Platinum-Catalyzed Hydrosilylation of 2,2-Divinyladamantane

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Only partial dihydrosilylation of 2,2-divinyladamantane with triethylsilane (Et_3SiH) mediated by a platinum(II) complex is observed in refluxing benzene after several days, while monosilylation occurs at room temperature within minutes. Steric effects may explain the longer reaction times. On the other hand, 2,2-divinyladamantane reacts with bis(hydrosilane) species in the presence of Zeise's dimer $[Pt_2Cl_4(CH_2CH_2)_2]$ to give disilacyclic compounds (double terminal addition) via an intramolecular process or acyclic compounds via an intermolecular process in high yields depending on nature, structure, and type of disilane used. Using *o*-bis(dimethylsilyl)benzene as the disilane, an unprecedented partial hydrogenation of 2,2-divinyladamantane catalyzed by a mononuclear platinum catalyst is observed.

Introduction

The surface of silicon has been studied intensively for many years because of its crucial importance in modern technology. At the beginning of the 90's, textured diamond films were grown on silicon(100) substrates by microwave plasma CVD (chemical vapor deposition) using a bias-enhanced nucleation process.[1−3] In 1993 oriented diamond films were deposited on silicon(100).[4] An enhanced nucleation density has been observed when the substrate is first fingerprinted (hydrocarbon residues), scratched with diamond powder,[5] or coated with layers of C−H,[6] glassy carbon,[7] carbon fibers, graphite, or carbon clusters (C_{60}, C_{70}).[8]

Olah suggested that hydrocarbon cage molecules[9] such as adamantane[10] could be possible embryos for diamond nuclei formation in the gas phase, and Linford and Chidsey recently reported the first example of a densely packed, stable organic monolayer covalently bonded directly to the silicon surface.[11,12]

Combination of these findings led us to the design of an adamantane derivative capable of being covalently attached 2-fold to the silicon surface. Molecular modeling revealed a chain length of two carbon atoms for fixing an adamantane molecule via two tethers to two adjacent silicon atoms of a (111) surface with minimal steric strain. The conclusions from these observations converged to 2,2-divinyladamantane (DVA) as target molecule (Figure 1).

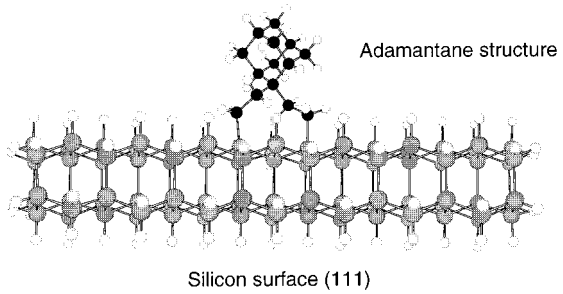

Figure 1. Molecular modeling of 2,2-divinyladamantane on a silicon(111) surface.

Consequently, starting from the 2-adamantanone, we synthesized this new derivative of adamantane containing two alkene chains in 6 steps and 38% overall yield,[13] with the aim of using it as a substrate for the nucleation and growth of oriented diamond on a silicon(111) surface.[14]

In our ongoing exploration of effective methods to prepare adamantane derivatives capable of being covalently attached to the silicon surface, we have investigated the hydrosilylation reaction of 2,2-divinyladamantane (**1**) with various types of silanes and different transition metal complexes, to get a better understanding of the mechanism of Si−adamantane derivative bond formation. Hydrosilylation of carbon−carbon multiple bonds has been studied extensively for the last half

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century.[15,16] In the early years, reactions were performed under free-radical conditions,[13,17−19] i.e. with ultraviolet light or organic peroxides as initiators. The choice of substrates, however, was limited to silanes,[20] such as Cl_3SiH and $MeCl_2SiH$, and to C−C multiple bonds substituted mostly with alkyls. The discovery that transition metals and their complexes catalyze hydrosilylation[21−24] superseded largely the other procedures.[16,21] Platinum catalysts, especially chloroplatinic acid, have become the most commonly used catalysts. Nickel, palladium, cobalt, rhodium, iridium, iron, ruthenium, and osmium catalysts have also been developed.[16,21,25] Some of these, irrespective of the nature of the silane, are very efficient and can be used for the simple preparation of a desired product as well as for asymmetric hydrosilylation. The role of transition metal catalysts represents a key aspect of all the studies.[15,21]

The results of our investigations with 2,2-divinyladamantane (**1**) as substrate will add to this collected knowledge and reveal that product distributions vary considerably depending on the silane structure, the catalyst, and the specific reaction conditions.

