

Formation of branched silanes via regiospecific hydrosilylation of vinylsilanes

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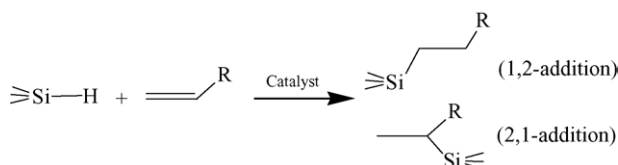
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Abstract

Metalocene complexes of type $\text{Cp}'_2\text{MCH}(\text{TMS})_2$ ($\text{Cp}' = \eta^5\text{-Me}_5\text{C}_5$, $\text{M} = \text{Y, Sm}$), $\text{Me}_2\text{SiCp}'_2\text{SmCH}(\text{TMS})_2$ ($\text{Cp}' = \eta^5\text{-Me}_4\text{C}_5$) catalyze rapid and clean hydrosilylation of $\text{CH}_2=\text{CH}-\text{SiMe}_2\text{R}$ ($\text{R} = \text{Me, Ph, NMe}_2, \text{O}^t\text{Bu}$) with PhSiH_3 . The distribution of 1,2-addition product versus 2,1-addition product was found to be sensitive to both catalysts and substrates. Generation of 2,1-addition product can best be achieved by use of more sterically accessible catalysts as well as substrates containing tethering functional groups. A four-centered transition state is invoked to explain these effects.



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1. Introduction

Catalytic hydrosilylation of α -olefins represents one of the most important industrial processes for the production of organosilicon compounds [1]. In principle, when a silane is added across a double bond, two regioisomers can be formed (Scheme 1): in one, the silicon adds to the less hindered side (linear silane, 1,2-addition); in the other, the silicon adds to the more hindered side (branched silane, 2,1-addition). In spite of extensive research in metal catalyzed hydrosilylation for many years, limited success has been achieved toward developing methods to produce the branched (2,1-addition) silane product. As a result, the synthesis of this technically very important intermediate still remains a scientific challenge [1,2]. Recently organolanthanide compounds have been shown to be efficient catalysts for olefin hydrosilylation [3–5]. Prudent selection of catalyst and substrate can sometimes lead to the formation of completely different regioisomers [3f,4]; however, factors governing the course of

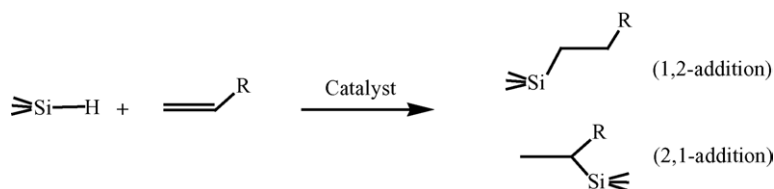
these processes are still poorly understood. We report herein the first attempt to elucidate these factors via hydrosilylation of various vinylsilanes catalyzed by metallocene compounds.

2. Results and discussion

In the presence of catalytic amounts of $\text{Cp}'_2\text{MCH}(\text{TMS})_2$ ($\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$; $\text{M} = \text{Y, Sm}$) or $\text{Me}_2\text{SiCp}'_2\text{SmCH}(\text{TMS})_2$ ($\text{Cp}' = \eta^5\text{-C}_5\text{Me}_4$) at room temperature, the reaction of $\text{CH}_2=\text{CH}-\text{SiMe}_2\text{R}$ ($\text{R} = \text{-Me, -Ph, -NMe}_2, \text{-O}^t\text{Bu}$) with PhSiH_3 proceeds cleanly on an NMR scale at room temperature, as monitored by ^1H NMR, to yield the corresponding hydrosilylated products (Table 1). Because of the slow initiation process with PhSiH_3 observed previously [4], a small amount of hydrogen was introduced prior to the beginning of the reaction so that the reaction rate can be measured accurately. The hydrogenolysis of $\text{M}-\text{CH}(\text{TMS})_2$ was shown to be instantaneous by ^1H NMR, generating catalytically active $\text{M}-\text{H}$ with the concomitant release of a stoichiometric amount of $\text{CH}_2(\text{TMS})_2$. The remainder of the H_2 was rapidly consumed by hydrogenation of the substrate ($N_t > 5000 \text{ h}^{-1}$) [6].

