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Reaction pathways of zirconocene-catalyzed silylation of alkenes with chlorosilanes

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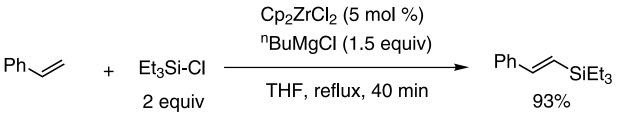
Abstract—Reaction pathways as well as stereochemistries and stoichiometries of zirconocene-catalyzed silylation of olefins with chlorosilanes in the presence of ^{n}BuMgCl were studied and discussed in detail. Rate determining steps were examined by kinetic studies and labeling experiments.

1. Introduction

Among a variety of reactions that have been developed for introducing R_3Si moieties into organic molecules, transition metal catalyzed silylation toward carbon–carbon unsaturated bonds have widely been employed as a straightforward and useful method of synthesizing organosilicon compounds.[1] As for the silylating reagents of such reactions, silanes,[2a] disilanes,[2b] silacyclobutanes[2c] or -propanes,[2d] silyl cyanides,[2e] silylgermanes,[2f] silylstannanes,[2g] silylselenides,[2f] and iodosilanes[2h–j] have been employed. Chlorosilanes are the most widely used and easily available silylating reagents in organic synthesis; however, their use in transition metal catalyzed reactions has been limited. This is due to the difficulty of the oxidative addition of the Si–Cl bond to low valent metal complexes.[3] We have reported the first example of transition metal catalyzed silylation of olefins with chlorosilanes by the use of Cp_2ZrCl_2.[4,5] For example, styrene reacted with Et_3SiCl in the presence of ^{n}BuMgCl and a catalytic amount of Cp_2ZrCl_2 in refluxing THF to afford the corresponding alkenylsilane with complete regio- and stereoselectivities as exemplified by Eq. 1. Ethylene gave a vinylsilane at 80 °C in good yield based on the chlorosilane used (Eq. 2). When allylbenzene was employed, only an *E*-allylsilane was obtained as a sole product at room temperature (Eq. 3), whereas alkyl-substituted olefins such as 1-octene affords a mixture of allyl- and vinylsilanes.[4] Herein, we wish to reveal the results obtained in a study performed to shed light on the reaction pathways of this zirconocene-catalyzed silylation of olefins with chlorosilanes.



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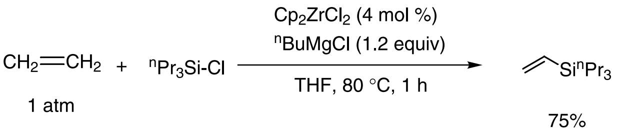

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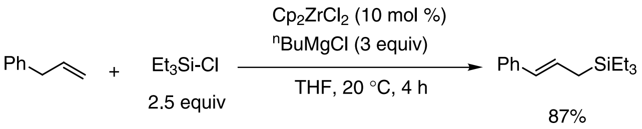

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2. Results and discussion

2.1. Stereochemistry

In all reactions using arylalkenes only *E*-isomers of vinylsilanes were formed. In order to determine whether the stereochemistry is controlled kinetically or thermodynamically, we carried out a reaction of *p*-methylstyrene with Et_3SiCl in the presence of *Z*-isomer of β-triethylsilylstyrene **1**. As shown in Eq. 4 only *E*-isomer of β-triethylsilyl-*p*-methylstyrene **2** was obtained in 97% yield and 72% of **1** was recovered as a 20:80 mixture of *E*/*Z* isomers. This result clearly indicates that the stereochemistries of

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Keywords: Zirconocene; Silylation; Chlorosilanes; Olefins; Grignard reagents.

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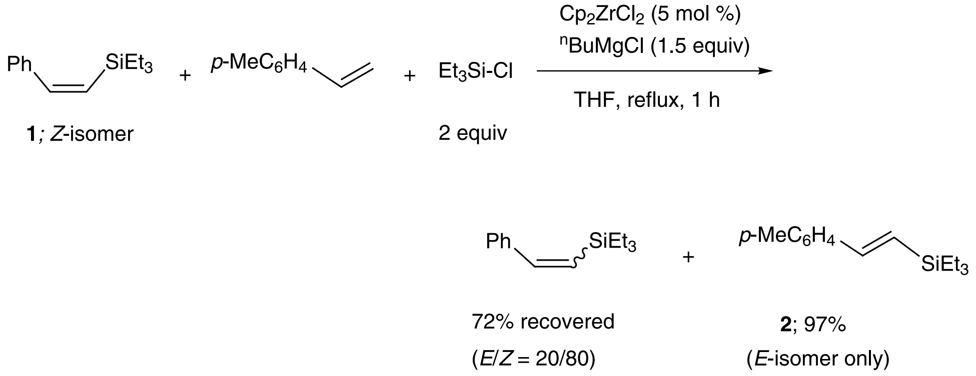
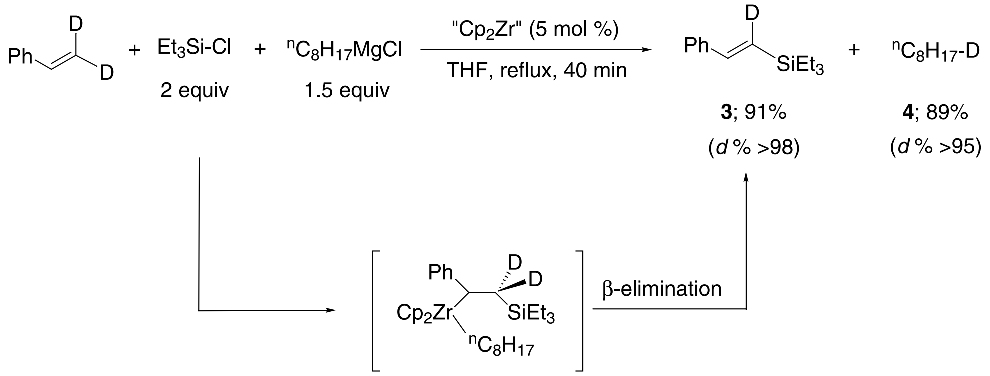
products are determined kinetically not by the isomerization of products.



