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Hydrosilylation of 1,4-bis(trimethylsilyl)-1-buten-3-ynes using late transition metal hydrides as catalyst precursors

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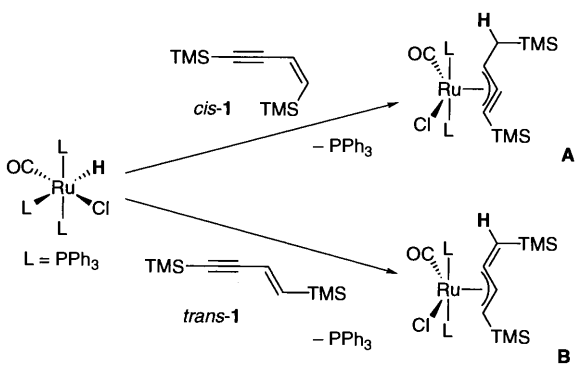
Abstract

Two geometrical isomers of 1,4-bis(trimethylsilyl)-1-buten-3-yne (*cis*- and *trans*-**1**) were subjected to catalytic hydrosilylation with $HSiR_3$ ($HSiMe_2Ph$ or $HSiMePh_2$) in the presence of catalytic amounts of late transition metal hydrides. Four kinds of regio- and stereoisomers of hydrosilylation products were formed: $(R_3Si)(Me_3Si)C{=}C{=}CHCH_2SiMe_3$ (**2**), (1*Z*,3*E*)-$CH(SiMe_3){=}C(SiR_3)$-$CH{=}CHSiMe_3$ (**3**), (1*Z*,3*E*)-$C(SiMe_3)(SiR_3){=}CHCH{=}CHSiMe_3$ (**4**), and (1*E*,3*E*)-$C(SiMe_3)(SiR_3){=}CHCH{=}CHSiMe_3$ (**5**). The product selectivity was strongly affected by the geometry of **1** as well as the catalyst precursor employed. Compounds **2**–**5** could be prepared in over 93% selectivity, respectively.

Keywords: Catalytic hydrosilylation; 1,4-Bis(trimethylsilyl)-1-buten-3-yne; Platinum catalyst; Rhodium catalyst; Ruthenium catalyst

1. Introduction

Insertion of a C–C multiple bond into a metal–hydrogen bond is a crucial elementary process in transition metal-catalyzed transformation of unsaturated hydrocarbons [1]. In general, a double bond is less reactive than a triple bond. However, Wakatsuki et al. previously reported that the insertion of *cis*-1,4-bis(trimethylsilyl)-1-buten-3-yne (*cis*-**1**) into RuH-$Cl(CO)(PPh_3)_3$ took place selectively at the double bond, giving an η^3-propargyl/allenyl complex **A** (Scheme 1) [2]. In contrast, the *trans* isomer (*trans*-**1**) underwent the insertion at the triple bond to give an η^3-butadienyl complex **B** [3,4]. Thus, a clear dependence of the insertion site upon the geometry of **1** has been documented.



Scheme 1.

We have been interested in this unique phenomenon found by Wakatsuki et al. and attempted in this study its application to catalytic reactions. That is, the two geometrical isomers of butenynes (*cis*-**1** and *trans*-**1**) were subjected to catalytic reactions including hydrogenation, hydrosilylation and hydroboration, and effect of the geometry upon product-selectivity was examined in the presence of catalytic amounts of late transition metal complexes [5]. Although no notable results were obtained for hydrogenation and hydroboration, the structures of hydrosilylation products were effectively altered by the starting butenynes as well as catalyst precursors. Thus, as summarized in Scheme 2, four kinds of regio- and stereoisomers (**2**–**4**) could be obtained in over 93% selectivities, respectively. Allenylsilane **2** is a 1,4-adduct of hydrosilane across the butenyne skeleton of **1**. Silylbutadienes **3**, **4** and **5** are

