

Hydrosilylation of 1,4-Bis(trimethylsilyl)butadiyne and Silyl-Substituted Butenynes

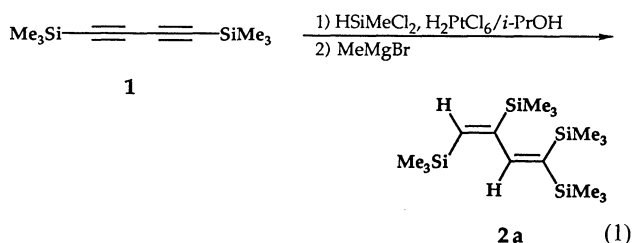
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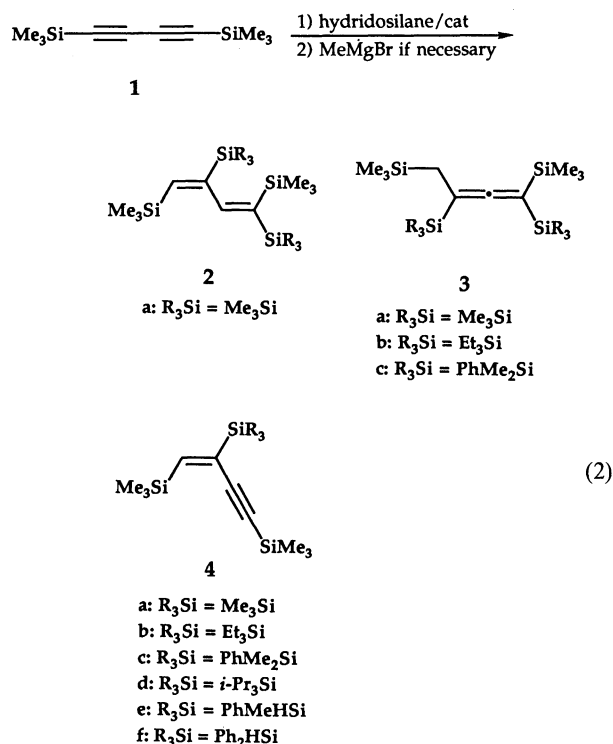
Hydrosilylation of 1,4-bis(trimethylsilyl)butadiyne using various hydrosilanes and Pt(IV), Pt(0), Rh(I) or Pd catalyst gave, depending on catalyst and hydrosilane, 1,1,3,4-tetrasilyl-substituted 1,3-butadienes or 1,1,3,4-tetrasilyl-substituted 1,2-butadienes. Formation of the 1,2-butadienes was proved to be attributable to second hydrosilylation of primary products 1,2,4-trisilyl-1-buten-3-yne. For the second hydrosilylation a mechanism was proposed that involves silylmatalation induced through a metalacyclopentene intermediate.

Alkylsilanes and vinylsilanes are versatile synthetic intermediates for carbon–carbon bond formation and/or functionalization.¹⁾ Alkylsilanes also are recently added to the category.²⁾ These are conveniently prepared by hydrosilylation of conjugated dienes, alkynes, and alkenes respectively using a transition metal catalyst.^{3,4)} The reaction proceeds usually in *cis*-fashion, though *trans*-addition of H and Si to alkynes are observed in some cases.⁵⁾ Regiochemical problem also arises for alkenes, conjugated dienes, enynes and diynes. Stereochemical and regiochemical selectivities depend on the kind of catalysts and hydrosilanes. Although 1,3-dienes have been well studied,⁶⁾ hydrosilylation of conjugated alkynes remained scarcely studied. Bock and Seidl reported that 1,4-bis(trimethylsilyl)butadiyne (**1**) gave in 40% yield a 1:2 adduct 1,1,3,4-tetrakis(trimethylsilyl)butadiene (**2a**) by the reaction with HSiCl₂Me and H₂PtCl₆ catalyst followed by methylation with MeMgBr.⁷⁾ We have been interested in new silyl-substituted building blocks useful for synthesis of silicon-containing materials and thus have studied introduction of two silyl groups into **1** through disilylation using disilanes and a palladium catalyst.⁸⁾ An alternative approach we considered promising was hydrosilylation of **1**.⁹⁾ We report herein details of experimental results to propose a new mechanism of hydrosilylation.



Hydrosilylation of **1** was carried out using excess hydrosilane and a transition metal catalyst in a sealed tube without solvent. The catalyst we used was hexachloroplatinic(IV) acid (H₂PtCl₆), chlorotris(triphenylphosphine)rhodium(I) (RhCl(PPh₃)₃), tetrakis(triphenylphosphine)platinum(0) (Pt(PPh₃)₄), dichlorobis(triphenylphosphine)palladium(II) (PdCl₂(PPh₃)₂), or

tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄). The hydrosilane we employed was chlorodimethylsilane (HSiClMe₂), dichloromethylsilane (HSiCl₂Me), trichlorosilane (HSiCl₃), trimethylsilane (HSiMe₃), triethylsilane (HSiEt₃), dimethylphenylsilane (HSiMe₂Ph), triisopropylsilane (HSi(*i*-Pr)₃), methylphenylsilane (H₂SiMePh) or diphenylsilane (H₂SiPh₂). When chlorosilane was applied, the remaining chlorine substituent of products was methylated with methylmagnesium bromide (MeMgBr), and the resulting methyl derivatives were isolated. Results are summarized in Table 1.



In accordance to the report of Bock and Seidl,⁷⁾ a combination of chlorosilane HSiClMe₂ and H₂PtCl₆ catalyst gave **2a** as a sole product (Run 1). The structural assignment is based on NMR: 4 trimethylsilyls and 2 olefinic hydrogens by ¹H NMR; 4 sp² carbons at δ=139.3 (d, ¹J=136 Hz), 139.4, 158.2 (dd, ³J=16 and

Table 1. Hydrosilylation of **1**^{a)}

Run	Catalyst	HSiR ₃	Conditions	Products (Yield/%) ^{b,c)}	
1	H ₂ PtCl ₆	HSiClMe ₂ ^{d)}	80 °C, 2 h	2a (54)	
2	H ₂ PtCl ₆	HSiEt ₃	80 °C, 0.5 h	3b (100)	
3	H ₂ PtCl ₆	HSiMe ₃	100 °C, 2 h	3a (46)	4a (40)
4	H ₂ PtCl ₆	HSiMe ₂ Ph	r.t., 1.5 h; 50–60 °C, 1 h	3c (10)	4c (70)
5	H ₂ PtCl ₆	HSi(<i>i</i> -Pr) ₃	90 °C, 8 h		4d (92)
6	RhCl(PPh ₃) ₃ ^{e)}	HSiCl ₂ Me ^{d)}	100 °C, 3 h	3a (18)	4a (76)
7	RhCl(PPh ₃) ₃	HSiEt ₃	90 °C, 0.9 h	3b (28)	4b (45)
8	RhCl(PPh ₃) ₃	HSiEt ₃	90 °C, 5 h	3b (83)	
9	RhCl(PPh ₃) ₃	HSiMe ₃	100 °C, 1 h	3a (90)	
10	RhCl(PPh ₃) ₃	HSiMe ₂ Ph	90 °C, 1 h	3c (36)	4c (27)
11	RhCl(PPh ₃) ₃	HSiMe ₂ Ph	100 °C, 2 h	3c (86)	
12	RhCl(PPh ₃) ₃	H ₂ SiMePh	100 °C, 2 h		4e (30)
13	RhCl(PPh ₃) ₃	H ₂ SiPh ₂	100 °C, 4 h		4f (49)
14	Pt(PPh ₃) ₃ ^{f)}	HSiCl ₂ Me ^{d)}	100 °C, 18 h		4a (96)
15 ^{g)}	Pt(PPh ₃) ₄	HSiCl ₂ Me ^{d)}	100 °C, 20 h		4a (67)
16	Pt(PPh ₃) ₄	HSiCl ₃ ^{d)}	100 °C, 90 h		4a (Trace)
17	Pt(PPh ₃) ₄	HSiEt ₃	90 °C, 2 h	3b (6)	4b (83)
18	Pt(PPh ₃) ₄	HSiEt ₃	90 °C, 18 h	3b (18)	4b (81)
19 ⁱ⁾	Pt(PPh ₃) ₄	HSiEt ₃	100 °C, 1 h		4b (100)
20	Pt(PPh ₃) ₄	HSiMe ₃	90 °C, 1 h	3a (2)	4a (69)
21	Pt(PPh ₃) ₄	HSiMe ₃	90 °C, 12 h	3a (94)	4a (1)
22	Pt(PPh ₃) ₄	HSiMe ₂ Ph	100 °C, 14 h		4c (60)
23 ^{j)}	Pt(PPh ₃) ₄	HSiMe ₂ Ph	100 °C, 2 h		4c (94)
24	PdCl ₂ (PPh ₃) ₂	HSiEt ₃	90 °C, 35 h		4b (18)
25	Pd(PPh ₃) ₄	HSiEt ₃	100 °C, 14 h		4b (8)

a) Typically a mixture of **1** (0.3 to 1 mmol), an excess (3 to 10 mol equiv) of hydridosilane, and the catalyst (0.2 mol% of H₂PtCl₆ in *i*-PrOH (0.1 M), 0.5 mol% of RhCl(PPh₃)₃ or 0.5 mol% of Pt(PPh₃)₄) was heated in a sealed tube under an argon atmosphere. b) Isolated yields after purification by preparative TLC or column chromatography. c) **a**: R₃Si=Me₃Si; **b**: R₃Si=Et₃Si; **c**: R₃Si=PhMe₂Si; **d**: R₃Si=(*i*-Pr)₃Si; **e**: R₃Si=PhMeHSi; **f**: R₃Si=Ph₂HSi. d) The reaction mixture was treated with MeMgBr. e) The catalyst amount was 3 mol%. f) The amount of the catalyst was 0.2 mol%. g) The amounts of **2** and Pt(PPh₃)₄ were 0.5 g and 0.8 mol% respectively. h) The catalyst 1 mol% was used. i) The substrate **1** (0.8 g), HSiEt₃ (1.2 mol equiv), and Pt(PPh₃)₄ (1 mol%) were used. j) The substrate **1** (0.5 g), HSiMe₂Ph (1.1 mol equiv), and Pt(PPh₃)₄ (1 mol%) were used.