(4)

2.2. Stoichiometry of Zr-catalyzed silylation reaction

In this silylation of olefins, vinylic hydrogen is replaced by a silyl group. In order to reveal the exact mass balance of this reaction, we carried out a reaction of styrene-*d*$_2$ with Et_3SiCl (2 equiv) and ^{n}OctMgCl (1.5 equiv) in the presence of 5 mol% of ‘Cp_2Zr’ generated in situ from Cp_2ZrCl_2 and ^{n}BuMgCl.[6] Refluxing the solution for 40 min followed by quenching with 0.1 N HCl_{aq} gave nearly equal amounts of monodeuterated vinylsilane **3** (deuterium content >98%) and octane **4** containing a deuterium at the terminal carbon (deuterium content >95%) (Eq. 5). This result shows that one of the deuterium atoms at the β-carbon of styrene-*d*$_2$ was transferred to the α-carbon of the octyl group of the Grignard reagent provably via β-elimination from dialkylzirconocene intermediate **5** (vide infra). The mechanism of β-hydrogen elimination of dialkylzirconocene complexes has been examined and a unique pathway involving direct transfer of a β-hydrogen of one of the alkyl substituents on Zr to an α-carbon of another alkyl group, not via a hydrozirconocene intermediate, has been proposed.[7]



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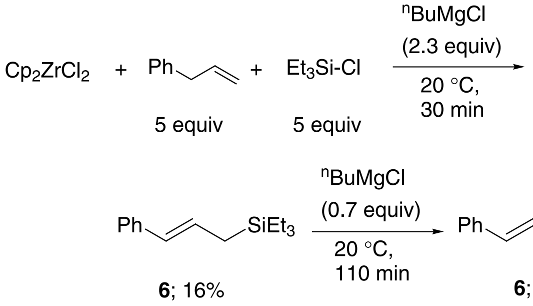
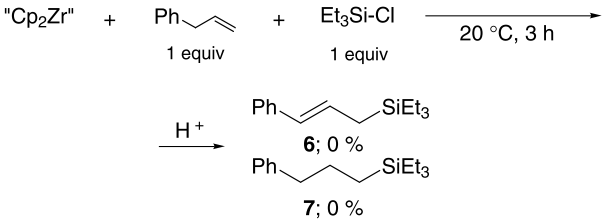
(5)

Present silylation reaction provides good yields of products based on the limiting substrates, either on olefins (Eqs. 1 and 3) or on chlorosilanes (Eq. 2); however, we encounter an interesting phenomenon when a limited amount of Grignard reagents was employed. When Cp_2ZrCl_2 was treated with 2.3 equiv. of ^{n}BuMgCl in the presence of 5 equiv. each of allylbenzene and Et_3SiCl, the corresponding allylsilane **6** was obtained only in 16% yield based on Cp_2ZrCl_2 used in 20 min (Eq. 6 and Figure 1). Although the yield of **6** was not improved by elongation of the reaction time, the yield increased up to 62% when 0.7 equiv of ^{n}BuMgCl was introduced additionally to the reaction mixture. It is known that Cp_2ZrCl_2 reacts with 2 equiv. of R-MgX to form Cp_2Zr.[6] This evidence along with the results shown in Eq. 6 and Figure 1 suggests that the products are formed only in the presence of Grignard reagents.



(6)

This phenomenon can more clearly be confirmed by the following control experiments. A reaction of allylbenzene with Et_3SiCl in the presence of a stoichiometric amount of Cp_2Zr, generated in situ by the reaction of Cp_2ZrCl_2 with 2 equiv. of ^{n}BuMgCl, gave no silylated products, such as **6** or **7**, even after quenching the resulting mixture with HCl_{aq} (Eq. 7). On the other hand, a similar reaction in the presence of 1 equiv. of ^{n}BuMgCl (i.e., total amount of ^{n}BuMgCl used is 3 equiv.) afforded **6** in 72% yield (Eq. 8). A reaction of Cp_2Zr with styrene (5 equiv.) and Et_3SiCl under THF reflux condition for 1 h did not afford any silylated products. However, 65% yield of the corresponding vinylsilane was obtained when a similar reaction was carried out in the presence of 1 equiv. of ⁿBuMgCl.



