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Chloroplatinic acid catalyzed cyclization of silanes bearing pendant acetylenic groups

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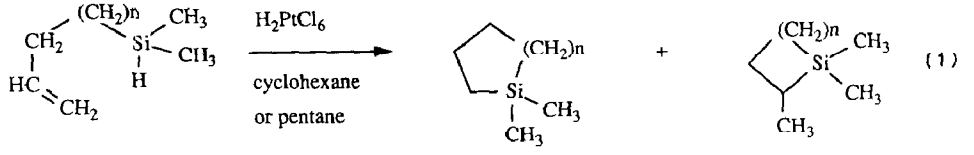
Abstract

Chloroplatinic acid catalyzed, intramolecular hydrosilylation of acetylenes of structure $HMe_2Si[CH_2]_nSiMe_2C{\equiv}CR$ (R = H or Ph, $n = 2$ or 3) proceeds via *syn* addition of the Si–H group to the carbon triple bond to give, predominantly, cyclic products having an exocyclic rather than an endocyclic double bond. When $n = 1$ (R = H), only recovered starting material is obtained. Closure of (4-hexynyl)dimethylsilane can also be effected to produce, exclusively, 1,1-dimethyl-2-methylene-1-silacyclopentane.

Introduction

The regioselectivity of platinum catalyzed, intramolecular hydrosilylation of alkenylsilanes of structure $HMe_2Si[CH_2]_nCH_2CH{=}CH_2$ (**1**) as a function of chain length n was studied by Swisher and Chen (eq. 1) [1]. For $n = 1$ the 1,1-dimethyl-1-silacycloalkane (**2**) was the predominant regioisomer formed, whereas the 1,1,2-trimethylsilacycloalkane (**3**) was strongly favored for $n = 2$ [1,2]. Only a slight preference (52–54/48–46) for formation of the smaller ring silacycloalkane **3** was observed for alkenylsilanes **1** of $n = 3$ and 4. We report results of a similar study of chloroplatinic acid catalyzed cyclization of a series of alkynylsilanes, in which the



(1)

1 (n = 1-5) **2** **3**

reacting acetylenic and hydrosilane groups are separated by two or more centers. Few examples of alkynylsilane intramolecular intramolecular cyclization have been previously reported [3,4]. Cyclization of propargyloxyhydrosilanes apparently occurs

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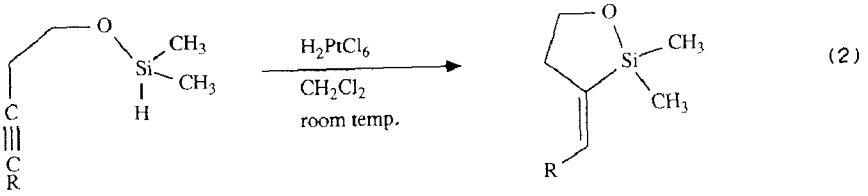
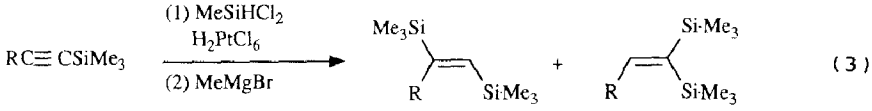
to form 4-methylene-1-sila-2-oxetanes [3]. Just recently, Tamao and coworkers [4] have shown that comparable cyclization of the hydrodimethylsilylethers of homopropargyl alcohols proceeds regio- and stereoselectively, as shown in eq. 2.



(2)

$R = n\text{-}C_6H_{13}$

In the case of acyclic alkynes the regioselectivity and stereoselectivity of transition metal catalyzed hydrosilylation has been extensively studied [3,5–9]. With few exceptions [8–11], hydrosilylation of acyclic alkynes leads to incorporation of silicon, preferentially at the terminal carbon of the alkyne, producing the *trans* alkene of net *syn* addition of the SiH group. While the regioselectivity probably reflects steric interactions, inductive effects can be important, as well as mesomeric



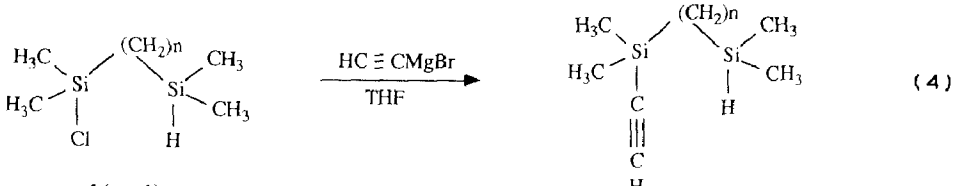
(3)

$R = n\text{-}C_6H_{13}$ 96% trace

effects in which conjugating electron withdrawing groups can significantly perturb product ratios towards the 1,1-disubstituted alkene product, whereas strong electron donating groups exercise an opposite effect [11,12]. With an unsymmetrical alkyne substituted by alkyl and trimethylsilyl groups the 1,2-bis(trimethylsilyl)alkene product is obtained in hydrosilylation (eq. 3) [13].

Results

The synthesis of acetylenic reactants **7–9** ($n = 1$–3) in Table 1 followed a procedure reported previously [14] involving reaction of ethynylmagnesium bromide with chlorosilanes **4–6** ($n = 1$–3) having the structure $ClMe_2Si[CH_2]_nSiMe_2H$ (eq. 4). The phenylacetylenes **12** and **13** ($n = 2$, 3) were obtained from reaction of



4 (n = 1)
5 (n = 2)
6 (n = 3)

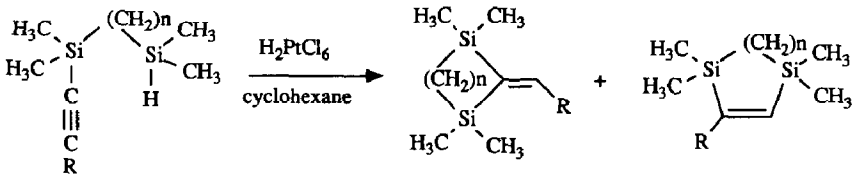
7 (n = 1)
8 (n = 2)
9 (n = 3)

(4)

phenylethynylmagnesium bromide with bis(chlorodimethylsilyl)alkanes $ClMe_2Si[CH_2]_nSiMe_2Cl$ ($n = 2$, 3), followed by lithium aluminum hydride reduction of chlorosilanes **10** and **11** (eq. 5). The substitution reaction of iodopropyldimethyl-

Table 1

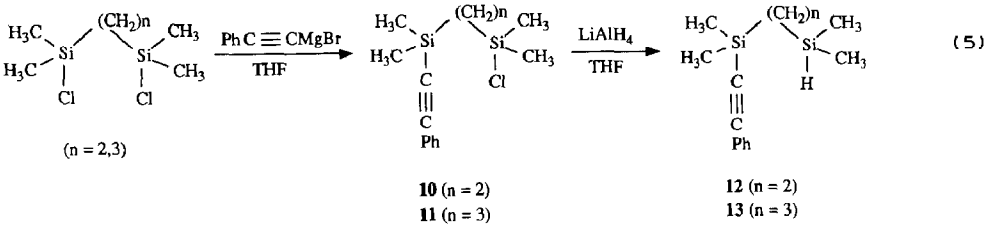
Hydrosilylation of acetylenic disilanes



exocyclic endocyclic

Reactant	Relative yield (area %) [a]		Isolated yield (%) [b]
	exocyclic	endocyclic	
7 ($n = 1$, R = H)	**16** [c]	**17** [c]	0
8 ($n = 2$, R = H)	**18** (100)	**19** [c]	58
9 ($n = 3$, R = H)	**20** (79.3)	**21** (20.7)	71
12 ($n = 2$, R = Ph)	**22** (100)	**23** [c]	42
13 ($n = 3$, R = Ph)	**24** (100)	**25** [c]	60

[a] Determined by GC. analysis. [b] Total products. [c] Not detected.