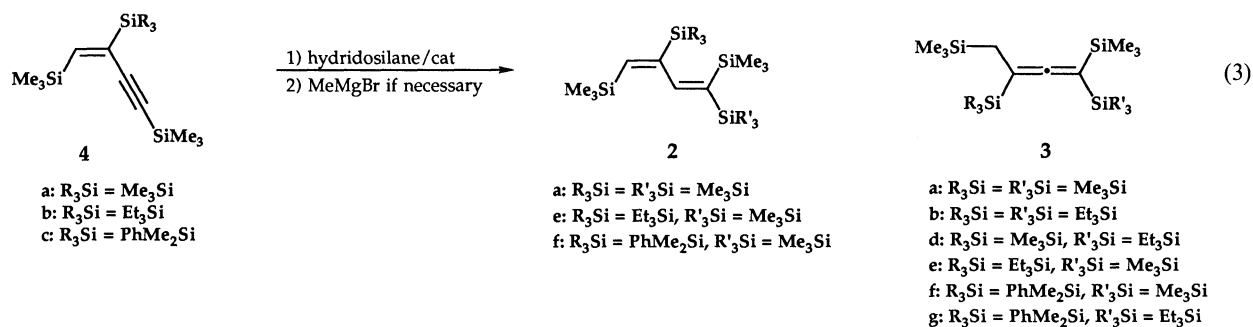
¹J=147 Hz, assigned to C(2)), and 169.4 by ¹³C NMR. However, the same reaction carried out using HSiEt₃ afforded allene **3b** in quantitative yield without any trace of a product of type **2** (Run 2). The structure of new product **3b** was determined by IR and ¹³C NMR. When bulkier hydridosilane HSi(*i*-Pr)₃ was applied, a 1:1 adduct **4d** was isolated as a sole product (Run 5). The butenyne structure was assigned on the basis of ¹³C NMR. Hydridosilane HSiMe₃ or HSiMe₂Ph underwent remarkable disilane formation and gave a mixture of products of type **3** and **4** but again with no trace of a product of type **2**.

Rhodium(I) catalyst always gave allenes **3** and/or enynes **4** without formation of **2** irrespective of the structure of hydridosilane. As the reactions with RhCl(PPh₃)₃ were slower, products of type **4** predominated at short reaction times, whereas after prolonged times 1:2 products of type **3** were accumulated (cf. Runs 7 vs. 8 and 10 vs. 11). Pt(PPh₃)₄ was proved to be much less reactive to give 1:1 products of type **4** except the reaction using a less bulky silane HSiMe₃. Pd(II) and Pd(0) exhibited impotent activity for **1** (Runs 24 and 25).

These results clearly show that hydrosilylation of **1** proceeds stepwise. First addition of hydridosilane

invariably takes place in a *cis*-manner with a regioselectivity that hydrogen adds at C(1) and silicon at C(2) to give products of type **4**. The regioselectivity compares well to that of non-conjugated 1-trimethylsilylalkynes.^{10,11)} Second addition of hydridosilane may take a route leading to products of type **2** via another 1,2-addition of C≡C of **4** but with different regioselectivity or alternatively a route leading to **3** via 1,4-addition. Although 1,2-addition of conjugated enynes has precedents to give butadienes,⁷⁾ no examples have appeared of giving allenes with high selectivity.¹²⁾ In order to get an insight into the selectivity difference, we studied hydrosilylation of **4a–c** using various sorts of hydridosilanes and catalysts and summarize the results in Table 2.

Reactions using H₂PtCl₆ catalyst and chlorosilanes such as HSiCl₃, HSiCl₂Me, and HSiClMe₂ resulted in predominant formation of butadienes **2** (Runs 1–3, 6–8, and 11–13). In contrast, HSiMe₃ and HSiEt₃ afforded allenes **3** only (Runs 5, 9, 10, 14, and 15) except the reaction of **4a** with HSiMe₃ (Run 4). Thus, the product selectivity is decisively governed by the kind of hydridosilane rather than the C(2)-substituent of **4** and parallels to the results of hydrosilylation of **1**. The

Table 2. Hydrosilylation of 4^{a)}

Run	Catalyst	R_3Si of 4 ^{b)}	HSiR'_3	Products (Yield/%) ^{c,d)}	
1	H_2PtCl_6	Me_3Si (a)	HSiCl_3	2a (67)	
2	H_2PtCl_6	Me_3Si (a)	HSiCl_2Me	2a (57)	
3	H_2PtCl_6	Me_3Si (a)	HSiClMe_2	2a (65)	
4	H_2PtCl_6	Me_3Si (a)	HSiMe_3	2a (30)	3a (20)
5	H_2PtCl_6	Me_3Si (a)	HSiEt_3		3d (58)
6	H_2PtCl_6	Et_3Si (b)	HSiCl_3	2e (56)	
7	H_2PtCl_6	Et_3Si (b)	HSiCl_2Me	2e (56)	
8	H_2PtCl_6	Et_3Si (b)	HSiClMe_2	2e (15)	
9	H_2PtCl_6	Et_3Si (b)	HSiMe_3		3e (9)
10	H_2PtCl_6	Et_3Si (b)	HSiEt_3		3b (99)
11	H_2PtCl_6	PhMe_2Si (c)	HSiCl_3	2f (39)	
12	H_2PtCl_6	PhMe_2Si (c)	HSiCl_2Me	2f (21)	
13	H_2PtCl_6	PhMe_2Si (c)	HSiClMe_2	2f (54)	
14	H_2PtCl_6	PhMe_2Si (c)	HSiMe_3		3f (17)
15	H_2PtCl_6	PhMe_2Si (c)	HSiEt_3		3g (93)
16	$\text{RhCl}(\text{PPh}_3)_3$	Me_3Si (a)	HSiCl_3		3a (46)
17	$\text{RhCl}(\text{PPh}_3)_3$	Me_3Si (a)	HSiCl_2Me		No reaction
18	$\text{RhCl}(\text{PPh}_3)_3$	Me_3Si (a)	HSiClMe_2		3a (47)
19	$\text{RhCl}(\text{PPh}_3)_3$	Me_3Si (a)	HSiMe_3		3a (96)
20	$\text{RhCl}(\text{PPh}_3)_3$	Me_3Si (a)	HSiEt_3		3d (46)
21	$\text{RhCl}(\text{PPh}_3)_3$	Et_3Si (b)	HSiCl_2Me		No reaction
22	$\text{RhCl}(\text{PPh}_3)_3$	Et_3Si (b)	HSiClMe_2		3e (44)
23	$\text{RhCl}(\text{PPh}_3)_3$	Et_3Si (b)	HSiMe_3		3e (86)
24	$\text{RhCl}(\text{PPh}_3)_3$	PhMe_2Si (c)	HSiCl_3		3f (16)
25	$\text{RhCl}(\text{PPh}_3)_3$	PhMe_2Si (c)	HSiCl_2Me		No reaction
26	$\text{RhCl}(\text{PPh}_3)_3$	PhMe_2Si (c)	HSiClMe_2		3f (63)
27	$\text{RhCl}(\text{PPh}_3)_3$	PhMe_2Si (c)	HSiMe_3		3f (77)
28	$\text{RhCl}(\text{PPh}_3)_3$	PhMe_2Si (c)	HSiEt_3		3g (100)
29	$\text{Pt}(\text{PPh}_3)_4$	Me_3Si (a)	HSiCl_3		No reaction
29	$\text{Pt}(\text{PPh}_3)_4$	Me_3Si (a)	HSiCl_3		No reaction
30	$\text{Pt}(\text{PPh}_3)_4$	Me_3Si (a)	HSiCl_2Me		No reaction
31	$\text{Pt}(\text{PPh}_3)_4$	Me_3Si (a)	HSiClMe_2		No reaction
32	$\text{Pt}(\text{PPh}_3)_4$	Me_3Si (a)	HSiMe_3		3a (15)
33	$\text{Pt}(\text{PPh}_3)_4$	Me_3Si (a)	HSiEt_3		3d (20)
34	$\text{Pt}(\text{PPh}_3)_4$	Et_3Si (b)	HSiMe_3		3e (54)

a) In a typical experiment a mixture of 4 (0.05 to 1 mmol), an excess (5 to 10 mol equiv) of hydridosilane, and the catalyst (0.5 to 1.0 mol% of H_2PtCl_6 in *i*-PrOH (0.1 M), $\text{RhCl}(\text{PPh}_3)_3$ or $\text{Pt}(\text{PPh}_3)_4$) was heated at 80 to 100 °C in a sealed tube under an argon atmosphere. When chlorosilanes were used, the reaction mixture was treated with MeMgBr. b) a: $\text{R}_3\text{Si} = \text{Me}_3\text{Si}$; b: $\text{R}_3\text{Si} = \text{Et}_3\text{Si}$; c: $\text{R}_3\text{Si} = \text{PhMe}_2\text{Si}$. c) Isolated yields after purification by preparative TLC, column chromatography or preparative GLC. d) a: $\text{R}_3\text{Si} = \text{R}'_3\text{Si} = \text{Me}_3\text{Si}$; b: $\text{R}_3\text{Si} = \text{R}'_3\text{Si} = \text{Et}_3\text{Si}$; d: $\text{R}_3\text{Si} = \text{Me}_3\text{Si}, \text{R}'_3\text{Si} = \text{Et}_3\text{Si}$; e: $\text{R}_3\text{Si} = \text{Et}_3\text{Si}, \text{R}'_3\text{Si} = \text{Me}_3\text{Si}$; f: $\text{R}_3\text{Si} = \text{PhMe}_2\text{Si}, \text{R}'_3\text{Si} = \text{Me}_3\text{Si}$; g: $\text{R}_3\text{Si} = \text{PhMe}_2\text{Si}, \text{R}'_3\text{Si} = \text{Et}_3\text{Si}$.

selectivity is apparently affected by electron density on silicon of hydridosilanes (*vide infra*).

When $\text{PhCl}(\text{PPh}_3)_3$ complex was used as the catalyst, HSiCl_3 as well as HSiClMe_2 also gave allenes 3 (Runs 16, 18, 22, 24, and 26) in contrast to the catalysis by H_2PtCl_6 .

It is curious but worthy to note that HSiCl_2Me did not give any hydrosilylation products (Runs 17, 21, and 25). HSiMe_3 and HSiEt_3 afforded allenes 3 as before (Runs 19, 20, 23, 27, and 28). $\text{Pt}(\text{PPh}_3)_4$ catalyst was proved to be less potent to catalyze the reaction, trialkylsilanes only

giving low yields of allenes **3** (Runs 32–34). We may conclude that low valent or electron-rich metals complexed by phosphine ligands prefer conjugate 1,4-addition of hydrosilanes to **4** to give **3** irrespective of the kind of the substituents of hydrosilanes.

The product selectivity observed above stimulated us to study the regioselectivity of hydrosilylation of disilylbutenyne **5** which lack trimethylsilyl group on terminal alkynyl carbon. The butenyne **5** was prepared by treatment of **4** with potassium fluoride in methanol. Hydrosilylation was carried out as before, and the results are summarized in Table 3. As readily seen, H_2PtCl_6 gave 1,2-*cis*-adducts **6** as exclusive products (Runs 1–5). The regioselectivity and stereoselectivity are the same as those of 1-alkynes and were again observed for the catalysis by $\text{RhCl}(\text{PPh}_3)_3$ and $\text{Pt}(\text{PPh}_3)_4$ (Runs 8–10, 12–14, and 17).^{3,13} Worthy to note is the fact that formation of *trans*-adducts of type **7** was recognized when the $\text{Pt}(0)$ catalyst was used (Runs 12 and 14). The same catalyst combined with HSiMe_3 or HSiEt_3 in particular afforded regioisomeric adducts of type **8** (Runs 15 and 16). Formation of a 1:2 adduct **9a** by $\text{Rh}(\text{I})$ -catalyzed reaction of HSiMe_3 (Run 7) is attributed to further 1,4-hydrosilylation of a primary adduct **8a**. Thus, hydrosilylation of terminal alkynes of type **5** using an electron-

rich metal complex and an electron-rich trialkylsilane resulted in inverse of regioselectivity.