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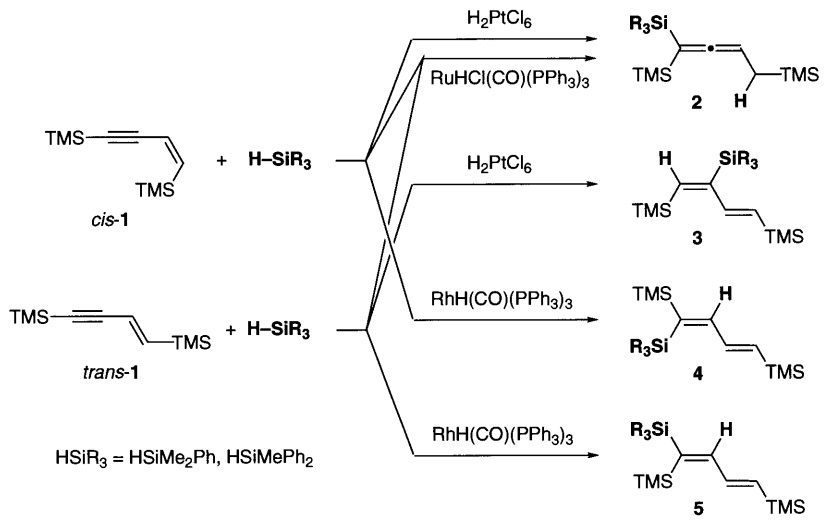


Scheme 2.

Table 1
Hydrosilylation of *cis*- and *trans*-**1** in the presence of platinum catalysts [a]

Entry	Butenyne	Catalyst	Hydrosilane	Reaction time (h)	Product ratio [b]				Total yield (%) [c]
					2	**3**	**4**	**5**	
1	*cis*-**1**	$H_2PtCl_6{\cdot}6H_2O$	$HSiMe_2Ph$	3	96	4	0	0	100
2		$H_2PtCl_6{\cdot}6H_2O$	$HSiMePh_2$	123	94	6	0	0	94
3		$PtCl_2$(cod)	$HSiMePh_2$	93	92	8	0	0	89
4		$Pt(cod)_2$	$HSiMePh_2$	69	94	6	0	0	96
5		$PtCl_2(PPh_3)_2$	$HSiMePh_2$	143	3	76	0	21	98
6		$Pt(PPh_3)_4$	$HSiMePh_2$	23	3	75	0	22	100
7	*trans*-**1**	$H_2PtCl_6{\cdot}6H_2O$	$HSiMe_2Ph$	3	0	93	0	7	100
8 [d]		$H_2PtCl_6{\cdot}6H_2O$	$HSiMePh_2$	18	1	94	0	5	98
9		$PtCl_2$(cod)	$HSiMePh_2$	4	2	91	0	7	91
10		$Pt(cod)_2$	$HSiMePh_2$	3	3	89	0	8	95
11		$PtCl_2(PPh_3)_2$	$HSiMePh_2$	148	1	77	0	22	100
12		$Pt(PPh_3)_4$	$HSiMePh_2$	30	0	78	0	22	100

[a] All reactions were run at 80°C without solvent unless otherwise noted. Initial ratio: **1**:hydrosilane:catalyst = 1:1.1:0.005.
[b] Determined by ^{1}H-NMR spectroscopy.
[c] Determined by GLC using tetradecane as an internal standard.
[d] The reaction was conducted at 60°C.

regio- and stereoisomers of 1,2-adducts across the triple bond. In the following sections, we describe details of the results according to catalyst precursors and discuss the reaction mechanisms [6].

2. Results and discussion

2.1. Catalytic reactions

Catalytic addition of hydrosilane ($HSiMe_2Ph$ or $HSiMePh_2$) to *cis*- and *trans*-**1** was examined at 80°C without solvent. The reaction products were analyzed by GLC, GC-mass spectrometry, and NMR spectroscopy, after removing the catalyst by column chromatography.

A distinct difference in the regioselectivity depending upon the geometry of **1** was noted for platinum-catalyzed reactions (Table 1). Treatment of *cis*-**1** with 1.1 molar ratio of $HSiMe_2Ph$ in the presence of a catalytic amount of $H_2PtCl_6{\cdot}6H_2O$ (0.005 molar ratio) led to 1,4-addition of hydrosilane, giving **2** in 96% selectivity (entry 1). In contrast, the reaction of *trans*-**1** under the same reaction conditions gave a 1,2-adduct **3** in 93% selectivity (entry 7). Almost the same selectivities were observed with $HSiMePh_2$ in place of $HSiMe_2Ph$, although the reactivity of $HSiMePh_2$ was considerably lower than that of $HSiMe_2Ph$ (entries 2 and 8). Platinum complexes bearing 1,4-cyclooctadiene (cod) ligand(s) also served as selective catalysts (entries 3, 4, 9, and 10). On the other hand, PPh_3-coordinated catalysts

afforded an 8:2 mixture of **3** and **5** irrespective of the geometry of **1** (entries 5, 6, 11, and 12).