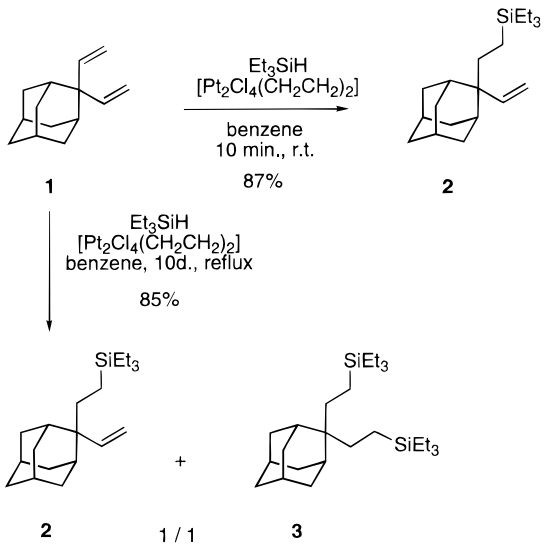
Results and Discussion

Reactions of 2,2-Divinyladamantane with Et_3SiH. Hydrosilylation of 2,2-divinyladamantane (DVA) (**1**) with triethylsilane (Et_3SiH) was studied first as a standard reaction to determine the role of the transition metal complexes.

At room temperature the reaction of DVA with Et_3SiH in benzene and in the presence of Zeise's dimer $[Pt_2Cl_4(CH_2CH_2)_2]$ as catalyst gave the corresponding monosilylated compound **2** in almost quantitative yield (Scheme 1). The reaction was complete within 1 h as revealed by GC monitoring (Table 1, entry 1). A small amount (3%) of dihydrosilylated product **3** was noted under these conditions, which is in contrast to the prolonged heating needed (10 days) in refluxing benzene with the same catalyst to reach higher conversions (45%, Table 1, entry 11). To increase the proportion of the dihydrosilylated product **3** other catalysts were tested.

Additions occur with high regioselectivity and yields (cf. Table 1). Formation of the anti-Markovnikov product is in agreement with a metal catalyst mechanism.[16,21,26,27] The triethylsilane adds exclusively to the less crowded end of the double bond yielding hydrosilylated compounds **2** and **3**, respectively, which argues against a concerted addition of the silicon hydride across the double bond.[28]

Scheme 1. Mono- and Dihydrosilylation of 1 Using Zeise's Dimer



Nearly all examined platinum complexes were found to catalyze good to excellently the formation of the monosilylated compound **2**. Indeed, a 5.3×10^{-5} M concentration of the Pt catalyst ([catalyst]/[DVA] $\sim 10^{-3}$ mol/mol) gave turnover numbers of ~1000 at turnover frequencies in the order of 0.0116 s^{-1} in most cases. The reaction failed in two cases, i.e. with tetrakis(triphenylphosphine)platinum $[Pt(PPh_3)_4]$ (it is known that triphenylphosphine reduces drastically the catalytic activity of platinum complexes)[29] and with Wilkinson's catalyst $[RhCl(PPh_3)_3]$, which has been reported to be relatively ineffective with substituted olefins[30] (Table 1, entries 9 and 10), and only the starting compound (**1**) was recovered. Speier's catalyst [H_2PtCl_6/2-propanol] afforded a poor yield of the desired product **2** and many side products (Table 1, entry 8). The different catalytic activity, i.e. addition of 2-propanol is required for reduction of the Pt(IV) species to the active Pt(II) catalyst prior to reaction, and the high reactivity of this complex may explain these results. Under the tested conditions only four catalysts led to formation of dihydrosilylated product **3** (Table 1, entries 2−5). Among them, the Pt(0) complex $[Pt(PPh_3)_2(C_6H_6)]$ was found to be unstable and no trace of it was left after 24 h reaction time (Table 1, entry 5): loss of a phosphine ligand converts it into the active species, a complex very soluble in benzene, analyzed as $[Pt(PPh_3)(C_6H_6)]_n$, mp > 287°, for which a cluster structure has been suggested.[31] Extending the reaction time with the remaining three catalysts (Table 1, entries 2−4) to 10 days resulted in a higher conversion to the disilylated product **3** without noticeable loss in yield.

