversion of olefin geometry) results from the geometrical requirements for optimum stabilization [1].

Electrophilic additions have been reported where the elimination of silicon was thwarted by bulky spectator ligands on silicon [3, 4]. Silicon retention has also been observed in cyclic adamantyl systems where conformational constraints restrict the interaction between the Si–C σ-orbital and the p orbital of the π bond (Scheme 1) [5].



Scheme 1.

More general examples of silicon retention involve electron-deficient silanes. In the early 1950s and 1960s Andrianov *et al.* [6] and Bailey *et al.* [7] observed that trichlorovinylsilanes undergo electrophilic addition reactions with benzene in the presence of aluminum chloride. Similar results were obtained by Tamao *et al.* [8] and Hagen and Mayr [9] for allylsilanes. Here the silicon is precluded from leaving due to the reduced β-stabilization afforded by the electron withdrawing chlorosilanes [10]. Attempts to examine the mechanism of these reactions or expand their synthetic utility have not been reported.

We have been primarily interested in using chlorosilanes to reduce the leaving group ability of silicon so that the silyl group can be used to control the formation of more than one C–C bond before finally being cleaved from the organic skeleton. Recently, we have shown that (*E*)-β-(trichlorosilyl)styrene (**1a**) and

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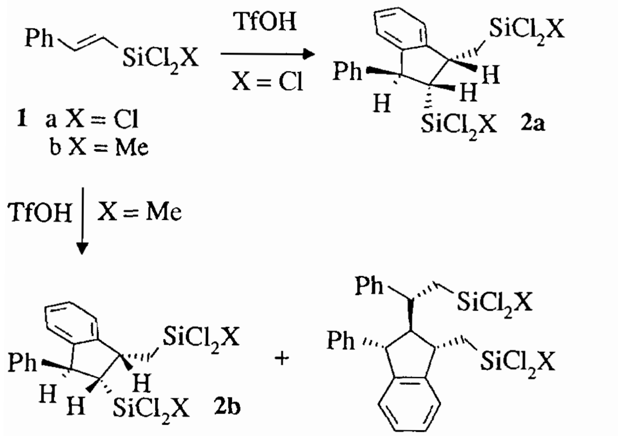
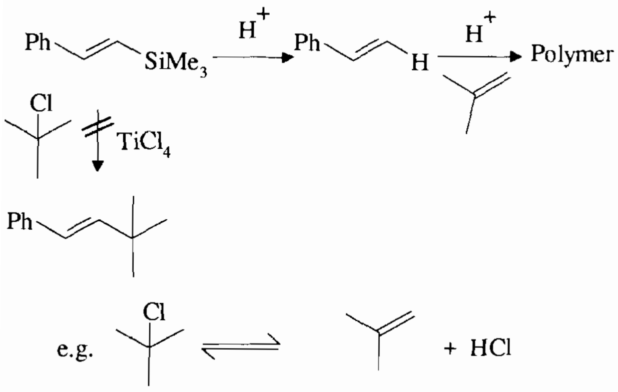


Scheme 2.



Scheme 3.

(E)-β-(dichloromethylsilyl)styrene (**1b**) can undergo diastereoselective dimerization and trimerization in the presence of trifluoromethanesulfonic acid, with retention of the silicon group **2a,b** (Scheme 2) [11].

To extend the utility of this approach, we have modified the ligands on silicon and examined the addition of carbon electrophiles. Our hope was that the diastereoselectivity observed in Scheme 2 could be extended to more complex systems in which the two bonds formed arise from different silyl nucleophiles. We have investigated, and herein report, the parameters required for the formation of acyclic and cyclic 1:1 addition products in the reactions of carbon electrophiles with (E)-β-(trichlorosilyl)styrene (**1a**) and (E)-β-(dichlorobenzylsilyl)styrene (**3**).

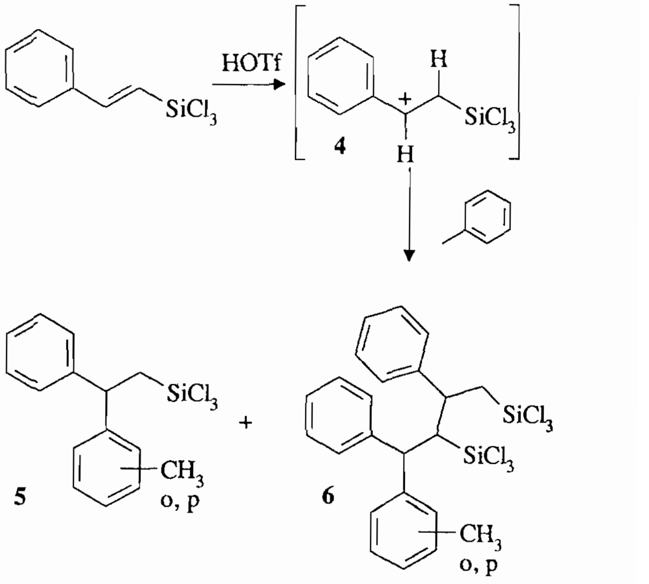
Results

Proton addition

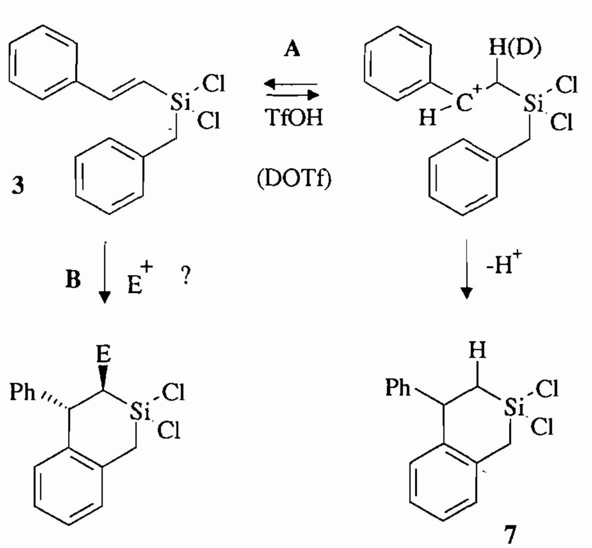
β-Trimethylsilylstyrene undergoes ready addition of a variety of carbon electrophiles such as $PhCH_2COCl$ [12], t-BuCl (e.g. Scheme 3), or PhRR'CCl (R, R' = Me, Ph) in the presence of Lewis acids. However, the reactions always produced desilylated materials. Protiodesilylation probably occurred first from adventitious protons, protons produced in a Friedel–Crafts reaction, or elimination of 3° cations, producing styrene which then polymerized (Scheme 3, shown for t-BuCl) or underwent reaction with the desired electrophile [13].