We studied also hydrosilylation of butenyne **10**¹⁴ with HSiEt_3 . In sharp contrast to the reaction of **4**, no 1,4-adducts were produced when H_2PtCl_6 was employed as the catalyst. Instead, 1,2-adducts **11** were produced exclusively. As compared with **4**, the $\text{C}\equiv\text{C}$ bond of **10**,

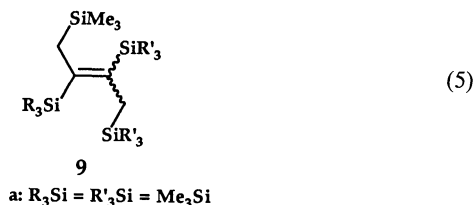
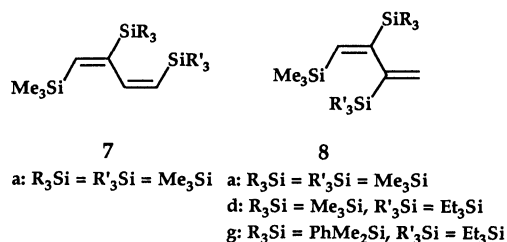
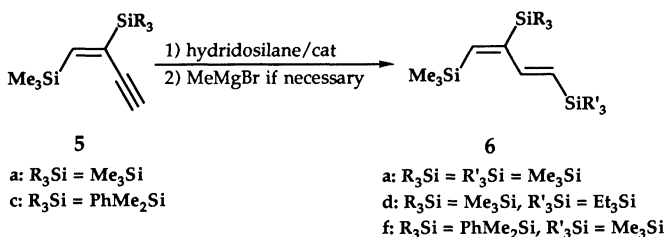
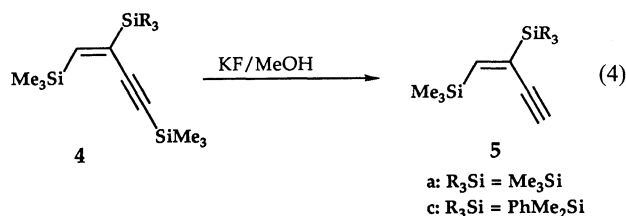
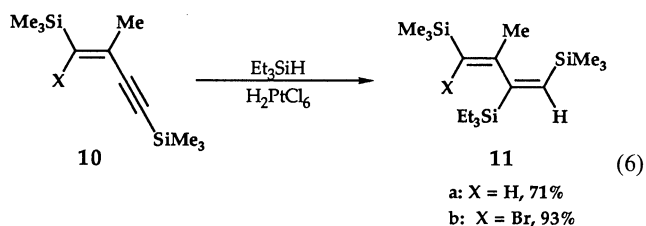


Table 3. Hydrosilylation of **5**^{a)}

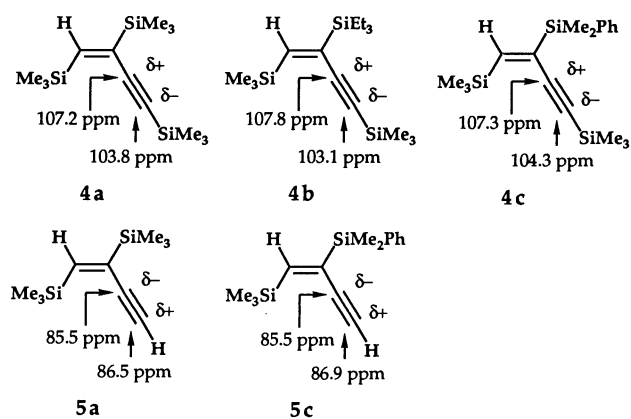
Run	Catalyst	5 ^{b)}	HSiR'_3	Products (Yield/%) ^{c,d)}	
1	H_2PtCl_6	5a	HSiEt_3	6d (63)	
2	H_2PtCl_6	5c	HSiCl_3	6f (73)	
3	H_2PtCl_6	5c	HSiCl_2Me	6f (77)	
4	H_2PtCl_6	5c	HSiClMe_2	6f (71)	
5	H_2PtCl_6	5c	HSiMe_3	6f (84)	
6	$\text{RhCl}(\text{PPh}_3)_3$	5a	HSiMe_3		9a (27)
7	$\text{RhCl}(\text{PPh}_3)_3$	5a	HSEt_3	8d (Trace)	
8	$\text{RhCl}(\text{PPh}_3)_3$	5c	HSiCl_3	6f (31)	
9	$\text{RhCl}(\text{PPh}_3)_3$	5c	HSiCl_2Me	6f (75)	
10	$\text{RhCl}(\text{PPh}_3)_3$	5c	HSiMe_2Cl	6f (76)	
11	$\text{RhCl}(\text{PPh}_3)_3$	5c	HSiEt_3		8g (Trace)
12	$\text{Pt}(\text{PPh}_3)_4$	5a	HSiCl	6a (20)	7a (12)
13	$\text{Pt}(\text{PPh}_3)_4$	5a	HSiCl_2Me	6a (32)	
14	$\text{Pt}(\text{PPh}_3)_4$	5a	HSiClMe_2	6a (24)	7a (35)
15	$\text{Pt}(\text{PPh}_3)_4$	5a	HSiMe_3	6a (41)	8a (32)
16	$\text{Pt}(\text{PPh}_3)_4$	5a	HSiEt_3		8d (59)
17	$\text{Pt}(\text{PPh}_3)_4$	5c	HSiClMe_2	6f (17)	

a) A typical experimental procedure follows. A mixture of **4** (0.3 to 1 mmol), an excess of hydrosilane (5 to 10 mol equiv) and the catalyst (0.5 to 1.0 mol%) was heated at 80°C to 100°C under an argon atmosphere. When chlorosilanes were used, the reaction mixture was treated with MeMgBr before purification. b) a: $\text{R}_3\text{Si} = \text{Me}_3\text{Si}$; c: $\text{R}_3\text{Si} = \text{PhMe}_2\text{Si}$. c) Isolated yields after purification by preparative TLC, column chromatography or preparative GLC. d) a: $\text{R}_3\text{Si} = \text{R}'_3\text{Si} = \text{Me}_3\text{Si}$; d: $\text{R}_3\text{Si} = \text{Me}_3\text{Si}, \text{R}'_3\text{Si} = \text{Et}_3\text{Si}$; f: $\text{R}_3\text{Si} = \text{PhMe}_2\text{Si}, \text{R}'_3\text{Si} = \text{Me}_3\text{Si}$; g: $\text{R}_3\text{Si} = \text{PhMe}_2\text{Si}, \text{R}'_3\text{Si} = \text{Et}_3\text{Si}$.

is obviously less hindered: Two trimethylsilyl groups on the olefinic carbons of **4** effectively block its C≡C bond, whereas substituents on the olefinic carbons of **10** are much less bulkier. Accordingly, 1,4-hydrosilylation of butenynes is concluded to take place only for the substrates whose C≡C bond is sterically crowded.



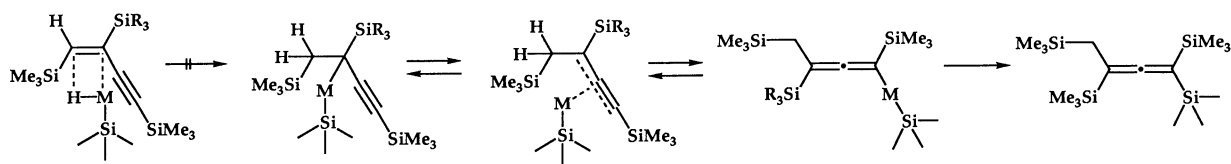
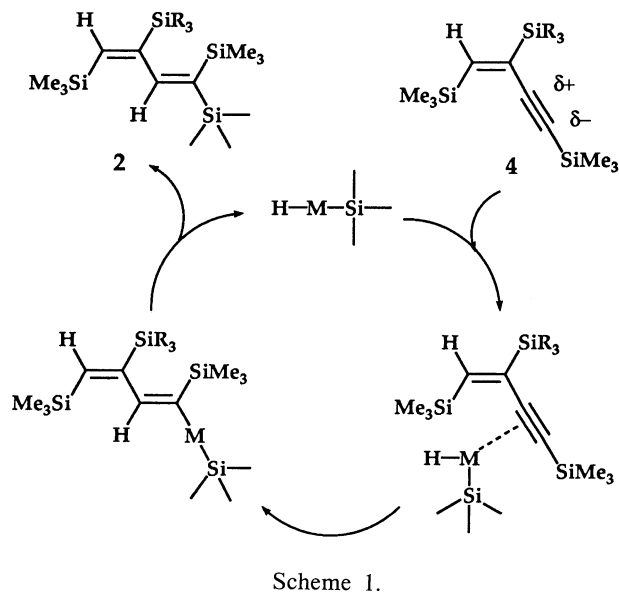
Mechanism of hydrosilylation has been explained by hydrometalation of H-M-Si species followed by reductive elimination of a resulting C(H)-C-M-Si species. The regiochemistry of the reaction is determined in a way that H prefers more electropositive olefinic (or acetylenic) carbon and M favors more electronegative position.¹⁵⁾ But this rule of thumb is said to be affected remarkably by steric environment. To examine whether the regioselectivities we observed follow the rule, we studied electron density distribution on acetylenic carbons through ¹³C NMR spectra.¹⁶⁾ Chemical shift data of **4a**, **4b**, **4c**, **5a**, and **5c** are shown below. It is clear that terminal carbons of trimethylsilyl substituted acetylenes **4a**—**c** are more electronegative than inner carbons, whereas the electron density distribution of **5a** and **5c** is opposite but with only tiny difference (1 to 1.4 ppm).

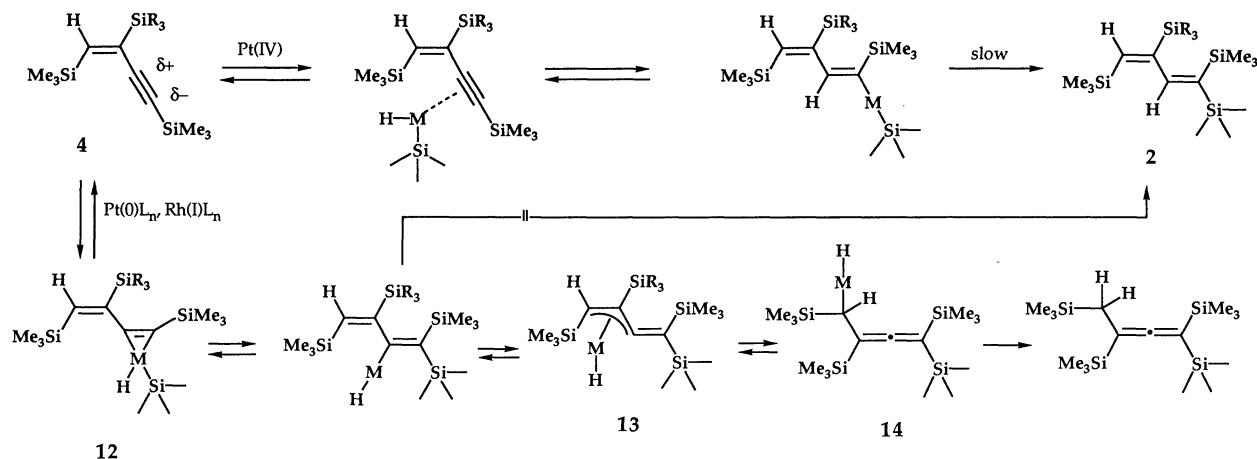


Formation of butadienes **2** when H₂PtCl₆ catalyst and chlorosilanes were applied is well explained by hydrosilylation-reductive elimination process (Scheme 1). Namely, hydride attaches at electropositive C(3) and silyl group at electronegative C(4).¹⁵⁾ However, application of this mechanism to the formation of allenes **3** results in reaction at a less reactive and more crowded olefinic moiety (Scheme 2). In addition, it is difficult to explain, through this mechanism, the regioselectivity dependence on kinds of catalyst metal and hydrosilanes.

