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Headline Articles

Aromatic *β*-Silylethenylation Reactions via Organogallium Compounds

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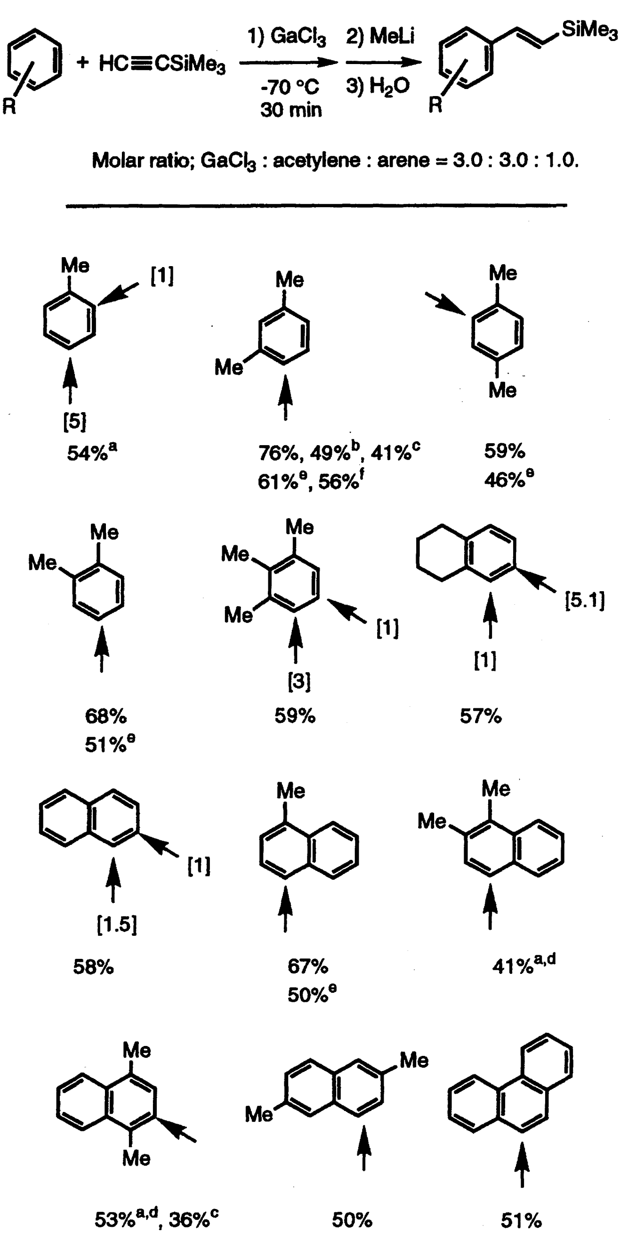
In the presence of $GaCl_3$, silylethyne reacted electrophilically with aromatic hydrocarbons to give *β*-silylethenylated arenes. The reaction proceeded via cationic species generated by the interaction of $GaCl_3$ and silylethyne. High reactivity of the intermediate was demonstrated by the rapid reaction rate at −78 °C using close to the equimolar amount of the substrates. *ipso*-Substitution reaction took place with 1,2,3-trimethoxybenzene. Structures and properties of several organogallium compounds involved in the reactions are discussed.

Ethenylarenes are some of the most fundamental chemicals in industry as well as in the laboratory; they are generally synthesized by stepwise methods. For example, styrene is produced in industry from benzene by electrophilic ethylation with ethylene, followed by dehydrogenation or oxidation–dehydration. Here, the C_2-unit is first introduced by the electrophilic substitution reaction, which is followed by the functional manipulation to generate ethenyl group. In the laboratory, organometallic ethenylation of halobenzenes[1] and the Wittig methylenation of aromatic aldehydes[2] are convenient methods. Although the direct conversion of aromatic $C(sp^2)$–H to $C(sp^2)$–$CH{=}CH_2$ is apparently the most straightforward method, it has not been employed. While the Friedel–Crafts methodology is effective to alkylate and acylate aromatic C–H bond, ethenylation reaction has been unsuccessful. Many attempts at the Friedel–Crafts ethenylation using ethyne, ethenyl halides, etc., failed even when it was conducted in the presence of arenes in large excess.[3] Instead of forming ethenylated products, poly(ethenylarene)s and 1,1-diarylethanes were the major products. Ethenylarenes are unstable under the reaction conditions. Protonation of the ethenylarene giving phenyl-stabilized ethyl cation is much more facile than the protonation of the ethenylating reagents such as ethyne or ethenyl halide which lacks such a stabilizing group.[4,5]

2-Propenyl cation is probably more stabilized than the ethenyl cation, and may be easier to generate. Furthermore, the propenylated arenes should be less sensitive to the oligomerization and polymerization. The aromatic 2-propenylation with propyne or 2-propenyl halides, however, gave very low yields of the products with various mixtures of by-products.[6] The results confirm the difficulty of aromatic ethenylation. On the other hand, alkenylation reactions using phenylacetylene, phenylethenyl halide, or phenylthioethenyl chloride were reported to give the products in higher yields.[7] These reactions involved ethenyl cations possessing powerful cation-stabilizing groups. Thus, the Friedel–Crafts alkenylation can give acceptable yields of the product only when the electrophilic reagent is heavily substituted and/or possesses a strong cation-stabilizing group. These discussions reveals that the low efficiency to generate ethenyl cation without the cation stabilizing group is another reason that the electrophilic aromatic ethenylation failed. The interpretation is supported by the fact that the aromatic compounds has been employed in large excess, typically as the solvent.[3,6,7] These reactions were generally conducted at 0 °C to room temperature.[8]

Gallium is a group 13 element, and sits just below aluminum in the periodic table. Its derivatives have rarely been used in organic synthesis,[9,10] although aluminum derivatives are quite popular. Attempts to utilize organogallium compounds generally revealed that they were less reactive than organoaluminum compounds. The reduced reactivity has been attributed to the less polarized nature of Ga–C bond compared to the Al–C bond, based on the relative electronegativity of the Ga (1.8) and Al (1.5).[11] We recently found that $GaCl_3$ possesses interesting propeties which have not been explored, and is much more effective in some C–C bond formation reactions compared to $AlCl_3$.[12,13] The findings led us to propose the following working hypotheses;

1) $GaCl_3$ can electrophilically activate carbon–carbon multiple bonds; 2) in the presence of $GaCl_3$, certain cationic species gain a long life-time; 3) organogallium compounds $RGaCl_2$ can participate in the carbometallation reaction with carbon–carbon multiple bonds. As an example, we reported the Friedel–Crafts β-silylethenylation of aromatic hydrocarbons with silylethyne, which directly introduced the C_2-olefin group to arenes.[14] The reaction proceeded at −78 °C without using aromatic compounds in large excess. Described here are the details of the reaction.

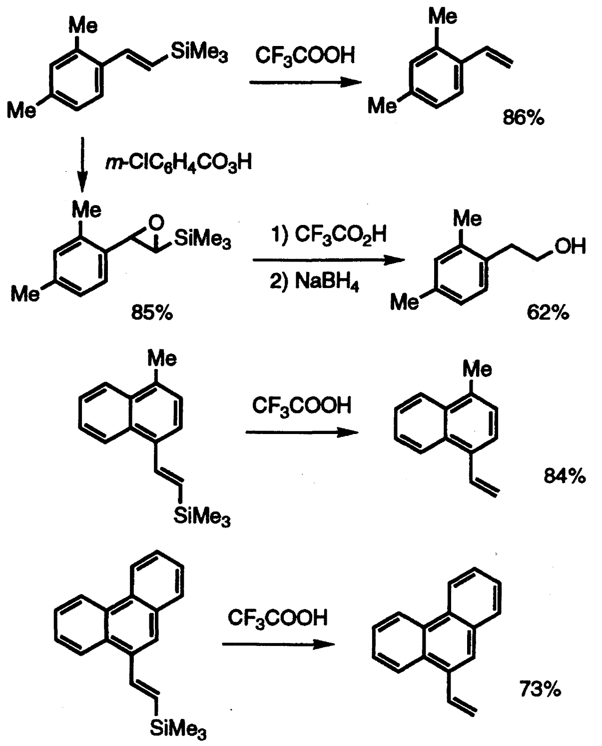


—►: Reaction site. []: Isomer ratio.
[a] Yield by GC. [b] Reaction in chlorobenzene.
[c] Molar ratio; $GaCl_3$: acetylene : arene = 1.0 : 1.0 : 1.0.
[d] Molar ratio; $GaCl_3$: acetylene : arene = 2.0 : 2.0 : 1.0.
[e] The reaction was quenched with THF and NH_4Cl.
[f] $GaBr_3$ was used.

Scheme 1.

Methylcyclohexane was employed for the solvent of the stock solution for $GaCl_3$, since it dissolved $GaCl_3$ and possessed a low melting point which allowed one to conduct reactions over a wide range of temperatures; from −120 to 100 °C.[15] Trimethylsilylethyne (3 mol equivalents) and an aromatic hydrocarbon (1 mol equivalent) were treated with $GaCl_3$ (3 mol equivalents) in a mixed solvent of methylcyclohexane and CH_2Cl_2 at −78 °C for 30 min. Then to the solution was added methyllithium in ether (methyllithium procedures); (*E*)-(β-trimethylsilylvinyl)arene was obtained by aqueous workup (Scheme 1). The addition of the organometallic reagent was essential to obtain reproducible results; methylmagnesium bromide or diethylzinc could also be used. It was later found that the treatment of the reaction mixture with THF at −78 °C followed by heating at reflux in aqueous NH_4Cl also gave comparable results (THF procedures). The C–C bond formation occurred at the β-carbon atom of the silylethyne, and the (*E*)-stereochemistry of the double bond was determined by ^1H NMR. Use of 1 mol equivalent of silylethyne and $GaCl_3$ to arene slightly decreased the yield. Dichloromethane and chlorobenzene were the preferred solvents, since they dissolved $GaCl_3$ and arenes at low temperatures. $GaBr_3$ also promoted the reaction.

The reaction sites on the aromatic rings were determined unambiguously by NMR studies and derivatization. The orientation of the aromatic substitution clearly indicates an electrophilic mechanism.[16] It is consistent with the low reactivity of chlorobenzene which can be used as solvent. Benzene reacted with the ethenylating reagent in low yield. Steric factors are important in some cases. For example, 2,6-dimethylnaphthalene reacted at the 4-position instead of the most reactive 1-position;[17] a substantial amount of 2-ethenylated product was obtained by the reaction of naphthalene. The electrophilic species involved here appear to be considerably bulky. Unlike previously reported Friedel–Crafts alkenylation,[3,6,7] this reaction does not require excess arene. Therefore, non-volatile polycyclic arenes can be β-silylethenylated without tedious separation of a large amount of unreacted starting materials. There was very little diethenylation under the present reaction conditions. Use of the gallium trihalides is critical; other Lewis acids ($AlCl_3$, $AlBr_3$, $InCl_3$, $SnCl_4$, $SbCl_5$, SbF_5), protic acids (CF_3SO_3H and HCl), or heterogeneous acids (Na-Montmorillonite, Sn-Montmorillonite, Montmorillonite K 10) did not promote the reaction. It should be emphasized that the β-silylethenylation is effectively promoted by $GaCl_3$ but not by $AlCl_3$. Triethylsilyl- and *t*-butyldimethylsilylethyne reacted with *m*-xylene to give the corresponding products in yields of 54 and 52%, respectively. When 1-methylnaphthalene was treated with $GaCl_3$ and ethyne at −78 °C, the arene was consumed within 30 min to give a considerable amount of polymeric substances. Thus, the silyl group not only directs the C–C bond formation at the β-carbon atom but also protects the olefin moiety of the products from side reactions. The (β-silylethenyl)arenes are useful synthetic intermediates for a variety of aromatic compounds (Scheme 2). For example,

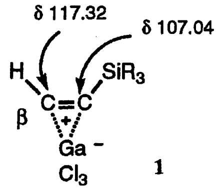


Scheme 2.

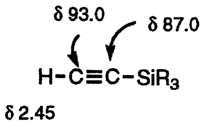
the trimethylsilyl group can be removed with trifluoroacetic acid to give the parent ethenylarenes. Epoxidation followed by treatment with an acid gave an arylacetaldehyde,[18] which was reduced to an arylethanol.

The present reaction proceeded via several organogallium intermediates, and their structure and reactivity were studied in detail. As noted in the introduction, the conventional aromatic alkenylation reactions were generally conducted at 0 °C to room temperature using the aromatic compounds in large excess.[3,6,7] In contrast, the present β-silylethenylation proceeded at -78 °C in less than 1 h employing close to an equimolar amount of the arene and silylethyne.[19] Apparently, highly reactive electrophilic ethenylating reagent is generated here. We previously reported that the linear trimerization of silylethyne took place in the absence of aromatic hydrocarbon.[13] The reactive electrophilic species can react even with the carbon–carbon triple bond of silylethyne. We assigned the intermediate to a $GaCl_3$-complexed silylethyne. The formation of an ethenyl cation by protonation of silylethyne with $HGaCl_4$[20] does not explain the results of the deuteration experiments (vide infra). Furthermore, addition of 2,6-di(*t*-butyl)-4-methylpyridine (0.3 mol equivalents) did not interfere with the reaction.