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Table 1. Study of the Transition Metal Catalyst Efficiency for Mono- and Dihydrosilylation of Compound 1

entry	catalyst[a]	time	*T* (°C)	ratio of **1**/**2**/**3**[b]	yield of **2**[c] (%)	yield of **3**[c] (%)
1	$Pt_2Cl_4(CH_2CH_2)_2$	1 h	20	0/97/3	91	3
2	$Pt_2Cl_4(CH_2CH_2)_2$	24 h	80	0/85/15	78	14
3	$Pt(acac)_2$	24 h	80	0/90/10	80	9
4	$[Pt(PPh_3)(C_6H_6)]_n$	24 h	80	0/91/9	82	8
5	$Pt(PPh_3)_2(C_6H_6)$	24 h	80	4/85/11	76	10
6	$PtCl_2(PPh_3)_2$	24 h	80	53/47/traces	43	traces
7	$Pt(PPh_3)_2(CH_2CH_2)$	24 h	80	67/33/traces	30	traces
8	H_2PtCl_6	24 h	80	80/20/0	14	0
9	$Pt(PPh_3)_4$	24 h	80	98/2/0	2	0
10	$RhCl(PPh_3)_3$	24 h	80	100/0/0	0	0
11	$Pt_2Cl_4(CH_2CH_2)_2$	10 d	80	0/50/50	45	46
12	$Pt(acac)_2$	10 d	80	0/50/50	44	44
13	$[Pt(PPh_3)(C_6H_6)]_n$	10 d	80	0/52/48	45	43

[a] Concentration = 5.3×10^{-5} M. [b] Ratio determined by GC. [c] Yield of isolated products.

Table 2. Effect of the Spacer between the Silicon Atoms on the Ratio of Products 5 and 6[a]

entry	compd	X	Si−X−Si angle (°)[b]	R_1, R_2	ratio of **5**/**6**[b]	Yield of **5**[c] (%)	Yield of **6**[c] (%)
1	**4a**	Si(Me, Ph)	108.9	Me, Ph	100/0	84	0
2	**4b**	NH	113.4	Me, Me	100/0	82	0
3	**4c**	CH_2	117.0	Me, Me	83/17	68	14
4	**4d**	O	147.1	Me, Me	78/22	62	18
5	**4e**		180	Me, Ph	70/30	55	24

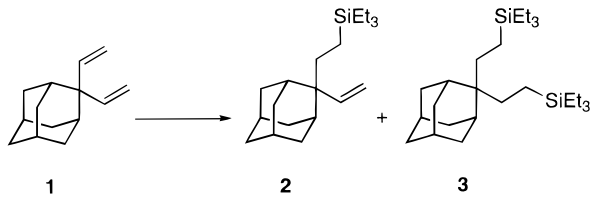
[a] Reactions run for 12 h at reflux in benzene (1 mL), [catalyst] = 5.3×10^{-5} M. See Experimental Section for reaction details. [b] Angles determined by modelization using CS Chem 3D Pro minimization. [c] Ratio determined by GC. [d] Yield of isolated products.

Although the monohydrosilylation is a rapid process, the dihydrosilylation requires considerably longer reaction times, which is explained by steric effects. In our study, catalysts derived from complexes of Pt(II) have shown to be slightly more effective than complexes of Pt(0) for both the mono- and the dihydrosilylation of 2,2-divinyladamantane. A similar effect has been observed by Kumada and co-workers.[31] But in contrast to the hydrosilylation of usual alkenes, dihydrosilylation of compound **1** needed high catalyst concentrations at reflux temperatures. Indeed, a benzene solution (1 mL) of triethylsilane (0.11 mmol) was added at room temperature to a mixture of 2,2-divinyladamantane (**1**, 5.3×10^{-5} mol) and tetrachlorobis(ethylene)diplatinum dissolved in benzene (1 mL). The mixture was heated and the reaction followed by GC analysis. When the platinum complex was used in high concentration (5.3×10^{-5} M, [catalyst]/[DVA] $\sim 10^{-3}$ mol/mol), the reaction occurred in 1 h and afforded the compound **2** in almost quantitative yield (>91%) (Table 1, entry 1). In contrast, lower catalyst concentrations (5.3×10^{-7} M, [catalyst]/[DVA] $\sim 10^{-5}$ mol/mol or 5.3×10^{-9} M, [catalyst]/[DVA] $\sim 10^{-7}$ mol/mol) slowed dramatically the reaction and gave after 1 h only a small amount of adduct **2** (<12%) along with starting product (>87%).