In the reactions using $RuHCl(CO)(PPh_3)_3$ as a catalyst precursor, allenylsilane **2** was produced from both isomers of **1** in high selectivities (entries 1–3 in Table 2). Predominant formation of **2** was also observed with $RuH_2(CO)(PPh_3)_3$ (entry 4), while $RuH_2(PPh_3)_4$ and $RuHCl(CO)(PPr^i_3)_2$ gave complicated mixtures (entries 5 and 6).

In the presence of $RhH(CO)(PPh_3)_3$ as a catalyst precursor, *cis*- and *trans*-**1** were converted into *anti*- and *syn*-1,2-addition products **4** and **5**, respectively (Table 3). The orientation of 1,2-addition was opposite to that observed for the platinum-catalyzed reactions of *trans*-**1** (see Scheme 2). The reaction of *cis*-**1** with $HSiMe_2Ph$ gave **4** in 95% selectivity (entry 1). On the other hand, *trans*-**1** was converted into **5** in 81% selectivity under the same reaction conditions (entry 3). The selectivity of **5** was improved to 93 or 96% by using toluene as a solvent (entry 4) or by using $HSiMePh_2$ in place of $HSiMe_2Ph$ (entry 5), respectively. The use of rhodium complexes other than $RhH(CO)(PPh_3)_3$ led to lower selectivities (entries 2 and 6–8).

2.2. Consideration for catalytic mechanisms

The regio- and stereochemical courses of the platinum- and rhodium-catalyzed reactions were clearly dictated by the *cis* and *trans* geometries of **1**. Thus, in the reactions catalyzed by $H_2PtCl_6{\cdot}6H_2O$, *cis*- and *trans*-**1** gave 1,4- and 1,2-addition products of $HSiMe_2Ph$ (**2** and **3**) in 96 and 93% selectivities, respectively (entries 1 and 7 in Table 1). On the other hand, in the $RhH(CO)(PPh_3)_3$-catalyzed reactions, *cis*- and *trans*-**1** underwent *anti*- and *syn*-addition of $HSiMe_2Ph$ in 95 and 93% selectivities, respectively (entries 1 and 4 in Table 3).

Catalytic hydrosilylation is generally thought to proceed via either the Chalk–Harrod or modified Chalk–Harrod cycle [7]. The former cycle has been commonly assumed for platinum-catalyzed reactions [8]. On the other hand, the latter cycle was well documented for

Table 2
Hydrosilylation of *cis*- and *trans*-**1** in the presence of ruthenium catalysts [a]