In contrast, in previous experiments it was determined that with the exception of triflic acid [11, 14] or bromine [15], electrophiles did not add to β-trichlorosilylstyrenes; the presence of the three Cl atoms significantly reduces the electron density in the alkene. In the presence of acceptable nucleophiles such as aryl groups, the first formed benzylic cation **4** could, however, be trapped. Thus, in toluene as solvent, treatment of trichlorosilylstyrene **1a** with triflic acid led to an intermolecular Friedel–Crafts reaction giving a monomeric **5** and dimeric species **6** (Scheme 4). This demonstrates that two different bond formation reactions can be controlled by a given silyl group.

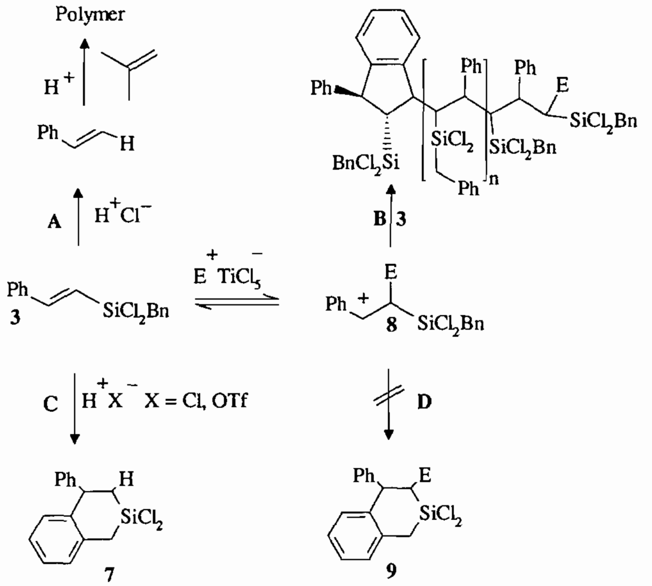
In order to increase the reactivity of the styryl double bond towards electrophiles, we replaced one of the chlorine groups with an alkyl group. We found that proton addition to dichloroallylsilanes led to the normal substitution reaction (protiodesilylation). Much more fruitful was the use of a benzyl group on silicon. This silyl group balances leaving group ability and electronic stabilization: the group has a sufficient β-effect to stabilize the intermediate cation, but a sufficiently poor leaving group ability that other reactions intervene before the silyl group is lost from the molecule, particularly the intramolecular Friedel–Crafts reaction with the silylbenzyl group. Thus, the addition of triflic acid to this system, leads to the formation of the tetrahydronaphthalene **7** (Scheme 5, A). In this process, two



Scheme 4.



Scheme 5.



Scheme 6.

bonds (C–H and C–C) are sequentially formed in the presence of the silyl group [16].

Carbon electrophiles

We have proceeded to determine if this system **3** could be used for the diastereoselective control of C–C bond formation (Scheme 5, B), by examining its reactivity with a series of carbon electrophiles. The reaction of t-butyl chloride with (*E*)-β-(dichlorobenzylsilyl)styrene (**3**) (Scheme 6, A), in the presence of titanium tetrachloride ($(CH_3)_3C^+$), led exclusively to the formation of an intractable polymeric mixture. Examination of the crude ^{1}H NMR allows one to draw the conclusion that a polymer containing primarily polystyryl units is the major constituent in the reaction products; small amounts of isobutylene and benzyl units (<5%) are incorporated although these polymers contained *no silicon groups* [13, 17]. The absence of silyl groups is consistent with initial protiodesilylation followed by polymerization of styrene in analogy with the process shown in Scheme 3.

Benzyl cations add to **3** to give an oligo/polymeric mixture in which most silicon groups have disappeared (>70%). The primary product appears to be an adduct between the benzyl cation and styrene or a styrene dimer.

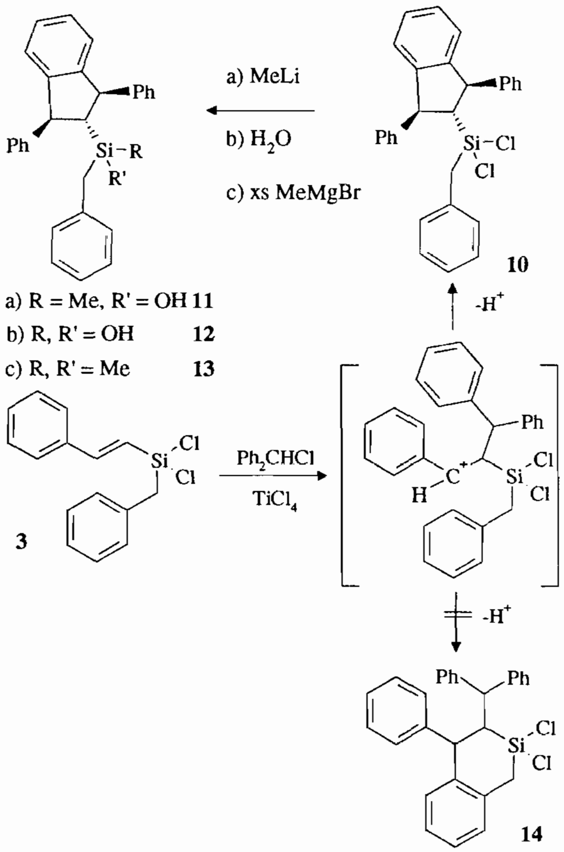
A small change in cationic stability led to a large difference in reaction products. The *p*-methoxybenzyl cation (*p*-$MeOC_6H_4CH_2Cl/TiCl_4$) reacted with **3** to give oligomeric products in which the silyl moiety was retained (60%) (Scheme 6, B) and, additionally, **7** (20%) (Scheme 6, C). There was no evidence for the expected tetrahydronaphthalene **9** (Scheme 6, D). The oligomer produced from the *p*-methoxybenzyl carbenium ion initiated reaction was of a relatively low molecular weight (MW=920).