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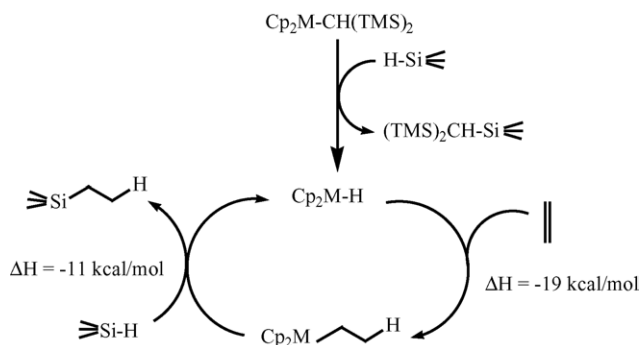
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Scheme 1. Regiochemistry of metal catalyzed olefin hydrosilylation.

As illustrated in Table 1, use of more sterically accessible catalyst (larger metal ions: $\text{Sm}^{3+} > \text{Y}^{3+}$ or more open ancillary ligation: $\text{Me}_2\text{SiCp}'_2\text{M} > \text{Cp}'_2\text{M}$) for the hydrosilylation of vinyltrimethylsilane (entries 1–3) not only leads to the increase of branched product from 0 to 50%, but also greatly accelerates the hydrosilylation reaction (N_t : 120–600 h^{-1}). The latter trend has been observed in a number of organolanthanide-catalyzed olefin transformations [4,6a,b,7]. The hydrosilylation of phenyl dimethyl vinylsilane gives similar results. Interestingly, when one of the substituents on silicon is replaced by $-\text{NMe}_2$, a better electron-donating group, the selectivity for the 2,1-addition product is increased to 67% (entry 9). For alkoxy-substituted vinylsilane, as high as 62% of 2,1-addition product was observed with the more sterically accessible bridged catalyst $\text{Me}_2\text{SiCp}'_2\text{SmR}$, although the turnover frequency is only one per hour. No competing silane coupling products were observed in any of the reactions [8].

A catalytic cycle involving $\text{M}-\text{H}$ as the active species is most likely based on previous mechanistic and kinetic studies (Scheme 2) [4]. The first step involves rapid and exothermic olefin insertion into $\text{M}-\text{H}$ bond, followed by the rate limiting and exothermic $\text{M}-\text{C}/\text{Si}-\text{H}$ transposition to give organosilicon product and regenerate $\text{M}-\text{H}$ [9]. The present result can be rationalized based on a four-centered transition state. Since kinetic and labeling experiments revealed that olefin insertion is rapid and irreversible [4], regiochemistry of olefin hydrosilylation is



Scheme 2. Catalytic cycle for metallocene catalyzed hydrosilylation.

most likely fixed on the first olefin insertion step. Vinylsilane derivative can approach the $\text{M}-\text{H}$ species in two different fashions (1,2-addition versus 2,1-addition), which gives rise to two different transition states: **I** and **II**. The relative energy of the two transition states apparently plays a key role in determining the regiochemistry of the reaction. Transition state **I** is energetically more favored over **II** because of its charge distribution (silyl groups tend to stabilize the adjacent negative charge) [10]. Therefore, under the conditions with no or only limited steric repulsion, 2,1-addition should be the preferred product, which is consistent with the results observed. Accordingly, it is reasonable to believe that the dominance of 1,2-addition product at

Table 1
Metallocene-catalyzed hydrosilylation of vinylsilanes with PhSiH_3^a

Entry	Substrate	Precatalyst ^b	Yield % ^c		N_t^d (h^{-1})
			1,2-Addition	2,1-Addition	
1		$\text{Cp}'_2\text{YR}$	1a (92)	1b (0)	120
2		$\text{Cp}'_2\text{SmR}$	1a (83)	1b (5)	300
3		$\text{Me}_2\text{SiCp}'_2\text{SmR}$	1a (46)	1b (50)	600 ^e
4		$\text{Cp}'_2\text{YR}$	2a (95)	2b (0)	100
5		$\text{Cp}'_2\text{SmR}$	2a (87)	2b (7)	200
6		$\text{Me}_2\text{SiCp}'_2\text{SmR}$	2a (46)	2b (48)	550
7		$\text{Cp}'_2\text{YR}$	3a (95)	3b (0)	75
8		$\text{Cp}'_2\text{SmR}$	3a (85)	3b (10)	180
9		$\text{Me}_2\text{SiCp}'_2\text{SmR}$	3a (31)	3b (67)	20
10		$\text{Cp}'_2\text{YR}$	4a (90)	4b (0)	20 ^f
11		$\text{Cp}'_2\text{SmR}$	4a (80)	4b (7)	20 ^f
12		$\text{Me}_2\text{SiCp}'_2\text{SmR}$	4a (30)	4b (62)	1 ^f