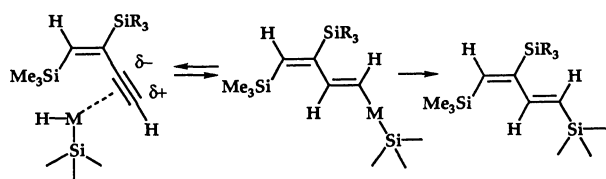
The fact that allenes **3** were produced particularly when a low valent metal with phosphine ligands and triorganohydrosilanes were used for hydrosilylation of silyl acetylenes **1** and **4** should be well understood in terms of a mechanism involving silylmatalation as shown in Scheme 3. Hereby the electron density at M of H-M-Si should be high to form a metalacyclopropene intermediate **12** through back-donation, and, in turn, a hydrometalation mechanism initiated by π -interaction of metal with acetylenic electrons being less plausible. Migration of silyl group from metal to electronegative C(4) then gives a π -allyl-type intermediate **13** which finally gives allenes by reductive elimination at C(1) of **14**. The silylmatalation mechanism, though often applied to vinylsilane formation through hydrosilylation of alkenes,¹⁷⁾ has had few precedents until recently.⁵⁾

As polarization of terminal acetylene bond of **5** was

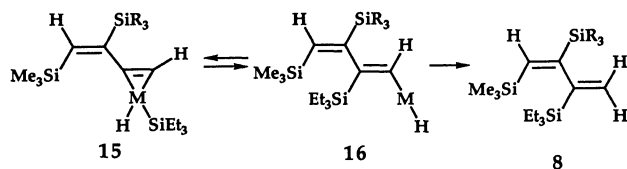




Scheme 3.



Scheme 4.



Scheme 5.

small, this substrate should be affected by steric factors: A bulky metal would prefer less crowded terminal carbon (Scheme 4). However, formation of **8**, as observed when $\text{Pt}(\text{PPh}_3)_4$ or $\text{RhCl}(\text{PPh}_3)_3$ catalyst was applied in combination with trialkylsilanes, is not explained by the mechanism of Scheme 4. We propose a new one which involves a metalacyclopentene intermediate (**15** in Scheme 5); silyl shift from metal to carbon takes place in a way that a bulky metal forms a bond with a less crowded terminal carbon with silyl group attaching to C(2) (e.g. **16**).

Silylmetalation mechanism is recently proposed for hydrosilylation of alkynes using trialkylsilanes and chromium,^{5a)} rhodium,^{5b)} or iridium catalyst.^{5c)} On the other hand, hydrosilylation of butenynes **4** by use of a combination of H_2PtCl_6 /trialkylsilanes and $\text{RhCl}(\text{PPh}_3)_3$ /chlorosilanes or trialkylsilanes exhibited striking regioselectivity which led us to propose silylmetalation mechanism for these reactions. Thus silyl-substituted butenynes **4** are considered to be good models for studying of hydrosilylation mechanism.

We have demonstrated that hydrosilylation of 1,4-

bis(trimethylsilyl)butadiyne (**1**) provides us with various silyl-substituted butenynes, 1,3-butadienes, and 1,2-butadienes which are apparently versatile synthetic reagents.¹⁾ In particular, hydrosilylation of silyl-substituted butenynes has afforded products whose formation should be ascribed to silylmetalation through a metalacyclopentene species.

Experimental

Melting and boiling points are uncorrected. Bulb-to-bulb distillation was carried out using a Shibata glass tube oven GTO 250R, and boiling points were determined by measurement of the bath temperature and given in °C/Torr (1 Torr=133.322 Pa). ^1H NMR spectra were obtained with a Varian EM-390, a Hitachi R-90, or a Bruker AM-400 spectrometer. ^{13}C NMR spectra with a Varian XL-100 or a Bruker AM-400 spectrometer. Chemical shifts are given in ppm units downfield from tetramethylsilane. Coupling constant J shown in ^{13}C NMR spectra means that between ^{13}C and H. IR spectra were recorded with a JASCO A-202 machine, MS were recorded with a RMU-6MG spectrometer under 70 eV. High-resolution mass spectra were recorded with a Hitachi M-80A spectrometer. TLC analyses were performed using Merck Silica gel 60 F₂₅₄ glass plates (0.25 mm). Preparative TLC (1.2 mm thick) were prepared from Merck Kiesel-gel PF₂₅₄. Column chromatography was carried out with silica gel (Wakogel C-200) at atmospheric pressure. 1,4-Bis(trimethylsilyl)butadiyne (**1**) was purchased from Aldrich and used directly.

Metal Catalyzed Hydrosilylation of 1,4-Bis(trimethylsilyl)butadiyne (1**) with Chlorosilanes.** A mixture of **1** (62 mg, 0.32 mmol), chlorodimethylsilane (255 mg, 2.7 mmol), and 0.1 M (1 M=1 mmol dm⁻³) hexachloroplatinic(IV) acid in 2-propanol (7 μl , 7×10^{-4} mmol) was placed in a 10 ml sealed tube and heated at 80°C for 10 h under an argon atmosphere. The reaction mixture was diluted with 5 ml of THF, and transferred into a two-necked flask, treated with 3 M methylmagnesium bromide in diethyl ether (1.4 ml, 4.2 mmol) at 0°C. The reaction mixture was stirred for 30 min at room temperature, hydrolyzed with sodium hydroxide aq solution (10 ml), and extracted with diethyl ether (25 ml). The ethereal layer was dried over anhydrous sodium sulfate and concentrated under

reduced pressure. Purification by preparative TLC (hexane, R_f 0.7) gave (*E*)-1,1,3,4-tetrakis(trimethylsilyl)-1,3-butadiene (**2a**) (59 mg, 54% yield) as a colorless oil, bp 75°C/0.3 Torr (lit.⁴⁾ 70–72°C/0.1 Torr). ^1H NMR (CDCl_3) δ =0.06 (s, 9H), 0.08 (s, 9H), 0.10 (s, 9H), 1.03 (s, 9H), 5.93 (d, J =2.4 Hz, 1H), 7.29 (d, J =2.4 Hz, 1H); ^{13}C NMR (CDCl_3) δ =−0.93 (septuple q, J =2 and 119 Hz, SiCH_3), 0.54 (mq, J =119 Hz, SiCH_3), 0.94 (septuple q, J =2 and 119 Hz, SiCH_3), 3.07 (septuple q, J =2 and 119 Hz, SiCH_3), 139.3 (md, J =136 Hz, $\underline{\text{C}}(4)$), 139.4 (m, $\underline{\text{C}}(1)$ or $\underline{\text{C}}(3)$), 158.2 (dd, J =16 and 147 Hz, $\underline{\text{C}}(2)$), 169.4 (m, $\underline{\text{C}}(1)$ or $\underline{\text{C}}(3)$); IR (neat) 2950, 2900, 2100, 1560, 1520, 1400, 1380, 1250, 1020, 930, 840, 750, 680, 650 cm^{-1} ; MS m/z (rel intensity) 342 (M^+ , 11), 239 (17), 181 (36), 73 (100), 45 (16). Found: m/z 342.2038. Calcd for $\text{C}_{16}\text{H}_{38}\text{Si}_4$: M, 342.2048.

In a similar manner, butadiyne **1** was allowed to react with HSiClMe_2 , HSiCl_2Me , and HSiCl_3 using $\text{RhCl}(\text{PPh}_3)_3$ or $\text{Pt}(\text{PPh}_3)_4$ catalyst. The crude products were treated with MeMgBr , and the products **3a** and/or **4a** were isolated.

1,1,3,4-Tetrakis(trimethylsilyl)-1,2-butadiene (3a). A colorless oil, bp 95°C/0.4 Torr, R_f 0.90 (hexane). ^1H NMR (CDCl_3) δ =0.08 (s, 18H), 0.15 (s, 18H), 1.14 (s, 2H); ^{13}C NMR (CDCl_3) δ =−1.29 (septuple q, J =2 and 119 Hz, SiCH_3), −0.51 (septuple q, J =2 and 119 Hz, SiCH_3), 0.68 (septuple q, J =2 and 119 Hz, $\text{Si}(\text{CH}_3)_2$), 14.3 (mt, J =120 Hz, $\underline{\text{C}}(4)$), 71.6 (m, $\underline{\text{C}}(1)$ or $\underline{\text{C}}(3)$), 78.0 (m, $\underline{\text{C}}(1)$ or $\underline{\text{C}}(3)$), 207.2 (t, J =7 Hz, $\underline{\text{C}}(2)$); IR (neat) 2970, 2920, 1890 ($\text{C}=\text{C}$), 1405, 1250, 1135, 900, 840, 760, 690, 615, 520 cm^{-1} ; MS m/z (rel intensity) 344 (M^+ +2, 13), 343 (M^+ +1, 22), 342 (M^+ , 59), 269 (34), 254 (26), 239 (39), 182 (19), 181 (92), 155 (40), 74 (20), 73 (100), 45 (36). Found: m/z 342.2025. Calcd for $\text{C}_{16}\text{H}_{38}\text{Si}_4$: M, 342.2048.

(*E*)-1,2,4-Tris(trimethylsilyl)-1-buten-3-yne (4a). A colorless oil, bp 61°C/0.35 Torr, R_f 0.80 (hexane). ^1H NMR (CDCl_3) δ =0.16 (s, 9H), 0.206 (s, 9H), 0.211 (s, 9H), 6.59 (s, 1H); ^{13}C NMR (CDCl_3) δ =−19.6 (septuple q, J =2 and 119 Hz, SiCH_3), −0.82 (mq, J =119 Hz, SiCH_3), 0.06 (septuple q, J =2 and 119 Hz, SiCH_3), 103.8 (decuplet, J =2 Hz, $\underline{\text{C}}(4)$), 107.2 (d, J =20 Hz, $\underline{\text{C}}(3)$), 145.5 (m, $\underline{\text{C}}(2)$), 155.3 (decuplet, d, J =2 and 137, $\underline{\text{C}}(1)$); IR (neat) 2980, 2150, 1410, 1250, 1055, 840, 760, 700, 610, 505 cm^{-1} ; MS m/z (rel intensity) 268 (M^+ , 16), 253 (15), 180 (18), 165 (29), 155 (49), 73 (100), 43 (22). Found: m/z 268.1474. Calcd for $\text{C}_{15}\text{H}_{28}\text{Si}_3$: M, 268.1496.