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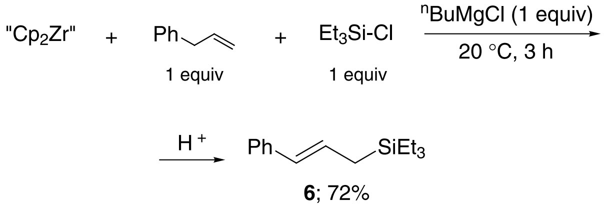


(8)

2.3. Reaction pathways

Taking into account these results mentioned above and the evidence that zirconocene–ethylene complex reacts with EtMgBr giving rise to zirconate complex,[8] we propose that the present reaction proceeds via zirconate complex **9** that reacts with R'_3SiCl to give dialkylzirconocene **11**, which then undergoes β-elimination to afford **12** (Scheme 1, path A). However, an alternative pathway that involves direct reaction of neutral olefin complexes **8** with chlorosilanes to give **10** may not be ruled out since a neutral zirconocene–ethylene complex $Cp_2Zr(CH_2{=}CH_2)$ reacts with chlorosilanes in the presence of Me_3P to form the corresponding β-silylalkylzirconocene complex.[9] If **10** is formed in only a small amount by an equilibrium process which is biased toward **8**, path B may not be contradicted by the results of Eqs. 6–8.

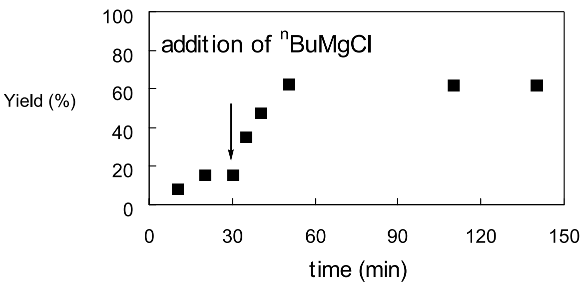
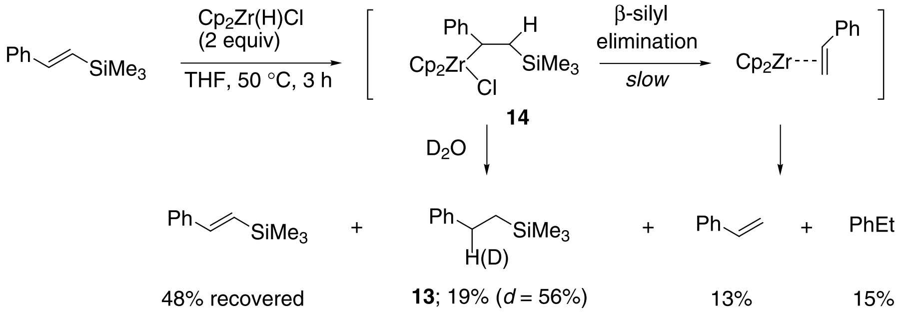


Figure 1.

In order to reveal which path is more likely, we examined whether β-Si elimination process from **10** to **8** can take place rapidly under the present reaction conditions. Since it is known that internal arylalkenes react with Cp_2ZrHCl to give benzylzirconocene complex predominantly,[10] we stirred a THF solution of β-trimethylsilylstyrene and Cp_2ZrHCl at 50 °C for 3 h and quenched the products with D_2O. NMR measurements showed that the resulting mixture contained unreacted β-trimethylsilylstyrene (48% recovered), 19% of saturated silane **13** having a deuterium atom at the benzylic position (56% of deuterium content), 13% of styrene, and 15% of ethylbenzene (Eq. 9). It is likely that incorporation of deuterium in **13** arises from the reaction of **14** with D_2O. Although the formation of styrene and ethylbenzene suggests that β-silyl elimination from **14** proceeds under these conditions, this can not be a rapid process since **14** remained under the conditions of Eq. 9 as suggested by formation of **13**. These results would rule out a possibility of the formation of **10** from **8** in the present reaction.