^a Reactions were carried out in C_6D_6 at room temperature and initiated with the addition of a small amount of H_2 (typical olefin/silane molar ratio = 1.2 and typical substrate/precatalyst molar ratio = 200).

^b $\text{R} = \text{CH}(\text{TMS})_2$.

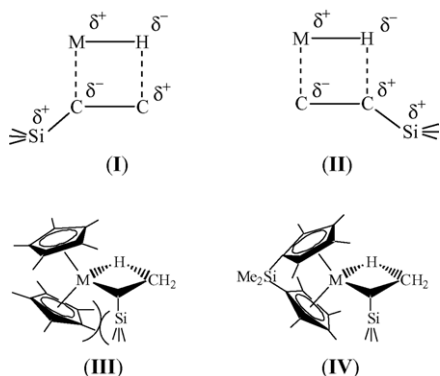
^c Yields were estimated based on GC analysis and the integration of ^1H NMR spectra.

^d Turn over frequency (N_t) was calculated based on the time required for 25% substrate consumption.

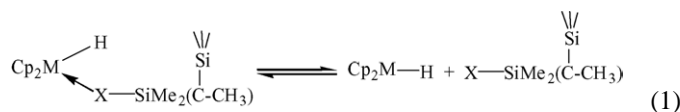
^e NMR scale and scale-up reactions.

^f Reaction temperature was 60 °C.

the sterically more encumbered metal center, such as $\text{Cp}'_2\text{YH}$, is largely due to unfavored steric repulsion between the silyl group and the Cp ring when the vinylsilane approaches the metal center (**III**), a similar substrate-ring effect has been noted in metallocene-mediated olefin polymerisation [11]. On the other hand, steric congestion is much smaller with the silylene-bridged catalysts (**IV**).



The enhancement of 2,1-regioselection in the case of vinylsilane with an amine ($-\text{NR}_2$) group on silicon seems to be inconsistent with what would be expected from transition state **I** because electron-donating substituent on the silicon tends to destabilize the transition state. As a result, the regio-selectivity for 2,1-addition product should be decreased. However, in viewing of the electronic donating ability of the amine substituent, it is plausible that the amine is acting as a tethering group and forms a transient chelate complex with the highly Lewis-acidic metal center that promotes the substrate being inserted into the $\text{M}-\text{H}$ bond preferably in a 2,1-addition fashion. The presence of such a tethering effect to the metal center is verified by a slower hydrosilylation rate (dissociation control, *vide infra*). Hydrosilylation of alkoxy-substituted vinylsilane also give a higher yield for the 2,1-addition product (62%). Its slower rate compared to that of the amine-substituted vinylsilane might be ascribed to the stronger affinity of oxygen to the electron deficient metal center (thermodynamic control) [12], which diminishes the rate of the substrate dissociation from the metal center after the 2,1-addition, and thus retards the catalytic cycle. Consequently, product dissociation most likely becomes the rate-limiting step (Eq. (1)). This explanation is supported by the decrease of hydrosilylation rate (N_t) in the order of $\text{CH}_2=\text{CH}-\text{SiMe}_3 > \text{CH}_2=\text{CH}-\text{SiMe}_2(\text{NMe}_2) > \text{CH}_2=\text{CH}-\text{SiMe}_2(\text{O}^t\text{Bu})$. The use of more sterically accessible precatalyst $\text{Me}_2\text{SiCp}'_2\text{NdCH}(\text{TMS})_2$ than its Sm counterpart fails to boost the formation of the 2,1-addition product, reflecting either the limitation of regioselective tunability or negligible energy difference between transition states **I** and **II** from the Sm to the Nd Catalyst.



In summary, we have shown that the regiochemistry of catalytic hydrosilylation is tunable with change of substrates and catalysts. Sterically more accessible catalysts (larger metal ions or more open ancillary ligation) as well as substrates with tethering groups favor formation of 2,1-regiospecific product.