Complex **1** formed from *t*-butyldimethylsilylethyne (**2**) and $GaCl_3$ could be detected by low temperature NMR in CD_2Cl_2. In order to avoid trimerization the bulky silyl derivative was employed. When $GaCl_3$ in CD_2Cl_2 was added to **2** at -78 °C, the chemical shifts of the acetylenic proton and carbon shifted low field: ^{1}H NMR $\delta = 4.77$; ^{13}C NMR $\delta = 107.04, 117.32$ (Fig. 1). The structure of the π-complex suggested by calculations (MP2/LanL2DZ) using HC≡CSiH$_3$ and GaF_3 is shown above. Although $AlBr_3$ was also reported to form such a complex with 2-butyne,[21] the behaviors of the aluminum derivative differed from gallium complex. While $AlBr_3$ promoted cyclobutane formation at a low temperature by the dimerization of 2-butyne,[21] treatment of 2-butyne with $GaCl_3$ in CH_2Cl_2 at 0 °C to room temperature gave hexamethylbenzene in 28% yield.



1



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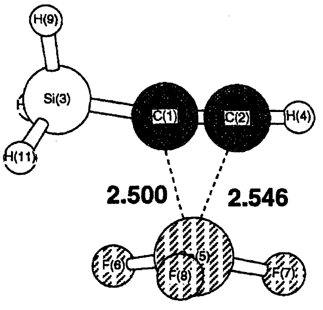


Fig. 1.

The next step of the β-silylethenylation is the nucleophilic attack of aromatic hydrocarbon to **1** at the β-carbon atom. The regioselectivity may be explained by the well-documented β-cation stabilizing effect of trialkylsilyl group.[22] As will be noted later, alkylacetylenes reacted at the internal carbon atom consistently with the interpretation. It should be noted that the electrophilic addition reaction to silylacetylene has been rare.[23] Generally, electrophilic activation of silylacetylene gives substitution products by expelling the silyl group rather than addition products (Fig. 2). A typical example is the Lewis acid promoted alkynylation of acid chloride with silylacetylene. Here, the electrophile, acylium cation, interacts with the carbon–carbon triple bond generating silicon-stabilized β-cation. Then the nucleophile, probably chloride ion, attacks the silicon atom giving the substitution product. In contrast, the electron-deficient carbon center is attacked by arene in the present reaction. This is an interesting example of the intermolecular trapping of the silicon-stabilized vinyl cation by carbon nucleophile.[24,25]

Another intriguing aspect of this addition reaction is its *cis*-stereochemistry. Such stereochemistry was also observed in

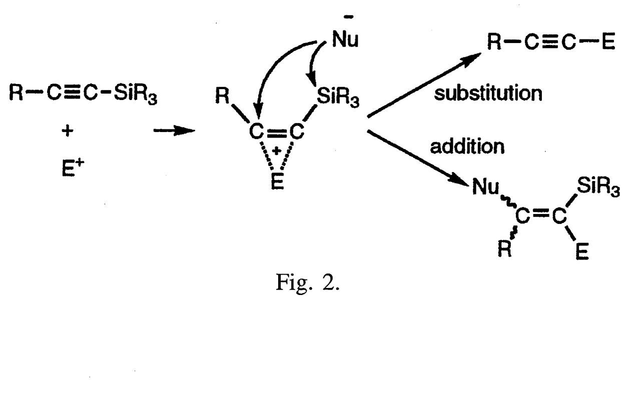


Fig. 2.

the first step of the trimerization of silylethyne.[13] The structure of the π-complex **1** in the Fig. 1 might be oversimplified since it should give the *trans*-addition product. A possible explanation is the involvement of a late transition state such as **3** or **4** which resembles the structure of the product (Fig. 3). In the latter, interaction of $GaCl_3$ and arene is presumed. Alternatively, the second and more reactive cationic intermediate with open structure such as **5** might be involved.[26] Formation of an ion-paired cationic species was previously suggested in the trimerization of silylethyne.[13] Silicon stabilized vinyl cations have recently attracted much interest.[27] However, their reactivity, particularly C–C bond formation reaction, was little investigated because of the competitive desilylation and the strong acidic conditions employed for their generation. The cationic species involved in the present reaction therefore appear to possess different properties from the known silicon stabilized vinyl cations: 1) It undergoes C–C bond formation at the cationic center, 2) it can be generated and reacted in non-polar solvents, 3) it resists the desilylation.

The arenium cation **6** could be detected by NMR (Scheme 3). *m*-Xylene was treated with *t*-butyldimethylsilylethyne and $GaCl_3$ in CD_2Cl_2 at −78 °C, and ^1H NMR spectra of the orange solution exhibited absorptions at $\delta = 9.6$—9.9. They may be assigned to the electron-deficient H(6) in **6**, although it appeared to be a mixture of several species.[28] Addition of THF followed by warming to room temperature caused the color of the solution to fade, and provided the next intermediate **7**, an olefin proton and carbon of which appeared at $\delta = 7.80$ and 157.17, respectively. When **6** was treated with methyllithium, the organogallium intermediate **8** was formed as detected by NMR (THF-d_8), which exhibited an olefin proton at $\delta = 7.71$ and carbon at $\delta = 149.17$. (*Z*)-Stereochemistry of **8** was deduced by NOE studies. The peaks of **8** disappeared with the addition of water, giving the (*E*)-silylethenylated product. Methyllithium and THF added before the aqueous workup deprotonated the arenium cation **6** giving the aromatized intermediates **7** and **8**. That the intense orange color of the solution faded as these reagents were added supports the interpretation. Reddish color of the arenium cation is well-documented.[29] Methyllithium at the same time converted $GaCl_n$ group to $GaMe_2$ group.

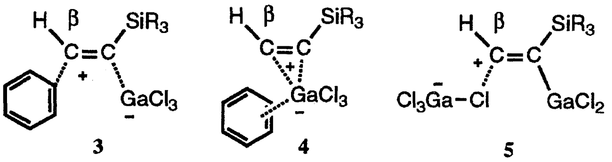
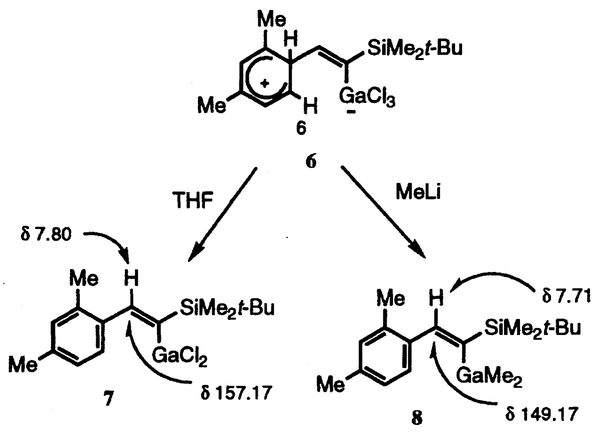


Fig. 3.

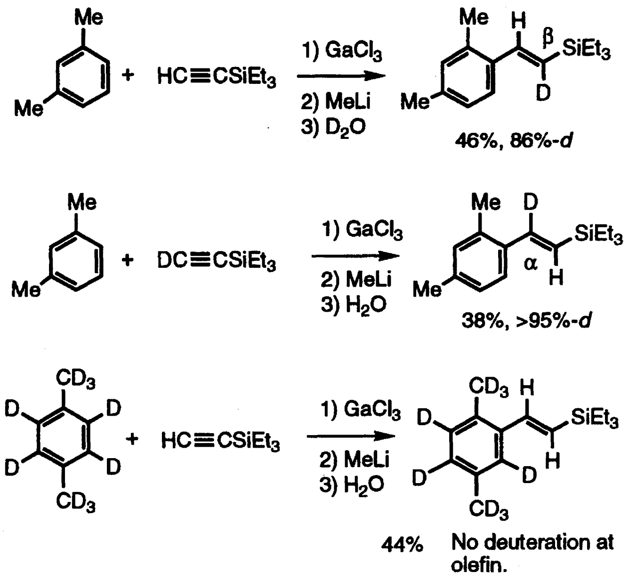


Scheme 3.

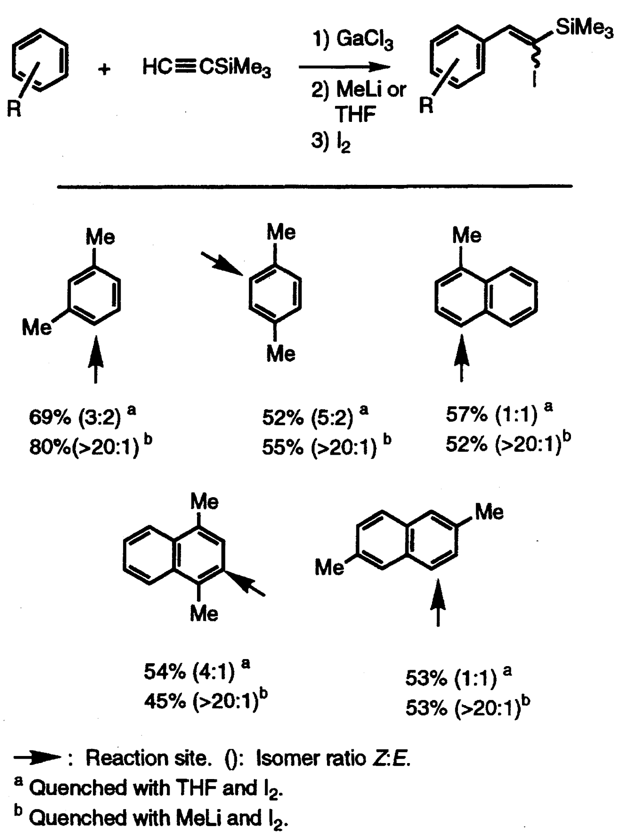
Deuteration experiments confirmed the formation of the organogallium intermediates (Scheme 4). When D_2O was added in the reaction of *m*-xylene and trimethylsilylethyne after methyllithium treatment, the ethenylarene was deuterated at the olefinic *β*-carbon atom. Such deuteration did not take place when the olefinic product was treated with methyllithium followed by D_2O either in the presence or in absence of $GaCl_3$. When a deuterated silylethyne was used, deuteration occurred at the *α*-carbon atom. No deuteration occurred at the olefin moiety with *p*-xylene-d_{10} as their other substrate.

The vinylgallium intermediates could be trapped with iodine (Scheme 5). Aromatic hydrocarbon and silylethyne were treated with $GaCl_3$ at −78 °C, and after reaction with methyllithium and iodine, (*Z*)-*β*-iodostyrene was obtained. The halogenation took place with retention of configuration. Addition of THF followed by iodine also worked effectively. In this reaction, however, mixtures of isomers were obtained. Since the vinyl iodides were configurationally stable under the ambient conditions, the stereochemistry of the product probably reflected the structure of the organogallium precursors. Such *α*-silylated vinyl halides were generally synthesized by the carbometallation reaction of organometallic reagents with silylacetylene followed by halogenation.[30] It is notable that the present method provides the compounds using aromatic hydrocarbon in place of the organometal reagent.

The mechanism of the *β*-silylethenylation thus may be



Scheme 4.



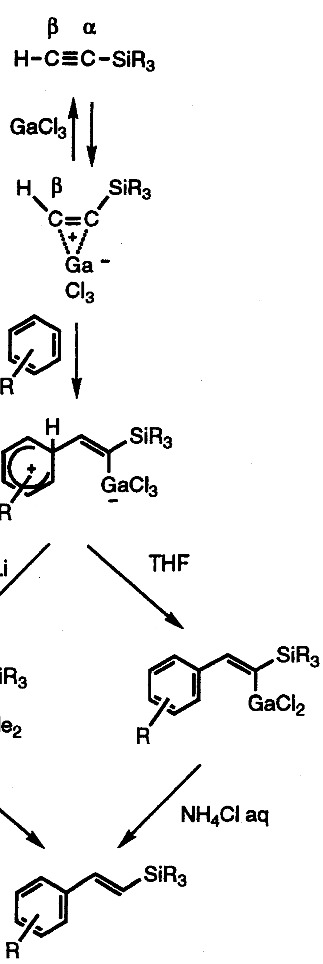
: Reaction site. (): Isomer ratio Z:E.

[a] Quenched with THF and I_2.

[b] Quenched with MeLi and I_2.

Scheme 5.