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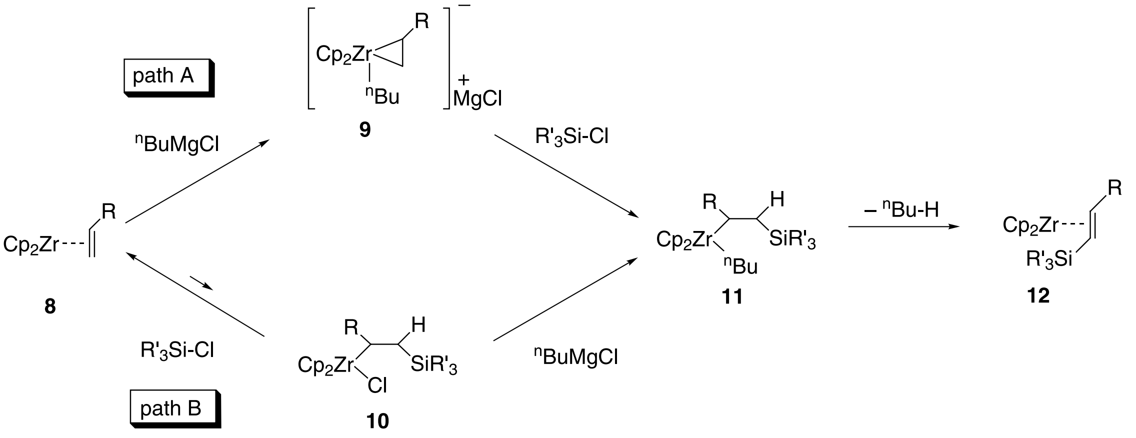
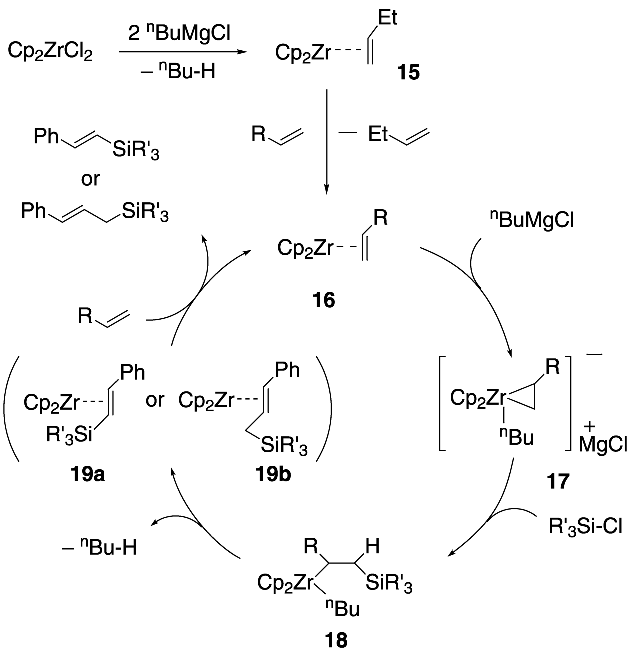


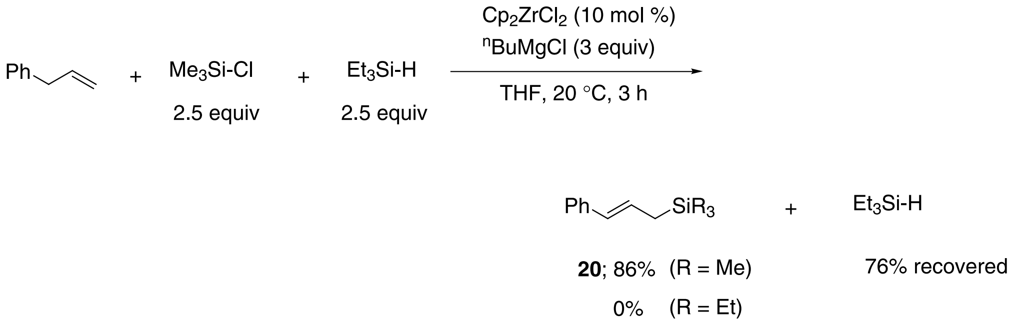
Scheme 1.

A plausible catalytic cycle is shown in Scheme 2. Zirconate complex **17**, formed by the reaction of zirconocene-olefin complex **16** with $^{n}BuMgCl$, reacts with chlorosilanes to give dialkylzirconocene complex **18** which undergoes β-hydrogen elimination with removal of one of the β-hydrogen to afford a vinylsilane or allylsilane.

In all of the present silylation reactions examined, a small amount of R_3SiH was formed along with the desired silylation product. Since it is known that Cp_2TiCl_2 catalyzes the reduction of R_3SiCl to R_3SiH[11] in the presence of $^{i}PrMgBr$ and that $Cp_2Zr^{n}Bu_2$ catalyzes the addition of R_3SiH to olefins,[12] there may still remain a possibility of an alternative pathway involving hydrosilylation process. So we then performed a reaction of allylbenzene with Me_3SiCl in the presence of Et_3SiH. The result that only a trimethylsilylated product **20** was obtained in 86% yield along with 76% recovery of Et_3SiH would suggest that R_3SiH is not involved in this catalytic cycle. When a similar reaction was carried out using styrene, Pr_3SiCl, and Et_3SiH, only tripropylsilylated vinylsilane was obtained in 76% yield and 97% of Et_3SiH was recovered unreacted.



Scheme 2.



(10)

2.4. Rate determining steps

To investigate the rate determining step of silylation of styrene with chlorosilanes, we ran the reaction employing different concentrations of substrates in THF at 50 °C for 5 min and quenched with H_2O (Eq. 11 and Fig. 2). Interesting to note, change of the concentration of Et_3SiCl did not affect the product yield indicating that Et_3SiCl is not involved either in the rate determining step or in the preceding equilibrium processes. On the other hand, the yield of the product obeys pseudo first-order kinetics ($k{=}3.9\times10^{-5}\ \mathrm{min}^{-1}$) on the concentration of styrene. These results suggest that the rate determining step is the ligand exchange process to regenerate zirconocene-styrene complex **21** from **24**. It was also surprising that decreasing the concentration of $^{n}BuMgCl$ increased the reaction rate. This unexpected phenomenon can be explained by assuming an equilibrium between **24** and **26**. High concentration of $^{n}BuMgCl$ shifted the equilibrium toward **26** resulting in retardation of the ligand exchange. In fact, when a reaction