3. Experimental

All manipulations of air-sensitive materials were performed with rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line, or interfaced to a high vacuum (10^{-5} Torr) line, or in a nitrogen-filled vacuum atmospheres glove box with a high capacity circulator (1–2 ppm O_2). Argon (Matheson, pre-purified) was purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Ether solvents were distilled under nitrogen from sodium benzophenone ketyl. Hydrocarbon solvents (toluene, pentane, heptane) were distilled under nitrogen from Na/K alloy. All solvents for vacuum line manipulations were stored in vacuo over Na/K alloy in resealable bulbs. Phenylsilane, trimethylvinylsilane were purchased from Aldrich, stirred over CaH_2 for 24 h, and vacuum transferred. Dimethylphenylvinylsilane, dimethyl(dimethylamino)silane, dimethyl(*tert*-butoxy)silane were prepared from the reaction of chlorodimethylvinylsilane with LiPh , LiNMe_2 , $\text{Li}(\text{O}^t\text{Bu})$, respectively, and dried over CaH_2 for 24 h. $\text{Cp}'_2\text{MCH}(\text{TMS})_2$ ($\text{Cp}' = \eta^5\text{-Me}_5\text{C}_5$; $\text{M} = \text{Y}, \text{Sm}$) and $\text{Me}_2\text{SiCp}'_2\text{MCH}(\text{TMS})_2$ ($\text{Cp}' = \eta^5\text{-Me}_4\text{C}_5$; $\text{M} = \text{Sm}, \text{Nd}$) were prepared according to literature methods [13].

NMR spectra were recorded on a Varian VXR 300 (FT, 300 MHz, ^1H ; 75 MHz, ^{13}C) instrument or a Varian XL-400 (FT, 400 MHz, ^1H ; 100 MHz, ^{13}C) instrument. GC/HRMS were performed on a VG 70-250 SE instrument with 70 eV electron impact ionization. Elemental analyses were performed by G.D. Searle Corp., Skokie, IL.

3.1. Typical procedure for the NMR scale catalytic reaction

In a glove box, precatalyst (0.005 mmol), olefin (1.2 mmol), phenylsilane (1.0 mmol), and benzene- d_6 (0.5 ml) were charged into a 5 mm NMR tube equipped with a Teflon valve. The tube was then closed and quickly removed from the glove box, and maintained at -78°C . Next, the tube was degassed on the vacuum line, back filled with H_2 (1 atm, 1.5–2.0 ml, 0.0067–0.0089 mmol) at -78°C , and further maintained at -78°C until NMR measurements began. The reaction was then monitored by a NMR spectrometer. After the completion of the reaction, the two regioisomers were separated by GC and analyzed by MS as well as high resolution MS (HRMS).

3.2. $\text{PhH}_2\text{Si}-(\text{CH}_2)_2-\text{SiMe}_3$ (**1a**)

^1H NMR (400 MHz, C_6D_6): δ 7.51 (m, 2H), 7.17 (m, 3H), 4.51 (t, $J = 3.6$ Hz, 2H), 0.75 (m, 2H), 0.52 (m, 2H), -0.06 (s, 9H). ^{13}C NMR (75 MHz, C_6D_6 , APT): δ 135.56 (CH), 132.93 (C_q), 129.83 (CH), 128.25 (CH), 10.78 (CH_2), 3.05 (CH_2), -2.14 (CH_3); MS (70 eV, EI, intensity%): 208.1 (M^+ ,

38.8), 193.0 (M^+-CH_3 , 77.4), 134.0 (M^+-SiMe_3-1 , 100), 121 ($M^+-SiMe_3-CH_2$, 52.3), 73.0 ($M^+-SiH_2Ph-CH_2-CH_2$, 90.6); HRMS for $C_{11}H_{20}Si_2$, calc.: 208.110; found: 208.1095.