The addition of acyl cations ($AcCl/TiCl_4$) to **3** also led to the formation of **7** (10%) and a oligomeric mixture (oligo(benzyldichlorosilyl)styrene) in which most of the silyl units had been retained (90%) but in which <5% acetyl groups had been incorporated. There was no evidence for the desired cyclized compound **9** (Scheme 6, D).

The formation of adduct **7** (Scheme 6, C) is the result of proton addition to **3** [16]. Presumably, once the electrophile (acyl or *p*-MeObenzyl cation) initiates the reaction, two manifolds exist: polymerization which terminates with a Friedel–Crafts condensation, concomitantly producing protons, and addition of those protons to produce **7**.

The reaction of chlorodiphenylmethane with **3** in the presence of $TiCl_4$ gave 73% of the 1:1 cyclized adduct 1,3-diphenyl-2-(dichlorobenzylsilyl)indan (**10**) (Scheme 7). The structural elucidation of **10** was accomplished after converting it to the methylhydroxysilyl derivative **11**. Direct hydrolysis of **10** gave the diol **12**. The reaction of **10** with 2 equivalents of methyl lithium resulted only in monomethylation giving **11**; steric congestion of the silicon afforded by the indan moiety effectively blocked the second methylation. This chloride was, however, susceptible to hydrolysis upon quenching the reaction mixture with water. Complete methylation to **13** was possible only after a huge excess of MeMgBr was allowed to react with **10** over an extended period of time. Again, there was no evidence for the six-ring **14**.

The ^{1}H NMR spectrum of the crude methylated product mixture, after removal of solvents, revealed that only a single, *meso* indan was produced. The structure was assigned *trans/trans* geometry based on nOe measurements, as well as the H–H scalar coupling constants and molecular modelling.



Scheme 7.

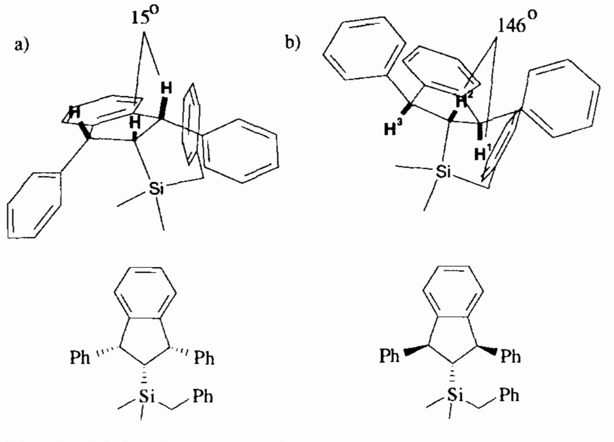


Fig. 1. Molecular mechanics calculations (MM2) of the (a) *trans,trans*(steric energy 26.4 kcal/mol) and (b) *cis,cis* isomers of **13** (steric energy 49.9 kcal/mol).

A coupling constant $J(H^1–H^2)$ of 11.8 Hz correlates better with a 180° (*trans*) dihedral angle on the Karplus scale, than to a 0° (*cis*) dihedral angle. Molecular mechanics calculations indicate that a dihedral angle of 146° for H^2–C–C–H^1 or H^2–C–C–H^3 **13** (Scheme 7), in which the hydrogens H^1, H^2 and H^3 are *trans* diaxial, corresponds to an energy minimum (Fig. 1(a)). In contrast, a dihedral angle of 15°, in which the hydrogens are *cis* to each other, is not an energy minimum since there is severe torsional strain as a result of the eclipsed, contiguous, bulky groups (Fig. 1(b)).

Upon exposure of **3** to the trityl cation (Ph_3C^+), no reaction was observed even at elevated temperatures (80 °C) irrespective of the nature of the counterion (BF_4^-, $SbCl_6^-$, PF_6^-).

Discussion

Reaction mechanism

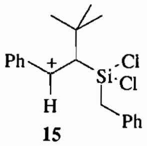
Clean addition reactions to the styrylsilane were observed with the combinations: **1**/HOTf/toluene and **3**/$Ph_2CHCl/TiCl_4$; the proton cyclized product **7** was observed in isolable quantities with the combination of **3**/*p*-$MeOPhCH_2Cl/TiCl_4$ (10%) and **3**/$MeCOCl/TiCl_4$ (20%). The nature of the products that arise from the reaction of **3** with other electrophiles is directly related to the ease of formation of the electrophile cation, the stability of **8**, the ease of its formation and the nucleophiles present in solution. The effect of each of these on the outcome of the reaction will be discussed in turn.

The first step in the reaction mechanism is the addition of the electrophile to the styryl double bond giving **8** (Scheme 6). This step is reversible; we have observed as much as 44.2% undeuterated **7** (39.4% monodeuterated and 16.4% dideuterated **7**), upon treating silylstyrene **7** (Scheme 7) with deuterated triflic acid ($E^+ = D^+$) [16]. The undeuterated species **7** (Scheme 7) must arise from protons ejected during the ultimate step in the Friedel–Crafts cyclization. The dideuterated species is formed by the sequential addition of D^+, loss of H^+ and addition again of D^+.

Cation stability

The addition of the tertiary cations t-Bu^+ and Ph_3C^+, in principle giving **15** and **16**, respectively, should be extremely slow because of the steric interactions. In the latter case, no reaction was observed. In the former, a different reaction course took place. As elimination of HCl is relatively facile, more facile than forming **15**, there are sufficient protons present for protiodesilylation (i.e. H^+ is the actual electrophile), and subsequent polymerization of styrene/isobutylene occurs (Scheme 6, A). The protiodesilylation step is likely facilitated by the nucleophilicity of Cl^- (*vide infra*).