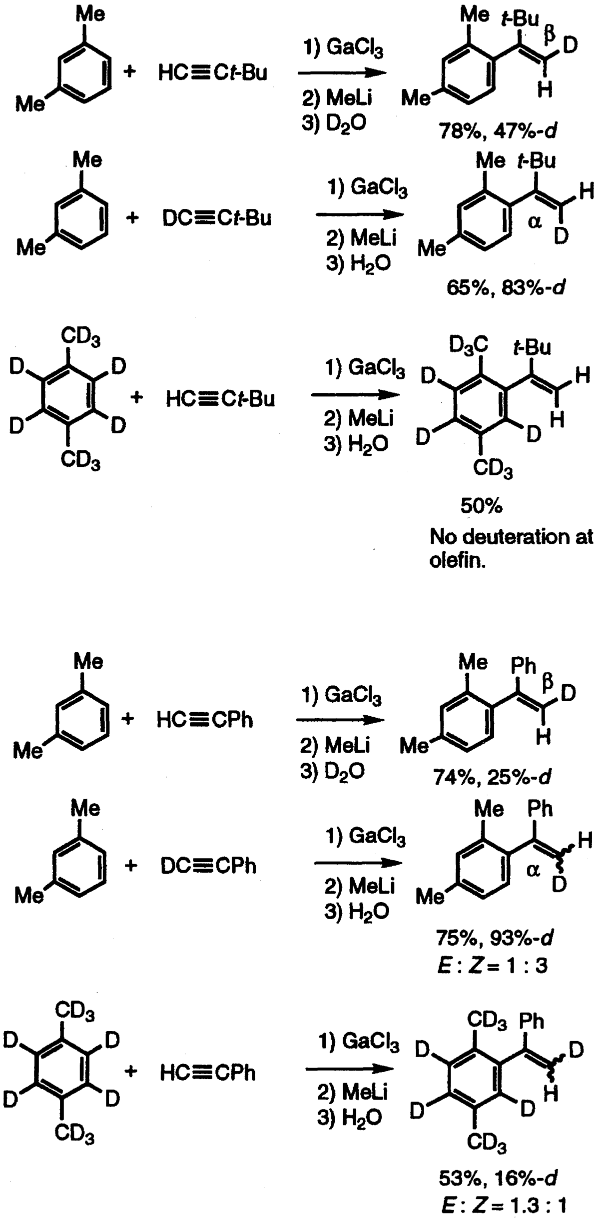
summarized as shown in Scheme 6. The activated silylethyne is attacked by aromatic hydrocarbon at the β-carbon atom. The resulting organogallium intermediate, (β-gallio-β-silylethenyl)arenium cation is then deprotonated either by methyllithium or THF, and (β-silylethenyl)arene is obtained by protodegallation.



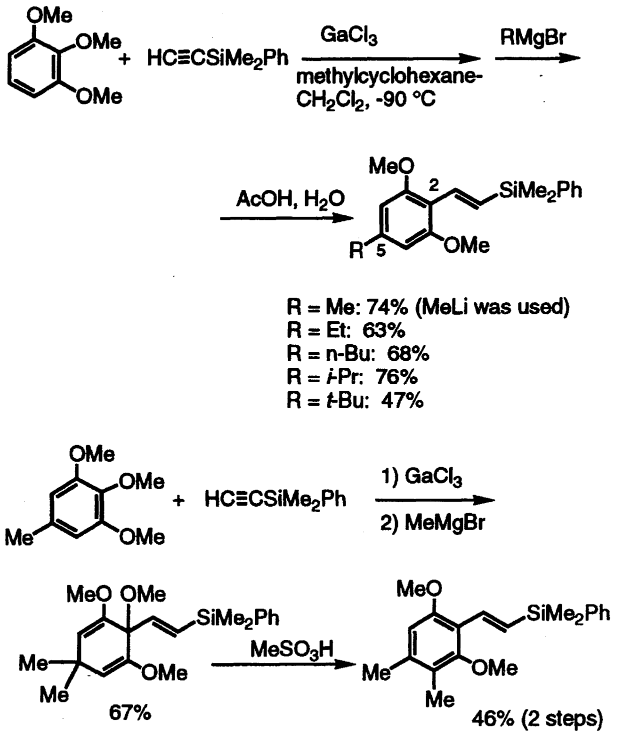
Scheme 6.

$GaCl_3$ promoted alkenylation as well as β-silylethenylation. When t-butylacetylene was treated with m-xylene and $GaCl_3$ followed by methyllithium and D_2O, an α-(t-butyl)styrene derivative was obtained with the β-carbon atom deuterated (Scheme 7). The regioselectivity in the alkenylation and silylethenylation can be ascribed to the ability of the substituents to stabilize the cations in the electrophilic intermediates. Stabilization of the β-cation by the silyl group is substantial, while the t-butyl group stabilizes the α-cation. Deuterated acetylene gave an isomeric deuterated product, which turned out to be the (Z)-isomer. Since the reaction with p-xylene-d_{10} did not lead to deuteration of the olefin moiety, the mechanism of the alkenylation must be similar to that of the β-silylethenylation involving the (Z)-gallio compound. Notably, *trans*-addition of arene and gallium metal took place in this alkenylation, which is contrasted to the *cis*-stereochemistry in the β-silylethenylation. The origin of the reversed stereochemistry is not clear at present. The reaction of phenylacetylene somewhat differed from that of t-butylacetylene. Although workup with D_2O gave β-deuterated product, the deuteration ratio was low: 25%-d. Reaction of phenylacetylene-d gave a mixture of isomeric products. Furthermore, some deuteration at the β-proton took place when p-xylene-d_{10} was employed. The observations suggested the involvement of 1-phenylethenyl cation to some extent; it should be formed by protonation of phenylacetylene.

Unusual *ipso*-substitution reaction took place with a trimethoxybenzene (Scheme 8).[31] When an equimolar amount of 1,2,3-trimethoxybenzene was treated with dimethylphenylsilylethyne in the presence of $GaCl_3$ at −90 °C which was followed by methyllithium and acetic acid, silylethenylated product was obtained. 1,2,3-Trimethoxybenzene was β-silylethenylated at a lower temperature than the aromatic hydrocarbons shown in the Scheme 1. Notably, the substitution of the 2-methoxy group with silylethenyl group occurred. In addition, a methyl group was introduced from methyllithium at 5-position. Two carbon–carbon bonds, one electrophilically and the other nucleophilically, were formed on a benzene ring. This is an unusual *ipso*-substitution reaction involving two carbon–carbon bond formations. The reaction was relatively insensitive to the substituents on the silicon atom; trimethylsilylethyne, triethylsilylethyne, t-butyldimethylsilylethyne, and triisopropylsilylethyne gave comparable results. The *ipso*-substitution, however, occurred only with 1,2,3-trimethoxybenzene derivatives, and arenes were recovered unchanged when methoxybenzene, 1,2-dimethoxybenzene, 1,3-dimethoxybenzene, or 1,3,5-trimethoxybenzene were reacted. Other organometallic reagents such



Scheme 7.



Scheme 8.

as ethylmagnesium bromide, could also be used, giving the corresponding 5-alkylated products. Even *t*-butyl group was introduced at the 5-position with *t*-butylmagnesium bromide. The reaction of 5-methyl-1,2,3-trimethoxybenzene gave silylethenylated cyclohexadiene, which rearranged to dimethylarene on treatment with acid.

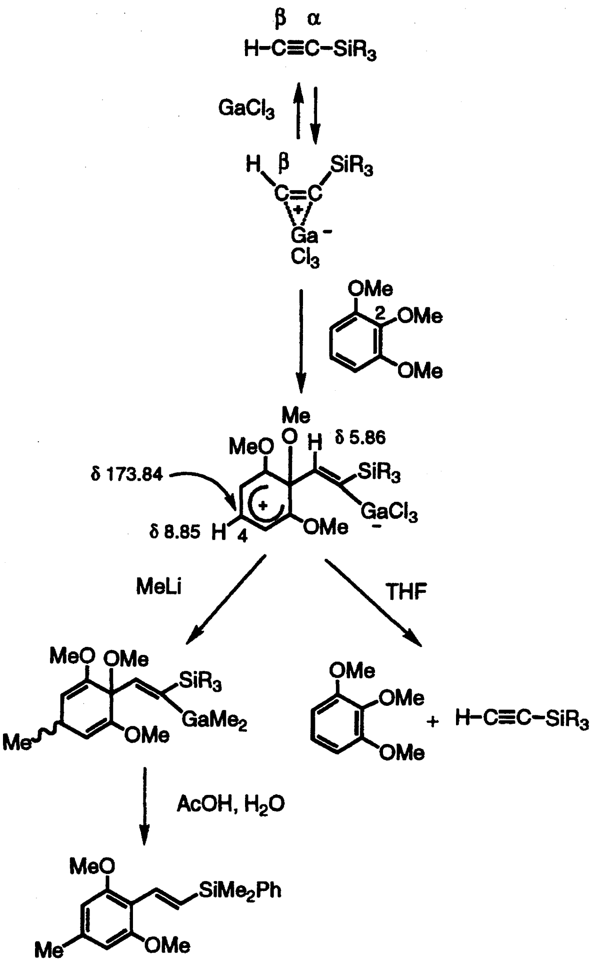
The mechanism of the *ipso*-substitution is summarized in Scheme 9. The first step is the electrophilic reaction of the gallium silylethyne complex with 1,2,3-trimethoxybenzene at 2-position. The arenium intermediate could be detected by low temperature NMR study; peaks at $\delta = 8.86$ and 173.84 were assigned to the electron deficient 4-proton and carbon, respectively. The intermediate appears to have a life-time long enough to be attacked by organometallic reagents. Methyllithium attacks at the 4-carbon, giving cyclohexadiene, which could be isolated by silica-gel chromatography as a mixture of two diastereomers. The major isomer possessed *cis*-configuration concerning 4-methyl and 1-ethenyl group as determined by NOE. It should be noted that the dimethylgallio moiety resides on the ethenyl group. The exceptional stability of the organogallium compound towards moisture may be due to the coordination of the adjacent oxygen atom. Such interaction might be the origin of the *ipso*-substitution of 1,2,3-trimethoxybenzene at 2-position. Finally, protodegallation and elimination of methanol gives the aromatized product. It was also noticed that the treatment of the arenium intermediate with THF regenerated 1,2,3-trimethoxybenzene and silylethyne. The C–C bond formation turned out to be reversible. Nucleophilic attack of THF at the gallium metal probably induced the β-elimination reaction.

In summary, $GaCl_3$ promotes the β-silylethenylation of aromatic hydrocarbons with silylethyne via novel organogallium intermediates. $GaCl_3$ appears to possess several interesting properties: 1) $GaCl_3$ strongly activates π-compounds. 2) In the presence of $GaCl_3$, otherwise unstable cationic species gain a long life-time.

Experimental

^1H NMR and ^{13}C NMR spectra were obtained on a Varian Gemini 200 (200 MHz), a JEOL α-500 (500 MHz), or a Varian Mercury 400 (400 MHz). Chemical shift values are given in ppm relative to internal Me_4Si. IR spectra were recorded on a JASCO FT/IR-410. MS spectra were taken with a JEOL JMXS-DX 303 and JEOL JMS-AX 500. Elemental analyses were conducted with a Yanaco CHN CORDER MT-5.

2,4-Dimethyl-1-[(*E*)-2-trimethylsilylethenyl]benzene. Methyllithium Procedures. Under an argon atmosphere, a solution of *m*-xylene (107 mg, 1.0 mmol) in CH_2Cl_2 (8 mL) was cooled



Scheme 9.

to −78 °C and a solution of $GaCl_3$ (1.0 M in methylcyclohexane, 3.0 mL, 1 M = 1 mol dm^{-3}) was added dropwise. To this mixture, trimethylsilylethyne (295 mg, 3.0 mmol) in CH_2Cl_2 (2 mL) was added slowly. After the mixture was stirred for 30 min at −78 °C, methyllithium (1.4 M in ether, 6.5 mL) was added dropwise, and stirring was continued for another 30 min. Then water was added, and the mixture was warmed to room temperature. The organic layer was separated and dried over $MgSO_4$. Solvents were removed in vacuo, and the residue was purified by flash column chromatography (silica-gel, hexane) to give the product (155 mg, 76%).

THF Procedures. The reaction was conducted as above, and THF (5 mL) was added in place of methyllithium. The mixture was stirred for 60 min, when saturated aqueous NH_4Cl (5 mL) was added. After being heated at reflux (bath temp 60 °C) for 30 min the mixture was cooled to room temperature. The organic layer was separated, washed with water, and dried over $MgSO_4$. Solvents were removed in vacuo, and the residue was purified by flash column chromatography (silica-gel, hexane) to give the product (126 mg, 61%). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 0.15 (9H, s), 2.30 (3H, s), 2.34 (3H, s), 6.32 (1H, d, J = 19.0 Hz), 6.95 (1H, br s), 6.97 (1H, br d, J = 9.1 Hz), 7.09 (1H, d, J = 19.0 Hz), 7.42 (1H, d, J = 7.8 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ = −1.1, 19.5, 21.1, 125.2, 126.8, 123.0, 131.0, 134.8, 135.1, 137.4, 141.1. IR (neat) 3008, 2958, 1601, 1499, 1450, 1249, 988, 868, 841, 797 cm^{-1}. MS (EI, 70 eV) m/z (%) 204 (M$^+$; 93), 189 (100), 173 (27), 163 (15), 73 (31), 59 (27). HRMS (EI, 70 eV) Calcd for $C_{13}H_{20}Si$: M$^+$, 204.1334. Found: m/z 204.1342 (M$^+$).