3.3. $CH_3-CH(SiH_2Ph)(SiMe_3)$ (**1b**)

1H NMR (400 MHz, C_6D_6): δ 7.52 (m, 2H), 7.17 (m, 3H), 4.58 (m, 1H), 4.43 (m, 1H), 1.06 (d, $J=7.4$ Hz, 3H), 0.11 (m, 1H), 0.02 (s, 9H); ^{13}C NMR (75 MHz, C_6D_6 , APT): δ 135.76 (CH), 133.16 (C_q), 129.75 (CH), 128.33 (CH), 10.67 (CH_3), 2.40 (CH), -1.83 (CH_3); MS (70 eV, EI, intensity%): 208.1 (M^+ , 27.6), 193.0 (M^+-CH_3 , -92.0), 134.0 (M^+-SiMe_3-1 , 100), 130.0 (M^+-Ph-1 , 23.3), 121 ($M^+-SiMe_3-CH_2$, 70.8), 73.0 ($M^+-SiH_2Ph-CH_2-CH_2$, 78.2); HRMS for $C_{11}H_{20}Si_2$, calc.: 208.1100; found: 208.1087.

3.4. $PhH_2Si-(CH_2)_2SiMe_2Ph$ (**2a**)

1H NMR (300 MHz, C_6D_6): δ 7.35–7.50 (m, 4H), 7.20–7.00 (m, 6H), 4.48 (bs, 2H), 0.76 (bs, 2H), 0.75 (bs, 2H), 0.15 (s, 6H); ^{13}C NMR (75 MHz, C_6D_6 , APT): δ 138.55 (C_q), 135.25 (CH), 133.65 (CH), 132.45 (C_q), 129.53 (CH), 128.01 (CH), 127.80 (CH), 127.72 (CH), 9.66 (CH_2), 2.77 (CH_2), -3.78 (CH_3); MS (70 eV, EI, intensity%): 270.1 (M^+ , 1.2), 269.1 (M^+-1 , 1.7), 255.1 (M^+-CH_3 , 11.1), 192.0 (M^+-Ph-1 , 60.0), 164.0 ($M^+-PhSiH$, 23.9), 135.1 (M^+-SiMe_2Ph , 100); HRMS for $C_{16}H_{22}Si_2$, calc.: 270.1260; found: 270.1258.

3.5. $CH_3-CH(SiH_2Ph)(SiMe_2Ph)$ (**2b**)

1H NMR (300 MHz, C_6D_6): δ 7.34–7.48 (m, 4H), 7.25–7.02 (m, 6H), 4.57 (m, 1H), 4.40 (m, 1H), 1.04 (d, $J=7.8$ Hz, 3H), 0.39 (m, 1H), 0.25 (s, 6H); ^{13}C NMR (75 MHz, C_6D_6 , APT): δ 138.25 (C_q), 135.48 (CH), 133.85 (CH), 132.69 (C_q), 129.46 (CH), 128.03 (CH), 128.01 (CH), 127.75 (CH), 10.69 (CH), 1.70 (CH_3), -4.22 (CH_3); MS (70 eV, EI, intensity%): 270.1 (M^+ , 2.1), 269.1 (M^+-1 , 1.2), 255.1 (M^+-CH_3 , 15.4), 192.0 (M^+-Ph-1 , 63.2), 177.1 ($M^+-Ph-CH_3-1$, 26.0), 135.1 (M^+-SiMe_2Ph , 100); HRMS for $C_{16}H_{22}Si_2$, calc.: 270.1260; found: 270.1245.

3.6. $PhH_2Si-(CH_2)_2SiMe_2(NMe_2)$ (**3a**)

1H NMR (400 MHz, C_6D_6): δ 7.52 (m, 2H), 7.16 (m, 3H), 4.53 (t, $J=3.5$ Hz, 2H), 2.36 (s, 6H), 0.80 (m, 2H), 0.60 (m, 2H), 0.01 (s, 6H). ^{13}C NMR (75 MHz, C_6D_6): δ 135.54 (CH), 133.03 (C), 129.79 (CH), 128.33 (CH), 38.13 (CH_3 of NMe_2), 10.18 (CH_2), 2.92 (CH_2), -3.30 (CH_3); MS (70 eV, EI, intensity%): 237.2 (M^+ , 17.9), 222.2 (M^+-CH_3 , 9.1), 130.2 ($M^+-PhSiH_2$, 25.2), 102.1 ($M^+-SiH_2Ph-CH_2-CH_2$, 100); HRMS for $C_{12}H_{23}Si_2N$, calc.: 237.1369; found: 237.1365. (This compound decomposes under GC conditions.)