Metal Catalyzed Hydrosilylation of 1 with Triethylsilane. In a sealed tube were placed **1** (75 mg, 0.39 mmol), HSiEt_3 (0.2 ml, 1.3 mmol), and H_2PtCl_6 (0.1 M 2-propanol solution, 8 μl , 8×10^{-4} mmol), and the mixture was heated at 80°C for 0.5 h under an argon atmosphere. The reaction mixture was filtered through a short silica gel column (Wakogel C-100, ϕ 20 mm $\times$ 20 mm). The column was washed with diethyl ether (30 ml), and the combined eluate was concentrated under reduced pressure. Purification by preparative TLC (hexane, R_f 0.9) gave 1,3-bis(triethylsilyl)-1,4-bis(trimethylsilyl)-1,2-butadiene (**3b**) (147 mg, 100% yield) as a colorless oil, bp 140°C/0.5 Torr. ^1H NMR (CDCl_3) δ =0.08 (s, 9H), 0.15 (s, 9H), 0.4–0.85 (m, 12H), 0.85–1.20 (m, 20H); ^{13}C NMR (CDCl_3) δ =−0.2 (mq, J =119 Hz, SiCH_3), 1.1 (mq, J =119 Hz, SiCH_3), 3.7 (qt, J =5 and 118 Hz, SiCH_2CH_3), 5.1 (qt, J =5 and 118 Hz, SiCH_2CH_3), 7.8 (tq, J =4 and 126 Hz, SiCH_2CH_3), 7.9 (tq, J =4 and 126 Hz, SiCH_2CH_3), 15.3 (mt, J =119 Hz, $\underline{\text{C}}(4)$), 69.5 (m, $\underline{\text{C}}(1)$ or $\underline{\text{C}}(3)$), 75.1 (m, $\underline{\text{C}}(1)$ or $\underline{\text{C}}(3)$), 208.7 (t, J =7 Hz, $\underline{\text{C}}(2)$); IR (neat) 3000, 2950, 2920, 1880 ($\text{C}=\text{C}$), 1460, 1420, 1250, 1040, 885, 840, 730 cm^{-1} ; MS m/z (rel intensity) 428 (M^+ +2, 14), 427 (M^+ +1, 26), 426 (M^+ , 60), 397 (10), 268 (69), 254

(45), 239 (22), 115 (74), 87 (100), 73 (92), 59 (80). Found: C, 62.14; H, 11.95%. Calcd for $\text{C}_{22}\text{H}_{50}\text{Si}_4$: C, 61.89; H, 11.80%.

In a similar manner **1** was allowed to react with HSiMe_3 , HSiMe_2Ph , $\text{HSi}(\text{i-Pr})_3$, H_2SiMePh , and H_2SiPh_2 using H_2PtCl_6 , $\text{RhCl}(\text{PPh}_3)_3$, or $\text{Pt}(\text{PPh}_3)_4$ as a catalyst. Results are summarized in Table I. The products **3c**, **4b**, **4c**, **4d**, **4e**, and **4f** gave following physical and analytical data.

1,3-Bis(dimethylphenylsilyl)-1,4-bis(trimethylsilyl)-1,2-butadiene (3c). A colorless oil, bp 155°C/0.5 Torr. R_f 0.6 (hexane). ^1H NMR (CDCl_3) δ =0.04 (s, 9H), 0.05 (s, 9H), 0.34 (s, 3H), 0.36 (s, 3H), 0.44 (s, 3H), 0.45 (s, 3H), 1.08 (d, J =12.5 Hz, 1H), 1.15 (d, J =12.5 Hz, 1H), 7.28–7.62 (m, 10H); IR (neat) 2970, 1885 ($\text{C}=\text{C}$), 1430, 1250, 1115, 890, 835, 810, 755, 730, 700 cm^{-1} ; MS m/z (rel intensity) 468 (M^+ +2, 8), 467 (M^+ +1, 14), 466 (M^+ , 29), 316 (16), 243 (27), 228 (26), 135 (100), 73 (62). Found: m/z 466.2343. Calcd for $\text{C}_{26}\text{H}_{42}\text{Si}_4$: M, 466.2361.

(*E*)-2-Triethylsilyl-1,4-bis(trimethylsilyl)-1-buten-3-yne (4b). A colorless oil, bp 61°C/0.35 Torr, R_f 0.85 (hexane). ^1H NMR (CDCl_3) δ =0.20 (s, 9H), 0.22 (s, 9H), 0.5–0.75 (m, 6H), 0.75–1.1 (m, 9H), 6.52 (s, 1H); ^{13}C NMR (CDCl_3) δ =−0.83 (mq, J =119 Hz, SiCH_3), −0.05 (septuple q, J =2 and 120 Hz, SiCH_3), 0.06 (mt, J =119 Hz, SiCH_2), 7.89 (tq, J =5 and 126 Hz, SiCH_2CH_3), 103.1 (decuplet, J =2 Hz, $\underline{\text{C}}(4)$), 107.8 (d, J =20 Hz, $\underline{\text{C}}(3)$), 142.5 (m, $\underline{\text{C}}(2)$), 155.3 (decuplet d, J =2 and 137 Hz, $\underline{\text{C}}(1)$); IR (neat) 2960, 2920, 2880, 2140, 1250, 1050, 1000, 840, 735 cm^{-1} ; MS m/z (rel intensity) 310 (M^+ , 13), 281 (39), 253 (38), 183 (66), 155 (45), 87 (62), 73 (100), 59 (66). Found: C, 61.74; H, 11.23%. Calcd for $\text{C}_{16}\text{H}_{34}\text{Si}_3$: C, 61.85; H, 11.03%.

(*E*)-2-Dimethylphenylsilyl-1,4-bis(trimethylsilyl)-1-buten-3-yne (4c). A colorless oil, bp 105°C/0.4 Torr, R_f 0.65 (hexane). ^1H NMR (CDCl_3) δ =0.20 (s, 9H), 0.22 (s, 9H), 0.45 (s, 6H), 6.58 (s, 1H), 7.3–7.48 (m, 3H), 7.48–7.68 (m, 2H); ^{13}C NMR (CDCl_3) δ =−3.26 (qq, J =2 and 120 Hz, $\text{Si}(\text{CH}_3)_2\text{Ph}$), −0.69 (mq, J =119 Hz, $\text{Si}(\text{CH}_3)_3$), −0.08 (septuple q, J =2 and 120 Hz, $\text{Si}(\text{CH}_3)_3$), 104.3 (decuplet, J =2 Hz, $\underline{\text{C}}(4)$), 107.2 (d, J =19 Hz, $\underline{\text{C}}(3)$), 127.7 (md, J =156 Hz, Ph), 129.2 (td, J =8 and 159 Hz, Ph), 134.2 (md, J =159 Hz, Ph), 137.4 (m, Ph), 143.4 (m, $\underline{\text{C}}(2)$), 157.4 (decuplet d, J =2 and 137, $\underline{\text{C}}(1)$); IR (neat) 2970, 2920, 2140, 1520, 1430, 1250, 1115, 1055, 835, 775, 760, 730, 700, 650, 625, 515 cm^{-1} ; MS m/z (rel intensity) 330 (M^+ , 43), 315 (24), 257 (25), 227 (23), 217 (33), 135 (100), 73 (83). Found: m/z 330.1637. Calcd for $\text{C}_{18}\text{H}_{30}\text{Si}_3$: M, 330.1653.

(*E*)-2-Tris(1-methylethyl)silyl-1,4-bis(trimethylsilyl)-1-buten-3-yne (4d). A colorless oil, bp 110°C/0.3 Torr, R_f 0.85 (hexane). ^1H NMR (CDCl_3) δ =0.16 (s, 9H), 0.22 (s, 9H), 1.0–1.4 (m, 21H), 6.6 (s, 1H); ^{13}C NMR (CDCl_3) δ =−0.78 (septuple q, J =2 and 119 Hz, SiCH_3), −0.14 (mq, J =120 Hz, SiCH_3), 11.1 (md, J =120 Hz, $\underline{\text{CH}}(\text{CH}_3)_2$), 18.6 (mq, J =120 Hz, $\underline{\text{CH}}(\text{CH}_3)_2$), 102.8 (decuplet, J =2 Hz, $\underline{\text{C}}(4)$), 108.9 (d, J =19 Hz, $\underline{\text{C}}(3)$), 143.4 (broad, s, $\underline{\text{C}}(2)$), 157.6 (decuplet d, J =2 and 139, $\underline{\text{C}}(1)$); IR (neat) 2960, 2880, 2140, 1465, 1250, 1150, 855, 840, 760, 740, 700, 645, 520 cm^{-1} ; MS m/z (rel intensity) 352 (M^+ , 3), 309 (34), 267 (40), 211 (58), 183 (16), 169 (16), 155 (18), 141 (22), 129 (14), 115 (11), 87 (14), 73 (100), 59 (45). Found: m/z 352.2421. Calcd for $\text{C}_{19}\text{H}_{40}\text{Si}_3$: M, 352.2435.

(*E*)-2-Methylphenylsilyl-1,4-bis(trimethylsilyl)-1-buten-3-yne (4e). A colorless oil, bp 160°C/0.5 Torr, R_f 0.5 (hexane). ^1H NMR (CDCl_3) δ =0.15 (s, 9H), 0.17 (s, 9H), 0.49 (d, J =3.7 Hz, 3H), 4.57 (d, J =3.7 Hz, 1H), 6.71 (s, 1H), 7.28–7.45 (m, 3H), 7.45–7.65 (m, 2H); IR (neat), 2960, 2130, 1425, 1250,

1110, 1050, 840, 760, 730, 700, 625, 510 cm^{-1} ; MS m/z (rel intensity) 316 (M^+ , 19), 301 (22), 243 (26), 228 (21), 227 (18), 135 (36), 73 (100). Found: m/z 316.1497. Calcd for $\text{C}_{17}\text{H}_{28}\text{Si}_3$: M, 316.1497.

(E)-2-Diphenylsilyl-1,4-bis(trimethylsilyl)-1-buten-3-yne (4f). A colorless oil, bp $180^\circ\text{C}/0.4$ Torr, R_f 0.45 (hexane). ^1H NMR (CDCl_3) δ =0.27 (s, 9H), 0.37 (s, 9H), 5.25 (s, 1H), 6.98 (s, 1H), 7.3—7.65 (m, 6H), 7.65—7.92 (m, 4H); IR (neat) 3100, 2970, 2150, 1430, 1250, 1115, 1055, 840, 800, 730, 700 cm^{-1} ; MS m/z (rel intensity) 378 (M^+ , 13), 363 (16), 305 (28), 290 (34), 183 (44), 182 (72), 181 (52), 135 (58), 105 (46), 73 (100). Found: m/z 378.1659. Calcd for $\text{C}_{22}\text{H}_{30}\text{Si}_3$: M, 378.1654.

Synthesis of 4a. In a sealed tube were placed **1** (0.50 g, 2.6 mmol), HSiCl_2Me (2.3 ml, 23 mmol), and $\text{Pt}(\text{PPh}_3)_4$ (24 mg, 0.02 mmol), and the resulting mixture was heated at 100°C for 20 h under an argon atmosphere. The reaction mixture was freed of excess HSiCl_2Me in vacuo. The residue was dissolved in THF (8 ml) and treated with 3 M MeMgBr in diethyl ether (2.5 ml, 7.5 mmol) at 20°C . The mixture was stirred for 2 h at room temperature before quenching with sodium hydroxide aq solution (30 ml) and extracted with diethyl ether (50 ml). The ethereal layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. Purification by column chromatography (hexane) gave **4a** (470 mg, 67% yield).