The product of acyl cation addition to **3**, **17**, will be destabilized by the electronic withdrawal by the acyl group. Rather than undergo intramolecular cyclization, the material reacts intermolecularly with more styryl monomers. Protons released in the Friedel–Crafts reactions that terminate the oligomerization (e.g. Scheme 2) can also initiate reaction and thus compete with the acyl cation. Similarly, a competition between p-MeOC$_6$H$_4$CH$_2{}^+$ addition giving **18** and H$^+$ addition giving **19** was observed. This type of competitive addition has previously been reported. Marcuzzi and Melloni for example, detected the products of HCl addition, formed during cyclization reactions of alkenes and alkynes with diphenylmethyl chloride in the presence of Lewis acids [18].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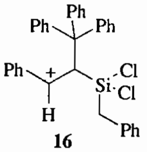
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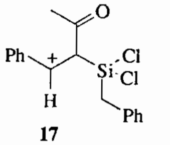
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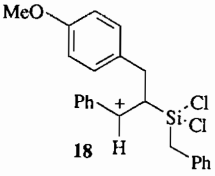
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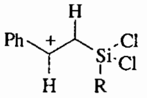
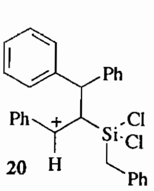

19 a R = Cl
b R = CH$_2$Ph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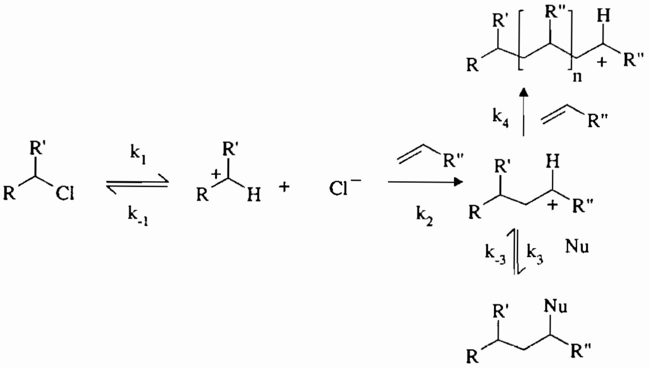
The cleanest reaction of those examined was with Ph$_2$CH$^+$, the most stable of the electrophiles which reacted, giving **20**, the most stable of the carbenium ions (**15**–**20**). There is clearly a correlation between the formation of the 1:1 addition product and the order of relative reactivity of the cations: tBu$^+$ $>p$-Me-OPhCH$_2{}^+$ $>$ MeCO$^+$ $\geq$ Ph$_2$CH$^+$. The less reactive cations produced more 1:1 addition product. There is at the same time an inverse relationship between electrophile stability and the extent of cationic polymerization.

A similar trend has been established by Mayr [19]. 1:1 addition products were observed when an alkene reacts faster with the educt ($k_2 > k_4$, alkyl chloride or aryl chloride, RCl, Nu = Cl, Scheme 8); polymerization occurs instead if the alkene reacts faster with the adduct **3** ($k_4 > k_2$). In our experiments, the carbenium ion is ultimately captured by an aryl group (Nu = Ph).



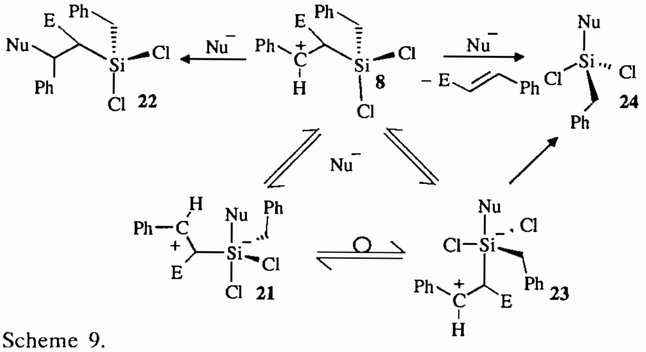
Scheme 8.

The point at which these two extremes meet can be seen by the results given above. Clean 1:1 addition reactions were observed with **1**/HOTf/toluene and **3**/Ph$_2$CHCl/TiCl$_4$ (via cations **19a**,**b**, **20**). In the other cases, polymerization was predominant due to a decreased stability of the carbenium ions **15**–**18** produced upon addition to the styryl group.

Leaving group ability

Silicon does not generally undergo S$_N$1 reactions: silylium ions are extremely rare in the condensed phase [20]. The elimination of silicon from the carbon skeleton requires bimolecular nucleophilic substitution reactions at silicon, with attack by the nucleophile as the requisite first step. The pentacoordinate intermediate produced (rather than a transition state for carbon), usually has the most electronegative (leaving) group in the apical position [21].

The BnCl$_2$Si group has a decreased leaving group ability compared to an Me$_3$Si group. This is readily understood from the proposed reaction mechanism. With an Me$_3$Si group, the alkyl carbenium ion will be the most apicophilic ligand on silicon. Thus, exposure to any nucleophile results in attack at silicon and cleavage of the silyl group from the carbon skeleton. In contrast, with the BnCl$_2$Si group, if the chloride has a higher apicophilicity than the carbocation [22], nucleophilic attack (Cl$^-$ or TiCl$_5{}^-$) to give the pentacoordinate species **21** (Nu = Cl) and subsequent substitution is a redundant reaction (Scheme 9). Nucleophilic attack at carbon, in these examples by an aromatic ring, leads to C–C bond formation **22** (Nu = Ph). If, however, the apicophilicity of the carbenium group is comparable to or greater than that of chloride, which is to be expected as the stability of the carbenium ion decreases, there will be an enhanced substitution at silicon via **23** leading to desilylation **24** of the carbon skeleton. The correlation between carbenium ion stability and desilylation can be directly seen (electrophile (% silyl group retention)) tBu$^+$ (0) < PhCH$_2{}^+$ (30) < p-MeOPhCH$_2{}^+$ (60) < CH$_3$CO$^+$ (90) < Ph$_2$CH$^+$ (100).



Scheme 9.