(*E*)-1-Methyl-4-(2-trimethylsilylethenyl)benzene and (*E*)-1-Methyl-2-(2-trimethylsilylethenyl)benzene. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.14 (9H, s, *para*), 0.16 (9H, s, *ortho*), 2.33 (3H, s, *para*), 2.37 (3H, s, *ortho*), 6.37 (1H, d, J = 19.2 Hz, *ortho*), 6.40 (1H, d, J = 19.3 Hz, *para*), 6.84 (1H, d, J = 19.0 Hz, *para*), 7.10—7.19 (4H, m, *ortho*), 7.12 (2H, d, J = 8.1 Hz, *para*), 7.32 (2H, br d, J = 8.1 Hz, *para*), 7.49—7.52 (1H, m, *ortho*). ^{13}C NMR (125 MHz, $CDCl_3$) *o*-isomer: δ = −1.19, 19.56, 125.25, 126.06, 127.66, 130.28, 131.34, 135.22, 137.64, 141.30. *p*-isomer: δ = −1.20, 21.20, 126.26, 128.12, 129.18, 135.69, 137.76, 143.47. IR (neat) 2958, 1609, 1512, 1249, 988, 868, 835, 787 cm^{-1}. MS (EI, 70 eV) m/z (%) 190 (M$^+$; 45), 175 (100), 159 (41), 149 (29), 73 (20), 59 (46). HRMS (EI, 70 eV) Calcd for $C_{12}H_{18}Si$: M$^+$, 190.1178. Found: m/z 190.1171 (M$^+$). Treatment of the product with $KMnO_4$ (pyridine–water, Na_2CO_3; r.t., 5 min) followed by diazomethane gave a mixture of methyl *para*-methylbenzoate and methyl *ortho*-methylbenzoate in 51% yield. Their structures were confirmed by comparison (^{1}H NMR) with the commercially available authentic sample.

(*E*)-1,4-Dimethyl-2-(2-trimethylsilylethenyl)benzene. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 0.16 (9H, s), 2.32 (3H, s), 2.33 (3H, s), 6.37 (1H, d, J = 18.9 Hz), 6.92—7.04 (2H, m), 7.10 (1H, d, J = 18.9 Hz), 7.34 (1H, br s). ^{13}C NMR (50 MHz, $CDCl_3$) δ = −1.1, 19.1, 21.1, 125.8, 128.5, 130.2, 130.9, 132.2, 135.3, 137.3, 141.4. IR (neat) 2958, 1601, 1493, 1249, 988, 866, 839, 804 cm^{-1}. MS (EI, 70 eV) m/z (%) 204 (M$^+$; 91), 189 (100), 173 (29), 73 (41), 59 (43). HRMS (EI, 70 eV) Calcd for $C_{13}H_{20}Si$: M$^+$, 204.1334. Found: m/z 204.1333 (M$^+$).

(*E*)-1,2-Dimethyl-4-(2-trimethylsilylethenyl)benzene. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.16 (9H, s), 2.26 (3H, s), 2.28 (3H, s), 6.42 (1H, d, J = 19.2 Hz), 6.84 (1H, d, J = 19.2 Hz), 7.09 (1H, d, J = 7.6 Hz), 7.19 (1H, br d, J = 8.3 Hz), 7.24 (1H, br s). ^{13}C NMR (125 MHz, $CDCl_3$) δ = −1.20, 19.52, 19.74, 123.84, 127.58, 127.90, 129.77, 130.58, 136.14, 136.45, 143.61. IR (neat) 2958, 1605, 1506, 1452, 1249, 986, 866, 839, 793 cm^{-1}. MS (EI, 70 eV) m/z (%) 204 (M$^+$; 52), 189 (100), 173 (34), 73 (26), 59(50). HRMS (EI, 70 eV) Calcd for $C_{13}H_{20}Si$: M$^+$, 204.1334. Found: m/z 204.1332 (M$^+$).

(*E*)-1,2,3-Trimethyl-4-(2-trimethylsilylethenyl)benzene and (*E*)-1,2,3-Trimethyl-5-(2-trimethyl-silylethenyl)benzene. ^{1}H NMR (500 MHz, $CDCl_3$) 2,3,4-isomer: δ = 0.15 (9H, s), 2.19 (3H, s), 2.27 (6H, s), 6.23 (1H, d, J = 18.8 Hz), 6.97 (1H, d, J = 8.1 Hz), 7.18 (1H, d, J = 18.8 Hz), 7.23 (1H, d, J = 8.1 Hz); 3,4,5-isomer: δ = 0.14 (9H, s), 2.15 (3H, s), 2.27 (6H, s), 6.39 (1H, d, J = 19.3 Hz), 6.79 (1H, d, J = 19.3 Hz), 7.08 (2H, s). ^{13}C NMR (125 MHz, $CDCl_3$) 2,3,4-isomer: δ = −1.12, 15.61, 15.80, 20.90, 123.21, 127.40, 130.87, 133.55, 135.00, 135.94, 136.39, 142.87; 3,4,5-isomer: δ = −1.18, 15.30, 20.55, 125.63, 127.73, 135.01, 135.42, 136.45, 143.71. IR (neat) 2958, 1605, 1485, 1446, 1249, 988, 868, 839 cm^{-1}. MS (EI, 70 eV) m/z (%) 218 (M$^+$; 63), 203 (81), 143 (25), 73 (100), 59 (93). HRMS (EI, 70 eV) Calcd for $C_{14}H_{22}Si$: M$^+$, 218.1491. Found: m/z 218.1505 (M$^+$).

(*E*)-1,2,3,4-Tetrahydro-5-(2-trimethylsilylethenyl)naphthalene and (*E*)-1,2,3,4-Tetrahydro-6-(2-trimethylsilylethenyl)-naphthalene. ^{1}H NMR (500 MHz, $CDCl_3$) 5-isomer: δ = 0.19 (9H, s), 1.82 (4H, quint., J = 3.7 Hz), 2.77—2.84 (4H, m), 6.35 (1H, d, J = 19.0 Hz), 7.16 (1H, d, J = 19.0 Hz), 7.02 (1H, br d, J = 8.1 Hz), 7.11 (1H, t, J = 8.1 Hz), 7.35 (1H, br d, J = 7.6 Hz); 6-isomer: δ = 0.18 (9H, s), 1.82 (4H, quint., J = 3.7 Hz), 2.75—2.81 (4H, m), 6.43 (1H, d, J = 19.0 Hz), 6.85 (1H, d, J = 19.0 Hz), 7.04 (1H, d, J = 7.8 Hz), 7.17 (1H, br s), 7.20 (1H, d, J = 7.8 Hz). ^{13}C NMR (125

MHz, $CDCl_3$) 5-isomer: $\delta = -1.15$, 22.73, 23.34, 26.42, 30.10, 123.03, 125.36, 128.86, 131.61, 135.77, 137.23, 138.10, 141.54; 6-isomer: $\delta = -1.20$, 23.23, 23.32, 29.24, 29.42, 123.44, 127.08, 127.93, 129.25, 135.77, 137.10, 137.16, 143.70. IR (neat) 2936, 1605, 1437, 1249, 986, 866, 837 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 230 (M^+; 58), 215 (100), 155 (43), 73 (40), 59 (81). HRMS (EI, 70 eV) Calcd for $C_{15}H_{22}Si$: M^+, 230.1491. Found: *m/z* 230.1483 (M^+). Treatment of the product with $KMnO_4$ (pyridine–water, Na_2CO_3; r.t., 5 min) followed by diazomethane gave a mixture of methyl 1,2,3,4-tetrahydro-5-naphthalenecarboxylate and methyl 1,2,3,4-tetrahydro-6-naphthalenecarboxylate in 49% yield. ^{1}H NMR (500 MHz, $CDCl_3$) 5-isomer: δ = 1.77—1.83 (4H, m), 2.80—2.85 (2H, m), 3.05 (2H, t, J = 6.3 Hz), 3.87 (3H, s), 7.13 (1H, t, J = 7.6 Hz), 7.21 (1H, br d, J = 7.1 Hz), 7.64 (1H, br d, J = 7.6 Hz); 6-isomer: δ = 1.79—1.82 (4H, m), 2.79—2.82 (4H, m), 3.89 (3H, s), 7.11 (1H, d, J = 7.8 Hz), 7.73 (1H, dd, J = 7.8, 1.7 Hz), 7.75 (1H, d, J = 1.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) 5-isomer: δ = 22.45, 23.10, 27.74, 30.21, 51.79, 124.95, 127.81, 130.25, 133.08, 138.37, 138.55, 168.62; 6-isomer: δ = 22.86, 22.96, 29.28, 29.62, 51.90, 126.50, 127.31, 129.16, 130.42, 137.29, 142.82, 167.42 (Chart 1)

(*E*)-2-(2-Trimethylsilylethenyl)naphthalene and (*E*)-1-(2-Trimethylsilylethenyl)naphthalene. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.24 (9H, s, β), 0.27 (9H, s, α), 6.59 (1H, d, J = 18.8 Hz, α), 6.65 (1H, d, J = 19.0 Hz, β), 7.09 (1H, d, J = 19.2 Hz, β), 7.45—7.57 (4H, m), 7.69—7.74 (2H, m), 7.79—7.88 (3H, m), 8.20 (1H, br d, J = 8.5 Hz, α). ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = -1.19$, -1.13, 123.34, 123.54, 123.56, 125.60, 125.65, 125.90, 125.97, 126.17, 126.59, 127.65, 128.08, 128.10, 128.16, 128.52, 130.03, 130.92, 133.28, 133.62, 133.64, 133.83, 135.83, 136.53, 140.71, 143.63. IR (neat) 3062, 2958, 1599, 1392, 1249, 986, 866, 839, 785 cm^{-1}. MS (EI) *m/z* (%) 226 (M^+; 100), 211 (57), 195 (33), 152 (76), 73 (82), 59 (67). HRMS (EI, 70 eV) Calcd for $C_{15}H_{18}Si$: M^+, 226.1178. Found: *m/z* 226.1176 (M^+). Treatment of the product with $KMnO_4$ (pyridine–water, Na_2CO_3; r.t., 5 min) followed by diazomethane gave a mixture of methyl 1-naphthoate and methyl 2-naphthoate in 72% yield. Their structures were confirmed by comparison (^{1}H NMR) with the commercially available authentic sample (Chart 2).

(*E*)-1-Methyl-4-(2-trimethylsilylethenyl)naphthalene. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.22 (9H, s), 2.68 (3H, s), 6.50 (1H, d, J = 19.0 Hz), 7.29 (1H, d, J = 7.5 Hz), 7.50—7.54 (2H, m), 7.55 (1H, d, J = 7.5 Hz), 7.65 (1H, d, J = 19.0 Hz), 7.98—8.02 (1H, m), 8.16—8.20 (1H, m). ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = -1.10$, 19.61, 123.30, 124.09, 124.60, 125.49, 125.60, 126.53, 130.98, 132.60, 132.86, 134.33, 134.99, 140.93. IR (neat) 2958, 1599, 1386, 1249, 986, 870, 837, 806, 756, 737 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 240 (M^+; 34), 166 (56), 73 (100), 59 (62). HRMS (EI, 70 eV) Calcd for $C_{16}H_{20}Si$: M^+, 240.1334. Found: *m/z* 240.1324 (M^+) (Chart 3).

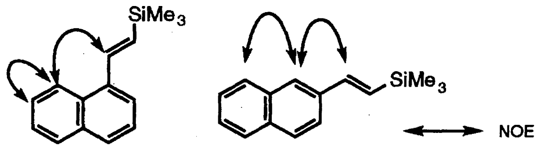


Chart 2.

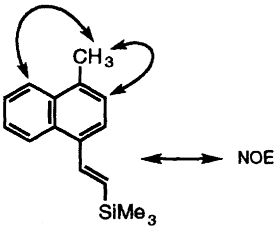


Chart 3.

(*E*)-1,2-Dimethyl-4-(2-trimethylsilylethenyl)naphthalene. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.26 (9H, s), 2.52 (3H, s), 2.62 (3H, s), 6.53 (1H, d, J = 19.0 Hz), 7.46—7.54 (2H, m), 7.53 (1H, br s), 7.67 (1H, d, J = 19.0 Hz), 8.07 (1H, d, J = 8.3 Hz), 8.17 (1H, d, J = 8.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = -1.09$, 14.70, 20.82, 116.21, 123.90, 124.19, 124.55, 125.52, 126.72, 129.70, 131.41, 132.63, 132.91, 134.10, 140.95. IR (neat) 2958, 1601, 1381, 1247, 986, 864, 839, 754, 737 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 254 (M^+; 36), 239 (10), 180 (61), 73 (100), 59 (60). HRMS (EI, 70 eV) Calcd for $C_{17}H_{22}Si$: M^+, 254.1491. Found: *m/z* 254.1490 (M^+). Small amounts of isomers and/or bis(β-silylethenyl) derivatives were also formed (Chart 4).