Synthesis of 4b. In a sealed tube were placed **1** (0.80 g, 4.2 mmol), HSiEt_3 (580 ml, 5 mmol), and $\text{Pt}(\text{PPh}_3)_4$ (51 mg, 0.04 mmol), and the mixture was heated at 100°C for 1 h under an argon atmosphere. Filtration through a short silica gel column (Wakogel C-100, ϕ 20 mm $\times$ 40 mm, elution with hexane (50 ml)) followed by concentration under reduced pressure afforded **4b** (1.28 g, 100% yield).

Synthesis of 4c. In a sealed tube were placed **1** (0.50 g, 2.6 mmol), HSiMe_2Ph (0.39 ml, 2.9 mmol), and $\text{Pt}(\text{PPh}_3)_4$ (33 mg, 0.026 mmol), and the mixture was heated at 100°C for 2 h under an argon atmosphere. The reaction mixture was filtered through a short silica gel column (Wakogel C-100, ϕ 20 mm $\times$ 40 mm, elution with diethyl ether (50 ml)) and concentrated under reduced pressure. Further purification by column chromatography (hexane) gave **4c** (0.8 g, 94% yield).

H_2PtCl_6 -Catalyzed Hydrosilylation of 4a with Chlorodimethylsilane. Butenyne **4a** (101 mg, 0.38 mmol) was allowed to react with HSiClMe_2 (0.15 ml, 1.35 mmol) and 0.1 M H_2PtCl_6 in 2-propanol (18 μl , 1.8×10^{-3} mmol) at 80°C for 10 h. After addition of THF (10 ml) and 3 M MeMgBr in diethyl ether (5 ml, 15 mmol) at 0°C , the resulting mixture was stirred for 2 h at room temperature and worked up. Purification by preparative TLC gave **2a** (82 mg, 65% yield).

In a similar manner **4a**, **4b**, and **4c** were allowed to react with HSiCl_3 , HSiCl_2Me , or HSiClMe_2 and gave **2e** and **2f** whose physical and analytical data follow.

(E)-3-Triethylsilyl-1,1,4-tris(trimethylsilyl)-1,3-butadiene (2e). A colorless oil, bp $125^\circ\text{C}/0.3$ Torr, R_f 0.7 (hexane). ^1H NMR (CDCl_3) δ =0.06 (s, 9H), 0.11 (s, 9H), 0.12 (s, 9H), 0.61 (q, J =7.8 Hz, 6H), 0.94 (t, J =7.8 Hz, 9H), 5.90 (d, J =2.3 Hz, 1H), 7.26 (d, J =2.3 Hz, 1H); ^{13}C NMR (CDCl_3) δ =0.66 (mq, J =119 Hz, SiCH_3), 0.88 (septuple q, J =2 and 119 Hz, SiCH_3), 3.20 (mt, J =119 Hz, SiCH_2CH_3), 3.60 (septuple q, J =2 and 118 Hz, SiCH_3), 7.72 (tq, J =5 and 126 Hz, SiCH_2CH_3), 138.5 (m, $\underline{\text{C}}(1)$ or $\underline{\text{C}}(3)$), 140.6 (md, J =133 Hz, $\underline{\text{C}}(4)$), 159.0 (dd, J =16 and 147 Hz, $\underline{\text{C}}(2)$), 166.6 (m, $\underline{\text{C}}(1)$ or $\underline{\text{C}}(3)$); IR (neat) 2975, 2925, 1730, 1560, 1520, 1460, 1420, 1380, 1250, 1020, 930, 890, 840, 760, 730, 690, 650, 620 cm^{-1} ; MS m/z (rel intensity) 384 (M^+ ,

20), 239 (32), 181 (50), 115 (30), 87 (41), 73 (100), 59 (37). Found: m/z 384.2493. Calcd for $\text{C}_{19}\text{H}_{44}\text{Si}_4$: M, 384.2517.

(E)-3-Dimethylphenylsilyl-1,1,4-tris(trimethylsilyl)-1,3-butadiene (2f). A colorless oil, bp $205^\circ\text{C}/0.3$ Torr, R_f 0.3 (hexane). ^1H NMR (CDCl_3) δ =0.04 (s, 9H), 0.06 (s, 9H), 0.08 (s, 9H), 0.315 (s, 6H), 6.03 (d, J =2.4 Hz, 1H), 7.25 (d, J =2.4 Hz, 1H), 7.33—7.35 (m, 3H), 7.48—7.50 (m, 2H); ^{13}C NMR (CDCl_3) δ =−2.70 (qq, J =2 and 120 Hz, $\text{Si}(\text{CH}_3)\text{MePh}$), −2.27 (qq, J =2 and 120 Hz, $\text{Si}(\text{CH}_3)\text{MePh}$), 0.49 (mq, J =119 Hz, SiCH_3), 0.88 (septuple q, J =2 and 119 Hz, SiCH_3), 2.98 (septuple q, J =2 and 119 Hz, SiCH_3), 127.7 (md, J =158 Hz, Ph), 129.0 (td, J =8 and 158 Hz, Ph), 134.3 (md, J =158 Hz, Ph), 138.2 (m, Ph), 140.1 (m, $\underline{\text{C}}(1)$ or $\underline{\text{C}}(3)$), 141.4 (md, J =133 Hz, $\underline{\text{C}}(4)$), 157.9 (dd, J =16 and 148 Hz, $\underline{\text{C}}(2)$), 166.9 (m, $\underline{\text{C}}(1)$ or $\underline{\text{C}}(3)$); IR (neat) 2950, 2900, 1890, 1730, 1560, 1520, 1430, 1385, 1250, 1110, 1020, 930, 840, 760, 730, 700, 640, 620 cm^{-1} ; MS m/z (rel intensity) 404 (M^+ , 11), 239 (17), 181 (36), 135 (72), 73 (100). Found: m/z 404.2218. Calcd for $\text{C}_{21}\text{H}_{40}\text{Si}_4$: M, 404.2205.

1-Triethylsilyl-1,3,4-tris(trimethylsilyl)-1,2-butadiene (3d). Butenyne **4a** (102 mg, 0.38 mmol) was allowed to react with HSiEt_3 (0.22 g, 1.9 mmol) and 0.1 M H_2PtCl_6 in 2-propanol (15 μl , 1.5×10^{-3} mmol) at 80°C for 13 h. Workup followed by preparative TLC (hexane, R_f 0.7) gave **3d** (82 mg, 58% yield) as a colorless oil, bp $130^\circ\text{C}/0.3$ Torr. ^1H NMR (CDCl_3) δ =0.04 (s, 9H), 0.05 (s, 9H), 0.11 (s, 9H), 0.61 (q, J =7.9 Hz, 6H), 0.95 (t, J =7.9 Hz, 9H), 0.96 (d, J =7.6 Hz, 1H), 1.25 (d, J =7.6 Hz, 1H); ^{13}C NMR (CDCl_3) δ =−1.1 (septuple q, J =2 and 119 Hz, SiCH_3), −0.4 (mq, J =119 Hz, SiCH_3), 0.9 (septuple q, J =2 and 119 Hz, SiCH_3), 5.0 (mt, J =119 Hz, SiCH_2CH_3), 7.8 (tq, J =5 and 126 Hz, SiCH_2CH_3), 14.8 (mt, J =119 Hz, $\underline{\text{C}}(4)$), 71.2 (m, $\underline{\text{C}}(1)$ or $\underline{\text{C}}(3)$), 75.1 (m, $\underline{\text{C}}(1)$ or $\underline{\text{C}}(3)$), 208.0 (dd, J =7 and 9 Hz, $\underline{\text{C}}(2)$); IR (neat) 2975, 2900, 1880 ($\text{C}=\text{C}=\text{C}$), 1460, 1420, 1385, 1250, 1180, 1140, 1070, 1000, 890, 840, 750, 730, 690 cm^{-1} ; MS m/z (rel intensity) 384 (M^+ , 44), 254 (62), 239 (40), 181 (32), 115 (55), 87 (71), 73 (100), 59 (53). Found: m/z 384.2493. Calcd for $\text{C}_{19}\text{H}_{44}\text{Si}_4$: M, 384.2517.

In a similar manner **4a**, **4b**, or **4c** was allowed to react with HSiEt_3 and to give **3e**, **3f**, or **3g**.

3-Triethylsilyl-1,1,4-tris(trimethylsilyl)-1,2-butadiene (3e). A colorless oil, R_f 0.9 (hexane). ^1H NMR (CDCl_3) δ =0.04 (s, 9H), 0.10 (s, 9H), 0.11 (s, 9H), 0.5—2.2 (m, 17H); IR (neat) 2980, 2920, 1885 ($\text{C}=\text{C}=\text{C}$), 1250, 1010, 895, 840, 760, 720, 690 cm^{-1} ; MS m/z (rel intensity) 384 (M^+ , 20), 269 (15), 254 (13), 239 (32), 181 (50), 115(30), 87 (41), 73 (100), 59 (37), 45 (16). Found: m/z 384.2501. Calcd for $\text{C}_{19}\text{H}_{44}\text{Si}_4$: M, 384.2517.

3-Dimethylphenylsilyl-1,1,4-tris(trimethylsilyl)-1,2-butadiene (3f). A colorless oil, bp $125^\circ\text{C}/0.6$ Torr, R_f 0.45 (hexane). ^1H NMR (CDCl_3) δ =−0.02 (s, 9H), 0.11 (s, 18H), 0.32 (s, 6H), 1.07 (s, 2H), 7.3—7.4 (m, 3H), 7.5—7.6 (m, 2H); ^{13}C NMR (CDCl_3) δ =−2.57 (qq, J =2 and 120 Hz, $\text{Si}(\text{CH}_3)_2\text{Ph}$), −0.48 (mq, J =119 Hz, SiCH_3), 0.75 (septuple q, J =2 and 119 Hz, $(\text{Si}(\text{CH}_3)_3)_2$), 14.7 (mt, J =119 Hz, $\underline{\text{C}}(4)$), 70.7 (m, $\underline{\text{C}}(1)$ or $\underline{\text{C}}(3)$), 78.4 (m, $\underline{\text{C}}(1)$ or $\underline{\text{C}}(3)$), 127.6 (md, J =159 Hz, Ph), 128.9 (td, J =7 and 159 Hz, Ph), 134.2 (md, J =157 Hz, Ph), 138.2 (m, Ph), 207.6 (t, J =7 Hz, $\underline{\text{C}}(2)$); IR (neat) 2950, 2900, 1890 ($\text{C}=\text{C}=\text{C}$), 1720, 1425, 1400, 1290, 1250, 1140, 1110, 1020, 1000, 930, 890, 840, 810, 770, 760, 730, 700, 620, 520 cm^{-1} ; MS m/z (rel intensity) 404 (M^+ , 23), 254 (19), 181 (26), 135 (63), 73 (100), 45 (15). Found: m/z 404.2224. Calcd for $\text{C}_{21}\text{H}_{40}\text{Si}_4$: M, 404.2205.