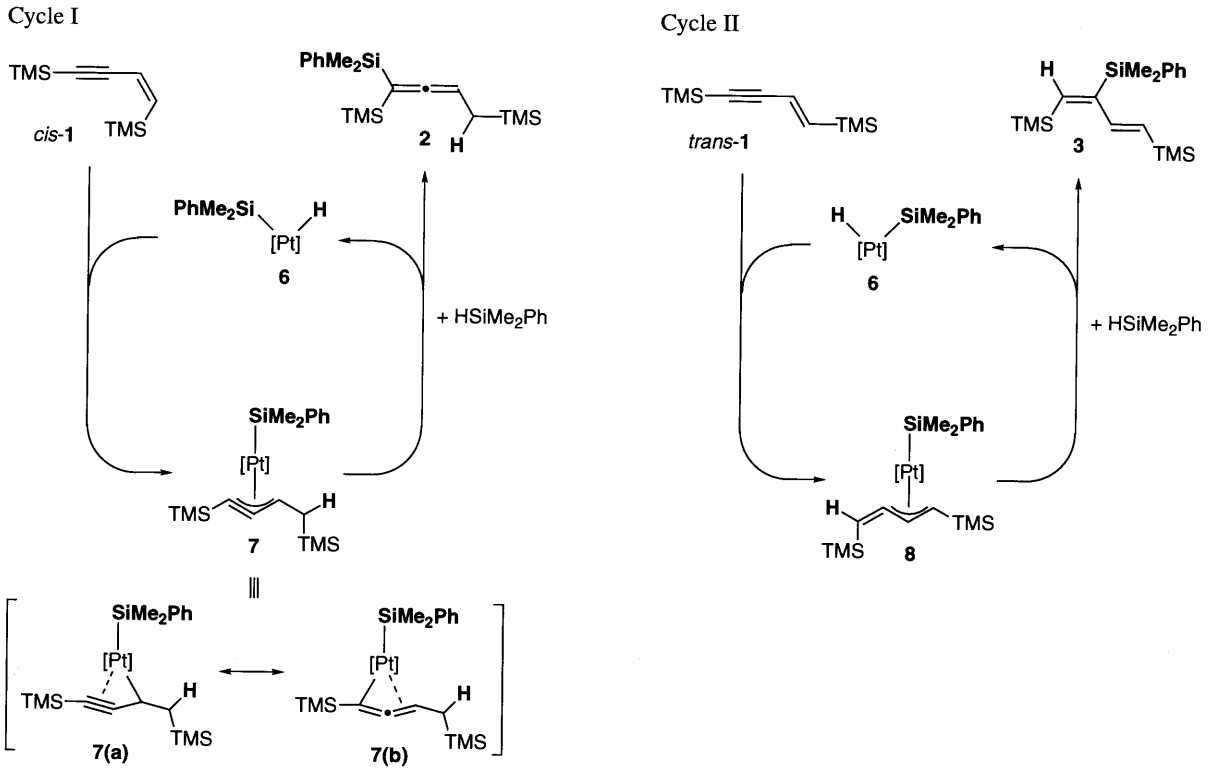
Entry	Butenyne	Catalyst	Hydrosilane	Reaction time (h)	Product ratio [b]				Total yield (%) [c]
					2	**3**	**4**	**5**	
1	*cis*-**1**	$RuHCl(CO)(PPh_3)_3$	$HSiMe_2Ph$	134	86	0	6	8	58
2	*trans*-**1**	$RuHCl(CO)(PPh_3)_3$	$HSiMe_2Ph$	142	91	0	2	7	95
3	*trans*-**1**	$RuHCl(CO)(PPh_3)_3$	$HSiMePh_2$	137	97	0	0	3	60
4	*trans*-**1**	$RuH_2(CO)(PPh_3)_3$	$HSiMe_2Ph$	142	92	0	1	7	92
5	*trans*-**1**	$RuH_2(PPh_3)_4$	$HSiMe_2Ph$	159	22	14	26	38	56 [d]
6	*trans*-**1**	$RuHCl(CO)(PPr^i_3)_2$	$HSiMe_2Ph$	207	62	12	3	23	48 [d]

[a] All reactions were run at 80°C without solvent unless otherwise noted. Initial ratio: **1**:hydrosilane:catalyst = 1:1.5:0.025.
[b] Determined by ^{1}H-NMR spectroscopy.
[c] Determined by GLC using tetradecane as an internal standard.
[d] Considerable amounts (30–40%) of unknown products were formed.

Table 3
Hydrosilylation of *cis*- and *trans*-**1** in the presence of rhodium catalysts [a]

Entry	Butenyne	Catalyst	Hydrosilane	Reaction time (h)	Product ratio [b]				Total yield (%) [c]
					2	**3**	**4**	**5**	
1	*cis*-**1**	$RhH(CO)(PPh_3)_3$	$HSiMe_2Ph$	19	0	0	95	5	98
2		$RhCl(PPh_3)_3$	$HSiMe_2Ph$	3	27	0	47	26	97
3	*trans*-**1**	$RhH(CO)(PPh_3)_3$	$HSiMe_2Ph$	19	10	0	9	81	96
4 [d]		$RhH(CO)(PPh_3)_3$	$HSiMe_2Ph$	24	5	0	2	93	93
5		$RhH(CO)(PPh_3)_3$	$HSiMePh_2$	24	4	0	0	96	99
6		$RhCl(PPh_3)_3$	$HSiMe_2Ph$	3	17	0	13	70	98
7		$[Rh(cod)_2]BF_4$	$HSiMe_2Ph$	3	5	44	0	51	100
8		$[Rh(cod)(dppp)]BF_4$	$HSiMe_2Ph$	3	2	48	0	50	98

[a] All reactions were run at 80°C without solvent unless otherwise noted. Initial ratio: **1**:hydrosilane:catalyst = 1:1.1;0.005.
[b] Determined by ^{1}H-NMR spectroscopy.
[c] Determined by GLC using tetradecane as an internal standard.
[d] The reaction was carried out in toluene.



Scheme 3.

Group 9 metal-catalyzed systems, even when the reactions were conducted with metal hydrides as catalyst precursors [9]. Although we presently have no direct information on the catalytic mechanisms, the alteration of reaction product depending upon the geometry of **1** was found to be reasonably accounted for by assuming the Chalk–Harrod and modified Chalk–Harrod cycles for the platinum- and rhodium-catalyzed reactions, respectively [10].