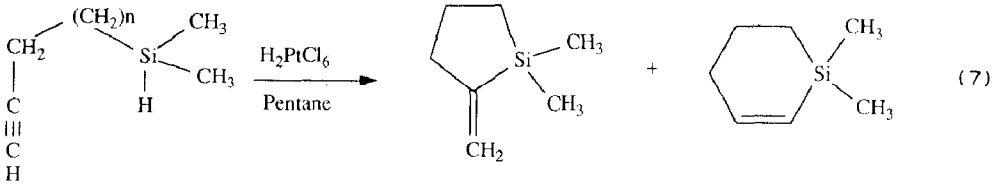
(n = 2,3) **10** (n = 2) **11** (n = 3) **12** (n = 2) **13** (n = 3) (5)

silane (14) with the ethylenediamine complex of lithium acetylide in dimethyl sulfoxide gave (4-pentynyl)dimethylsilane (**15**) (eq. 6). Detailed procedures and physical and spectroscopic data are given in the Experimental section.

14 **15** (6)

Intramolecular hydrosilylation of disilalkynes **7**–**9**, **12**, and **13** under high dilution conditions in refluxing cyclohexane was effected with chloroplatinic acid as catalyst in the isolated yields reported in Table 1. Product yields for the closure of monosilylacetylene **15** utilizing pentane as the solvent are given in eq. 7. The reactions were followed by GC–MS analyses and by ^{1}H NMR spectroscopy, noting the disappearance of the Si–H and/or C≡CH proton absorptions of reactants and the appearance of the olefinic protons of the disilacycloalkenes which were formed. Relative yields of the regioisomeric alkene products were determined by GC analysis and checked by ^{1}H NMR (Table 1). Controls were performed to insure that carbosilanes **20** and **21** did not interconvert under the reaction conditions. GC–MS

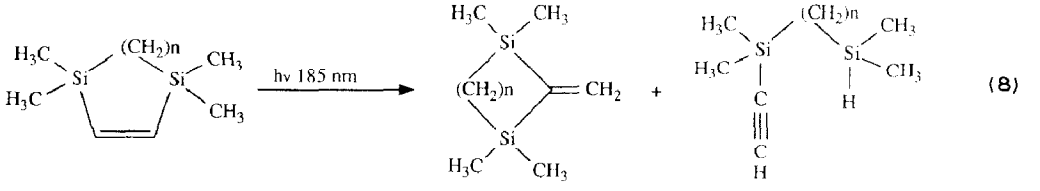
analyses showed only the presence of reactant and no products of isomerization in refluxing cyclohexane in the presence of catalyst.



15 (n = 2) **26** (69%) **27** (0%)

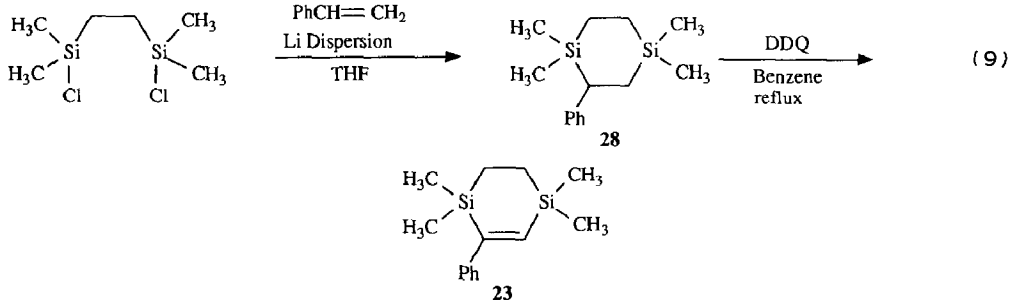
Only in the case of the alkynylmonosilane (**15**) were significant amounts of high molecular weight products detected by capillary GC–MS analysis. Of these, one exhibited a molecular ion at *m/z* 252 and thus appeared to be dimeric. It constituted 11% of the total products by peak area, while another 13% corresponded to products still higher in molecular weight, which appeared at longer retention times. On the other hand, dimerization or oligomerization was not observed by GC–MS analysis in the case of disilylacetylene (**7**), although such reactivity might have been expected given the failure of **7** to undergo intramolecular hydrosilylation under the conditions used for the hydrosilylations of Table 1. The starting material was in fact recovered in 90% yield and checked by ^{1}H NMR analysis.

Except for products **22**, **24**, and **26**, which were only characterized spectroscopically, product structures were elucidated by comparison of spectral data to independently synthesized samples. Disilacyclopentene (**17**) [15,16], disilacyclohexene (**19**) [17], and methylenedisilacyclopentane (**18**) [17] were known compounds that were prepared in previous studies [14,18] by flash vacuum pyrolyses followed by preparative GC isolation. Bis(triphenylphosphine)palladium(II) chloride catalyzed addition of acetylene and phenylacetylene to 1,1,2,2-tetramethyl-1,2-disilacyclopentane gave disilacycloheptenes (**21** and **25**) [19]. Methylenedisilacycloalkenes (**16** and **20**) were obtained from 185 nm photolyses of **17** [14] and **21** [20], respectively (eq. 8), followed by preparative GC to separate alkynes **7** and **9**, which were also produced



17 (n = 1) **16** **7**
21 (n = 3) **20** **9**

in both cases. 2-Phenyl-1,4-disilacyclohexene (**23**) was synthesized in two steps, as shown in eq. 9. The first step gave 2-phenyl-1,1,4,4-tetramethyl-1,4-disilacyclohexane (**28**) in 50% yield by reaction of styrene and chlorodimethyl[2-(chlorodimethylsilyl)ethyl]silane with lithium dispersion in THF. Disilacycloalkene (**23**) was then obtained in 22% yield after DDQ oxidation and medium pressure liquid chromatography to remove a small amount of an isomeric impurity. The first step of the



(9)