To summarize, Zeise's dimer $[Pt_2Cl_4(CH_2CH_2)_2]$, used in high concentration, has proved to be the best catalyst for the present reaction.

Reaction of 2,2-Divinyladamantane with Disilanes. Of particular importance among transition metal catalyzed syntheses of silicon compounds is the double silylation of unsaturated hydrocarbons with disilanes to give cyclic compounds.[23] Double silylation of conjugated dienes with disilanes occurs generally by 1,4-addition (terminal addition), and our studies have revealed that 2,2-divinyladamantane (**1**) readily undergoes disilylation with bis(hydrosilane) species to give disilacyclic compounds (terminal addition) in high yields.

Scheme 2

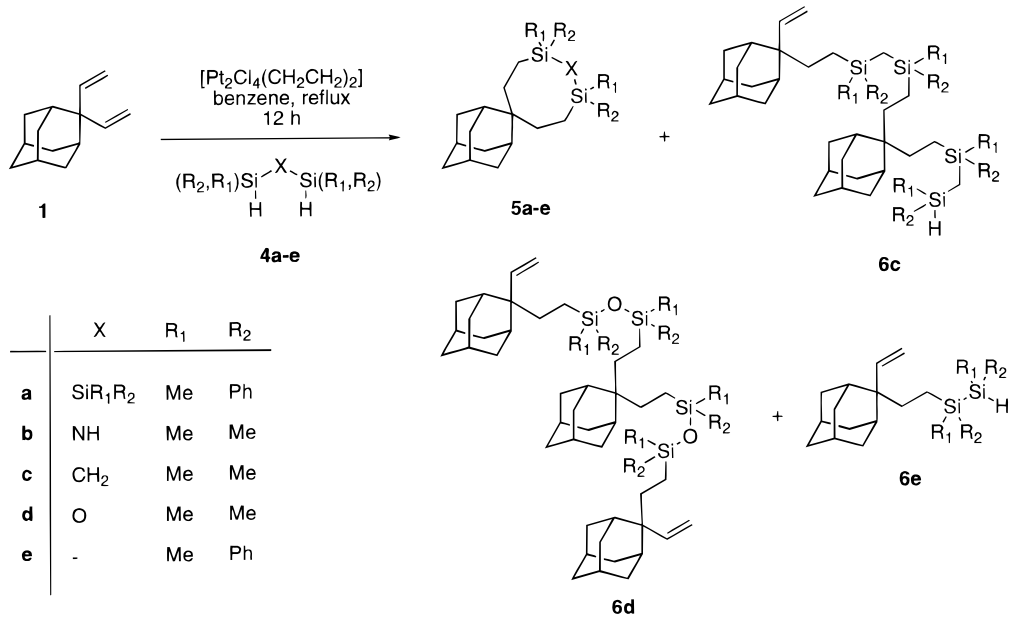


As concluded from the results obtained with monosilanes, dihydrosilylation proceeds mainly in two steps. After the first addition of silane to one double bond, the formed intermediate can react in two ways: either it cyclizes to yield bicyclic derivatives (**5a**−**e**) by an intramolecular reaction which is normally favored or an intermolecular addition occurs to give acyclic compounds (**6c**−**e**). The latter reaction is preferred when the angle of the Si−X−Si unit increases, the distance between the silane and the double bond being not so efficient for cyclization.