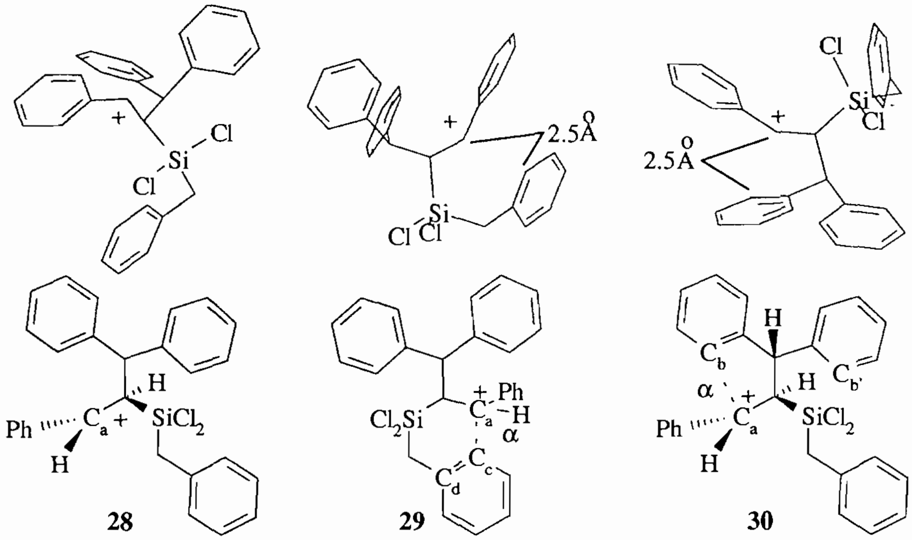


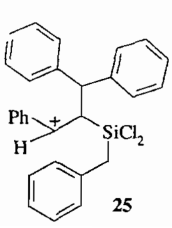
Fig. 2. MMX calculated structures of **28**, **29** and **30** with $\alpha = 2.5$ Å.

As indicated above, the t-Bu cation is unlikely to add to the styryl group. In this case protiodesilylation is a consequence of the much higher H^+ concentration in this reaction due to the facile elimination of HCl from t-BuCl. Although the carbocation will primarily occupy the equatorial position **21** ($E = H$, $Nu = Cl$), even a low amount of reaction through **23** will inevitably lead to, essentially irreversible, protiodesilylation.

Reaction with Ph_2CH^+

Six-ring versus five-ring formation

Initially, we anticipated that, in analogy to **7**, a six-membered ring would be formed from the addition of Ph_2CH^+ to **3**. However, only the five-membered ring was formed. In the latter case, there are three aryl rings that can react to cyclize, with a statistical advantage for the formation of the five-membered rings from two diastereotopic phenyl rings. In order to determine if other factors are operating, we calculated (AM1) the relative stability of the three cations: the open cation **25**, the six-membered ring cation **26** and the five-membered ring cation **27**. The open cation **25** was found to have a heat of formation of 181.6 kcal/mol, whereas **26** and **27** were found to have heats of formation of 188.0 and 180.9 kcal/mol, respectively. Thus, on thermodynamic grounds, the formation of **27** is not surprising.



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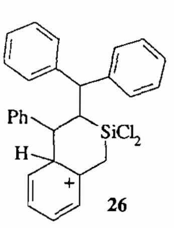

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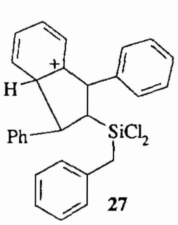

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In order to examine the steric interactions that might be incurred leading from **25** to **26** and **27**, we examined the conformational energy on the path to the transition state using molecular mechanics calculations on the dimethylsilyl derivatives **28**, **29** and **30***. These calculations provide some insight into the differences in the two approaches.

The distances between the benzylic carbon (C_a) and the aromatic carbons (C_b in **29** and C_c in **30**, respectively) were fixed at 2.5 Å. Minimization using the MMX parameter set, which has preliminary parameters for carbenium ions, also suggested that formation of the five-ring **30** (steric energy 65.05 kcal/mol) would be more facile than the six-membered ring **29** (steric energy 79.10 kcal/mol, Fig. 2); the open cation **28** was least strained (steric energy 58.00 kcal/mol). These results suggest formation of the indans such as **2** and **10** are normal. The formation of **7** is anomalous because the benzyl group is the only viable nucleophile in the reaction.

Importance of the β-effect

The β-effect has been shown to be angularly dependent (torsional angle between the Si–C σ-bond and the empty p orbital) in a type of Karplus relationship with an optimum stabilization at 180° [3]. As the reaction proceeds from **28** to **29** the dihedral angle changes from 123° (Si–C–C_a^+-p orbital) to 178° (Si–C–C_d^+-p orbital), respectively. This implies that the β-effect can operate, and will have an increased magnitude as the Friedel–Crafts process occurs. However, the fact that

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*Since MMX parameters for the Si–Cl bond do not exist, the modelling was undertaken on the dimethyl derivatives shown.

the five-membered ring is formed suggests that the β-effect of a Cl_2BnSi group is not sufficiently strong to control the regiochemistry of the reaction and **30** is preferentially formed [15].

Only one diastereomer of **30** was observed both at lower (−35 °C) and more elevated temperatures (42 °C). Although this contrasts with the results of the protonation of **1** [11], it is consistent with the addition of diarylcarbenium ions to *Z*- and *E*-alkenes which have been shown to stereospecifically form *trans*/*trans* 1,3-disubstituted indans as a result of a less crowded transition state or intermediate [23].

Conclusions

The change from trialkylsilyl to benzyldichlorosilyl groups has a significant impact on the reactivity of the alkene to which they are bonded. One important difference is that the silicon has a lower β-effect and thus the reactivity of the alkene towards electrophiles is diminished. At the same time, the leaving group ability is lower and the silicon can remain on the molecule to be further exploited. In order for the 1:1 addition products to be produced, the reaction in which the silicon stabilized carbenium ion intermediate is trapped must normally be intramolecular. The utilization of electron poor silanes of this type, therefore, requires a judicious choice of carbon electrophiles. They must not place extreme steric demands on the alkenylsilane, must be relatively stable carbenium ions and, furthermore, must have non-nucleophilic counterions.

Experimental

Apparatus, materials and methods

The continuous wave ^1H NMR spectra were recorded on a Varian EM-390 (90 MHz) spectrometer and the Fourier spectra on a Bruker AM-500 (500 MHz) spectrometer, Bruker AC-300 (300 MHz) spectrometer or Bruker AC-200 (200 MHz) spectrometer. ^{13}C and ^{29}Si NMR were performed on a Bruker AC-200 (at 200 MHz for protons), and a Bruker AC-300 (at 300 MHz for protons), respectively. Chemical shifts are reported with respect to tetramethylsilane as standard, set to 0 ppm. Coupling constants (J) are recorded in hertz (Hz). The abbreviations s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, m = multiplet, are used in reporting the spectra.