(*E*)-1,4-Dimethyl-2-(2-trimethylsilylethenyl)naphthalene. Mp 107.0—109.5 °C (methanol). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.20 (9H, s), 2.67 (3H, s), 2.68 (3H, s), 6.46 (1H, d, J = 19.0 Hz), 7.42 (1H, d, J = 19.1 Hz), 7.46—7.53 (2H, m), 7.51 (1H, s), 7.94—7.98 (1H, m), 8.07—8.10 (1H, m). ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = -1.10$, 14.00, 19.44, 124.51, 124.63, 125.00, 125.27, 125.65, 128.96, 131.92, 132.07, 132.47, 133.18, 133.85, 142.13. IR (KBr) 2954, 2362, 1597, 1249, 986, 868, 837, 750 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 254 (M^+; 66), 239 (24), 179 (22), 73 (100), 59 (76). HRMS (EI, 70 eV) Calcd for $C_{17}H_{22}Si$: M^+, 254.1491. Found: *m/z* 254.1489 (M^+). Small amounts of isomers and/or bis(β-silylvinyl) derivatives were also formed (Chart 5).

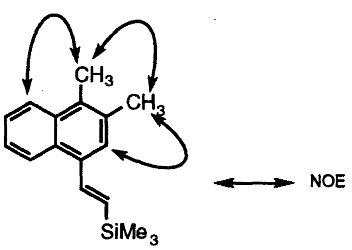


Chart 4.

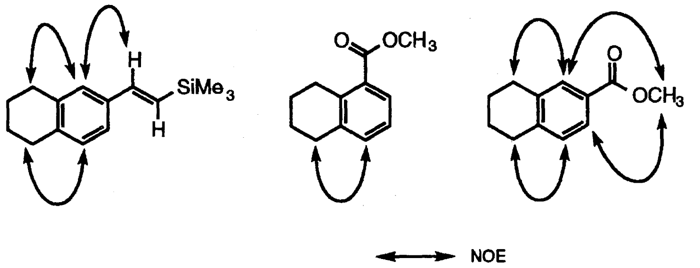


Chart 1.

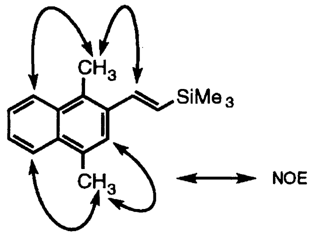


Chart 5.

(*E*)-3,7-Dimethyl-1-(2-trimethylsilylethenyl)naphthalene. ^{1}H NMR (500 MHz, CDCl$_3$) δ = 0.23 (9H, s), 2.48 (3H, s), 2.52 (3H, s), 6.52 (1H, d, J = 18.8 Hz), 7.28 (1H, dd, J = 8.3, 2.0 Hz), 7.48 (1H, br s), 7.50 (1H, br s), 7.63 (1H, d, J = 19.0 Hz), 7.64 (1H, d, J = 8.1 Hz), 7.84 (1H, br s). ^{13}C NMR (125 MHz, CDCl$_3$) δ = −1.10, 21.56, 22.05, 122.33, 125.80, 126.99, 127.69, 127.91, 129.38, 132.18, 133.07, 134.05, 134.63, 135.57, 140.84. IR (neat) 2958, 1607, 1439, 1247, 986, 864, 839 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 254 (M$^+$; 38), 239 (16), 180 (55), 73 (100), 59 (56). HRMS (EI, 70 eV) Calcd for $C_{17}H_{22}Si$: M$^+$, 254.1491. Found: *m/z* 254.1493 (M$^+$) (Chart 6).

(*E*)-9-(2-Trimethylsilylethenyl)phenanthrene. ^{1}H NMR (500 MHz, CDCl$_3$) δ = 0.30 (9H, s), 6.67 (1H, d, J = 18.8 Hz), 7.58—7.73 (5H, m), 7.90 (1H, s), 7.91 (1H, dd, J = 1.5, 7.5 Hz), 8.23 (1H, dd, J = 2.0, 7.5 Hz), 8.67 (1H, d, J = 8.0 Hz), 8.74 (1H, dd, J = 1.5, 8.0 Hz). ^{13}C NMR (125 MHz, CDCl$_3$) δ = −1.09, 122.49, 123.07, 124.40, 124.52, 126.38, 126.46, 126.55, 126.69, 128.73, 130.24, 130.35, 130.40, 131.85, 134.36, 135.69, 141.44 (one peak overlapped). IR (neat) 2956, 1601, 1493, 1452, 1381, 1247, 986, 866, 839, 737 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 276 (M$^+$; 46), 204 (37), 202 (100), 73 (99), 59 (97). HRMS (EI, 70 eV) Calcd for $C_{19}H_{20}Si$: M$^+$, 276.1334. Found: *m/z* 276.1340 (M$^+$) (Chart 7).

(1-*t*-Butylethenyl)-2,4-dimethylbenzene. ^{1}H NMR (500 MHz, CDCl$_3$) δ = 1.10 (9H, s), 2.21 (3H, s), 2.30 (3H, s), 4.73 (1H, d, J = 1.5 Hz), 5.27 (1H, d, J = 1.5 Hz), 6.92 (2H, m), 7.00 (1H, br s). ^{13}C NMR (125 MHz, CDCl$_3$) δ = 20.44, 20.98, 29.83, 36.89, 112.25, 125.09, 129.33, 130.64, 135.63, 135.74, 139.65, 157.79. IR (neat) 2960, 1628, 1464, 1361, 905, 822 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 188 (M$^+$; 59), 173 (76), 131 (100), 115 (14). HRMS (EI, 70 eV) Calcd for $C_{14}H_{20}$: M$^+$, 188.1565. Found: *m/z* 188.1555 (M$^+$) (Chart 8).

2,4-Dimethyl-1-(1-phenylethenyl)benzene. ^{1}H NMR (200 MHz, CDCl$_3$) δ = 2.01 (3H, s), 2.35 (3H, s), 5.17 (1H, d, J = 1.5 Hz), 5.74 (1H, d, J = 1.5 Hz), 7.00—7.16 (3H, s), 7.29 (5H, br s). ^{13}C NMR (125 MHz, CDCl$_3$) δ = 20.05, 21.09, 114.75, 126.32, 126.51, 127.48, 128.28, 129.97, 130.88, 135.94, 137.11, 138.77, 140.85, 149.41. IR (neat) 3026, 2922, 1613, 1493, 1446, 903, 828, 779, 708 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 208 (M$^+$; 57), 193 (100), 178 (40), 89 (7). HRMS (EI, 70 eV) Calcd for $C_{16}H_{16}$: M$^+$, 208.1252. Found: *m/z* 208.1250 (M$^+$).

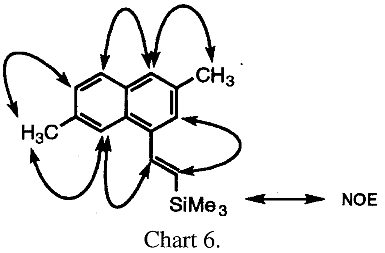


Chart 6.

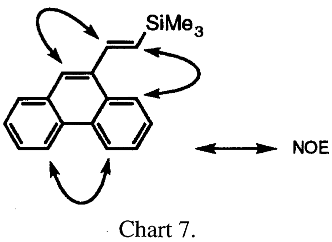


Chart 7.

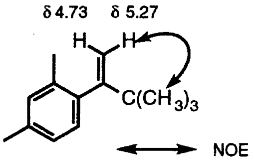


Chart 8.

(*E*)-2,4-Dimethyl-1-(2-triethylsilylethenyl)benzene. ^{1}H NMR (200 MHz, CDCl$_3$) δ = 0.65 (6H, q, J = 8.0 Hz), 0.99 (9H, t, J = 8.0 Hz), 2.30 (3H, s), 2.33 (3H, s), 6.24 (1H, d, J = 19.2 Hz), 6.96 (1H, s), 6.98 (1H, d, J = 7.7 Hz), 7.20 (1H, d, J = 19.2 Hz), 7.41 (2H, d, J = 7.8 Hz). ^{13}C NMR (50 MHz, CDCl$_3$) δ = 3.6, 7.4, 19.5, 21.1, 125.2, 126.4, 126.8, 131.0, 135.0, 135.2, 137.4, 142.5. IR (neat) 2958, 1613, 1597, 1249, 793, 772, 723 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 246 (M$^+$; 29), 217 (100), 189 (14), 159 (10). HRMS (EI, 70 eV) Calcd for $C_{16}H_{26}Si$: M$^+$, 246.1804. Found: *m/z* 246.1804 (M$^+$).

(*E*)-1-[2-(*t*-Butyldimethylsilyl)ethenyl]-2,4-dimethylbenzene. ^{1}H NMR (200 MHz, CDCl$_3$) δ = 0.11 (6H, s), 0.92 (9H, s), 2.30 (3H, s), 2.34 (3H, s), 6.30 (1H, d, J = 19.0 Hz), 6.91—7.02 (2H, m), 7.10 (1H, d, J = 19.0 Hz), 7.41 (1H, d, J = 7.8 Hz). ^{13}C NMR (50 MHz, CDCl$_3$) δ = −6.0, 16.7, 19.5, 21.1, 26.5, 125.3, 126.0, 127.5, 131.0, 135.0, 135.2, 137.4, 142.6. IR (neat) 2956, 1603, 1470, 1249, 990, 828, 762 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 246 (M$^+$; 9), 205 (44), 189 (100), 173 (11), 163 (87), 73 (11), 59 (18). HRMS (EI, 70 eV) Calcd for $C_{16}H_{26}Si$: M$^+$, 246.1804. Found: *m/z* 246.1806 (M$^+$).

1-Ethenyl-4-methylnaphthalene. Trifluoroacetic acid (3.9 mL, 50 mmol) was added dropwise to a solution of (*E*)-1-methyl-4-(2-trimethylsilylethenyl)naphthalene (120 mg, 0.5 mmol) in ether (5 mL) and water (0.5 mL) at −78 °C. The mixture was warmed to room temperature, and stirred for 3 h. Then the reaction was quenched by adding saturated aqueous NaHCO$_3$, and the organic materials were extracted with ether. The organic layer was washed with brine, dried over MgSO$_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (silica-gel, hexane) to give 1-ethenyl-4-methylnaphthalene (71 mg, 84%). ^{1}H NMR (200 MHz, CDCl$_3$) δ = 2.70 (3H, s), 5.43 (1H, dd, J = 10.8, 1.6 Hz), 5.75 (1H, dd, J = 17.2, 1.7 Hz), 7.31 (1H, br d, J = 7.2 Hz), 7.47 (1H, dd, J = 17.2, 10.8 Hz), 7.49—7.58 (2H, m), 7.98—8.07 (1H, m), 8.11—8.18 (1H, m). ^{13}C NMR (50 MHz, CDCl$_3$) δ = 19.6, 116.3, 123.3, 124.3, 124.5, 125.5, 125.6, 126.4, 131.1, 132.5, 134.0, 134.3, 134.5. IR (neat) 3074, 2950, 1626, 1593, 1516, 1427, 988, 913, 835, 783 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 168 (M$^+$; 100), 153 (87), 141 (4), 115 (7). HRMS (EI, 70 eV) Calcd for $C_{13}H_{12}$: M$^+$, 168.0939. Found: *m/z* 168.0954 (M$^+$).

1-Ethenyl-2,4-dimethylbenzene. ^{1}H NMR (200 MHz, CDCl$_3$) δ = 2.30 (3H, s), 2.32 (3H, s), 5.23 (1H, dd, J = 11.0, 1.5 Hz), 5.59 (1H, dd, J = 17.5, 1.5 Hz), 6.91 (1H, dd, J = 17.5, 11.0 Hz), 6.97 (1H, br s), 6.98 (1H, br d, J = 7.7 Hz), 7.38 (1H, br d, J = 8.0 Hz). ^{13}C NMR (50 MHz, CDCl$_3$) δ = 19.6, 21.0, 114.1, 125.2, 126.8, 131.0, 133.9, 134.6, 135.2, 137.4. IR (neat) 2924, 1613, 1502, 1454, 990, 907, 822 cm^{-1}.

9-Ethenylphenanthrene.[32] ^{1}H NMR (200 MHz, CDCl$_3$) δ =

5.53 (1H, dd, J = 10.8, 1.8 Hz), 5.86 (1H, dd, J = 17.2, 1.8 Hz), 7.48 (1H, dd, J = 17.2, 10.8 Hz), 7.55—7.76 (4H, m), 7.80—7.93 (2H, m), 8.13—8.20 (1H, m), 8.43—8.77 (2H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 117.5, 122.5, 123.0, 124.6 (2 carbons), 126.4, 126.5, 126.6, 126.7, 128.7, 130.2, 130.3, 130.5, 131.8, 134.6, 135.0. IR (neat) 3080, 2928, 1628, 1495, 1452, 1423, 1307, 986, 917, 893, 768, 748, 725 cm^{-1}.