Thus selectivity for cyclic products depends very much on the spacer between the silicon atoms (Table 2): it decreases from 100 to 70% with increasing angle Si−X−Si (108.9−180.0°) of the starting compound **4a**−**e** (Scheme 3). Only the trisilane $PhMeSi(SiPhMeH)_2$ (**4a**) and the 1,1,3,3-tetramethyldisilazane (**4b**) (Table 2, entries 1 and 2) gave selectively the disilacyclic compounds **5a**,**b** in high yield (>82%). Disilanes **4c**−**e** afford the wanted disilacyclic compounds **5c**−**e** in moderate yields (68−55%), accompanied by acyclic compounds **6c**−**e** (14−24%), respectively.

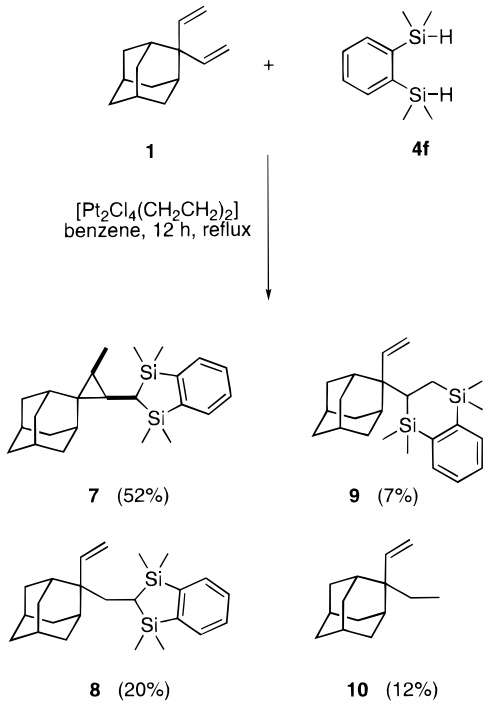
Whereas the secondary product of 1,1,2,2-tetramethyldisilane (**4e**) stops at the terminally monoalkylated product **6e** (Table 2, entry 5), 1,2-bis(dimethylsilyl)-methane (**4c**) yields the corresponding dimer **6c** (Table

Scheme 3



	X	R_1	R_2
a	SiR_1R_2	Me	Ph
b	NH	Me	Me
c	CH_2	Me	Me
d	O	Me	Me
e	-	Me	Ph

Scheme 4



2, entry 3). Formation of the byproduct **6d** in the case of 1,1,3,3-tetramethyldisiloxane (**4d**) is more difficult to explain (Table 2, entry 4), because the logical precursor of this product, the dialkylated disilane, was not found in the reaction mixture. In this case, the presence of a larger trihedral angle favors competitively intermolecular reactions.

In contrast to the substrates discussed so far, *o*-bis(dimethylsilyl)benzene (**4f**) reacts completely unselectively by 1,1- and 1,2-double silylation as the major reaction pathways. 1,1-Double silylation affords compounds **7** and **8** in 52% and 20% yield, respectively, and 1,2-double silylation gives **9** in 7% yield (Scheme 4).

In accordance with a previous study of Eaborn et al.,[33] formation of the 1,2-adduct **9** is explained by the formation of the cyclic bis(silyl)platinum complex **II**. As reported by Tanaka et al., formation of 1,1-adducts (**7**, **8**) can be explained by intramolecular insertion of the C=C bond into a Pt−Si or Pt−H bond of an intermediate complex **III** which is formed via either path A, i.e. olefin insertion into one of the two Si−Pt bonds of complex **II** and subsequent β-elimination of the resulting product,[32] or path B, i.e. dehydrogenative silylation of an olefin with one of the two Si−H bonds of **4f**.[23] In our case, formation of the cis-configured spirocyclic compound **7** provides evidence for an intramolecular insertion of the double bond into the Pt−Si bond of complex **III**. Either oxidative elimination of the resulting complex **IV** gives **8** or a new intramolecular insertion of the second double bond into the Pt−C or Pt−H bond of the resulting complex produces **7** (Scheme 5, paths A and B).