Electron impact (EI) and chemical ionization (CI, NH_3) mass spectra were recorded at 70 eV with a source temperature of *c*. 200 °C on a VG analytical ZAB-E mass spectrometer equipped with a VG 11-250 data system. High resolution mass spectral (HRMS) data were obtained with the VG-ZAB-E instrument by the EI method. IR spectra were run on a Perkin Elmer 283 spectrometer and Fourier spectra on a BIO RAD FTS-40 spectrometer, as a neat film.

The purity of new volatile compounds was confirmed by an HP-5890A gas chromatograph; 2-3755 glass capillary column, SPB-1, 30 m, 0.075 mm ID after distillation.

The molecular weight distributions of the copolymers were analyzed using a Waters gel permeation chromatograph equipped with a Waters 410 differential refractive index detector. Two Jordi mixed bed columns in series were utilized with 1,1,1-trichloroethane as solvent flowing at 1.5 ml/min. Narrow molecular weight polystyrene standards from Polymer Laboratories were used for calibration of the chromatographic system.

All solvents were thoroughly dried before use. Dichloromethane was distilled over P_2O_5. Diethyl ether, THF and hexane were distilled over Na/benzophenone. NEt_3 was dried by refluxing with NaOH and distilling over BaO.

Due to the tendency of halo groups on silicon to hydrolyze easily, all reactions were carried out in dry apparatus under a nitrogen atmosphere with the use of septa and syringes for the transfer of reagents.

The standard work-up procedure for all reaction products, unless otherwise indicated, was extraction with diethyl ether, washing with distilled water, removal of solvent under reduced pressure and purification by radial chromatography and/or distillation or Kugelrohr distillation.

Addition of toluene to trichlorosilylstyrene (1)

To a solution of **1** (0.95 g, 4.00 mmol) and toluene (0.50 ml, 4.70 mmol) at 0 °C was added triflic acid (0.06 ml, 0.68 mmol). The reaction mixture immediately turned bright red–orange and two layers formed. After stirring for 3 h, the solution was diluted with Et_2O (10 ml) and quenched with MeMgBr (3.0 M in Et_2O, 7.0 ml, 21 mmol). Two compounds were isolated by radial chromatography.

5 (equal portions *para* and *ortho* products): yield 52% (650 mg). ^1H NMR ($CDCl_3$ 200 MHz): δ 0.04, 0.06 (s, 9H), 1.61 (d, 2H, J = 8.1 Hz), 2.47, 2.49 (s, 3H), 4.25 (t, 1H, J = 8 Hz), 7.27–7.49 (m, 9H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ −1.12, 20.96, 24.30, 46.96, 47.33, 124.56, 125.87, 126.69, 127.41, 128.30, 128.98, 135.28, 137.69, 144.13, 147.05, 147.34. ^{29}Si NMR ($CDCl_3$, 49.7 MHz): δ 0.65. IR (neat): ν 3020, 2940, 2890, 1595, 1485, 1445, 1410, 1240, 1170, 1010, 850, 830, 750, 690. HRMS (m/z): M^+ calc. for $C_{18}H_{24}Si$ 268.1647; found 268.1635.

6 (≈ equal portions *para* and *ortho* products): yield 19% (170 mg). ^1H NMR ($CDCl_3$ 200 MHz): δ −0.18, −0.12 (m, 18H), 1.38–1.47 (m, 4H), 2.28–2.33 (m, 3H), 4.01–4.13 (m, 1H), 7.04–7.32 (m, 14H). IR (neat): ν 3060, 3020, 2950, 2900, 1600, 1490, 1450, 1410, 1245, 1170, 1015, 850, 755, 690. HRMS (m/z): M^+ calc. for $C_{29}H_{40}Si_2$ 444.2669; found 444.2668.

(E)-β-(Dichlorobenzylsilyl)styrene (3)

To a solution of **1** [24] (48.1 g, 204 mmol) in Et_2O (500 ml) was added benzylmagnesium chloride (1 M in Et_2O, 102 ml, 102 mmol, 0.5 equiv.). After stirring overnight at −50 °C, the reaction mixture was allowed to warm to ambient temperature (20 °C) and stirred at that temperature for 1 h. Yield 28 g (95%, with reference to BzMgCl), obtained after removing excess trichlorosilylstyrene at 97 °C/5 Torr followed by distillation of (*E*)-β-(dichlorobenzylsilyl)styrene at 170 °C/0.1 Torr. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 2.63 (s, 2H), 6.19 (d, 1H, $J=18.0$ Hz), 7.11 (d, 1H, $J=18.0$ Hz), 7.05–7.23 (m, 10H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 150.39, 136.06, 133.81, 129.67, 128.89, 128.45, 128.31, 127.17, 125.75, 118.76, 30.18. ^{29}Si NMR ($CDCl_3$, 49.7 MHz): δ 15.67. MS (EI, *m/z*): 292(10), 257(12), 201(55), 165(100), 91(38), 77(20), 63(15), 51(10). HRMS (*m/z*, M^+): calc. for $C_{15}H_{14}Cl_2Si$ 292.0206; found 292.0224. IR (neat): 3027, 2895, 1602, 1493, 1450, 1396, 1210, 1175, 1100, 1058, 1029, 989, 908, 833, 803, 764, 733, 697, 591, 500, 459 cm^{-1}.

Reactions of 3 with carbon electrophiles

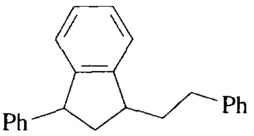
t-Butyl cation as electrophile

3 (4.64 g, 15.8 mmol) was added to a mixture of titanium tetrachloride (2.0 ml, 17.4 mmol) and t-butyl chloride (1.61 ml, 17.4 mmol) in dichloromethane (400 ml) at −40 °C. The reaction mixture was stirred at −40 °C (20 h), −10 °C (1 h) and 0 °C (2 h) followed by removal of dichloromethane under reduced pressure at ambient temperature (22–25 °C). Alkylation was effected by using MeMgBr (3.0 M, 53 ml in diethyl ether, 159 mmol) and stirring for 16 h at ambient temperature. The reaction yielded a complex oligo/polymeric mixture, primarily polystyrene with some isobutylene ($\approx 10\%$).