Our proposals for the platinum-catalyzed systems are depicted in Scheme 3, which postulate the participation of a common hydrido(silyl)platinum intermediate **6**, and the occurrence of the insertion of butenynes into the Pt–H bond of **6** according to the regiochemistries given in Scheme 1. Thus, when the Pt–H bond is added to the double bond of *cis*-**1**, an η^3-propargyl/allenyl intermediate **7** will be produced (cycle I) [11]. The subsequent C–Si reductive elimination that reflects the allenyl structure **7(b)** gives allenylsilane **2**. When *trans*-**1** undergoes the insertion into the Pt–H bond at the triple bond, an η^3-butadienyl intermediate **8** is generated (cycle II). The subsequent C–Si coupling at the less hindered site of the η^3-butadienyl ligand provides **3**.

Scheme 4 illustrates the proposed catalytic cycles for the rhodium systems. While the Chalk–Harrod cycles in Scheme 3 invoke the insertion of **1** into a Pt–H bond, the modified Chalk–Harrod cycles given in Scheme 4 invoke the insertion into a Rh–Si bond. Since product **5** formed from *trans*-**1** is a simple *syn*-1,2-adduct, its formation may be easily interpreted by a typical modified Chalk–Harrod process given in cycle IV. Thus, *syn*-addition of a silylrhodium species **9** to the triple bond of *trans*-**1** gives an η^3-butadienyl intermediate **15**. Oxidative addition of $HSiMe_2Ph$ to **15**, followed by C–H reductive elimination from the resulting **16** affords **5**.

The structure of **4** derived from *cis*-**1** indicates two characteristic points related to the catalytic mechanism. One is *anti*-addition of hydrosilane, and the other is *cis* to *trans* isomerization of the ene part of *cis*-**1**. These phenomena can be rationalized by the hydrosilylation process given in cycle III. The first step is *syn*-addition of a silylrhodium species **9** to the triple bond of *cis*-**1**. This process is similar to cycle IV. However, while the insertion complex **15** in cycle IV has a *syn*-π-allyl structure, the corresponding **10** in cycle III has an *anti*-π-allyl structure that causes a significant steric repulsion between the trimethylsilyl group and the rhodium moiety. The steric demand inherent in **10** will be effectively reduced by its isomerization to the *syn*-π-allyl isomer **13** via allenylmethyl intermediates **11** and **12**. It was observed that the rhodium moiety is shifted from the *syn* position to *the* anti position with respect to the $SiMe_2Ph$ group during the isomerization. Therefore, after oxidative addition of $HSiMe_2Ph$ to **13** followed by C–H reductive elimination from **14**, the *anti*-addition product **4** is produced with the *cis* to *trans* isomerization of the ene part.