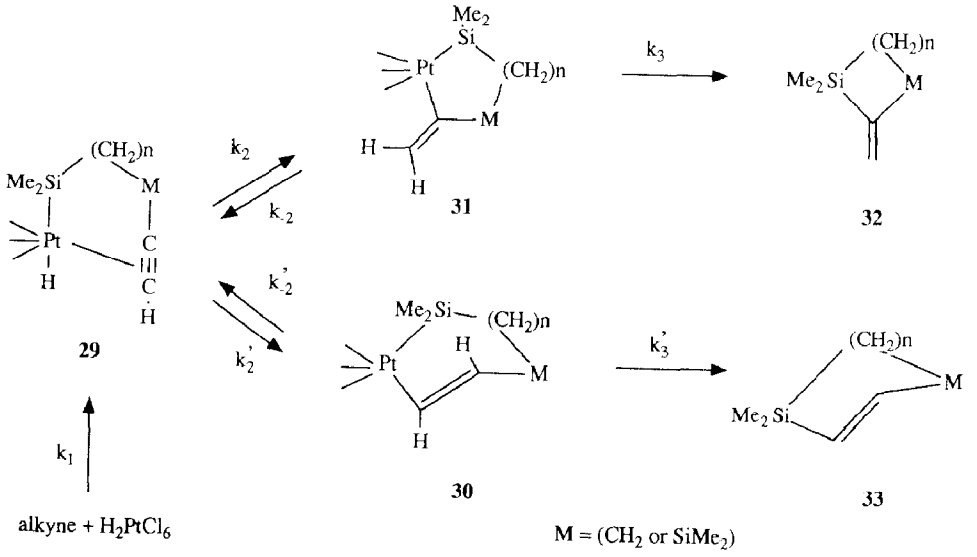
sequence is reminiscent of the reaction of chlorotrimethylsilane and styrene [21] with lithium wire in THF at 40 °C to produce 1,2-bis(trimethylsilyl)-1-phenylethane.

The spectroscopic characterization of products **22**, **24**, and **26** was unambiguous. In contrast to the 2-phenyldisilacycloalkenes (**23** and **25**), which exhibited ^{1}H NMR absorptions for an olefinic proton at δ 6.59 and 6.44, respectively, the corresponding proton singlets of **22** and **24** were farther downfield at δ 7.69 and 7.71, respectively. The ^{13}C NMR spectrum was instrumental in assigning the structure of methylenesilacyclopentane (**26**) and showed the presence of an olefinic quaternary carbon and an olefinic methylene group. Furthermore, the ^{1}H NMR data clearly indicated that the compound was not **27** [22].

Discussion

The results of Table 1 and eq. 7 indicate a strong preference for α addition to form methylenesilacycloalkanes for chain lengths $n = 2$ and 3, in contrast to the more typical β regioselectivity of platinum catalyzed hydrosilylation of acyclic alkenes and alkynes [3,5–9,13]. Significant yields of endocyclic regioisomer are obtained only in the case of alkynylsilane (**9**) ($n = 3$). While there is an apparent parallel between preferential formation of 1,1,2-trimethyl-1-silacyclopentane (**3**, $n = 2$) from 4-pentenyldimethylsilane (**1**, $n = 2$) in the Swisher and Chen study [1] and the formation of products **18**, **22**, and **26** from alkynes **8**, **12**, and **15**, the low regioselectivity for cyclization of 5- and 6-alkenyldimethylsilanes (**1**, $n = 3$, 4) (eq. 1) is not mirrored by alkynes **9** and **13**, which maintain high *exo* regioselectivity in intramolecular hydrosilylation. Moreover, 1,1-dimethylsilacyclopentane (**2**, $n = 1$) is produced in good yield from 3-butenyldimethylsilane (**1**, $n = 1$) [1], whereas only unreacted starting material is recovered in the attempted closure of its alkyne counterpart, **7**, which gave no detectable **16** or **17**.

The regioselectivity of chloroplatinic acid catalyzed intramolecular hydrosilylation of alkynes can be discussed in the context of the mechanism of Scheme 1, which is analogous to the mechanism proposed [1,3,5,6] for hydrosilylation of alkenes. Except for 3-butenyldimethylsilane (**1**, $n = 1$), in which ring strain determines product ratios in the final product forming step, the regiospecificities observed for 4, 5, and 6-alkenylsilanes (**1**, $n = 2$–4) are consistent with preferential formation of the less strained, intermediate σ complex of the alkene with platinum, although this preference is only pronounced in the case of the 4-pentenylsilane (**1**, $n = 2$) [1]. Strain energy considerations suggest that the alkyne regioselectivities for $n = 2$ and 3 may reflect the relative stabilities of σ complexes **30** and **31**. Complex **31** is likely to be the more stable intermediate, since the *syn* stereoselectivity



Scheme 1

generally observed in platinum catalyzed alkyne hydrosilylations (vide supra) requires incorporating a *trans* double bond into a medium ring in the case of **30**.

The relative stability of intermediates **30** and **31** is not the only factor to consider as potentially controlling the ratios of **32**/**33** for various values of n. If the final step is rate determining the rate constants k_3 and k_3' assume importance in the rate expression for the product ratio (eq. 10). Imposition of the *syn* stereochemical constraint for intramolecular SiH addition to alkynes would require the endocyclic regioisomers to be formed with *trans* stereochemistry at the double bond, suggesting that $k_3 > k_3'$. This is in keeping with the conclusion that in acyclic alkene [23] and alkyne [6] hydrosilylations silicon is transferred to carbon in the final step with retention of configuration at carbon.

$$\frac{[\mathbf{32}]}{[\mathbf{33}]} = \frac{k_2/k_{-2}}{k_2'/k_{-2}'} \times \frac{k_3}{k_3'} \tag{10}$$

Actually, it is not known for certain whether the final step is rate determining in alkyne hydrosilylation. Kinetic parameters [24] have been determined for the hydrosilylation of 1-hexyne. The small loss in entropy of activation (-2 e.u.) is consistent with minimal reorganization of the reacting species in attaining the transition state, which has been construed [24] as π complexation of the alkyne and platinum species (shown as intermediate **29** in Scheme 1) prior to the rate-determining step.

Experimental

Spectra were recorded with the following spectrometers: Varian EM 360L (60 MHz, ^{1}H NMR), JEOL FX60Q (^{13}C), Analect FX 6200 (FTIR). A Hewlett Packard 5890 GC equipped with a HP 5970 mass selective detector and a 0.25 mm $\times$ 30 m DB-1 capillary column, programmed at 35 °C for 3 min and then 250 °C at 10 °C min^{-1}, was used for GC–MS analyses, which were performed at 70 eV.

Preparative GC separations were performed on a Gow-Mac (model 580) gas chromatograph with He as carrier gas at 30 ml min^{-1} flow rate on a 9 ft × 1/4 in 15% didecylphthalate column (column A) on 80–100 mesh Chromosorb P-AW. A Varian 1400 gas chromatograph equipped with flame ionization detector, an HP 3390A electronic integrating recorder, and a 12 ft × 1/8 in 10% didecylphthalate on 100–120 mesh Supelcoport column (column B) was used for analytical separations. Nitrogen was the carrier gas at a flow rate of 30 ml min^{-1}.

Preparative liquid chromatographic separations were effected by medium pressure liquid chromatography (MPLC) with a 82 cm × 2.5 cm column of 40–60 μm silica gel (EM, grade 60, 230–400 mesh) and hexanes as eluant. The column was connected via a septum injector to a Gilson Model 302 pump equipped with a 100 ml min^{-1} capacity head, and the eluant was passed through an ISCO UA-5 UV detector.