3-Dimethylphenylsilyl-1-triethylsilyl-1,4-bis(trimethylsilyl)-

1,2-butadiene (3g). A colorless oil, bp 150°C/0.3 Torr, R_f 0.75 (hexane). ^1H NMR (CDCl_3) δ = -0.06 (s, 9H), 0.12 (s, 9H), 0.32 (s, 6H), 0.48–0.8 (m, 6H), 0.8–1.08 (m, 10H), 1.22 (d, J = 13.5 Hz, 1H), 7.28–7.42 (m, 3H), 7.43–7.65 (m, 2H); IR (neat) 2970, 1880 (C=C=C), 1425, 1245, 1115, 1000, 858, 835, 810, 775, 765, 700 cm^{-1} ; MS m/z (rel intensity) 449 (M^+ + 3, 4), 448 (M^+ + 2, 13), 447 (M^+ + 1, 25), 446 (M^+ , 52), 316 (25), 268 (49), 254 (27), 243 (29), 228 (30), 135 (62), 115 (45), 87 (86), 73 (100), 19 (63). Found: m/z 466.2657. Calcd for $\text{C}_{24}\text{H}_{46}\text{Si}_4$: M, 466.2674.

Rhodium(I)-Catalyzed Hydrosilylation of 4a with Trichlorosilane. Butenyne **4a** (100 mg, 0.37 mmol) was allowed to react with HSiCl_3 (0.18 ml, 1.8 mmol) and $\text{RhCl}(\text{PPh}_3)_3$ (3.0 mg, 3.2×10^{-3} mmol) at 100°C for 12 h. After addition of THF (10 ml) and 3 M MeMgBr in diethyl ether (4 ml, 12 mmol) at 0°C, the reaction mixture was stirred for 2 h at room temperature and then worked up. Purification by preparative TLC gave **2a** (58 mg, 46% yield).

In a similar manner **4a**, **4b**, and **4c** were allowed to react with HSiCl_3 , HSiCl_2Me , and HSiClMe_2 to afford **3a**, **3e**, and **3f**, respectively.

Rhodium(I)-Catalyzed Hydrosilylation of 4a with Trimethylsilane. Butenyne **4a** (100 mg, 0.37 mmol) was allowed to react with HSiMe_3 (0.31 g, 4.2 mmol) and $\text{RhCl}(\text{PPh}_3)_3$ (10 mg, 0.01 mmol) at 100°C for 13 h. The reaction mixture was filtered through a short silica gel column. Purification by preparative TLC gave **2a** (121 mg, 96% yield).

In a similar manner **4a**, **4b**, and **4c** were allowed to react with HSiMe_3 or HSiEt_3 using $\text{RhCl}(\text{PPh}_3)_3$ or $\text{Pt}(\text{PPh}_3)_4$ catalyst, to yield **3a**, **3d**, **3e**, **3f**, or **3g**.

(E)-1,2-Bis(trimethylsilyl)-1-buten-3-yne (5a). Potassium fluoride (5.7 g, 98 mmol) was added to a methanol (20 ml) solution of (*E*)-1,2,4-tris(trimethylsilyl)-1-buten-3-yne (**4a**) (2.6 mg, 9.8 mmol). The mixture was heated to reflux for 5 h and then concentrated. The residue was dissolved in hexane (50 ml) and washed with water (30 ml $\times$ 3). Concentration followed by distillation gave **5a** (1.05 g, 55% yield) as a colorless oil, bp 105°C/18 Torr, R_f 0.6 (hexane). ^1H NMR (CDCl_3) δ = 0.14 (s, 9H), 0.18 (s, 9H), 3.44 (d, J = 0.9 Hz, 1H), 6.62 (d, J = 0.9 Hz, 1H); ^{13}C NMR (CDCl_3) δ = -2.03 (septuple q, J = 2 and 120 Hz, SiCH_3), -0.85 (mq, J = 120 Hz, SiCH_3), 85.5 (dd, J = 20 and 48 Hz, $\underline{\text{C}}(3)$), 8.65 (d, J = 249 Hz, $\underline{\text{C}}(4)$), 114.4 (m, $\underline{\text{C}}(2)$), 156.5 (md, J = 136 Hz, $\underline{\text{C}}(1)$); IR (neat) 3325, 2980, 2900, 2080, 1245, 840, 760, 690, 610, 450 cm^{-1} ; MS m/z (rel intensity) 196 (M^+ , 12), 181 (37), 83 (15), 73 (100), 45 (14), 28 (14). Found: C, 60.84; H, 10.21%. Calcd for $\text{C}_{10}\text{H}_{20}\text{Si}_2$: C, 61.14; H, 10.26%.

(E)-2-Dimethylphenylsilyl-1-trimethylsilyl-1-buten-3-yne (5c). In a similar manner **4c** (7.1 g, 21.5 mmol) was allowed to react with KF (12.5 g, 215 mmol) for 7 h at 70°C. Workup and purification by column chromatography (hexane, R_f 0.4) gave **5c** (4.65 g, 87% yield). Mp 38°C. ^1H NMR (CDCl_3) δ = 0.19 (s, 9H), 0.45 (s, 6H), 3.44 (s, 1H), 6.66 (s, 1H), 7.12–7.68 (m, 5H); ^{13}C NMR (CDCl_3) δ = -3.03 (qq, J = 2 and 120 Hz, SiCH_3), -1.15 (mq, J = 119 Hz, SiCH_3), 85.5 (dd, J = 20 and 48 Hz, $\underline{\text{C}}(3)$), 86.9 (dd, J = 1 and 249 Hz, $\underline{\text{C}}(4)$), 127.8 (md, J = 167 Hz, Ph), 129.3 (dtd, J = 1, 7, and 159 Hz, Ph), 134 (md, J = 167 Hz, Ph), 137.1 (m, Ph), 142.0 (octet, J = 2 Hz, $\underline{\text{C}}(2)$), 158.8 (md, J = 138 Hz, $\underline{\text{C}}(1)$); IR (neat) 3325, 2980, 2900, 2080, 1245, 840, 760, 690, 610, 450 cm^{-1} ; MS m/z (rel intensity) 196 (M^+ , 12), 181 (37), 83 (15), 73 (100), 45 (14), 28 (14). Found: C, 69.61; H, 8.77%. Calcd for $\text{C}_{15}\text{H}_{22}\text{Si}_2$: C, 69.69; H, 8.58%.

(E,E)-1,2,4-Tris(trimethylsilyl)-1,3-butadiene (6a). Butenyne **5a** (107 mg, 0.54 mmol) was allowed to react with HSiCl_2Me (613 mg, 5.3 mmol) and $\text{Pt}(\text{PPh}_3)_4$ (7.0 mg, 5.6×10^{-3} mmol) at 100°C for 2 h. After addition of THF (15 ml) and 3 M MeMgBr in diethyl ether (5 ml, 15 mmol) at -20°C, the reaction mixture was stirred for 2 h at room temperature. Workup and purification by preparative TLC gave **6a** (47 mg, 32% yield) as a colorless oil, bp 80°C/0.3 Torr, R_f 0.64 (hexane). ^1H NMR (CDCl_3) δ = 0.09 (s, 9H), 0.13 (s, 9H), 0.14 (s, 9H), 5.80 (d, J = 19.2 Hz, 1H), 6.17 (d, J = 1.1 Hz, 1H), 6.88 (dd, J = 1.1 and 19.2 Hz, 1H); ^{13}C NMR (CDCl_3) δ = -1.18 (mq, J = 118 Hz, SiCH_3), 0.37 (septuple q, J = 2 and 119 Hz, SiCH_3), 0.57 (mq, J = 119 Hz, SiCH_3), 132.8 (md, J = 134 Hz, $\underline{\text{C}}(1)$ or $\underline{\text{C}}(4)$), 145.9 (md, J = 136 Hz, $\underline{\text{C}}(1)$ or $\underline{\text{C}}(4)$), 147.9 (ddd, J = 7, 17 and 148 Hz, $\underline{\text{C}}(3)$), 162.9 (md, J = 7 Hz, $\underline{\text{C}}(2)$); IR (neat) 2970, 1730, 1590, 1410, 1385, 1250, 1090, 985, 840, 750, 695, 620 cm^{-1} ; MS m/z (rel intensity) 270 (M^+ , 8), 182 (13), 167 (50), 73 (100), 45 (18). Found: m/z 270.1654. Calcd for $\text{C}_{13}\text{H}_{30}\text{Si}_3$: M, 270.1654.

Similar reaction of **5a** or **5c** with HSiCl_3 , HSiCl_2Me , HSiClMe_2 , HSiMe_3 , or HSiEt_3 using H_2PtCl_6 , $\text{RhCl}(\text{PPh}_3)_3$ or $\text{Pt}(\text{PPh}_3)_4$ as a catalyst afforded **6d**, **6f**, **7a**, **8a**, **8d**, **8g**, or **9a**.

(E,E)-4-Triethylsilyl-1,2-bis(trimethylsilyl)-1,2-butadiene (6d). A colorless oil, bp 90°C/0.4 Torr, R_f 0.7 (hexane). ^1H NMR (CDCl_3) δ = 0.138 (s, 9H), 0.143 (s, 9H), 0.51–0.64 (m, 6H), 0.95 (t, J = 7.8 Hz, 9H), 5.77 (d, J = 19.3 Hz, 1H), 6.17 (d, J = 0.9 Hz, 1H), 6.90 (dd, J = 0.9 and 19.3 Hz, 1H); ^{13}C NMR (CDCl_3) δ = -0.33 (septuple q, J = 2 and 119 Hz, SiCH_3), 0.56 (mq, J = 119 Hz, SiCH_3), 3.59 (mt, J = 117 Hz, SiCH_2CH_3), 7.52 (tq, J = 5 and 126 Hz, SiCH_2CH_3), 129.5 (md, J = 133 Hz, $\underline{\text{C}}(1)$ or $\underline{\text{C}}(4)$), 145.7 (md, J = 136 Hz, $\underline{\text{C}}(1)$ or $\underline{\text{C}}(4)$), 149.0 (ddd, J = 7, 16 and 149 Hz, $\underline{\text{C}}(3)$), 163.0 (m, $\underline{\text{C}}(2)$); IR (neat) 2950, 2875, 1730, 1580, 1460, 1420, 1380, 1250, 1090, 1010, 980, 840, 750, 720, 680 cm^{-1} ; MS m/z (rel intensity) 312 (M^+ , 4), 167 (35), 115 (21), 87 (54), 73 (100), 59 (33), 45 (22). Found: m/z 312.2122. Calcd for $\text{C}_{16}\text{H}_{36}\text{Si}_3$: M, 312.2122.