Interestingly, the formation of the hydrogenated compound **10** results from the reduction of one of the double bonds of DVA (**1**). We propose that this hydrogenation occurs by the following mechanism (Scheme 5, path C): oxidative addition of the Si−H bond to the mononuclear platinum complex functioning as hydrogenation catalyst gives complex **I** which is converted to complex **V** by hydroplatination of a double bond of DVA.[34−36] Further oxidative addition of the second Si−H bond leads to an intermediate **VI** which undergoes reductive elimination of the product **10** to the Pt complex **II**. This complex **II** could either be involved in a subsequent 1,1-addition (as a substitute for the above-mentioned path A), take up H_2 (reversed path A), or reductively eliminate 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclobut-3-ene[37] (**11**) to close a catalytic cycle (Scheme 5, path C). However, the absence of disilacy-

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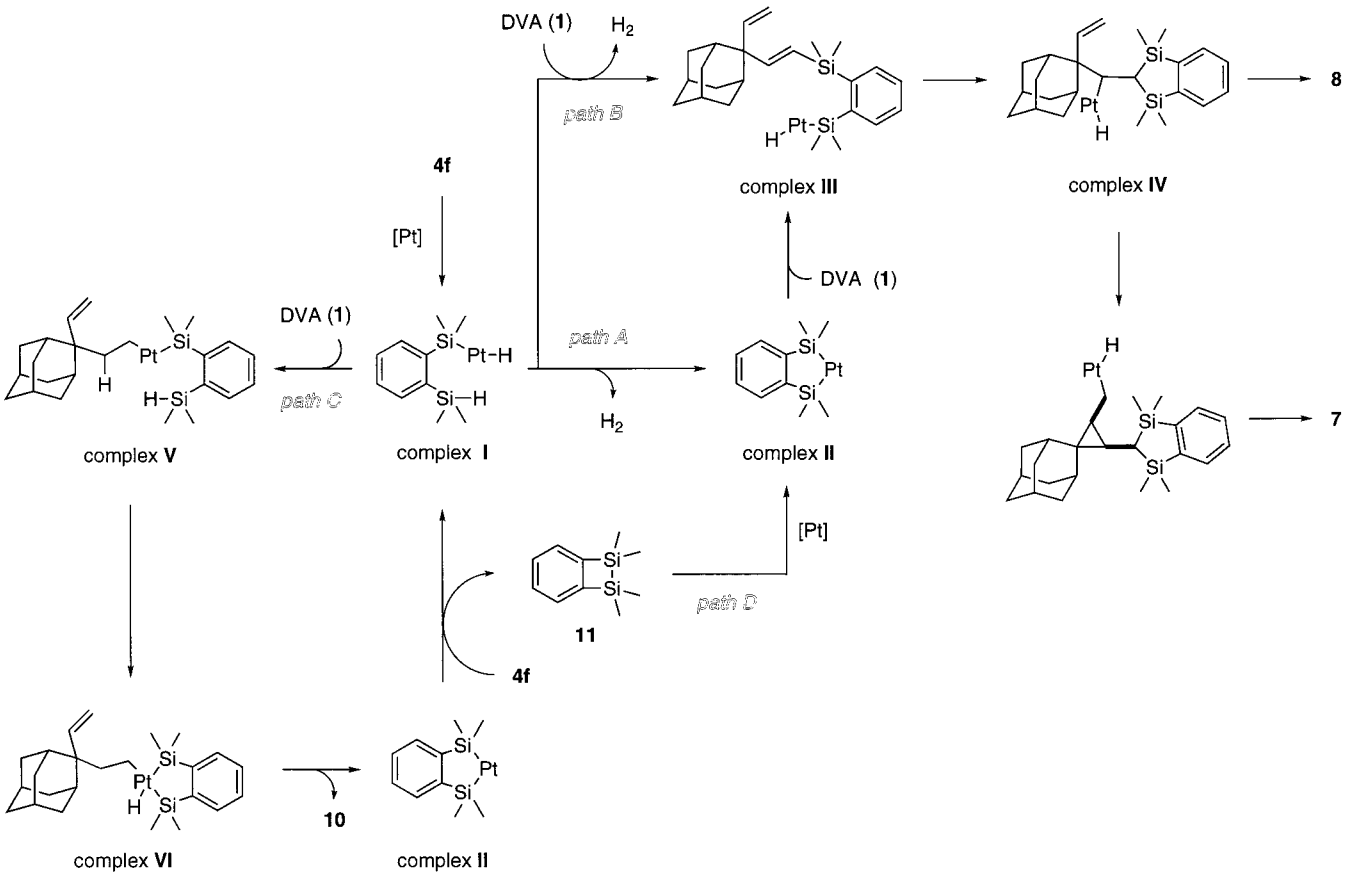
Scheme 5. Hydrogenative and Dehydrogenative Mechanism