Cyclohexane (Aldrich) and pentane (EMS, Omnisolv) were used as solvents in hydrosilylations.

[2-(Dimethylsilyl)methyl]ethynyldimethylsilane (7). Silane **7** was prepared from chloro[(dimethylsilyl)methyl]dimethylsilane (**4**) as described previously [14].

[2-(Dimethylsilyl)ethyl]ethynyldimethylsilane (8). A slurry of 1.75 g (46.1 mmol) of lithium aluminum hydride in 100 ml of ether was added dropwise with stirring to a solution of 36.2 g (169 mmol) of chloro[2-(chlorodimethylsilyl)ethyl]dimethylsilane (Hüls-Petrarch) in 150 ml of ether while refluxing under nitrogen. After 3 h additional reflux, the mixture was cooled and filtered. Distillation of the solvent and most of the low boiling component, [2-(dimethylsilyl)ethyl]dimethylsilane, which was a byproduct formed through overreduction, gave a colorless liquid. The above hydride reduction was repeated twice more on the same scale and the crude product from each run was combined with the first batch of monochlorosilane. The combined crude product was then distilled using a 6 in Vigreux column to obtain 18.6 g of product, b.p. 84–85 °C (70 mmHg). The product contained 14.9 g (83.2 mmol) of [2-(chlorodimethylsilyl)ethyl]dimethylsilane (**5**) by GC–MS and ^1H NMR analysis. The yield of monochlorosilane **5** from the combined preparations was thus 16%. The contaminants were the bisreduction product and a smaller amount of unreacted starting material. The GC–MS data of the monochlorosilane were as follows: *m/z* (relative intensity) 180 (M^+, 1.5), 167 (10), 165 (26), 137 (10), 95 (15), 93 (38), 86 (100), 78 (7), 73 (18), 71 (26), 67 (6), 65 (20), 63 (13), 59 (85), 58 (65), 57 (7), 55 (5), 45 (12), 43 (33).

Commercial acetylene was passed through a 100 cm × 2 cm column of activated alumina and bubbled into 100 ml of dry THF (successively distilled from sodium and lithium aluminium hydride) at 5 °C for 40 min. A solution of 120 mmol of ethylmagnesium bromide in 80 ml of dry THF was then added dropwise with mechanical stirring while continuing the acetylene flow. After 30 min of additional stirring and bubbling of acetylene, 18.6 g of the 77% pure chloro[2-(dimethylsilyl)ethyl]dimethylsilane (**5**) containing 83.2 mmol of monochlorosilane (vide supra) in 40 ml of THF was added dropwise under nitrogen. After 2 h the acetylene flow was discontinued and the reaction mixture was warmed to room temperature and stirred overnight. Excess Grignard was destroyed by slow addition of 100 ml of cold water at 5 °C. The organic fraction was extracted with 100 ml of ether and the aqueous layer was washed twice with 25 ml of ether. The combined ether extracts were then washed five times with 75 ml of water, once with saturated

sodium chloride solution, and dried over anhydrous sodium sulfate. After removing the solvent by distillation through a 6 in Vigreux column, 10.0 g (71% yield based on 83.2 mmol of **5**) of alkyne **8** was obtained by distillation, b.p. 89–91°C (102 mmHg). The spectral data were as follows: ^{1}H NMR (CCl_4) δ 0.12 (d, J 4 Hz, 6H, methyl), 0.19 (s, 6H, methyl), 0.59–0.62 (m, 4H, methylene), 2.25 (s, 1H, alkynyl), 3.69–4.05 (br m, 1H, SiH); IR (CCl_4) 3.08, 3.35, 3.40, 3.41, 3.48, 4.29, 4.70, 4.76, 4.91, 6.41, 7.11, 7.91, 8.03, 8.77, 8.83, 9.40, 9.51, 11.02, 11.59 μm; GC–MS retention time 8.09 min, m/z (relative intensity) 170 (M^+ 0.60), 169 (2.1), 155 (62), 142 (8.2), 127 (60), 116 (4.7), 111 (5), 97 (17), 95 (21), 83 (100), 73 (37), 69 (12), 59 (61), 53 (17), 43 (52). Anal. Found: C, 56.08; H, 10.50. $C_8H_{18}Si_2$ calcd.: C, 56.37; H, 10.65%. High resolution MS–EI for $C_8H_{18}Si_2$: Calcd. 170.0947; Found, 170.0933.

*Ethynyldimethyl[3-(dimethylsilyl)propyl]silane (**9**).* A portion of 40 g (194 mmol) of 3-chloropropyldimethylsilane, prepared by the literature method [25,26], in 200 ml of dry THF was added to 14.3 g (588 mmol) of preheated granular magnesium under nitrogen, and the reaction was initiated with a crystal of iodine. The remainder of the chloropropyldimethylsilane was added while heating to reflux, and the reaction mixture was refluxed an additional 1 h after addition was complete. The mixture was then transferred via cannula to an addition funnel connected to a 1 l three-necked flask and added dropwise with stirring to a refluxing solution of 75.3 g (588 mmol) of dichlorodimethylsilane in 120 ml of THF under nitrogen. After refluxing overnight the reaction mixture was cooled and suction filtered followed by distillation of the THF. Benzene was added to precipitate additional salts, which were removed by suction filtration. Distillation through a 6 in Vigreux column gave 22.4 g (39.0% yield) of chlorodimethyl[3-(dimethylsilyl)propyl]silane (**6**), b.p. 76–78°C (25 mmHg), which was used without further purification. The spectral data were as follows: ^{1}H NMR (CCl_4) δ 0.09 (d, J 4 Hz, 6H, methyl), 0.39 (s, 6H, methyl), 0.65–0.99 (m, 4H, methylene), 1.25–1.70 (m, 2H, methylene), 3.65–4.05 (m, 1H, SiH); GC–MS retention time 10.3 min, m/z (relative intensity) 194 (M^+, 0.82), 183 (3.8), 181 (11.67), 179 (28.77), 151 (2.62), 135 (1.6), 134 (1.27), 121 (1.39), 119 (2.19), 100 (30), 99 (12.4), 95 (18.25), 93 (49.6), 85 (50.4), 72 (70), 65 (23), 59 (100), 43 (51).

Alkyne **9**, b.p. 61–64°C (15 mmHg), was prepared in 76% yield (16 g, 87.0 mmol) from 22.4 g (115 mmol) of chlorodimethyl[3-(dimethylsilyl)propyl]silane (**6**) by the procedure for the synthesis of alkyne **8** (vide supra). The spectral data were as follows: ^{1}H NMR (CCl_4) δ 0.07 (d, J 4 Hz, 6H, methyl), 0.15 (s, 6H, methyl), 0.47–0.54 (m, 4H, methylene), 1.2–1.69 (m, 2H, methylene), 2.20 (s, 1H, alkynyl), 3.64–4.04 (br m, 1H, SiH); IR (CCl_4), 3.03, 3.37, 3.43, 3.47, 4.73, 4.9, 7.07, 7.48, 8.0, 8.73, 9.54, 10.88, 11.28, 11.84, 12.47, 13.4 μm. GC–MS retention time 9.87 min, m/z (relative intensity), no parent, 183 (0.22), 169 (19), 155 (1.47), 143 (11.5), 141 (35), 127 (5), 125 (4), 109 (20), 99 (8.2), 95 (4.0), 85 (18.5), 84 (14), 83 (100), 73 (40), 69 (12), 67 (19.6), 59 (80), 58 (17), 55 (25), 53 (17), 45 (15), 43 (71). Anal. Found C, 58.44; H, 10.95. $C_9H_{20}Si_2$ calcd.: C, 58.61; H, 10.93%.