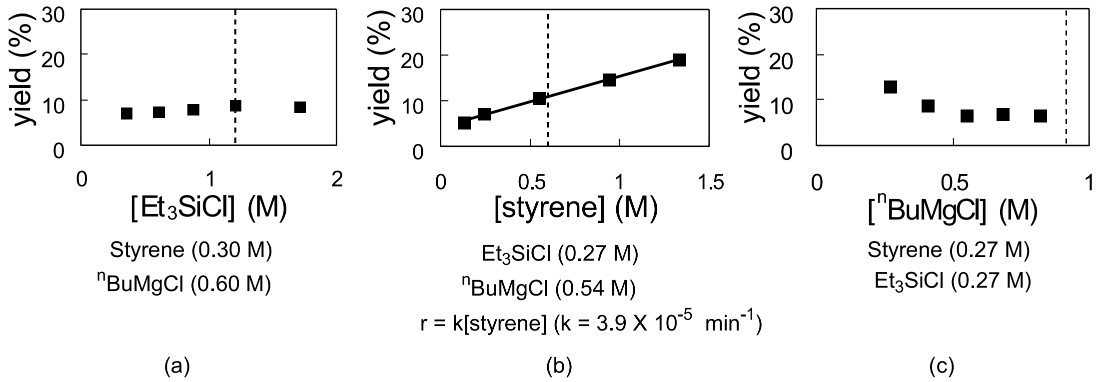
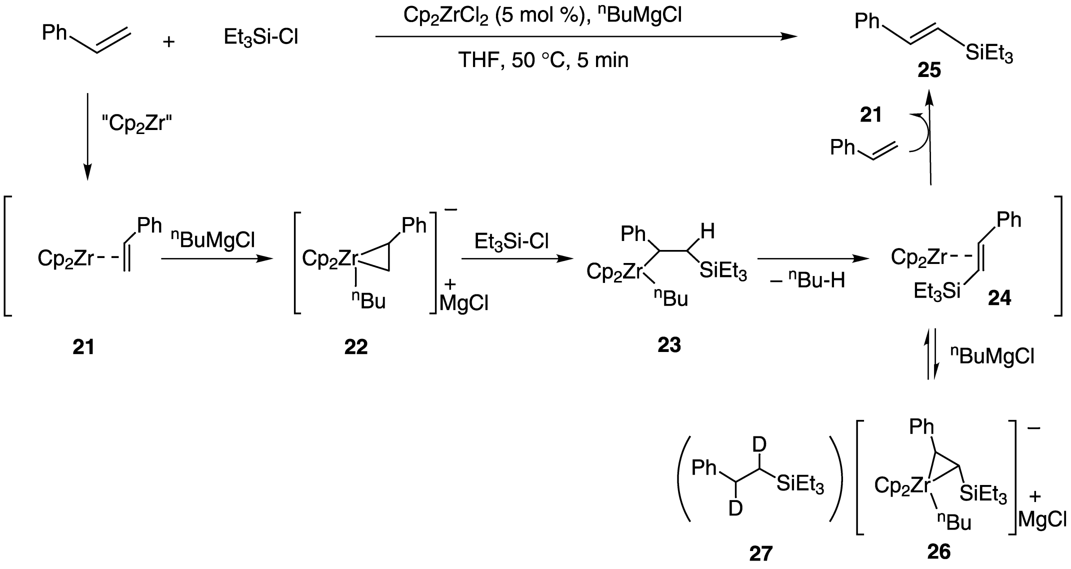


Figure 2. Plots of yields of **25** against concentration of (a) Et_3SiCl, (b) styrene, and (c) $^{n}BuMgCl$. The dotted line shows a representative concentration of the standard conditions of this silylation.

mixture was quenched with D_2O after the reaction, a dideuterated silane **27** was obtained, probably by the reaction of **26** with D_2O, in almost the same amount of zirconocene catalyst employed (Fig. 2).



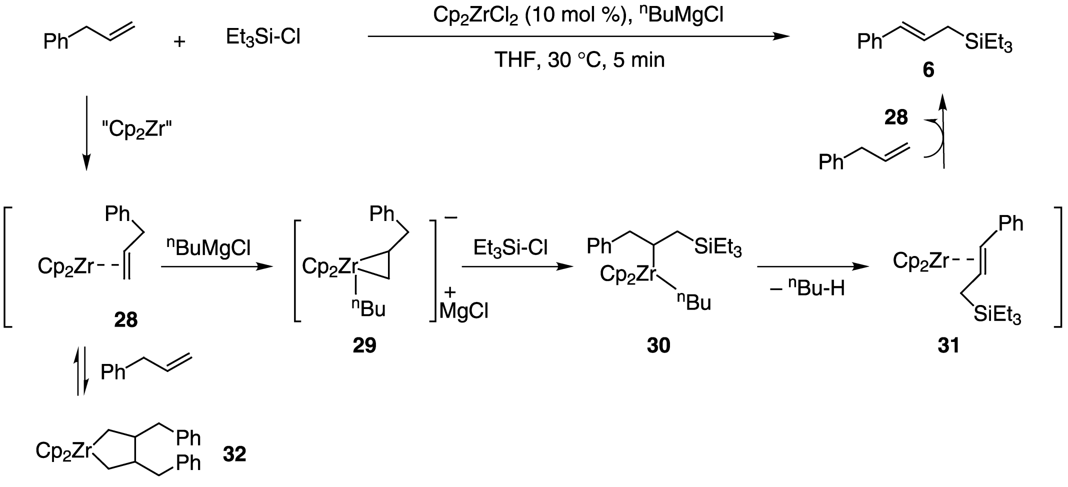
(11)