2-(2,4-Dimethylphenyl)ethanol. A suspension of (*E*)-2,4-dimethyl-1-(2-triethylsilylethenyl)benzene (350 mg, 1.5 mmol) and $NaHCO_3$ (840 mg, 10 mmol) in CH_2Cl_2 (10 mL) was cooled to 0 °C. Then a solution of *m*-chloroperbenzoic acid (345 mg, 2.0 mmol) in CH_2Cl_2 (10 mL) was added dropwise, and the resulting mixture was stirred for 1.5 h at 0 °C and for 3 h at room temperature. The reaction was quenched by adding aqueous $NaHSO_3$, and the organic materials were extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (silica-gel, hexane–ethyl acetate 10 : 1) to give (*E*)-1-(2,4-dimethylphenyl)-2-triethylsilyloxirane (263 mg, 67%). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 0.69 (6H, t, J = 7.3 Hz), 1.01 (9H, q, J = 7.3 Hz), 2.19 (1H, d, J = 3.5 Hz), 2.30 (3H, s), 2.36 (3H, s), 3.85 (1H, d, J = 3.5 Hz), 6.96 (1H, br s), 6.98 (1H, br d, J = 8.4 Hz), 7.12 (1H, d, J = 7.6 Hz). A solution of the oxirane (112 mg, 0.43 mmol) and trifluoroacetic acid (49 mg, 0.43 mmol) in tetrahydrofuran–water (10 : 1, 2.2 mL) was stirred at room temperature for 12 h. After addition of aqueous $NaHCO_3$, the organic materials were extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The crude aldehyde was dissolved in methanol (3 mL), and $NaBH_4$ (32 mg, 0.86 mmol) was added at 0 °C. After 10 min, water was added, and the organic materials were extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo . The residue was purified by flash column chromatography (silica-gel, hexane–ethyl acetate 5 : 1) to give 2-(2,4-dimethylphenyl)ethanol (40 mg, 62%). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.42 (1H, br t, J = 5.1 Hz), 2.30 (6H, s), 2.86 (2H, t, J = 6.8 Hz), 3.81 (2H, dt, J = 6.6, 5.1 Hz), 6.96 (1H, br d, J = 8.7 Hz), 6.99 (1H, br s), 7.06 (1H, d, J = 7.5 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 19.3, 20.9, 35.9, 62.7, 126.6, 129.5, 131.2, 133.2, 136.0, 136.3. IR (neat) 3334, 2948, 2876, 1618, 1506, 1450, 1044, 818 cm^{-1}. ^{1}H NMR data coincided with those reported in the literature.[33]

Complex 1 of *t*-Butyldimethylsilylethyne and $GaCl_3$. In a dry NMR sample tube, (*t*-butyldimethylsilyl)ethyne (28 mg, 0.20 mmol) was dissolved in CD_2Cl_2 (0.20 mL) under an argon atmosphere. This solution was cooled to −78 °C; then a solution of $GaCl_3$ in CD_2Cl_2 (1.0 M, 0.40 mmol) was added to it slowly. The tube was gently shaken in the cooling bath at −78 °C for 10 min. After the mixture was allowed to stand at this temperature for 30 min, the NMR spectra of **1** were recorded at −85 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 0.38 (6H, s), 0.96 (9H, s), 4.77 (1H, s). ^{13}C NMR (100 MHz, CD_2Cl_2) δ = −6.82, 17.57, 24.28, 107.04, 117.32.

Arenium Cation 6 and Vinylgallium 7 from *m*-Xylene. Under an argon atmosphere, a solution of *m*-xylene (25 μL, 0.20 mmol) and *t*-butyldimethylsilylethyne (28 mg, 0.20 mmol) in CD_2Cl_2 (0.3 mL) was cooled to −78 °C in a NMR sample tube. Then a 2.0 M solution of $GaCl_3$ in CD_2Cl_2 (0.3 mL) was added slowly, and the resulting mixture was gently shaken until $GaCl_3$ dissolved. The resulting orange solution was allowed to stand at −78 °C for 30 min, and NMR spectra of **6** were obtained at −85 °C. ^{1}H NMR (400 MHz, CD_2Cl_2, −85 °C) δ = 9.6—9.9. ^{13}C NMR (100 MHz, CD_2Cl_2, −85 °C) δ = 204.28, 204.56. When dry THF (0.1 mL) was added, **6** disappeared. The mixture was allowed to warm to room temperature; after the solution turned to pale purple NMR spectra of **7** were obtained. ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 6.93 (1H, s), 6.99 (1H, d, J = 10.4 Hz), 7.33 (1H, d, J = 7.8 Hz), 7.80 (1H, s). ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 125.86, 127.17, 127.64, 129.73, 134.59, 137.62, 138.70, 157.17.

^{1}H NMR Studies on the Vinylgallium 8. Under an argon atmosphere, a methylcyclohexane solution of $GaCl_3$ (1.0 M, 0.40 mL) was added to *m*-xylene (0.25 mL, 0.20 mmol) in CH_2Cl_2 (2 mL) at −78 °C. To this mixture, (*t*-butyldimethylsilyl)ethyne (28 mg, 0.20 mmol) in CH_2Cl_2 (1.0 mL) was added. After stirring for 30 min at this temperature, methyllithium (1.4 M in ether, 0.85 mL) was added, and stirring was continued for a further 30 min. The cooling bath was removed, and the solution was concentrated in vacuo. The residue was dissolved in THF-d_8 (1.0 mL), and a part of the solution was transferred to NMR tube under an argon atmosphere. NMR spectra of **8** were recorded immediately. ^{1}H NMR (THF-d_8, 500 MHz) δ = −1.03 (6H, br s), 0.09 (6H, s), 0.97 (9H, s), 2.22 (3H, s), 2.24 (3H, s), 6.72 (1H, br s), 6.73 (1H, br d, J = 7.6 Hz), 7.44 (1H, br d, J = 7.3 Hz), 7.71 (1H, br s). ^{13}C NMR (THF-d_8, 125 MHz) δ = −1.19 (C7), 21.91 (C1), 22.83 (C3), 30.24 (C8), 126.97 (C4), 130.63 (C2), 132.20 (C5), 134.60 (C9), 136.27 (C10), 145.64 (C11), 149.17 (C6) (Charts 9 and 10). Addition of a small amount of water to the NMR tube resulted in the disappearance of the peaks of **8**, and (*E*)-1-[2-(*t*-butyldimethylsilyl)ethenyl]-2,4-dimethylbenzene was formed. THF-d_8 solution of **8** left in the flask was also treated with water, and the products were combined. The organic materials were extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (silica-gel, hexane) to give the silylvinylarene (16 mg, 33%).

Deuteration Experiment. Under an argon atmosphere, to a solution of $GaCl_3$ (1.0 M in methylcyclohexane, 1.5 mL) and *m*-xylene (0.63 mL, 5.0 mmol) in CH_2Cl_2 (10 mL) was added triethylsilylethyne (140 mg, 1.0 mmol) in methylcyclohexane (1.0 mL) at −78 °C. After being stirred for 30 min at −78 °C, methyllithium (1.4 M in ether, 3.5 mL) was added, and stirring was continued for 30 min. Then, the reaction was quenched by addition of D_2O (2.0 mL). (*E*)-1-(2-Deutero-2-trimethylsilylethenyl)-2,4-dimethylbenzene (112 mg, 46% yield, 86% deuterated) was obtained by the workup described above.

1-(2-Iodo-2-trimethylsilylethenyl)-2,4-dimethylbenzene. Methyllithium Procedures. Under an argon atmosphere, a solu-

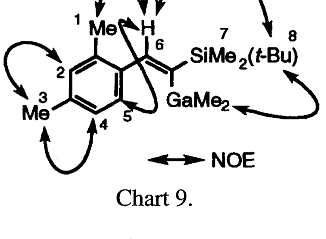


Chart 9.

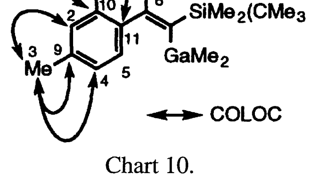


Chart 10.

tion of *m*-xylene (107 mg, 1.0 mmol) in CH_2Cl_2 (8 mL) was cooled to −78 °C, and a solution of $GaCl_3$ (1.0 M in methylcyclohexane, 3.0 ml) was added dropwise. Then, trimethylsilylethyne (295 mg, 3.0 mmol) in CH_2Cl_2 (2.0 mL) was added slowly, and the mixture was stirred for 30 min at −78 °C. After addition of methyllithium (1.14 M in ether, 9.0 mmol) stirring was continued for another 30 min. A solution of iodine (5.1 g, 20 mmol) in THF (20 mL) was then added, and the mixture was warmed to 0 °C. The reaction was quenched with saturated aqueous Na_2SO_3, and the organic layer was separated, washed with brine, and dried over $MgSO_4$. Solvents were removed in vacuo, and the residue was purified by flash column chromatography (silica-gel, hexane) to give (*Z*)-1-(2-iodo-2-trimethylsilylethenyl)-2,4-dimethylbenzene (240 mg, 79%).

THF Procedures. The reaction was conducted as above, and THF (0.78 mL) was added in place of methyllithium. After the mixture was stirred for 30 min, iodine (1.27 g, 5.0 mmol) was added, and the mixture was warmed to 0 °C. Saturated aqueous Na_2SO_3 was added, and the organic layer was separated, washed with brine, and dried over $MgSO_4$. Solvents were removed in vacuo, and the residue was purified by flash column chromatography (silica-gel, hexane) to give (*E*)-1-(2-iodo-2-trimethylsilylethenyl)-2,4-dimethylbenzene (90 mg, 27%) and (Z)-1-(2-iodo-2-trimethylsilylethenyl)-2,4-dimethylbenzene (139 mg, 42%).

(*Z*)-1-(2-Iodo-2-trimethylsilylethenyl)-2,4-dimethylbenzene: ^1HNMR (400 MHz, $CDCl_3$) δ = 0.28 (9H, s), 2.18 (3H, s), 2.33 (3H, s), 7.01 (1H, s), 7.02 (1H, d, *J* = 8.4 Hz), 7.23 (1H, s), 7.24 (1H, d, *J* = 8.0 Hz). ^{13}CNMR (100 MHz, $CDCl_3$) δ = −1.08, 19.69, 21.38, 114.38, 125.92, 127.90, 130.48, 134.89, 136.86, 137.42, 144.70. IR (neat) 2954, 1613, 1492, 1249, 838, 758 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 330 (M^+; 39), 315 (2), 203 (5), 185 (28), 73 (100). HRMS (EI, 70 eV) Calcd for $C_{16}H_{19}ISi$: M^+, 330.0298. Found: *m/z* 330.0288 (M^+).

(*E*)-1-(2-Iodo-2-trimethylsilylethenyl)-2,4-dimethylbenzene: ^1HNMR (400 MHz, $CDCl_3$) δ = −0.01 (9H, s), 2.19 (3H, s), 2.29 (3H, s), 6.94 (2H, s), 6.97 (1H, s), 8.22 (1H, s). ^{13}CNMR (100 MHz, THF-d_8) δ = 0.83, 20.02, 21.35, 111.89, 126.69, 129.40, 131.06, 135.79, 138.01, 138.71, 155.76. IR (neat) 2955, 1614, 1492, 1248, 897, 838 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 330 (M^+; 62), 315 (5), 203 (15), 185 (33), 73 (100). HRMS (EI, 70 eV) Calcd for $C_{16}H_{19}ISi$: M^+, 330.0298. Found: *m/z* 330.0295 (M^+).

(Z)-1-(2-Iodo-2-trimethylsilylethenyl)-2,5-dimethylbenzene. ^1HNMR (400 MHz, $CDCl_3$) δ = 0.28 (9H, s), 2.17 (3H, s), 2.34 (3H, s), 7.06 (1H, d, *J* = 6.8 Hz), 7.08 (1H, d, *J* = 7.2 Hz), 7.11 (1H, br s), 7.25 (1H, s). ^{13}CNMR (100 MHz, $CDCl_3$) δ = −0.98, 19.38, 21.21, 114.79, 128.46, 128.55, 129.70, 131.88, 134.70, 139.83, 145.16. IR (neat) 2954, 1249, 840, 759 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 330 (M^+; 40), 203 (6), 185 (29), 73 (100). HRMS (EI, 70 eV) Calcd for $C_{13}H_{19}ISi$: M^+, 330.0298. Found: *m/z* 330.0298 (M^+).