clobutene **11** in the reaction mixture can be best explained by its reaction with the platinum catalyst, as reported by Ishikawa,[38,39] to produce complex **II**. Path D illustrates a possible mechanistic interpretation of the observed reaction course. The formation of products **7** and **8** involves oxidative addition of an ethenyl C−H bond in 2,2-divinyladamantane (**1**) to platinum *o*-quinodisilane complex **II**. A shift of a ethenyl group from the platinum atom onto a silene silicon atom affords platinum hydride complex **III**. Finally, intramolecular hydrosilylation of **III** gives complex **IV** and the latter produces **7** and **8** (Scheme 5, path D).

Conclusion

Our systematic study aiming at the synthesis of dihydrosilylated compounds has shown that the reaction of 2,2-divinyladamantane with triethylsilane is best catalyzed by Zeise's dimer [$Pt_2Cl_4(CH_2CH_2)$]. In the same way, different bis(hydrosilanes) gave selectively disilacyclic compounds in high yields. The observed competition between the intra- and intermolecular processes, leading to disilacyclic compounds and oligomers, respectively, illustrates the critical importance of the bis(hydrosilane) geometry for the selectivity. However, no disilacyclic product was found using *o*-bis(dimethylsilyl)benzene (**4f**). It reacts completely unselectively via 1,1- and 1,2-double silylation reaction pathways. Finally, isolation of the hydrogenated compound **10** from this reaction mixture allowed us to propose a hydrogenation mechanism involving a mononuclear platinum complex.

Experimental Section

General Conditions. All experiments involving air-sensitive compounds were performed under N_2 or argon using standard Schlenk techniques. THF and Et_2O were freshly distilled from Na/benzophenone under an argon atmosphere prior to use; CH_2Cl_2, DMF, and benzene were distilled from CaH_2 under N_2 and toluene from Na under N_2. Deuterated solvents were obtained from Armar AG. Solvents for chromatography were used after distillation. Flash column chromatography (FC) and filtration were performed with Baker silica gel (0.063−0.200 mm). TLC were run on Merck silica gel 60 F_{254} analytical plates; detection were carried either with UV or spraying with a solution of $KMnO_4$ (3 g), K_2CO_3 (20 g), H_2O (300 mL), and 5% NaOH (5 mL), followed by heating. Melting points were determined on a Reichert Thermovar apparatus. NMR: Bruker Avance DRX-500 (^{1}H 500.13 MHz and ^{13}C 125.77 MHz); for ^{1}H δ are in ppm relative to $CDCl_3$ (=7.27 ppm), for ^{13}C δ are in ppm relative to $CDCl_3$ (=77.1 ppm), and coupling constants *J* are given in Hz. Assignments were confirmed by NOESY, COSY, and HETCOR experiments. MS: Vacuum Generators Micromass VG 70/70E; EI (70 eV) [*m*/*z* (%)]. Elemental analysis: Ciba Specialities Mikrolabor, Marly, Switzerland. Quantitative GC analyses were carried out on a Fisons HRGC MEGA 2 series gas chromatograph equipped with a flame ionization detector and a Permabond SE 54 25 m × 0.32 mm capillary column. The synthesis of 2,2-divinyladamantane (DVA) is reported elsewhere.[13] Bis(triphenylphosphine)ethyleneplatinum(0),[40,41] bis(triphenylphos-

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phine)benzeneplatinum(0), and $[Pt(PPh_3)(C_6H_6)]_n$[31] were prepared as previously described. The disilane **4e** and trisilane **4a** were synthesized by the method of Corey,[42,43] and bis(dimethylsilyl)methane (**4c**) was synthesized by following the procedure of Dunoguès.[44] All other materials were commercially available and were used as received.