Crude material: ^{1}H NMR ($CDCl_3$ 90 MHz): δ 1.2 (broad s, ≈ 0.6 H), 1.5–2.3 (m, 3H), 7.3–7.6 (m, 5H).

Benzyl cation as electrophile

3 (2.0 g, 6.8 mmol) was added to a mixture of titanium tetrachloride (3.4 ml, 29.6 mmol) and *p*-methoxybenzyl chloride (0.78 ml, 6.8 mmol) in dichloromethane (140 ml) under reflux. The reaction mixture was stirred under reflux for 48 h followed by removal of dichloromethane under reduced pressure at ambient temperature (22–25 °C). Alkylation was effected by using MeMgBr (3.0 M, 90 ml in diethyl ether, 270 mmol) and stirring for 16 h at ambient temperature. The crude ^{1}H NMR showed the presence of $\approx 30\%$ Me_2Si groups. Otherwise, the oligomeric mixture contained primarily styryl monomers and dimers initiated by a benzyl cation, e.g.



^{1}H NMR ($CDCl_3$, 90 MHz): δ 0.1–0.35 (m, <30% based on aryl protons, $SiMe_2$), 1.4–1.7 (m, 6H), 2.1–2.3 (m, 1H), 3.5–4.2 (m, 1H), 7.3–7.6 (m, 14H).

p-Methoxybenzyl cation as electrophile

3 (2.0 g, 6.8 mmol) was added to a mixture of titanium tetrachloride (3.4 ml, 29.6 mmol) and *p*-methoxybenzyl chloride (0.92 ml, 6.8 mmol) in dichloromethane (140 ml) under reflux. The reaction mixture was stirred under reflux for 48 h followed by removal of dichloromethane under reduced pressure at ambient temperature (22–25 °C). Alkylation was effected by using MeMgBr (3.0 M, 90 ml in diethyl ether, 270 mmol) and stirring for 16 h at ambient temperature. The reaction yielded 20% **7** (0.34 g, 1.36 mmol), along with polymeric material.

3,3-Dimethyl-1-phenyl-3-sila-tetrahydronaphthalene (7). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.10 (s, 3H), 0.29 (s, 3H), 1.29 (dd, 1H, $J=4.63$, -14.21 Hz), 1.34 (dd, 1H, $J=10.40$, -14.20 Hz), 2.12 (d, 1H, $J=-14.55$ Hz), 2.18 (d, 1H, $J=-14.59$ Hz), 4.26 (dd, 1H, $J=4.58$, 10.36 Hz), 6.77–7.48 (m, 9H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 145.12, 144.82, 138.59, 130.41, 129.85, 128.89, 127.75, 126.86, 126.76, 125.38, 45.35, 21.78, 18.84, −1.20. ^{29}Si NMR ($CDCl_3$, 49.7 MHz): δ 0.51. MS (EI, *m/z*): 252(100), 237(41), 224(7.5), 209(7.5), 191(7.5), 178(41), 161(64), 141(48), 133(40), 121(26), 114(20), 105(21), 91(14), 59(21), 43(13). MS (CI, *m/z*): $M^+ + NH_4$ 270(100), 252(35), 237(18), 207(15), 180(40), 152(18), 91(10), 76(15). HRMS (*m/z*, M^+): calc. for $C_{17}H_{20}Si$ 252.1334; found 252.1340. IR (neat): 3002, 2800, 1590, 1470, 1430, 1225, 1190, 1140, 1030, 820, 770, 730, 675 cm^{-1}. *Anal.* Calc. for $C_{17}H_{20}Si$: C, 80.97; H, 8.00. Found: C, 80.71; H, 8.06%. MW from GPC 920.

Residue (mainly poly(*p*-methoxybenzyl): ^{1}H NMR ($CDCl_3$, 200 MHz): −0.18 (bs, 1H, $SiMe_2$), 0.8–1.0 (m, 0.1H, adjacent $SiMe_2$), 1.2–1.5 (0.4H, oligostyrene CH), 2.0 (0.2H, CH_2Ph added to styryl system), δ 3.3–4.2 (m, 2H), 6.6–7.4 (m, 4H, benzyl+styryl).

Acylium ion as electrophile

3 (1.0 g, 3.4 mmol) was added to a mixture of titanium tetrachloride (1.65 ml, 14.4 mmol) and acetyl chloride (0.29 g, 3.7 mmol) in dichloromethane (70 ml) at ambient temperature (22–25 °C). The reaction mixture was stirred while refluxing for 20 h. Following removal of dichloromethane under reduced pressure at ambient temperature and replacing with 30 ml diethyl ether, alkylation was effected using MeLi (1.5 M, 46 ml in diethyl ether, 69 mmol). After addition of the lithium reagent, the reaction mixture was stirred for 16 h at ambient temperature. The reaction yielded 10% **7** (0.85 g, 3.37 mmol), in addition to an intractable mixture of oligomeric species. There was no evidence for acyl groups or the Me_2OH groups expected to be produced upon methylation with MeLi.

Crude: ^{1}H NMR ($CDCl_3$, 90 MHz): δ 0.1–0.4 (m, 5.5H), 1.5–2.3 (m, 2H), 2.5 (broad s, 2H), 7.3–7.6 (m, 10H).