*Dimethyl(phenylethynyl)[2-(dimethylsilyl)ethyl]silane (**12**).* A solution of 0.11 mol of ethylmagnesium bromide in 80 ml of dry THF was prepared under nitrogen from 3.30 g (0.136 mol) of magnesium and 12.3 g (8.68 ml, 0.113 mol) of bromoethane. A solution of 13.0 g (14.0 ml, 0.127 mol) phenylacetylene in 40 ml dry THF was added dropwise with stirring followed by 30 min of refluxing. The phenylacetylide reaction mixture was then added dropwise, under nitrogen, to a stirred solution of 21.4 g

(0.0995 mol) chloro[2-(chlorodimethylsilyl)ethyl]dimethylsilane (Hüls-Petrarch) over a 1.5 h period, followed by heating at 40–50 °C overnight. After cooling and suction filtration, the mixture was concentrated in vacuo and 50 ml of ether was added to the residue. Suction filtration and concentration gave 29 g of an oil which was distilled through a 6 in Vigreux column to obtain 12.8 g (45.8% yield) of chlorodimethyl(2-[dimethyl(phenylethynyl)silyl]ethyl)silane (**10**), b.p. 99–101 °C (0.28 mmHg). The spectral data were as follows: ^{1}H NMR (CCl_4) δ 0.26 (s, 6H, methyl), 0.46 (s, 6H, methyl), 0.74–0.92 (m, 4H, methylene), 7.19–7.59 (m, 5H, phenyl); GS–MS retention time 16.26 min, *m/z* (relative intensity) 280 (M^+, 3.5), 265 (23), 160 (24), 159 (100), 145 (11), 129 (15), 105 (11), 93 (12), 86 (12), 43 (17).

A solution of 10.7 g (38.2 mmol) of chlorosilane **10** in 20 ml of dry THF was added dropwise with stirring to 1.45 g (38.2 mmol) of lithium aluminum hydride in 50 ml of dry THF. The mixture was refluxed 4 h and then cooled in an ice-bath, followed by dropwise addition of 50 ml of wet ether and 75 ml of water. The phases were separated and the aqueous phase was extracted with 50 ml ether. The combined organic phases were washed five times with 50 ml water, once with saturated sodium chloride, followed by drying over anhydrous sodium sulfate. Concentration in vacuo afforded 8.6 g of crude product, which was subjected to short path distillation, collecting 5.48 g (58% yield) of silane (**12**), b.p. 79–81 °C (0.28 mmHg). The distilled product was contaminated by ca. 1–2% of isomeric impurities flanking the product peak according to GS–MS analysis. The impurity at the earlier GC retention time was collected by MPLC in the first peak eluted and identified by NMR as 1,1,4,4-tetramethyl-2-phenyl-1,4-disilacyclohex-2-ene (**23**) (vide infra). The impurity at the later GC retention time was cut from the tail of the silane **12** liquid chromatographic fraction, but was obtained in too small an amount to be identified. The spectral data of **12** were as follows: ^{1}H NMR (CCl_4) δ 0.17 (d, *J* 2 Hz, 6H, methyl), 0.27 (s, 6H, methyl), 0.69–0.79 (m, 4H, methylene), 3.75–4.19 (br m, 1H, SiH), 7.19–7.62 (m, 5H, phenyl); IR (CCl_4) 3.37, 3.43, 3.47, 4.63, 4.74, 6.70, 7.11, 7.99, 8.19, 8.80, 9.47, 11.30, 12.0, 12.40, 12.58, 12.70, 12.91, 14.49 μm. GC–MS retention time 14.50 min, *m/z* (relative intensity) 246 (M^+, 2), 231 (71), 218 (13), 203 (48), 187 (7), 173 (15), 171 (7), 159 (100), 145 (25), 143 (9), 135 (19), 131 (10), 129 (20), 105 (17), 103 (4), 85 (5), 73 (16), 59 (21), 53 (5), 43 (23). Anal. Found: C, 68.07; H, 8.85. $C_{14}H_{22}Si_2$ calcd.: C, 68.22; H, 9.00%.

*Dimethyl(phenylethynyl)[3-(dimethylsilyl)propyl]silane (**13**).* A solution of 0.050 mol of ethylmagnesium bromide in 40 ml of dry THF was prepared under nitrogen from 1.5 g (0.062 mol) of magnesium and 5.4 g (3.8 ml, 0.050 mol) of bromoethane. A solution of 5.1 g (5.5 ml, 0.050 mol) of phenylacetylene in 20 ml dry THF was added dropwise with stirring over a 20 min period followed by 30 min of refluxing. The phenylacetylide reaction mixture was then added dropwise, under nitrogen, to a stirred solution of 10 g (0.044 mol) of chloro[3-(chlorodimethylsilyl)propyl] dimethylsilane [27] in 50 ml of dry THF over a 45 min period, followed by heating at 40–50 °C overnight. After cooling and suction filtration, the mixture was concentrated in vacuo and 50 ml of ether was added to the residue. Suction filtration and concentration gave 9.8 g of crude chlorodimethyl(3-[dimethyl(phenylethynyl)silyl]propyl)silane (**11**) as an oil which was dissolved in 20 ml of dry THF. The THF solution of crude chlorosilane **11** was added dropwise to 2.5 g (0.66 mol) of lithium aluminum hydride in 50 ml of dry THF over a period of 20 min. The mixture was refluxed 5 h and then stirred overnight without heating. The cold

reaction mixture was hydrolyzed by dropwise addition of 100 ml of water. Two phases appeared after hydrolysis, which were separated. The aqueous phase was extracted with 100 ml of ether, and the combined organic phases were washed four times with 50 ml of water, once with 50 ml of saturated sodium chloride, followed by drying over anhydrous sodium sulfate. Concentration in vacuo afforded 8.1 g of crude product, which was subjected to short path distillation, collecting 2.2 g (19% yield) of ^{1}H NMR pure silane **13**, b.p. 77–80 °C (0.2 mmHg). The spectral data were as follows: ^{1}H NMR (CCl_4) δ 0.18 (d, J 4 Hz, 6H, methyl), 0.33 (s, 6H, methyl), 0.65–1.03 (m, 4H, methylene), 1.33–1.90 (m, 2H, methylene), 3.97 (nonet, J 4 Hz, 1H, SiH), 7.2–7.7 (m, 5H, aromatic); IR (CCl_4) 3.25, 3.26, 3.30, 3.36, 3.41, 3.47, 4.60, 4.72, 6.25, 6.73, 6.94, 7.04, 7.46, 8.00, 8.20, 8.73, 9.34, 9.76, 10.87, 11.24, 11.76, 14.39 μm; GC–MS m/z (relative intensity) 260 (M^+, 1.7), 259 (2.8), 245 (5.1), 217 (20.3), 203 (16.6), 160 (20.2), 159 (100), 145 (41.0), 143 (17.7), 135 (40.7), 131 (12.7), 129 (18.2), 105 (20.7), 73 (25.8), 72 (9.5), 59 (55.9), 45 (11.8), 43 (50.0). MS–EI for $C_{15}H_{24}Si_2$, calcd. 260.1417, found 260.1420.