3. Experimental

3.1. General procedures

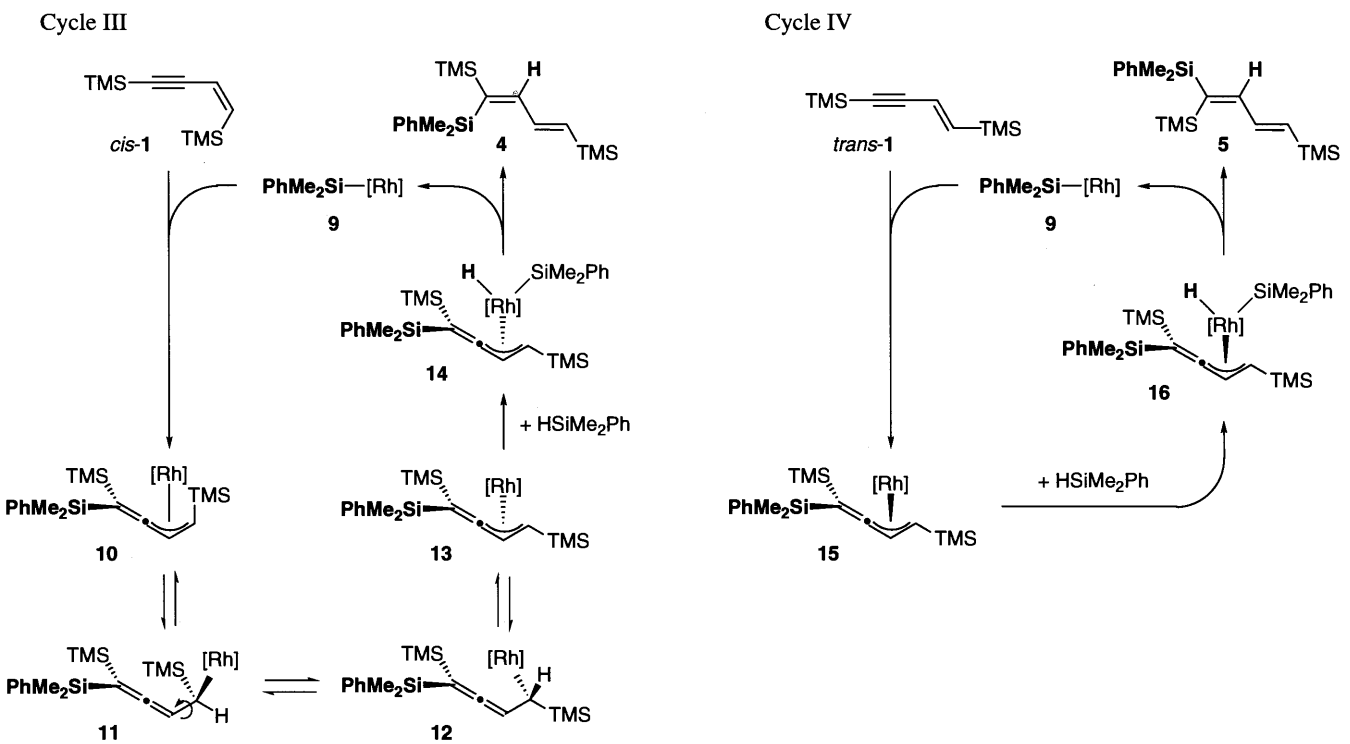
All manipulations were carried out under a nitrogen atmosphere using conventional Schlenk techniques. Nitrogen gas was dried by passage through P_2O_5 (Merck, SICAPENT). NMR spectra were recorded on a JEOL JNM-A400 spectrometer (^{1}H-NMR, 399.65 MHz; ^{13}C-NMR, 100.40 MHz). Chemical shifts are reported in δ ppm referred to an internal $SiMe_4$ standard. Mass spectra were measured with a Shimadzu QP-5000 spectrometer (EI, 70 eV). GLC analysis was performed with a Shimadzu GC-8A instrument equipped with a TCD detector and a Silicone OV-1 column (1 m). The starting butenynes (*cis*- and *trans*-**1**) [5b,12] and catalyst precursors ($Pt(cod)_2$ [13], $PtCl_2(cod)$ [14], $PtCl_2(PPh_3)_2$ [15], $Pt(PPh_3)_4$ [16], $RuHCl(CO)(PPh_3)_3$ [17], $RuH_2(PPh_3)_4$ [18], $RuHCl(CO)(PPr^i_3)_2$ [19], $RhH(CO)(PPh_3)_3$ [20], $RhCl(PPh_3)_3$ [21], $[Rh(cod)_2]BF_4$ [22], and $[Rh(cod)(dppp)]BF_4$ [23]) were synthesized according to literature methods. All other compounds were obtained from commercial sources and used without purification.

3.2. Catalytic reactions

Entry 1 in Table 1 represents a typical procedure. To a Schlenk tube containing $H_2PtCl_6{\cdot}6H_2O$ (1.6 mg, 3.1 μmol) were added *cis*-**1** (120 mg, 0.611 mmol), $HSiMe_2Ph$ (92.3 mg, 0.678 mmol), and tetradecane (20.5 mg, 0.103 mmol) as an internal standard for GLC analysis. The pale yellow solution was heated at 80°C with stirring for 3 h, giving a brown solution. At this stage, a 100% yield of the hydrosilylation products was obtained as confirmed by GLC. The reaction mixture was passed through an Al_2O_3 column using hexane as an eluent and concentrated under reduced pressure. ^{1}H-NMR analysis of the resulting oily material revealed the formation of **2** and **3** in a 96:4 ratio. Since these isomers could not be separated from each other by column chromatography, further purification was performed by bulb-to-bulb distillation under reduced pressure (95–110°C/0.1 mmHg), giving 161 mg of the product mixture. Anal. Calc. for $C_{18}H_{32}Si_3$: C, 64.98; H, 9.69. Found: C, 64.92; H, 9.58%.