(*E*)-1-(2-Iodo-2-trimethylsilylethenyl)-2,5-dimethylbenzene. ^1HNMR (400 MHz, $CDCl_3$) δ = 0.01 (9H, s), 2.19 (3H, s), 2.30 (3H, s), 6.87 (1H, br s), 7.02 (2H, br s), 8.21 (1H, s). ^{13}CNMR (100 MHz, $CDCl_3$) δ = 0.79, 19.65, 21.02, 111.83, 128.67, 129.43, 129.50, 132.10, 134.62, 139.71, 154.72. IR (neat) 2955, 1595, 1492, 1248, 901, 878, 839 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 330 (M^+; 39), 203 (6), 185 (25), 73 (100). HRMS (EI, 70 eV) Calcd for $C_{13}H_{19}ISi$: M^+, 330.0298. Found: *m/z* 330.0294 (M^+).

(Z)-1-(2-Iodo-2-trimethylsilylethenyl)-4-methylnaphthalene. ^1HNMR (400 MHz, $CDCl_3$) δ = 0.36 (9H, s), 2.72 (3H, s), 7.35 (1H, d, *J* = 7.2 Hz), 7.44 (1H, d, *J* = 7.2 Hz), 7.53 (2H, d-quint., *J* = 7.6, 2.0 Hz), 7.63 (1H, br s), 7.84 (1H, dd, *J* = 8.0, 1.6 Hz), 8.04 (1H, dd, *J* = 8.0, 1.2 Hz). ^{13}CNMR (100 MHz, $CDCl_3$) δ = −0.97, 19.74, 116.17, 124.52, 124.66, 125.60, 125.66, 125.78, 125.83, 130.37, 132.41, 134.45, 136.14, 144.05. IR (neat) 2955, 1591, 1510, 1388, 1248, 897, 837, 753 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 366 (M^+; 18), 239 (7), 223 (7), 185 (15), 73 (100). HRMS (EI, 70 eV) Calcd for $C_{16}H_{19}ISi$: M^+, 366.0298. Found: *m/z* 366.0296 (M^+).

(*E*)-1-(2-Iodo-2-trimethylsilylethenyl)-4-methylnaphthalene. ^1HNMR (400 MHz, $CDCl_3$) δ = −0.10 (9H, s), 2.66 (3H, s), 7.16 (1H, d, *J* = 7.6 Hz), 7.25 (1H, d, *J* = 7.6 Hz), 7.50—7.59 (2H, m), 7.89—7.97 (1H, m), 7.98—8.07 (1H, m), 8.60 (1H, br s). ^{13}CNMR (100 MHz, Acetone-d_6) δ = 1.58, 20.47, 114.36, 126.01, 127.02, 127.27, 127.48, 127.59, 127.61, 132.65, 133.89, 136.59, 137.57, 155.22. IR (neat) 2953, 1591, 1510, 1419, 1389, 1249, 838, 757 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 366 (M^+; 22), 239 (6), 223 (7), 185 (13), 73 (100) HRMS (EI, 70 eV) Calcd for $C_{16}H_{19}ISi$: M^+, 366.0298. Found: *m/z* 366.0292 (M^+).

(Z)-2-(2-Iodo-2-trimethylsilylethenyl)-1,4-dimethylnaphthalene. ^1HNMR (400 MHz, $CDCl_3$) δ = 0.33 (9H, s), 2.54 (3H, s), 2.69 (3H, s), 7.17 (1H, s), 7.51—7.56 (2H, m), 7.55 (1H, s), 7.97—8.02 (1H, m), 8.06—8.11 (1H, m). ^{13}CNMR (100 MHz, $CDCl_3$) δ = −1.04, 15.62, 19.46, 116.04, 124.51, 124.66, 125.28, 125.45, 126.58, 128.57, 131.64, 132.07, 132.72, 137.06, 146.36. IR (neat) 2953, 1599, 1508, 1444, 1386, 1248, 840, 752 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 380 (M^+; 33), 237 (2), 185 (13), 165 (11), 73 (100). HRMS (EI, 70 eV) Calcd for $C_{16}H_{19}ISi$: M^+, 380.0457. Found: *m/z* 380.0457 (M^+).

(*E*)-2-(2-Iodo-2-trimethylsilylethenyl)-1,4-dimethylnaphthalene. ^1HNMR (400 MHz, $CDCl_3$) δ = −0.05 (9H, s), 2.57 (3H, s), 2.66 (3H, s), 7.05 (1H, s), 7.51—7.55 (2H, m), 7.96—8.00 (1H, m), 8.03—8.06 (1H, m), 8.42 (1H, s) ^{13}CNMR (100 MHz, $CDCl_3$) δ = 0.61, 16.02, 19.40, 112.48, 124.60, 124.67, 125.45, 125.82, 127.67, 128.96, 131.53, 132.16, 132.53, 136.47, 155.28. IR (neat) 2953, 1600, 1444, 1408, 1387, 1249, 841, 753 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 380 (M^+; 32), 237 (2), 185 (12), 165 (7), 73 (100). HRMS (EI, 70 eV) Calcd for $C_{17}H_{21}ISi$: M^+, 380.0457. Found: *m/z* 380.0450 (M^+).

(Z)-1-(2-Iodo-2-trimethylsilylethenyl)-3,7-dimethylnaphthalene. ^1HNMR (400 MHz, $CDCl_3$) δ = 0.38 (9H, s), 2.51 (3H, s), 2.53 (3H, s), 7.30 (1H, d, *J* = 8.0 Hz), 7.36 (1H, br s), 7.51 (1H, d, *J* = 0.4 Hz), 7.57 (1H, br s), 7.60 (1H, s), 7.69 (1H, d, *J* = 8.4 Hz). ^{13}CNMR (100 MHz, $CDCl_3$) δ = −0.97, 21.70, 22.14, 115.99, 122.89, 126.79, 127.55, 128.05, 128.24, 128.73, 131.84, 133.49, 134.54, 136.82, 144.01. IR (neat) 2954, 1605, 1439, 1248, 888, 867, 840, 753 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 380 (M^+; 30), 237 (6), 185 (15), 165 (8), 156 (15), 73 (100). HRMS (EI, 70 eV) Calcd for $C_{17}H_{21}ISi$: M^+, 380.0457. Found: *m/z* 380.0457 (M^+).

(*E*)-1-(2-Iodo-2-trimethylsilylethenyl)-3,7-dimethylnaphthalene. ^{11}HNMR (400 MHz, $CDCl_3$) δ = −0.05 (9H, s), 2.47 (3H, s), 2.51 (3H, s), 7.08 (1H, br s), 7.30 (1H, dd, *J* = 8.4, 1.5 Hz), 7.54 (1H, br s), 7.61 (1H, br s), 7.65 (1H, d, *J* = 8.4 Hz), 8.58 (1H, s). ^{13}CNMR (100 MHz, $CDCl_3$) δ = 0.87, 21.66, 22.11, 113.45, 123.93, 127.09, 127.36, 128.34, 128.52, 129.51, 131.68, 133.37, 135.01, 136.88, 153.41. MS (EI, 70 eV) *m/z* (%) 380 (M^+; 19), 237 (5), 185 (10), 165 (6), 73 (100). Calcd for $C_{17}H_{21}ISi$: M^+, 380.0457. Found: *m/z* 380.0449 (M^+).

(*E*)-2-(2-Phenyldimethylsilylethenyl)-1,3-dimethoxy-5-methylbenzene. Under an argon atmosphere, a solution of 1,2,3-trimethoxybenzene (34 mg, 0.20 mmol) in CH_2Cl_2 (4 mL) was cooled to −90 °C, and a solution of $GaCl_3$ (1.0 M in methylcyclohexane, 1.0 mL) was added dropwise. To this mixture, dimethylphenylsilylethyne (32 mg, 0.20 mmol) in CH_2Cl_2 (1 mL) was added slowly. After stirring for 15 min at −90 °C, methyllithium (0.93 M in ether, 3.0 mmol) was added, and the mixture was stirred for a further 30 min. After warming to room temperature AcOH (30 mmol)/H_2O (1 : 1) was added, and the mixture was stirred for 9 h. The organic layer was separated, washed with saturated aqueous $NaHCO_3$ twice, and dried over $MgSO_4$. Solvents were removed in vacuo, and the residue was purified by flash column chromatography (silica-gel, hexane : ethyl acetate = 30 : 1) to give (*E*)-2-(2-phenyldimethylsilylethenyl)-1,3-dimethoxy-5-methylbenzene (41 mg, 66%). Mp 61.2—61.9 °C (MeOH). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.41$ (6H, s), 2.32 (3H, s), 3.80 (6H, s), 6.36 (2H, s), 6.88 (1H, d, $J = 19.8$ Hz), 7.26 (1H, d, $J = 19.6$ Hz), 7.31—7.36 (3H, m), 7.56—7.52 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = -2.14$, 22.22, 55.68, 104.94, 113.14, 127.46, 128.48, 130.05, 133.85, 135.98, 138.73, 139.63, 158.50. IR (NaCl) 2955, 1605, 1463, 1410, 1245, 1116, 1002, 834, 731, 700 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 312 (M^+; 27), 297 (100), 282 (22), 267 (53), 219 (13), 135 (17), 91 (17). HRMS (EI, 70 eV) Calcd for $C_{19}H_{24}O_2Si$: M^+, 312.1544. Found: *m/z* 312.1547 (M^+). Anal. Calcd for $C_{19}H_{24}O_2Si$: C, 73.03; H, 7.74%. Found: C, 72.93; H, 7.86%.

(*E*)-1,3-Dimethoxy-5-methyl-2-(2-trimethylsilylethenyl)benzene. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.13$ (9H, s), 2.31 (3H, s), 3.81 (6H, s), 6.35 (2H, s), 6.76 (1H, d, $J = 19.6$ Hz), 7.15 (1H, d, $J = 19.6$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = -0.86$, 22.24, 55.71, 104.94, 113.10, 132.84, 134.12, 138.47, 158.40. IR (neat) 2952, 1593, 1564, 1456, 1404, 1244, 1196, 1117, 1002, 864, 837, 811, 751 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 250 (M^+; 64), 235 (80), 220 (66), 205 (100), 163 (49), 73 (25). HRMS (EI, 70 eV) Calcd for $C_{14}H_{22}O_2Si$: M^+, 250.1388. Found: *m/z* 250.1389 (M^+).

(*E*)-1,3-Dimethoxy-5-methyl-2-(2-triethylsilylethenyl)benzene. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.65$ (6H, q, $J = 7.9$ Hz), 0.99 (9H, t, $J = 7.9$ Hz), 2.32 (3H, s), 3.81 (6H, s), 6.36 (2H, s), 6.66 (1H, d, $J = 19.8$ Hz), 7.13 (1H, d, $J = 19.9$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 3.86$, 7.69, 22.23, 55.82, 105.13, 113.66, 129.42, 135.30, 138.33, 158.35. IR (neat) 2952, 2873, 1606, 1462, 1414, 1245, 1207, 1121, 1003, 809, 784, 734 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 292 (M^+; 22), 263 (95), 248 (18), 219 (100), 191 (17), 96 (13), 59 (14). HRMS (EI, 70 eV) Calcd for $C_{17}H_{28}O_2Si$: M^+, 292.1857. Found: *m/z* 292.1849 (M^+).

(*E*)-(2-*t*-Butyldimethylsilylethenyl)-1,3-dimethoxy-5-methylbenzene. Mp 74.8—76.0 °C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.10$ (6H, s), 0.92 (9H, s), 2.33 (3H, s), 3.81 (6H, s), 6.36 (2H, s), 6.71 (1H, d, $J = 20.4$ Hz), 7.11 (1H, d, $J = 20.0$ Hz). ^{13}C NMR (100 MHz, C_6D_6) $\delta = -4.57$, 18.17, 23.18, 27.96, 56.32, 106.19, 115.33, 131.13, 137.44, 139.25, 159.97. IR (NaCl) 2925, 2852, 1596,1461, 1409, 1244, 1203, 1113, 1006, 834, 814 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 292 (M^+; 4), 277 (4), 235 (100), 220 (57), 205 (61). HRMS (EI, 70 eV) Calcd for $C_{17}H_{28}O_2Si$: M^+, 292.1857. Found: *m/z* 292.1854 (M^+). Anal. Calcd for $C_{17}H_{28}O_2Si$: C, 69.81; H, 9.65%. Found: C, 69.81; H, 9.62%.

(*E*)-1,3-Dimethoxy-5-methyl-2-(2-triisopropylsilylethenyl)benzene. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.10$ (18H, d, $J = 6.1$ Hz), 1.12—1.21 (3H, m), 2.32 (3H, s), 3.80 (6H, s), 6.37 (2H, s), 6.56 (1H, d, $J = 20.0$ Hz), 7.10 (1H, d, $J = 20.0$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 11.17$, 18.92, 22.20, 55.93, 105.30, 114.32, 127.60, 136.08, 138.15, 158.25. IR (neat) 2940, 2863, 1605, 1462, 1410, 1246, 1211, 1120, 1003, 908, 882, 816, 761, 734 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 334 (M^+; 12), 291 (100), 249 (12), 233 (66), 205 (19), 191 (14). HRMS (EI, 70 eV) Calcd for $C_{20}H_{34}O_2Si$: M^+, 334.2326. Found: *m/z* 334.2333 (M^+).