*3-Iodopropyldimethylsilane (**14**).* The procedure differed from the previous method [25] in using 2-butanone [28] instead of acetone as the solvent. To a refluxing, turbid solution of 46.9 g (312 mmol) of anhydrous sodium iodide in 300 ml 2-butanone was added dropwise 33 g (242 mmol) of 3-chloropropyldimethylsilane [25,26] with stirring under nitrogen. The reaction mixture was refluxed for additional 12 h, cooled, and then filtered to remove the sodium chloride. The filtrate was diluted with 250 ml of pentane and the mixture was washed six times with 200 ml of water, once with dilute sodium bicarbonate, water, saturated sodium chloride solution, and dried over anhydrous sodium sulfate. After distilling the pentane, 44.1 g (79.7% yield) of 3-iodopropyldimethylsilane (**14**) was collected at 82–84 °C (35 mmHg) (lit. [25] b.p. 179–181 °C) using a 18 in Vigreux column. The ^{1}H NMR spectrum was identical to that reported previously [25]. IR (CCl_4) 3.37, 3.4, 4.72, 7.98, 8.3, 10.7, 10.96, 11.2, 11.95, 12.3, 13.5, 18.85 μm; GC–MS retention time 9.65 min, m/z (relative intensity) no parent ion, 227 (0.2), 213 (19), 185 (17), 171 (30), 127 (7), 101 (5), 73 (18), 59 (100), 43 (33).

*Dimethyl(4-pentynyl)silane (**15**).* A slurry of 22.6 g (231 mmol) of lithium acetylide ethylenediamine complex (Aldrich) in 110 ml of dimethyl sulfoxide was prepared under nitrogen. After stirring for 45 min 43.2 g (189 mmol) of 3-iodopropyldimethylsilane (**14**) (vide supra) was added dropwise with stirring, maintaining the temperature between 5–8 °C with an ice-water bath. Stirring was continued for another 2 h at room temperature. The reaction mixture was then treated with 150 ml of pentane followed by slow addition of 200 ml of water. The organic layer was separated and the aqueous layer was washed twice with 100 ml of pentane. The organic fractions were then combined, washed six times with 200 ml of water, once with saturated sodium chloride solution and dried over anhydrous sodium sulfate. Distillation through an 18 in Vigreux column gave 3.76 g (15.8% yield) of alkyne **15**, b.p. 43–45 °C (40 mmHg). The spectral data were as follows: ^{1}H NMR (CCl_4) δ 0.09 (d, J 4 Hz, 6H, methyl), 0.52–0.89 (m, 2H, methylene), 1.35–1.85 (m, 2H, methylene), 1.80 (s, 1H, acetylenic), 2.07–2.35 (m, 2H, methylene), 3.69–4.05 (m, 1H, SiH); IR (CCl_4) 3.0, 3.37, 3.4, 4.7, 7.0, 8.0, 11, 11.95, 12.7, 13.5, 15.8 μm; GC–MS retention time 5.6 min, m/z (relative intensity) 126 (M^+, 0.24), 125 (1.1), 111 (30), 98 (14), 87 (21), 83 (43), 69 (7), 67 (7), 59 (100), 55 (9), 43 (44). Anal. Found: C, 66.54; H, 11.24. $C_7H_{14}Si$ calcd.: C, 66.58; H, 11.18%.

Cyclization of [2-(dimethylsilyl)ethyl]ethynyldimethylsilane (8). To a refluxing solution of 0.5 ml of 0.2 *M* chloroplatinic acid in isopropyl alcohol and 1.0 l of cyclohexane under nitrogen was added, dropwise with stirring, 6.46 g (38.0 mmol) of alkyne **8** in 400 ml of cyclohexane. The addition took 6 h. After an additional 2 h of reflux the reaction mixture was analyzed by GC–MS and then stirred overnight at room temperature, followed by GC–MS analysis and filtration. The solvent was removed by distillation through a 6 in Vigreux column and the crude product was analyzed by ^{1}H NMR and GC–MS. Further distillation gave 3.76 g (58.2% yield) of NMR pure 1,1,3,3-tetramethyl-2-methylene-1,3-disilacyclopentane (**18**), b.p. 101–102°C (154 mmHg). The spectral data of the product matched a sample previously prepared by a different method in this laboratory [18], as originally reported by Barton and coworkers [17]. The spectral data were as follows: ^{1}H NMR (CCl_4) δ 0.07 (s, 12H, methyl), 0.76 (s, 4H, methylene), 6.34 (s, 2H, vinyl); IR (CCl_4): 3.34, 3.38, 3.42, 6.27, 6.97, 7.0, 8.0, 8.87, 9.74, 10.39, 11.77, 12.25, 12.53, 12.87, 13.0, 13.26 μm. GC–MS retention time 7.9 min, *m/z* (relative intensity), 170 (M^+, 34), 155 (70), 142 (22), 129 (17), 127 (100), 116 (7), 97 (15), 95 (20), 85 (18), 83 (24), 73 (62), 69 (13), 59 (48), 55 (15), 45 (26), 43 (68).

Cyclization of ethynyldimethyl[3-(dimethylsilyl)propyl]silane (9). The cyclization procedure described for alkyne **8** was used with 0.7 ml of 0.2 *M* chloroplatinic acid in isopropyl alcohol as catalyst and 1.25 l of cyclohexane as solvent, to which was added a solution of 9.17 g (49.8 mmol) of alkyne **9** in 400 ml of cyclohexane. GC–MS of the crude reaction mixture showed no starting material and two isomeric products with retention times 10.6 min (product **A**, the major peak) and 11.1 min (minor product **B**); on column B at 110°C products **A** and **B** appeared at 13.4 min and 16.6 min retention times, respectively, in a ratio of areas of 3.84/1. The crude product mixture was distilled to give 6.5 g (71% yield), b.p. 75–78°C (20 mmHg). The area ratio of the distilled product mixture was 2.89/1, indicating enrichment of the higher boiling product. Products **A** and **B** were isolated by preparative GC on column A at 130°C and identified by ^{1}H NMR, IR and GC–MS. Product **A** was found to be 1,1,3,3-tetramethyl-2-methylene-1,3-disilacyclohexane (**20**), which was obtained as one of the products of photolysis of disilacycloheptene **21** (eq. 8) [20]. Comparison of spectral data to an authentic sample and GC–MS coinjection led to the assignment of product **B** as 1,1,4,4-tetramethyl-1,4-disilacyclohept-2-ene (**21**) [19]. The spectral data for methylenedisilacyclohexane (**20**) were as follows: ^{1}H NMR (CCl_4) δ 0.04 (s, 12H, methyl), 0.62 (t, *J* 6 Hz, 4H, methylene), 1.64–2.07 (m, 2H, methylene), 6.17 (s, 2H, vinyl); IR (CCl_4) 3.38, 3.42, 3.45, 3.50, 8.00, 8.77, 10.4, 10.7, 11, 11.9, 12.2, 12.6, 12.65, 12.7, 13.2, 13.35, 13.5 μm. GC–MS retention time 10.67 min, *m/z* (relative intensity) 184 (M^+, 19), 169 (100), 156 (3), 141 (88), 127 (13), 113 (7), 109 (24), 99 (14), 97 (9), 85 (27), 73 (92), 59 (65), 55 (16), 53 (9), 45 (32), 43 (76). Anal. Found: C, 58.54; H, 10.92. $C_9H_{20}Si_2$ calcd.: C, 58.61; H, 10.93%.