3.7. $CH_3-CH(SiH_2Ph)[SiMe_2(NMe_2)]$ (**3b**)

1H NMR (300 MHz, C_6D_6): δ 7.51 (m, 2H), 7.12 (m, 3H), 4.58 (m, 1H), 4.46 (m, 1H), 2.37 (s, 6H), 1.80 (d, $J=7.5$ Hz, 3H), 0.35 (m, 1H), 0.05 (s, 6H); ^{13}C NMR (75 MHz, C_6D_6 ,

APT): δ 135.73 (CH), 133.45 (C_q), 128.36 (CH), 128.18 (CH), 38.36 (CH_3 of NMe_2), 10.73 (CH_3), 4.32 (CH), -3.00 (CH_3); MS (70 eV, EI, intensity%): 237.1 (M^+ , 16.1), 222.1 (M^+-CH_3 , 7.2), 135.1 ($M^+-SiMe_2(NMe_2)$, 3.0), 130.2 ($M^+-PhSiH_2$, 9.5), 102.1 ($M^+-SiH_2Ph-CH_3-CH$, 100); HRMS for $C_{12}H_{23}Si_2N$, calc.: 237.1369; found: 237.1383.

3.8. $PhH_2Si(CH_2)_2-SiMe_2(O^tBu)$ (**4a**)

1H NMR (300 MHz, C_6D_6): δ 7.40 (m, 2H), 7.15 (m, 3H), 4.54 (t, $J=3.6$ Hz, 2H), 1.16 (s, 9H), 0.90 (m, 2H), 0.68 (m, 2H), 0.11 (s, 6H). ^{13}C NMR (75 MHz, C_6D_6 , APT): δ 135.90 (CH), 133.01 (C_q), 129.62 (CH), 128.18 (CH), 32.20 (CH_3 of tBu), 12.90 (CH_2), 2.73 (CH_2), 0.59 (CH_3); MS (70 eV, EI, intensity%): 266.1 (M^+ , 0.3), 209.0 (M^+-^tBu , 5.6), 131.0 ($M^+-SiH_2Ph-CH_2-CH_2$, 26.7), 75.0 ($M^+-PhSiH_2-CH_2-CH_2-^tBu+1$, 100); HRMS for $C_{14}H_{26}Si_2O$, calc.: 266.1522; found: 266.1490.

3.9. $CH_3-CH(SiH_2Ph)[SiMe_2(O^tBu)]$ (**4b**)

1H NMR (300 MHz, C_6D_6): δ 7.60 (m, 2H), 7.15 (m, 3H), 4.67 (m, 1H), 4.52 (m, 1H), 1.18 (d, 3H), 1.16 (s, 9H), 0.28 (m, 1H), 0.09 (s, 6H); ^{13}C NMR (75 MHz, C_6D_6 , APT): δ 136.12 (CH), 133.65 (C_q), 129.89 (CH), 128.39 (CH), 32.09 (CH_3 of tBu), 10.34 (CH_3), 4.97 (CH), 1.12 (CH_3); MS (70 eV, EI, intensity%): 266.1 (M^+ , 0.1), 209.0 (M^+-^tBu , 21.8), 195.0 (M^+-^tBu , 21.6), 189.0 (M^+-Ph , 16.5), 131.0 ($M^+-SiH_2Ph-CH_2-CH_2$, 25.4), 75.0 ($M^+-PhSiH_2-CH_2-CH_2-^tBu+1$, 100); HRMS for $C_{14}H_{26}Si_2O$, calc.: 266.1522; found: 266.1514.

3.10. Preparative scale hydrosilylation of trimethyl vinylsilane

In a glove box, $Me_2SiCp_2''SmCH(TMS)_2$ (30.5 mg, 0.05 mmol), benzene (10 ml), trimethylvinylsilane (2.00 g, 20 mmol) and $PhSiH_3$ (2.16 g, 20 mmol) were added successively into a 50-ml flask equipped with a J-Young vial. The mixture was stirred at room temperature for 3 h. Volatiles were then removed by a rotary pump, yielding viscous oil that was purified by flash chromatography with pentane as an elutant to yield colorless oil, 3.95 g (95%). The colorless oil is a mixture of two regioisomers **1a** (47%) and **1b** (53%) and their NMR data and mass spectral parameters are identical to the products obtained from the NMR scale reactions. Anal. calc. for $C_{11}H_{20}Si_2$ (a mixture of the two regioisomers): C, 63.43; H, 9.61. Found: C, 63.58; H, 9.60

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