Diphenylcarbenium ion as electrophile

1,3-Diphenyl-2-(dimethylbenzylsilyl)indan (13). **3** (5.0 g, 17.2 mmol) was added to a mixture of titanium tetrachloride (8.5 ml, 74.2 mmol) and chlorodiphenylmethane (3.4 ml, 17.2 mmol) in dichloromethane (250 ml) under reflux. The reaction mixture was stirred under reflux for 24 h. Following removal of dichloromethane under reduced pressure at ambient temperature (22–25 °C), alkylation was effected using MeMgBr (3.0 M, 186 ml in diethyl ether). After addition of the Grignard reagent, the reaction mix was stirred for 1 week at ambient temperature. The result after radial chromatography was **13**. Yield 73% (5.25 g); b.p. 220 °C/2.0 torr. ^{1}H NMR ($CDCl_3$, 300 MHz): δ −0.15 (s, 6H), 1.94 (s, 2H), 2.22 (dd, 1H, J = 11.1, 11.2 Hz), 4.38, (d, 2H, J = 11.1 Hz), 6.78–7.41 (m, 19H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 148.01, 145.15, 139.54, 128.88, 128.41, 128.08, 127.94, 126.64, 126.55, 124.25, 123.82, 53.34, 45.56, 24.72, −3.7. ^{29}Si NMR ($CDCl_3$, 49.7 MHz): δ 3.06. MS (EI, m/z): 418(20), 403(15), 327(30), 267(100), 191(30), 165(16), 149(30), 135(80), 91(15), 59(20). High resolution MS (m/z, M^+): calc. for $C_{30}H_{30}Si$ 418.2156; found 418.2136. IR (neat); ν 3061.5, 3025.4, 2954.9, 2892.3, 1599.4, 1493.6, 1452.6, 1251.0, 1205.9, 1156.9, 1075.8, 1029.4, 908.5, 831.1, 754.0, 700.1 cm^{-1}.

1,3-Diphenyl-2-(dihydroxybenzylsilyl)indan (12) and 1,3-diphenyl-2(methylhydroxybenzylsilyl)indan (11). A similar reaction to that above was used, with less Grignard reagent: **3** (1.1 g, 3.7 mmol); $TiCl_4$ (1.7 ml, 14.8 mmol); chlorodiphenylmethane (0.74 ml, 3.7 mmol); in CH_2Cl_2 (70 ml). After 17 h, the acids were neutralized with triethylamine (37 mmol) followed by removal of dichloromethane under reduced pressure at ambient temperature (22–25 °C). Alkylation was effected using MeMgBr (3.0 M, 14.8 ml in diethyl ether), with stirring for 17 h at ambient temperature. The reaction yielded 17% (0.27 g) 1.3-diphenyl-2-(dihydroxybenzylsilyl)-indan (**12**), 21% (0.33 g), 1,3-diphenyl-2-(methylhydroxybenzylsilyl)indan (**11**) and 2% **13**.

1,3-Diphenyl-2-(dihydroxybenzylsilyl)indan (12). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.00 (s, 2H, CH_2), 2.10 (dd, 1H, CH, J = 11.36, 11.40), 2.73 (broad s, OH), 4.55 (d, 2H, CH, J = 11.37), 6.86–7.44 (m, aromatic H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 148.17, 145.21, 137.73, 129.39, 129.30, 129.14, 128.85, 127.44, 127.39, 125.07, 124.92, 52.78, 47.60, 25.44. ^{29}Si NMR ($CDCl_3$, 49.7 MHz): δ −10.9. MS (EI, m/z): 422(75), 404(10), 331(28), 268(40), 191(40), 153(65), 139(60), 91(100), 63(32). High resolution MS (m/z, M^+): calc. for $C_{28}H_{26}SiO_2$ 422.1702; found 422.1702. IR (neat): ν 3603.0, 3387.1, 3081.5, 3026.5, 2795.3, 1599.8, 1594.0, 1452.5, 1400.4, 1261.0, 1210.4, 1166.6, 1075.9, 1030.3, 991.7, 909.4, 842.5, 816.7, 735.2, 700.5 cm^{-1}. *Anal.* Calc. for $C_{28}H_{26}O_2Si$: C, 79.59; H, 6.21. Found: C, 79.33, H, 6.01%.

1,3-Diphenyl-2-(methylhydroxybenzylsilyl)indan (11). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.07 (s, 3H, CH_3), 1.4 (broad s, 1H, OH), 1.90 (d, 1H, CH_2, J = −14.0), 1.95 (d, 1H, CH_2, J = −14.0), 2.12 (dd, 1H, CH, J = 11.3, 11.3), 4.33 (d, 1H, CH, J = 11.3), 4.38 (d, 1H, J = 11.3), 6.77–7.37 (m, 14H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 147.84, 144.76, 138.28, 128.81, 128.69, 128.33, 126.75, 124.27, 52.74, 52.60, 47.55, 26.24, −2.36. ^{29}Si NMR ($CDCl_3$, 49.7 MHz): δ −21.94. MS (EI, m/z) 420(20), 402(5), 329(16), 267(22), 191(10), 151(2), 137(55), 84(100), 61(37), 49(20). High resolution MS (m/z, M^+): calc. for $C_{29}H_{28}SiO$ 420.1874; found 420.1876. IR (neat): ν 3364, 2896, 2797, 2248, 1599, 1493, 1452, 1258, 1206, 1157, 1008, 909, 820, 733, 700 cm^{-1}.

Ampac

AM1 calculations on the proposed intermediate cations **25**, **26** and **27** were performed with AMPAC version 2.1 [25] ported to an IBM RS/6000 computer. The keyword PRECISE was used to tighten the convergence criteria. The input files were created with PCMODEL, originally minimized using the MMX force field, which is also the source of the structures shown above. The heats of formation of the three compounds were calculated to be 181.6, 188.0 and 180.9 kcal/mol for compounds **25**, **26** and **27**, respectively.

Molecular modelling

Molecular modelling was done using PC-Model (Serena Software, Bloomington, Indiana) using the supplied MM2X force constants. As appropriate force constants are not available for Cl–Si bonds, the intermediates **28**, **29** and **30** were modelled with Si–Me groups instead. The C_a–C_b distances in **30** and C_a–C_c in **29** were constrained to 2.5 Å in order to mimic the transition state for bond formation between these two centres. The Si–C–C$^+$-p orbital angles in the minimized structures were found to be 172 and 123° in **30** and **29**, respectively. The angle to the product pentadienyl cation

(Si–C–C_d^+-p orbital after the Friedel–Crafts reaction has occurred) in **29** was found to be 178°. Thus, had this reaction occurred, the magnitude of the β-effect should have increased during the bond formation. However, there is very little stabilization provided to the carbenium ion in the initial geometry (123°).

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