Cyclization of dimethyl(phenylethynyl)[2-(dimethylsilyl)ethyl]silane (12). A solution of 2.82 g (11.5 mmol) of alkyne **12** (vide supra) in 120 ml of cyclohexane was added over a 4 h period to a solution of 161 μl of 0.20 *M* chloroplatinic acid in isopropyl alcohol in 320 ml of cyclohexane while refluxing under nitrogen. The reaction mixture was then refluxed 3 h and stirred at room temperature an additional 12 h, whereupon capillary GC–MS analysis showed only one peak corresponding to benzylidenedisilacyclopentane **22**. No trace of 1,1,4,4-tetramethyl-

2-phenyl-1,4-disilacyclohex-2-ene (**23**) (vide infra) was detected. Removal of the solvent in vacuo gave 2.08 g of a dark brown residue, which was subjected to short path distillation to give 1.18 g (42% yield), b.p. 74–77 °C (0.28 mmHg). The spectral data were as follows: ^{1}H NMR (CCl_4) δ 0.19 (s, 6H, methyl), 0.22 (s, 6H, methyl), 0.82–0.92 (m, 4H, methylene), 7.32 (m, 5H, phenyl), 7.69 (s, 1H, vinyl); IR (CCl_4) 3.26, 3.30, 3.38, 3.44, 6.29, 6.38, 6.69, 6.91, 7.09, 7.99, 9.30, 9.73, 10.78, 11.25, 11.73, 12.17, 12.25, 12.87, 13.04, 13.40, 14.38, 14.93 μm; GC–MS retention time 14.34 min, *m/z* (relative intensity) 246 (M^+, 17) 231 (15), 219 (25), 218 (100), 204 (21), 203 (98), 177 (5), 159 (21), 145 (39), 135 (10), 131 (7), 129 (7), 105 (13), 101 (7), 85 (10), 73 (60), 59 (23), 58 (9), 45 (10), 43 (28). Anal. Found: C, 68.03; H, 8.84. $C_{14}H_{22}Si_2$ calcd.: C, 68.22; H, 9.00%.

*Cyclization of dimethyl(phenylethynyl)[3-(dimethylsilyl)propyl]silane (**13**).* A solution of 1.85 g (7.12 mmol) of the alkyne (vide supra) in 75 ml of cyclohexane was added over a 6 h period to a solution of 100 μl of 0.20 *M* chloroplatinic acid in isopropyl alcohol in 200 ml of cyclohexane while refluxing under nitrogen. The reaction mixture was then refluxed 3 h and stirred at room temperature an additional 12 h, whereupon capillary GC–MS analysis showed a 7.3/1 ratio of benzylidenedisilacyclohexane (**24**): starting alkyne at 13.05 min and 12.80 min, respectively. No trace of 1,1,4,4-tetramethyl-2-phenyl-1,4-disilacyclohept-2-ene (**25**), which was synthesized by the literature method [19], was detected at 12.89 min retention time. Removal of the solvent in vacuo gave 1.91 g of a dark brown residue, which was subjected to MPLC on a 80 cm × 2.5 cm column of 40–60 μm silica gel eluting with hexanes at a flow rate of 12 ml min^{-1} to obtain 1.12 g (60.5% yield) of NMR and GC–MS pure benzylidenedisilacyclohexane (**24**). Final purification of the benzylidenedisilacyclohexane (**24**) was effected by molecular distillation at a bath temperature of 75 °C (0.2 mmHg). The spectral data were as follows: ^{1}H NMR (CCl_4) δ 0.067 (s, 6H, methyl), 0.32 (s, 6H, methyl), 0.52–1.02 (m, 4H, methylene), 1.75–2.25 (m, 2H, methylene), 7.28 (s, 5H, aromatic), 7.71 (s, 1H, vinyl); IR (CCl_4) 3.24, 3.26, 3.31, 3.38, 3.45, 3.50, 6.31, 6.41, 6.71, 6.94, 7.08, 7.97, 9.01, 9.66, 10.58, 11.05, 11.98, 14.28, 15.62, 16.13 μm; GC–MS *m/z* (relative intensity) 260 (M^+, 36.4), 245 (26.3), 218 (27.6), 217 (32.0), 204 (19.7), 203 (81.8), 187 (10.0), 161 (10.3), 160 (17.3), 159 (48.4), 148 (57.9), 146 (11.1), 145 (60.3), 143 (15.4), 135 (34.7), 131 (14.7), 129 (13.4), 115 (10.2), 105 (23.8), 101 (10.6), 99 (20.5), 85 (11.3), 83 (12.4), 73 (79.6), 72 (15.5), 71 (10.5), 59 (100), 58 (20.4), 55 (11.3), 53 (12.2), 45 (35.0), 43 (94.0. MS–EI for $C_{15}H_{24}Si_2$, calcd. 260.1417, found, 260.1417.

*Cyclization of dimethyl(4-pentynyl)silane (**15**).* The cyclization procedure described for alkyne **8** was used with 0.28 ml of 0.20 *M* chloroplatinic acid in isopropyl alcohol as catalyst, and 216 ml pentane as the solvent, to which was added a solution of 2.5 g (19.8 mmol) of alkyne **15**. The reaction was monitored by GC–MS and the crude product was analyzed by ^{1}H NMR spectroscopy. Distillation of the crude product gave 1.67 g (66.8% yield) of NMR pure 1,1-dimethyl-2-methylenesilacyclopentane (**26**), b.p. 46–48 °C (60 mmHg), which was subjected to preparative GC on column A at 110 °C to obtain a sample for elemental analysis. The spectral data of the analytically pure sample were as follows: ^{1}H NMR (CCl_4) δ 0.07 (s, 6H, methyl), 0.59–0.82 (t, *J* 7 Hz, 2H, methylene), 1.45–1.90 (m, 2H, methylene), 2.1–2.44 (m, 2H, methylene), 5.19–5.32 (m, 1H, vinyl), 5.57–5.70 (m, 1H, vinyl); ^{13}C NMR ($CDCl_3$) δ −2.20, 13.82, 24.99, 38.95, 120.25, 155.50. IR (CCl_4) 3.29, 3.39, 3.45, 3.50, 3.54, 6.98, 7.06, 8.0, 9.02, 9.26, 9.9, 10.42, 10.9, 11.55,

11.8, 12, 12.18, 12.41, 12.57, 13.4, 13.5 μm. GC–MS retention time 5.06 min, *m/z* (relative intensity) 126 (M^+, 14), 111 (53), 109 (18), 98 (100), 85 (23), 83 (74), 72 (31), 67 (13), 59 (46) 55 (17), 53 (16), 45 (16), 43 (77). Anal. Found: C, 66.53; H, 10.98. $C_7H_{14}Si$ calcd.: C, 66.58; H, 11.18%.