We next examined the rate determining step of the silylation reaction of allylbenzene by the similar procedures (Eq. 12 and Fig. 3). The rate of allylsilane formation is independent on the concentration of Et_3SiCl as in the case of styrene and also on that of ^{n}BuMgCl. However, the rate surprisingly decreased when the concentration of allylbenzene increased in the region of >0.2 M. With these observations, we would like to propose that the rate determining step is the β-elimination process since the reaction rate was not affected by the concentrations of any substrates in the region of [allylbenzene] <0.2 M. Higher concentration of allylbenzene (>0.2 M) would retard the reaction probably by converting **28** to zirconacyclopentane **32** which is a resting stage of the catalyst. GC and GC-MS analyses of the resulting mixture after quenching with aqueous HCl suggested the formation of a dimerized product of allylbenzene arising by hydrolysis from **32** in ca. 40% based on Cp_2Zr employed (Fig. 3).

2.5. Mechanisms of C–Si bond forming step

As discussed above carbon–silicon bond forming process is rapid and is not the rate determining step of this silylation reaction. Adopting the intermediary of the ate complex **33**, we would like to propose three possible mechanisms for this process as shown in Scheme 3. Mechanism A involves electrophilic outside attack of R_3SiCl to the coordinated olefin to give a silylzirconation product **34**. Mechanism B affords **35** via σ-metathesis and mechanism C involves oxidative addition of R_3SiCl to **33** affording a Zr(IV) intermediate and subsequent insertion. In mechanism A, Si and Zr were introduced at vinylic carbons from the opposite sides of olefins and, contrary to this, addition proceeds in *syn* fashion in mechanisms B and C. In order to determine the stereochemistry of this C–Si bond forming process, we prepared *p*-methylstyrenes having one deuterium atom at *trans*- or *cis*-position on the β-carbon (**36** and **37**, respectively) and subjected them to the present silylation reaction.

As mentioned above, only *E*-vinyl silanes were formed from styrenes by kinetic control. If β-elimination of dialkylzirconocene complexes proceeds intramolecularly via direct H shift from the β-carbon of an alkyl group on Zr to the β-carbon



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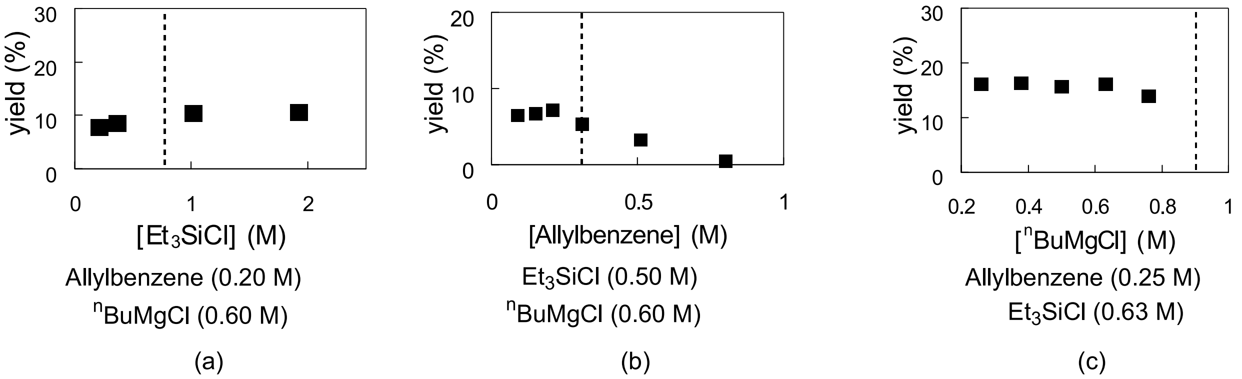


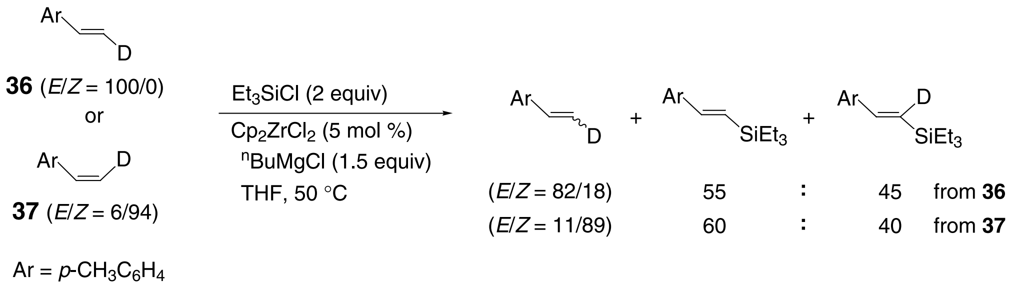
Figure 3. Plots of yields of **6** against concentration of (a) Et_3SiCl, (b) allylbenzene, and (c) ^nBuMgCl. The dotted line shows a representative concentration of the standard conditions of this silylation.

of the other as demonstrated by Negishi et al.,[7] the stereochemistry of this step should be *cis*. So it was expected that D and H contents at the β-carbon of the product reflects the stereochemistry of this process. Unfortunately, both **36** and **37** gave similar mixtures of products with nearly 1:1 ratio of d_0- and d_1-vinylsilanes as shown in Eq. 13 and we could not determine the stereochemistry of this process; however, these experiments provide useful information about relative rates of C–Si bond formation, *cis-trans* isomerization,[13] and ligand exchange process as shown below.