All catalytic reactions reported in this paper were similarly carried out. The structural assignments of the products were based on the following NMR data and NOE experiments. Analytical data for the reaction products with $HSiMePh_2$ (entry 8 in Table 1) was as follows. Anal. Calc. for $C_{23}H_{34}Si_3$: C, 69.98; H, 8.68. Found: C, 70.12; H, 8.77%.

2a ($SiMe_2Ph$): ^{1}H-NMR ($CDCl_3$): δ −0.04 (s, 9H, $Si(CH_3)_3$), 0.00 (s, 9H, $Si(CH_3)_3$), 0.36 (s, 6H, $SiPh(CH_3)_2$), 1.25 (d, $J = 8.3$ Hz, 2H, CH_2), 4.38 (t, $J = 8.3$ Hz, 1H, =CH), 7.24–7.65 (m, 5H, Ph). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ −1.7 ($Si(CH_3)_3$), −1.3 ($SiPh(CH_3)_2$), 0.1 ($Si(CH_3)_3$), 15.6 (CH_2), 72.0 (=CH), 86.4 (=CSi), 127.5 (Ph), 128.8 (Ph), 133.9 (Ph), 139.5



Scheme 4.

(Ph), 213.3 (=*C*=). MS, *m*/*z* (relative intensity, %): 332 [M^+, 8], 317 (1), 258 (5), 244 (33), 229 (18), 182 (26), 167 (41), 135 (100), 109 (17), 73 (81), 45 (56), 43 (48).

3a ($SiMe_2Ph$): ^{1}H-NMR ($CDCl_3$): δ 0.00 (s, 9H, $Si(CH_3)_3$), 0.15 (s, 9H, $Si(CH_3)_3$), 0.38 (s, 6H, $SiPh(CH_3)_2$), 5.69 (d, $J = 19.0$ Hz, 1H, =C(*H*)Si), 6.27 (s, 1H, =C(*H*)Si), 6.88 (d, $J = 19.0$ Hz, 1H, =C*H*), 7.24–7.60 (m, 5H, Ph). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ −1.7 ($SiPh(CH_3)_2$), −1.4 ($Si(CH_3)_3$), 0.4 ($Si(CH_3)_3$), 127.6 (Ph), 128.7 (Ph), 134.0 (Ph), 134.1 (=*C*H), 139.1 (Ph), 147.2 (=*C*H), 148.2 (=*C*H), 160.3 (=*C*Si). MS, *m*/*z* (relative intensity, %): 332 [M^+, 3], 317 (1), 258 (18), 244 (38), 229 (45), 167 (58), 135 (100), 73 (99), 45 (59), 43 (54).

4a ($SiMe_2Ph$): ^{1}H-NMR ($CDCl_3$): δ −0.12 (s, 9H, $Si(CH_3)_3$), 0.13 (s, 9H, $Si(CH_3)_3$), 0.43 (s, 6H, $SiPh(CH_3)_2$), 5.90 (d, $J = 18.1$ Hz, 1H, =C*H*(Si)), 6.60 (dd, $J = 18.1$ and 10.2 Hz, 1H, =C*H*), 7.12 (d, $J = 10.7$ Hz, 1H, =C*H*), 7.45–7.60 (m, 5H). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ −1.6 ($Si(CH_3)_3$), 0.2 ($Si(CH_3)_3$)), 0.7 ($SiPh(CH_3)_2$)), 127.8 (Ph), 128.6 (Ph), 133.7 (Ph), 138.4 (=*C*H), 140.9 (Ph), 143.6 (=*C*Si(Si)), 145.1 (=*C*H), 156.5 (=*C*H). MS, *m*/*z* (relative intensity, %): 332 [M^+, 1], 317 (1), 258 (49), 244 (42), 229 (50), 167 (46), 135 (85), 73 (100), 45 (52), 43 (44).

5a ($SiMe_2Ph$): ^{1}H-NMR ($CDCl_3$): δ 0.06 (s, 9H, $Si(CH_3)_3$), 0.10 (s, 9H, $Si(CH_3)_3$), 0.36 (s, 6H, $SiPh(CH_3)_2$), 6.01 (d, $J = 18.1$ Hz, 1H, =C*H*(Si)), 6.96 (dd, $J = 18.1$, 10.7 Hz, 1H, =C*H*), 7.12 (d, $J = 10.7$ Hz, 1H, =C*H*), 7.24–7.60 (m, 5H, Ph); ^{13}C{^{1}H}-NMR ($CDCl_3$): δ −1.4 ($Si(CH_3)_3$), −1.2 ($SiPh(CH_3)_2$), 1.7 ($Si(CH_3)_3$), 127.6 (Ph), 128.7 (Ph), 134.0 (Ph), 138.8 (=*C*H), 139.9 (Ph), 144.1 (=*C*Si(Si)), 144.6 (=*C*H), 157.1 (=*C*H). MS, *m*/*z* (relative intensity, %): 332 [M^+, 1], 317 (1), 258 (34), 244 (30), 229 (34), 167 (31), 135 (65), 73 (100), 45 (37), 43 (28).