(*E*)-2-(2-Dimethylphenylsilylethenyl)-5-ethyl-1,3-dimethoxybenzene. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.41$ (6H, s), 1.23 (3H, t, $J = 7.7$ Hz), 2.61 (2H, q, $J = 7.7$ Hz), 3.81 (6H, s), 6.39 (2H, s), 6.89 (1H, d, $J = 19.6$ Hz), 7.26 (1H, d, $J = 19.8$ Hz), 7.32—7.35 (3H, m), 7.58—7.61 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = -2.14$, 15.55, 29.60, 55.68, 103.72, 113.41, 127.45, 128.46, 130.08, 133.84, 136.02, 139.63, 145.20, 158.58. IR (neat) 2961, 1605, 1566, 1457, 1417, 1246, 1199, 1119, 835, 731, 700 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 326 (M^+; 27), 311 (100), 296 (19), 281 (46), 271(26), 135 (19), 91 (16). HRMS (EI, 70 eV) Calcd for $C_{20}H_{26}O_2Si$: M^+, 326.1701. Found: *m/z* 326.1702 (M^+).

(*E*)-2-(2-Dimethylphenylsilylethenyl)-5-isopropyl-1,3-dimethoxybenzene. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.41$ (6H, s), 1.24 (6H, d, $J = 6.8$ Hz), 2.85 (1H, septet, $J = 6.8$ Hz), 3.82 (6H, s), 6.41 (2H, s), 6.88 (1H, d, $J = 19.8$ Hz), 7.26 (1H, d, $J = 19.6$ Hz), 7.31—7.35 (3H, m), 7.57—7.61 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = -2.12$, 23.96, 34.86, 55.70, 103.24, 113.65, 127.45, 128.47, 130.14, 133.86, 136.06, 139.65, 149.90, 158.59. IR (neat) 2958, 1604, 1564, 1457, 1417, 1243, 1200, 1117, 1002, 835, 730, 700 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 340 (M^+; 31), 325 (100), 310 (20), 295 (44), 135 (19), 91 (15). HRMS (EI, 70 eV) Calcd for $C_{21}H_{28}O_2Si$: M^+, 340.1857. Found: *m/z* 340.1863 (M^+).

(*E*)-5-Butyl-2-(2-dimethylphenylsilylethenyl)-1,3-dimethoxybenzene. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.41$ (6H, s), 0.93 (3H, t, $J = 7.3$ Hz), 1.36 (2H, sextet, $J = 7.7$ Hz), 1.53—1.64 (2H, m), 2.57 (2H, t, $J = 7.7$ Hz), 3.81 (6H, s), 6.37 (2H, s), 6.89 (1H, d, $J = 19.6$ Hz), 7.26 (1H, d, $J = 19.8$ Hz), 7.31—7.36 (3H, m), 7.57—7.62 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = -2.13$, 14.09, 22.53, 33.57, 36.46, 55.75, 104.31, 113.37, 127.46, 128.48, 130.11, 133.89, 136.03, 139.70, 143.91, 158.53. IR (neat) 2955, 1605, 1566, 1456, 1416, 1245, 1200, 1119, 1002, 835, 730, 700 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 354 (M^+; 26), 339 (100), 309 (18), 282 (15), 135 (14), 91 (11). HRMS (EI, 70 eV) Calcd for $C_{22}H_{30}O_2Si$: M^+, 354.2013. Found: *m/z* 354.2007 (M^+).

(*E*)-5-(*t*-Butyl)-2-(2-dimethylphenylsilylethenyl)-1,3-dimethoxybenzene. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.42$ (6H, s), 1.31 (9H, s), 3.83 (6H, s), 6.57 (2H, s), 6.90 (1H, d, $J = 19.8$ Hz), 7.26 (1H, d, $J = 19.6$ Hz), 7.32—7.35 (3H, m), 7.58—7.61 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = -2.12$, 31.34, 35.32, 55.84, 101.74, 113.51, 127.48, 128.49, 130.40, 133.91, 135.97, 139.73, 152.18, 158.32. IR (neat) 2957, 1604, 1559, 1454, 1410, 1247, 1201, 1126, 1113, 1002, 837, 730, 700 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 354 (M^+; 32), 339 (100), 324 (16), 309 (34), 283 (14), 205 (21), 135 (21), 57 (32). HRMS (EI, 70 eV) Calcd for $C_{22}H_{30}O_2Si$: M^+, 354.2013. Found: *m/s* 354.2019 (M^+).

(*E*)-6-(2-Dimethylphenylsilylethenyl)-1,5,6-trimethoxy-3,3-dimethyl-1,4-cyclohexadiene. Under an argon atmosphere, to a solution of 3,4,5-trimethoxytoluene (36 mg, 0.20 mmol) in CH_2Cl_2 (4 mL) was added a solution of $GaCl_3$ (1.0 M in methylcyclohexane, 1.0 mL) at −90 °C. Then dimethylphenylsilylethyne (160 mg, 1.0 mmol) in CH_2Cl_2 (1 mL) was added slowly. After the mixture was stirred for 15 min at −90 °C, methylmagnesium bromide (0.93 M in THF, 3.0 mmol) was added, and the mixture was allowed to warm to 0 °C. After 30 min, water was added. The organic layer was separated, and dried over $MgSO_4$. Solvents were removed in vacuo, and the residue was purified by flash column chromatography (Et_3N-treated silica-gel, hexane : chloroform = 8 : 1, then silica-gel, hexane : ethyl acetate = 15 : 1) to give (*E*)-6-(2-dimethylphenylsilylethenyl)-1,5,6-trimethoxy-3,3-dimethyl-1,4-cyclohexadiene (49 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.31$ (6H, s), 1.15 (3H, s), 1.19 (3H, s), 3.13 (3H, s), 3.56 (6H, s), 4.89 (2H, s), 5.99 (1H, d, $J = 19.1$ Hz), 6.21 (1H, d, $J = 18.8$ Hz), 7.28—7.32 (3H, m), 7.47—7.50 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = -2.34$, 31.95, 32.69, 33.75, 51.16, 54.79, 79.55, 109.10, 126.86, 127.42, 128.56, 133.83, 138.96, 148.45, 149.41. IR (neat) 2954, 1686, 1650, 1465, 1355, 1249, 1206, 1102, 825, 733, 700 cm^{-1}. MS

(EI, 70 eV) *m/z* (%) 358 (M^+; 2), 343 (63), 317 (21), 197 (26), 183 (17), 135 (100). HRMS (EI, 70 eV) Calcd for $C_{21}H_{30}O_3Si$: M^+, 358.1962. Found: *m/z* 358.1970 (M^+).

(*E*)-2-(2-Dimethylphenylsilylethenyl)-1,3-dimethoxy-4,5-dimethylbenzene. The reaction was conducted as above, and the crude product was dissolved in ether (10 mL). After cooling to 0 °C, H_2O (1 mL) and methanesulfonic acid (1.3 mL, 20 mmol) were added, and the mixture was stirred for 1 h at 0 °C. Then saturated aqueous $NaHCO_3$ was added, and the organic layer was separated, washed with saturated aqueous $NaHCO_3$ twice, and dried over $MgSO_4$. Solvents were removed in vacuo, and the residue was purified by flash column chromatography (silica-gel, hexane : ethyl acetate = 20 : 1) to give (*E*)-1,3-dimethoxy-2-(2-phenyldimethylsilylethenyl)-4,5-dimethylbenzene (30 mg, 46%). ^1H NMR (400 MHz, $CDCl_3$) $\delta = 0.42$ (6H, s), 2.12 (3H, s), 2.25 (3H, s), 3.60 (3H, s), 3.79 (3H, s), 6.50 (1H, s), 6.93 (1H, d, $J = 19.8$ Hz), 7.16 (1H, d, $J = 19.8$ Hz), 7.31—7.36 (3H, m), 7.56—7.62 (2H, m) ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = -2.28$, 11.74, 20.74, 55.68, 60.19, 108.81, 117.85, 121.79, 127.52, 128.60, 131.27, 133.83, 136.78, 137.76, 139.25, 156.19, 157.23. IR (neat) 2952, 1604, 1465, 1247, 1200, 1119, 1013, 845, 733, 700 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 326 (M^+; 51), 311 (100), 296 (39), 281 (48), 233 (17), 177 (23), 135 (27). HRMS (EI, 70 eV) Calcd for $C_{20}H_{26}O_2Si$: M^+, 326.1701. Found: *m/z* 326.1697 (M^+).

(*E*)-6-[2-(*t*-Butyldimethylsilyl)-2-dimethylgallioethenyl]-1,5,6-trimethoxy-3-methyl-1,4-cyclohexadiene. Under an argon atmosphere, to a solution of 1,2,3-trimethoxybenzene (34 mg, 0.20 mmol) in CH_2Cl_2 (4 mL) was added a solution of $GaCl_3$ (1.0 M in methylcyclohexane, 1.0 mL) at −90 °C dropwise. To this mixture, dimethylphenylsilylethyne (140 mg, 1.0 mmol) in CH_2Cl_2 (1.0 mL) was added slowly. After the mixture was stirred for 15 min at −90 °C, methyllithium (0.93 M in ether, 3.0 mmol) was added, and the mixture was stirred for 30 min. Then water was added, and the organic layer was separated, and dried over $MgSO_4$. Solvents were removed in vacuo, and the residue was purified by flash column chromatography (silica-gel, hexane : ethyl acetate = 20 : 1) to give the product as a mixture of diastereomers (61 mg, 72%).

Major diastereomer: ^1H NMR (500 MHz, $CDCl_3$) $\delta = -0.40$ (6H, s), −0.02 (6H, s), 0.84 (9H, s), 1.13 (3H, d, $J = 7.1$ Hz), 3.03 (1H, m), 3.16 (3H, s), 3.50 (6H, s), 4.98 (2H, d, $J = 3.8$ Hz), 6.03 (1H, s). ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = -5.26$, −4.58, 16.98, 24.43, 26.77, 29.85, 50.55, 54.71, 85.74, 104.03, 144.10, 149.40, 156.14 (Chart 11).

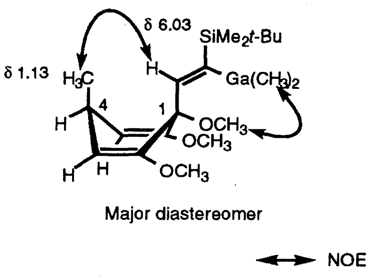


Chart 11.

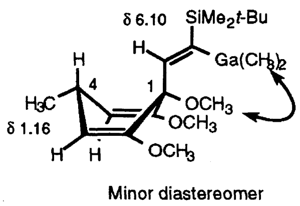


Chart 12.

Minor diastereomer: ^1H NMR (500 MHz, $CDCl_3$) $\delta = -0.40$ (6H, s), −0.02 (6H, s), 0.83 (9H, s), 1.16 (3H, d, $J = 7.1$ Hz), 3.03 (1H, m), 3.16 (3H, s), 3.49 (6H, s), 4.94 (2H, d, $J = 3.8$ Hz), 6.10 (1H, s). ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = -5.22$, −4.58, 16.77, 23.54, 26.77, 29.81, 50.39, 54.71, 85.96, 103.96, 143.50, 149.08, 156.08. IR (neat, mixture) 2952, 2853, 1685, 1655, 1561, 1463, 1358, 1237, 1214, 1104, 888, 827, 763 cm^{-1} (Chart 12).

Arenium Cation Formed from 1,2,3-Trimethoxybenzene. Under an argon atmosphere, a solution of 1,2,3-trimethoxybenzene (17 mg, 0.10 mmol) and *t*-butyldimethylsilylethyne (14 mg, 0.10 mmol) in CD_2Cl_2 (0.35 mL) was cooled to −90 °C in a NMR sample tube. A solution of 2.0 M $GaCl_3$ in CD_2Cl_2 (0.25 mL) was added slowly, and the resulting mixture was gently shaken until $GaCl_3$ dissolved. The resulting orange solution was allowed to stand at −90 °C for 30 min, and NMR spectra were obtained at −90 °C. ^1H NMR (400 MHz, CD_2Cl_2) $\delta = 0.13$ (6H, s), 0.80 (9H, s), 3.96 (3H, s), 4.35 (6H, s), 5.86 (1H, s), 6.76 (2H, d, $J = 8.8$ Hz), 8.85 (1H, d, $J = 8.8$ Hz). ^{13}C NMR (100 MHz, CD_2Cl_2) $\delta = -6.62$, 16.38, 25.16, 60.44, 62.04, 89.12, 106.35, 138.87, 147.59, 173.84, 183.13. When THF-d_8 (0.1 mL) was added to this mixture, the color of the solution faded. NMR indicated the formation of 1,2,3-trimethoxybenzene and *t*-butyldimethylsilylethyne.

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