It was confirmed by NMR and GC-Mass analyses that vinylsilanes having more than one deuterium were not formed and the deuterium was attached only to the β-carbon (the carbon bearing a silyl group). The *E*/*Z* ratios of the recovered *p*-methylstyrene-d_1, were 82:18 from **36** and 11:89 from **37** indicating that *cis-trans* isomerization of starting olefin proceeds only to a small extent. These results suggest; (1) *cis-trans* isomerization takes place rapidly on Zr metal, (2) this isomerization reaction is much faster than the competing silylation process leading the products, and (3) this silylation process proceeds faster than olefin exchange reaction on Zr, i.e., most of the coordinated olefin molecules go to the products without dissociation from Zr. These results also show another important feature of this reaction. It has been reported that the first isotope effect on β-hydrogen elimination of dialkylzirconocene complexes is nearly 6.[14] However, no isotope effect was observed in the reactions of Eq. 13. This evidence indicates that C–Si bond forming process is irreversible under the conditions employed or β-Si elimination, if proceeds, is much slower than the β-hydrogen elimination.

3. Conclusion

Zr-catalyzed silylation of olefins with chlorosilanes have been examined in detail focusing on the reaction pathway and mechanisms of this reaction. Important results obtained are (i) it is likely that this reaction proceeds via zirconocene–olefin ate complexes, (ii) the rate determining step of this catalytic cycle is ligand exchange process in the case of styrene and is β-hydrogen elimination step in the case of allylbenzene, (iii) the C–Si bond forming process is irreversible and faster than olefin exchange reaction on Zr, and (iv) *cis-trans* isomerization of coordinated olefins proceeds rapidly on



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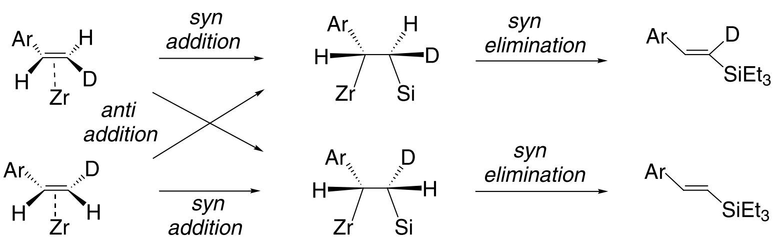

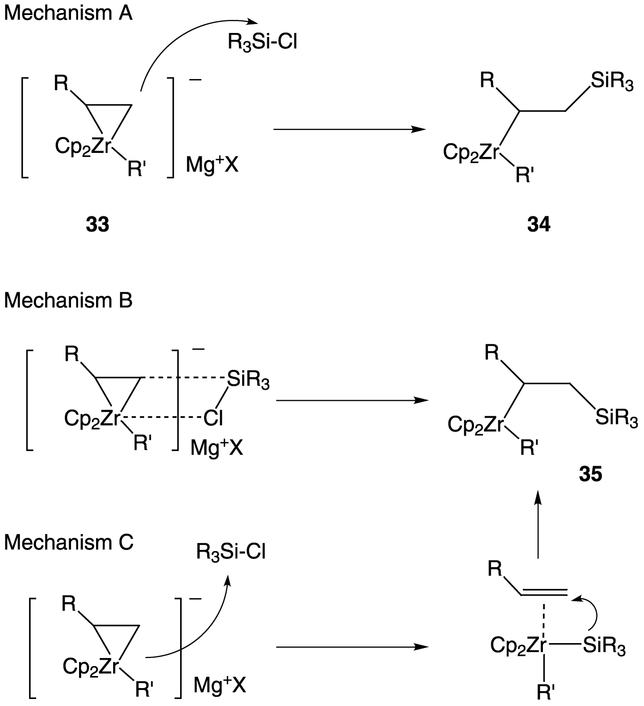

Scheme 3.

Zr and is faster than the C–Si bond forming process. In this reaction the olefinic carbon acts as a nucleophilic center toward chlorosilanes. This unique reactivity may arise from strong back donation from zirconium to olefins and this effect would be enhanced by complexation to form ate complexes.