2b ($SiMePh_2$): ^{1}H-NMR ($CDCl_3$): δ −0.09 (s, 9H, $Si(CH_3)_3$), −0.06 (s, 9H, $Si(CH_3)_3$), 0.63 (s, 3H, $SiPh_2(CH_3)$), 1.15 (dd, $J = 14.6$ and 7.8 Hz, 1H, C*H*(H)), 1.22 (dd, $J = 14.6$ and 8.8 Hz, 1H, CH(*H*)), 4.35 (dd, $J = 8.8$ and 7.8 Hz, 1H, =C*H*), 7.24–7.60 (m, 10H, Ph). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ −1.8 ($SiPh_2(CH_3)$), −1.8 ($Si(CH_3)_3$), 0.1 ($Si(CH_3)_3$), 15.4 (CH_2), 72.7 (=*C*H), 84.8 (=*C*Si), 127.5 (Ph), 129.1 (Ph), 135.0 (Ph), 137.1 (Ph), 214.9 (=*C*=). MS, *m*/*z* (relative intensity, %): 394 [M^+, 5], 320 (3), 306 (10), 244 (30), 229 (14), 197 (100), 182 (13), 167 (12), 135 (25), 119 (8), 105 (13), 73 (68), 45 (36), 43 (16).

3b ($SiMePh_2$): ^{1}H-NMR ($CDCl_3$): δ −0.04 (s, 9H, $Si(CH_3)_3$), 0.15 (s, 9H, $Si(CH_3)_3$), 0.67 (s, 3H, $Si(CH_3)Ph_2$), 5.68 (d, $J = 19.0$ Hz, 1H, =C(*H*)Si), 6.26 (s, 1H, =C(*H*)Si), 6.96 (d, $J = 19$ Hz, 1H, =C*H*), 7.24–7.60 (m, 10H, Ph). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ −2.6 ($Si(CH_3)Ph_2$), −1.5 ($Si(CH_3)_3$), 0.4 ($Si(CH_3)_3$), 127.6 (Ph), 129.0 (Ph), 135.1 (Ph), 135.2 (=*C*H), 136.8 (Ph), 146.9 (=*C*H), 151.2 (=*C*H), 158.1 (=*C*Si). MS, *m*/*z* (relative intensity, %): 394 [M^+, 1], 320 (32), 316 (25), 306 (5), 291 (8), 244 (45), 229 (34), 197 (100), 181 (8), 167 (28), 135 (34), 119 (10), 105 (14), 73 (59), 45 (39), 43 (29).

5b ($SiMePh_2$): ^{1}H-NMR ($CDCl_3$): δ 0.06 (s, 9H, $Si(CH_3)_3$), 0.07 (s, 9H, $Si(CH_3)_3$), 0.67 (s, 3H, $SiPh_2(CH_3)$), 5.86 (d, $J = 17.6$ Hz, 1H, =C*H*(Si)), 6.89 (d, $J = 10.7$ Hz, 1H, =C*H*), 6.97 (dd, $J = 17.6$ and 10.3 Hz, 1H, =C*H*), 7.24–7.60 (m, 10H, Ph); ^{13}C{^{1}H}-NMR ($CDCl_3$): δ −2.3 ($SiPh_2(CH_3)$), −1.4 ($Si(CH_3)_3$), 1.7 ($Si(CH_3)_3$), 127.7 (Ph), 129.0 (Ph), 135.1 (Ph), 137.3 (Ph), 139.3 (=*C*H), 142.1 (=*C*Si(Si)), 144.4 (=*C*H), 159.7 (=*C*H). MS, *m*/*z* (relative intensity, %): 394 [M^+, 1], 320 (35), 306 (7), 305 (9), 291 (13), 244 (32), 229 (35), 197 (55), 135 (73), 105 (15), 73 (100), 45 (38), 43 (22).

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