Attempted cyclization of (dimethylsilylmethyl)ethynyldimethylsilane (7). The cyclization procedure described for alkyne **8** was used with 0.9 ml of 0.20 *M* chloroplatinic acid in isopropyl alcohol as catalyst and 1.25 l of cyclohexane as solvent, to which was added 10 g (64 mmol) of alkyne **7** in 400 ml of cyclohexane over a 5 h period at reflux. The refluxing reaction mixture was monitored by GC–MS analysis for 20 h, during which time no components other than starting material were detected. After distilling the solvent, 9.0 g (90% yield) of the starting material was recovered by distillation at 70–72 °C (95 mmHg). The spectral data of the distillate matched unreacted alkyne **7** and no products were detected, including 1,1,3,3-tetramethyl-1,3-disilacyclopentene (**17**) [14,16,29] or 1,1,3,3-tetramethyl-2-methylene-1,3-disilacyclobutane (**16**) [14,29].

Synthesis of 1,1,4,4-tetramethyl-2-phenyl-1,4-disilacyclohexane (28). A solution of 36.7 g (0.171 mol) of chloro[2-(chlorodimethylsilyl)ethyl]dimethylsilane (Hüls-Petrarch) and 20.0 ml (18.2 g, 0.174 mol) of styrene in 150 ml of dry THF was added dropwise to 11 g (0.40 mol lithium) of lithium dispersion in mineral oil with stirring under nitrogen. Periodic cooling was needed to control the exothermic reaction. The reaction mixture was stirred at 30 °C overnight. The reaction mixture was hydrolysed by dropwise addition of 100 ml of water, 100 ml of ether was added, and the aqueous phase was separated and extracted with 50 ml of ether. The combined ether phases were washed five times with 75 ml water, once with saturated sodium chloride, and dried over anhydrous sodium sulfate. Concentration in vacuo gave 48 g of crude product which was distilled through a 6 in Vigreux to obtain 21.3 g (50.2% yield) of the 2-phenyl-1,4-disilacyclohexane (**28**), b.p. 71–74 °C (0.28 mmHg), as a colorless liquid. The spectral data were as follows: ^{1}H NMR (CCl_4) δ 0.07 (s, 6H, methyl), 0.13 (s, 3H, methyl), 0.19 (s, 3H, methyl), 0.49–1.32 (m, 6H, methylene), 2.16–2.46 (m, 1H, methine), 6.96–7.29 (m, 5H, phenyl); IR (CCl_4) 3.24, 3.26, 3.30, 3.38, 3.45, 3.57, 6.25, 6.69, 6.89, 7.08, 7.99, 9.44, 11.98, 12.42, 12.57, 12.65, 12.73, 13.04, 13.12, 14.33 μm; GC–MS retention time 14.59 min, *m/z* (relative intensity) 248 (M^+, 33), 233 (8), 219 (8), 191 (5), 163 (7), 161 (19), 147 (36), 145 (27), 144 (28), 135 (18), 129 (7), 121 (9), 116 (100), 105 (7), 101 (9), 85 (14), 78 (4), 73 (40), 59 (47), 53 (3), 43 (33). Anal. Found: C, 67.64; H, 9.82. $C_{14}H_{24}Si_2$ calcd.: C, 67.66; H, 9.73%.

Synthesis of 1,1,4,4-tetramethyl-2-phenyl-1,4-disilacyclohex-2-ene (23). A mixture of 6.69 g (0.0270 mol) of 1,1,4,4-tetramethyl-2-phenyl-1,4-disilacyclohexane (**28**) and 9.45 g (0.0416 mol) of dichlorodicyanoquinone in benzene was refluxed under argon with stirring for 1.75 h, at which point GC–MS analysis indicated complete consumption of reactant to form the disilacyclohexene as well as minor amounts (ca. 14% by peak area) of an isomeric impurity. After cooling in an ice bath 200 ml of hexane was added followed by suction filtration through a pad of celite. The filtrate was concentrated in vacuo to give a purple oil, which was subjected to short path distillation to obtain 1.89 g of crude product, b.p. 74–77 °C (0.2 mmHg). The crude distillate was chromatographed on a 1 m × 2.5 cm column of 40–60 μm silica gel, eluting with hexane. The peak centered at 35 min retention time was collected, cutting the leading and trailing edges, to obtain 1.49 g (22% yield) of NMR pure

disilacyclohexene **23**. An analytically pure sample was obtained by molecular distillation. The spectral data were as follows: ^{1}H NMR (CCl_4) δ 0.16 (s, 12H, methyl), 0.96 (s, 4H, methylene), 6.59 (s, 1H, vinyl), 7.19 (s, 5H, phenyl); IR (CCl_4) 3.25, 3.26, 3.38, 3.44, 6.72, 6.94, 7.09, 7.99, 9.51, 9.68, 10.83, 11.48, 11.66, 11.98, 12.37, 12.49, 12.57, 12.65, 12.73, 12.82, 13.04, 13.12, 13.25, 13.40, 13.77, 14.33 μm; GC–MS retention time 14.10 min, *m/z* (relative intensity) 246 (M^+, 54), 231 (100), 218 (22), 203 (83), 173 (22), 159 (20), 146 (31), 135 (44), 121 (10), 116 (9), 105 (15), 101 (7), 85 (13), 73 (53), 59 (37), 58 (13), 45 (16), 43 (40). Anal.Found: C, 68.19; H, 9.02. $C_{14}H_{22}Si_2$ calcd.: C, 68.21; H, 8.99%.

*Control. Stability of 1,1,3,3-tetramethyl-2-methylene-1,3-disilacyclohexane (**20**) and 1,1,4,4-Tetramethyl-1,4-disilacycloheptene (**21**) under hydrosilylation conditions.* A mixture of 50 mg (0.272 mmol) of methylenedisilacyclohexane **20**, nonane as internal standard, and 3.8 μL of 0.2 *M* chloroplatinic acid in isopropyl alcohol in 7 ml of cyclohexane was refluxed with stirring under nitrogen for 20 h while monitoring by GC–MS. A duplicate experiment was performed with disilacycloheptene **21**. No isomerization of **20** to give **21** or the converse was detected in either run, and no other products were found. In each case only the reactant alkene and nonane were present in the reaction mixtures at the end of the runs.

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