4. Experimental

4.1. (*E*)-Triethyl(2-phenylethenyl-1-*d*)silane (3)

Ethenyl-2,2-*d2*-benzene was prepared in 87% yield from PhCHO and CD_3I following a reported procedure.[15] A THF solution of Cp_2Zr was prepared by the addition of 2 equiv. of ^{n}BuMgCl (0.9 M in THF, 0.22 ml, 0.20 mmol) to Cp_2ZrCl_2 (29 mg, 0.10 mmol) at −78 °C followed by stirring for 1 h at the temperature. Into this solution were added Ethenyl-2,2-*d2*-benzene (212 mg, 2.0 mmol), Et_3SiCl (603 mg, 4.0 mmol) and ^{n}OctMgCl (1.0 M in THF, 3.0 ml, 3.0 mmol) and the mixture was refluxed for 40 min. The addition of benzaldehyde in order to trap the remaining ^{n}OctMgCl and subsequent quenching with 0.1 N HClaq afforded monodeuterated products **3** (91% NMR yield) and **4** (89% GC yield).

Compound **3**. (Deuterium content >98%), purified by HPLC. IR (NaCl) 2953, 2909, 2874, 1494, 1015, 722, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J*=7.1 Hz, 2H), 7.32 (t, *J*=7.5 Hz, 2H), 7.24 (t, *J*=5.4 Hz, 1H), 6.88 (s, *J*=2.4 Hz, 1H), 0.98 (t, *J*=7.8 Hz, 9H), 0.65 (q, *J*=7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 138.2, 128.3, 127.6, 126.1, 125.3 (t, *J*=20.7 Hz,), 7.5, 3.6; MS (EI) *m/z* (relative intensity, %) 219 (M^+, 19), 191 (24), 190 (100), 162 (64), 134 (31), 132 (25). HRMS calcd for $C_{14}H_{21}DSi$ 219.1570, found 219.1547. The deuterium content was determined by a comparison of its mass spectrum with that of the corresponding non-deuterated triethyl(2-phenylethenyl)silane.

4.1.2. Octane-1-*d* (4) (deuterium content >95%). The deuterium content of octane-1-*d* (**4**) was determined similarly by mass spectroscopy. The evidence that only a terminal carbon shows a triplet peak at δ 13.9 (t, *J*=19 Hz) in the ^{13}C NMR spectrum (100 MHz, $CDCl_3$) indicates that a deuterium is incorporated at the terminal carbon.

4.1.3. (*E*)-1-Phenyl-3-(triethylsilyl)prop-1-ene (6). To a mixture of allylbenzene (382.9 mg, 3.24 mmol), Et_3SiCl (487.9 mg, 3.24 mmol) and a catalytic amount of Cp_2ZrCl_2 (34.0 mg, 0.12 mmol) was added ^{n}BuMgCl (0.90 M in THF, 1.7 mL, 1.49 mmol) at 20 °C under nitrogen. After stirring the solution for 30 min at 20 °C, a small portion of reaction mixture was treated with 1 N HCl_{aq}, followed by the same workup as mentioned above gave **6** in 16% GC yield. To a remaining reaction mixture was added ^{n}BuMgCl (0.90 M in THF, 0.5 mL, 0.45 mmol) at 20 °C under nitrogen. Additional stirring the solution for 90 min at 20 °C, **6** was obtained in 62% GC yield. Purification by silica gel column chromatography with hexane as the eluent afforded 80 mg (53%) of **6**. IR (NaCl) 2952, 2910, 2874, 2360, 960, 728, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 7.30 (m, 4H), 7.11–7.16 (m, 1H), 6.24 (m, 2H), 1.69 (m, 2H), 0.95 (t, *J*=8.0 Hz, 9H), 0.56 (q, *J*=8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 128.3, 128.0, 127.9, 126.0, 125.3, 19.0, 7.6, 3.5; MS (EI) *m/z* (relative intensity, %) 232 (M^+, 32), 115 (100), 87 (91), 59 (28). HRMS calcd for $C_{15}H_{24}Si$ 232.1647, found 232.1634. Anal. calcd: C, 77.51; H, 10.41. Found: C, 77.36; H, 10.61.

4.1.4. (*E*)-1-Phenyl-3-(trimethylsilyl)prop-1-ene (20). To a mixture of allylbenzene (138.8 mg, 1.17 mmol), Me_3SiCl (319 mg, 2.94 mmol), Et_3SiH (341 mg, 2.94 mmol) and a catalytic amount of Cp_2ZrCl_2 (34.2 mg, 0.12 mmol) was added ^{n}BuMgCl (0.90 M in THF, 3.90 mL, 3.51 mmol) at 20 °C under nitrogen. Stirring the solution for 3 h at 20 °C, 1 N HCl_{aq} was added to the solution at 0 °C, and the mixture was again warmed to 20 °C. A saturated aqueous NH_4Cl solution (50 mL) was added, and the product was extracted with ether (50 mL), dried over $MgSO_4$, and evaporated to give **20** (86% NMR yield) along with recovery of Et_3SiH (89% GC yield). Purification by silica gel column chromatography with hexane as the eluent afforded 172 mg (78%) of **20**. IR (NaCl) 3023, 2954, 1248, 1148, 961, 862, 740, 693 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.31 (m, 4H), 7.11–7.17 (m, 1H), 6.21–6.26 (m, 2H), 1.65 (m, 2H), 0.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 128.3, 128.1, 127.7, 126.1, 125.4, 24.1, −1.6. HRMS calcd for $C_{12}H_{18}Si$ 190.1178, found 190.1174. Anal. calcd: C, 75.72; H, 9.53. Found: C, 75.59; H, 9.60.

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