(E,E)-2-Dimethylphenylsilyl-1,4-bis(trimethylsilyl)-1,3-butadiene (6f). A colorless oil, bp 115°C/0.3 Torr, R_f 0.5 (hexane). ^1H NMR (CDCl_3) δ = 0.02 (s, 9H), 0.16 (s, 9H), 0.39 (s, 6H), 5.70 (d, J = 19.2 Hz, 1H), 6.28 (d, J = 1.0 Hz, 1H), 6.89 (dd, J = 1.0 and 19.2 Hz, 1H), 7.30–7.35 (m, 3H), 7.46–7.53 (m, 2H); ^{13}C NMR (CDCl_3) δ = -1.56 (qq, J = 2 and 119 Hz, $\text{Si(CH}_3\text{)Ph}$), 1.26 (mq, J = 119 Hz, SiCH_3), 0.60 (mq, J = 119 Hz, SiCH_3), 127.7 (md, J = 158 Hz, Ph), 128.8 (td, J = 7 and 159 Hz, Ph), 134.09 (md, J = 158 Hz, Ph), 134.14 (md, J = 135 Hz, $\underline{\text{C}}(1)$ or $\underline{\text{C}}(4)$), 139.2 (m, Ph), 147.3 (ddd, J = 7, 17 and 149 Hz, $\underline{\text{C}}(3)$), 148.2 (md, J = 136 Hz, $\underline{\text{C}}(1)$ or $\underline{\text{C}}(4)$), 160.6 (m, $\underline{\text{C}}(2)$); IR (neat) 2950, 2900, 1720, 1580, 1520, 1430, 1380, 1250, 1110, 1090, 980, 870, 860, 830, 730, 700, 620, 470 cm^{-1} ; MS m/z (rel intensity) 332 (M^+ , 4), 244 (25), 229 (20), 167 (31), 135 (74), 73 (100), 45 (15). Found: m/z 332.1820. Calcd for $\text{C}_{18}\text{H}_{32}\text{Si}_3$: M, 332.1813.

(E,E)-1,2,4-Tris(trimethylsilyl)-1,3-butadiene (7a). A colorless oil, bp 85°C/0.3 Torr, R_f 0.67 (hexane). ^1H NMR (CDCl_3) δ = 0.07 (s, 9H), 0.17 (s, 9H), 0.18 (s, 9H), 5.32 (d, J = 14.4 Hz, 1H), 6.40 (d, J = 1.7 Hz, 1H), 7.08 (dd, J = 1.7 and 14.4 Hz, 1H); ^{13}C NMR (CDCl_3) δ = 0.54 (mq, J = 119 Hz, SiCH_3), 0.91 (mq, J = 119 Hz, SiCH_3), 1.10 (septuple q, J = 2 and 119 Hz, SiCH_3), 127.1 (md, J = 133 Hz, $\underline{\text{C}}(1)$ or $\underline{\text{C}}(4)$), 145.6 (md, J = 128 Hz, $\underline{\text{C}}(1)$ or $\underline{\text{C}}(4)$), 156.7 (ddd, J = 6, 13 and 150 Hz, $\underline{\text{C}}(3)$), 163.6 (m, $\underline{\text{C}}(2)$); IR (neat) 2960, 2900, 1725, 1575, 1410, 1250, 1010, 980, 875, 840, 750, 695, 660, 630, 500 cm^{-1} ; MS

m/z (rel intensity) 270 (M^+ , 8), 182 (13), 167 (50), 73 (100), 45 (18). Found: m/z 270.1650. Calcd for $C_{13}H_{30}Si_3$: M , 270.1654.

(E)-1,2,3-Tris(trimethylsilyl)-1,3-butadiene (8a). A colorless oil, bp 125°C/0.8 Torr, R_f 0.70 (hexane). 1H NMR ($CDCl_3$) δ =0.04 (s, 9H), 0.05 (s, 9H), 0.13 (s, 9H), 5.27 (s, 2H), 5.88 (s, 1H); ^{13}C NMR ($CDCl_3$) δ =-0.63 (septuple q, J =2 and 119 Hz, $SiCH_3$), 0.04 (septuple q, J =2 and 119 Hz, $SiCH_3$), 1.14 (mq, J =119 Hz, $SiCH_3$), 123.1 (dt, J =2 and 133 Hz, $C(4)$), 138.7 (md, J =133 Hz, $C(1)$), 158.3 (m, $C(3)$), 170.1 (m, $C(2)$), IR (neat) 2950, 2900, 1545, 1400, 1240, 980, 910, 830, 750, 680, 630, 610, 490, 450 cm^{-1} ; MS m/z (rel intensity) 270 (M^+ , 10), 182 (17), 167 (38), 73 (100), 45 (19). Found: m/z 270.1645. Calcd for $C_{13}H_{30}Si_3$: M , 270.1654.

(E)-3-Triethylsilyl-1,2-bis(trimethylsilyl)-1,3-butadiene (8d). A colorless oil, bp 85°C/0.4 Torr, R_f 0.80 (hexane). 1H NMR ($CDCl_3$) δ =0.05 (s, 9H), 0.06 (s, 9H), 0.57-0.74 (m, 6H), 0.98 (t, J =7.8 Hz, 9H), 5.21 (d, J =3.6 Hz, 1H), 5.29 (d, J =3.6 Hz, 1H), 5.86 (s, 1H); ^{13}C NMR ($CDCl_3$) δ =-0.40 (septuple q, J =2 and 119 Hz, $SiCH_3$), 1.21 (mq, J =119 Hz, $SiCH_3$), 4.32 (mt, J =118 Hz, $SiCH_2CH_3$), 7.80 (tq, J =5 and 125 Hz, $SiCH_2CH_3$), 124.2 (ddd, J =2, 155, and 157 Hz, $C(4)$), 139.1 (decouple d, J =2 and 133 Hz, $C(1)$), 155.6 (md, J =12 Hz, $C(3)$), 170.5 (m, $C(2)$); IR (neat) 2975, 1730, 1250, 1010, 970, 910, 840, 750, 730, 685, 665 cm^{-1} ; MS m/z (rel intensity) 312 (M^+ , 14), 255 (28), 167 (43), 115 (50), 87 (100), 73 (93), 59 (59). Found: m/z 312.2104. Calcd for $C_{16}H_{36}Si_3$: M , 312.2122.

(E)-2-Dimethylphenylsilyl-3-triethylsilyl-1-trimethylsilyl-1,3-butadiene (8g). A colorless oil, R_f 0.70 (hexane). 1H NMR ($CDCl_3$) δ =0.04 (s, 9H), 0.33 (s, 6H), 0.4-0.7 (m, 6H), 0.87 (t, J =7.3 Hz, 9H), 5.19 (d, J =3.5 Hz, 1H), 5.29 (d, J =3.5 Hz, 1H), 5.97 (s, 1H), 7.25-7.4 (m, 3H), 7.4-7.6 (m, 2H); IR (neat) 2950, 1245, 1110, 1010, 910, 830, 720, 695 cm^{-1} .

1,2,3,4-Tetrakis(trimethylsilyl)-2-butene (9a). A colorless oil, bp 105°C/0.3 Torr, R_f 0.72 (hexane). 1H NMR ($CDCl_3$) δ =0.03 (s, 18H), 0.17 (s, 18H), 1.85 (s, 4H); ^{13}C NMR ($CDCl_3$) δ =0.43 (septuple q, J =2 and 119 Hz, $SiCH_3$), 2.88 (septuple q, J =2 and 119 Hz, $SiCH_3$), 26.83 (mt, J =119 Hz, $C(1)$), 147.0 (m, $C(2)$); IR (neat) 2970, 2900, 1570, 1500, 1410, 1250, 1200, 1150, 1030, 840, 750, 690, 640, 560, 440 cm^{-1} ; MS m/z (rel intensity) 344 (M^+ , 5), 168 (38), 73 (100), 45 (11). Found: m/z 344.2197. Calcd for $C_{16}H_{40}Si_4$: M , 344.2208.

(E,E)-2-Methyl-3-triethylsilyl-1,4-bis(trimethylsilyl)-1,3-butadiene (11a). In a sealed tube were placed (*E*)-2-methyl-1,4-bis(trimethylsilyl)-1-buten-3-yne (**10a**) (95 mg, 0.45 mmol), $HSiEt_3$ (0.23 ml, 1.4 mmol), and H_2PtCl_6 (0.1 M 2-propanol solution, 10 μ l, 1×10^{-3} mmol), and the resulting mixture was heated at 90°C for 0.5 h under an argon atmosphere. Workup and purification by preparative TLC gave **11a** (104 mg, 71% yield) as a colorless oil, R_f 0.9 (hexane). 1H NMR ($CDCl_3$) δ =0.07 (s, 9H), 0.12 (s, 9H), 0.59 (q, J =7.9 Hz, 6H), 0.92 (t, J =7.9 Hz, 9H), 1.83 (d, J =0.8 Hz, 3H), 4.96 (q, J =0.8 Hz, 1H), 5.80 (s, 1H); ^{13}C NMR ($CDCl_3$) δ =-0.00 (mq, J =119 Hz, $SiCH_3$), 0.64 (mq, J =119 Hz, $SiCH_3$), 3.32 (mt, J =119 Hz, $SiCH_2CH_3$), 7.41 (tq, J =5 and 126 Hz, $SiCH_2CH_3$), 23.0 (dq, J =12.5 and 126 Hz, $C(2)-CH_3$), 123.17 (md, J =134 Hz, $C(1)$), 140.0 (md, J =133 Hz, $C(4)$), 159.33 (qd, J =7 and 21 Hz, $C(2)$), 169.3 (m, $C(3)$); IR (neat) 2980, 1600, 1550, 1460, 1420, 1250, 1115, 1105, 930, 840 cm^{-1} ; MS m/z (rel intensity) 326 (M^+ , 5), 297 (22), 195 (26), 181 (60), 115 (31), 87 (52), 73 (100), 59 (40). Found: m/z 326.2250. Calcd for $C_{17}H_{38}Si_3$: M , 326.2279.

(1Z,3E)-1-Bromo-2-methyl-3-triethylsilyl-1,4-bis(trimethyl-

silyl)-1,3-butadiene (11b). In a similar way (*E*)-1-bromo-2-methyl-1,4-bis(trimethylsilyl)-1-buten-3-yne (**10b**) (328 mg, 1.6 mmol) was allowed to react with $HSiEt_3$ (0.5 ml, 3.1 mmol), and H_2PtCl_6 (0.1 M, 2-propanol solution, 30 μ l, 3×10^{-3} mmol), and gave **11b** (476 mg, 93% yield) as a colorless oil, R_f 0.75 (hexane). 1H NMR ($CDCl_3$) δ =0.1 (s, 9H), 0.3 (s, 9H), 0.45-0.83 (m, 6H), 0.83-1.15 (m, 9H), 1.83 (s, 3H), 5.92 (s, 1H); ^{13}C NMR ($CDCl_3$) δ =-0.30 (mq, J =120 Hz, $SiCH_3$), 0.75 (mq, J =120 Hz, $SiCH_3$), 4.04 (mt, J =118 Hz, $SiCH_2CH_3$), 7.52 (tq, J =5 and 126 Hz, $SiCH_2CH_3$), 24.0 (q, J =128 Hz, $C(3)-CH_3$), 119.5 (m, $C(3)$), 140.8 (md, J =132 Hz, $C(4)$), 153.9 (qd, J =6 and 13.5 Hz, $C(2)$), 166.0 (m, $C(1)$); IR (neat) 2970, 1590, 1460, 1415, 1250, 1070, 1020, 850, 840, 735, 690 cm^{-1} ; MS m/z (rel intensity) 377 (M^+ +2-Et, 8), 375 (M^+ -Et, 8), 223 (35), 195 (72), 125 (30), 111 (28), 97 (80), 87 (47), 73 (100), 59 (41). Found: m/z 404.1372 and 406.1388. Calcd for $C_{17}H_{37}BrSi_3$: M , 404.1385 and $M+2$, 406.1365.

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