General Procedure 1 for the Hydrosilylation of 2,2-Divinyladamantane (Table 1). A 10 mL round-bottomed flask equipped with a magnetic stirring bar, dry argon inlet, reflux condenser, and septum was charged with 2,2-divinyladamantane (**1**) (10 mg, 0.053 mmol) and a solution of platinum complex ([C] = 5.3×10^{-5} mol/L) in 1 mL of dry benzene. The solution was degassed and stirred at room temperature for 1 h. Triethylsilane (13 mg, 0.11 mmol) was added slowly, the resulting mixture was refluxed under an inert atmosphere, and the reaction was monitored by GC analysis. The reaction mixture was evaporated and filtered through a short column of silica gel. Selectivity was determined from GC and ^{1}H NMR. For analysis the product was repurified by FC (hexane).

2: colorless liquid. ^{1}H NMR ($CDCl_3$): $\delta = 5.55$ (dd, $J = 18.1$ Hz, 11.2 Hz, 1H, C*H*═CH_2), 5.14 (dd, $J = 11.2$ Hz, 1.7 Hz, 1H, CH_2═CH cis), 4.87 (dd, $J = 18.1$ Hz, 1.7 Hz, 1H, CH_2═CH trans), 2.03 (br d, $J = 12.3$ Hz, 2H, C(8)-H_{syn}, C(10)-H_{syn}), 2.00 (br d, $J = 12.5$ Hz, 2H, C(4)-H_{syn}, C(9)-H_{syn}), 1.83 (m, 1H, C(7)-*H*), 1.79 (m, C(5)-*H*), 1.72 (br s, 2H, C(1)-*H*, C(3)-*H*), 1.65 (br s, 2H, C(6)H_2), 1.56 (br d, $J = 12.3$ Hz, 2H, C(8)-H_{anti}, C(10)-H_{anti}), 1.52 (br d, $J = 12.5$ Hz, 2H, C(4)-H_{anti}, C(9)-H_{anti}), 1.44 (m, 2H, C$H_2$$CH_2$Si), 0.91 (t, $J = 8.0$ Hz, 9H, C$H_3$$CH_2$Si), 0.48 (q, $J = 8.0$ Hz, 6H, CH_3CH_2Si), 0.34 (m, 2H, CH_2Si). ^{13}C NMR ($CDCl_3$): $\delta = 147.1$ (d, *C*H═CH_2), 112.7 (t, *C*H_2═CH), 45.2 (s, C(2)), 39.0 (t, C(6)), 34.0 (t, C(4), C(9)), 33.5 (d, C(1), C(3)), 32.5 (t, C(8), C(10)), 30.5 (t, *C*$H_2$$CH_2$Si), 28.5 (d, C(5)), 27.9 (d, C(7)), 7.6 (q, *C*$H_3$$CH_2$), 3.3 (t, *C*$H_2$$CH_3$), 2.4 (t, CH_2*C*H_2Si). CI-MS: *m*/*z* (%) = 304 (5, M^+), 276 (11), 193 (43), 143 (8), 115 (100), 87 (2), 59 (2). Anal. Calcd for $C_{20}H_{36}Si$ (304.26): C, 78.88; H, 11.92. Found: C, 78.76; H, 11.87.

3: colorless liquid. ^{1}H NMR ($CDCl_3$): $\delta = 2.11$ (br d, $J = 13.2$ Hz, 4H, C(4)-H_{syn}, C(8)-H_{syn}, C(9)-H_{syn}, C(10)-H_{syn}), 1.82 (br s, 2H, C(1)-*H*, C(3)-*H*), 1.72 (br s, 2H, C(5)-*H*, C(7)-*H*), 1.64 (br s, 2H, C(6)H_2), 1.49 (br d, $J = 13.2$ Hz, 4H, C(4)-H_{anti}, C(8)-H_{anti}, C(9)-H_{anti}, C(10)-H_{anti}), 1.43 (m, 4H, C$H_2$$CH_2$Si), 0.94 (t, $J = 7.9$ Hz, 18H, C$H_3$$CH_2$), 0.52 (q, $J = 7.9$ Hz, 12H, CH_2-CH_3), 0.24 (m, 4H, CH_2CH_2Si). ^{13}C NMR ($CDCl_3$): $\delta = 40.0$ (t, C(6)), 39.9 (s, C(2)), 33.1 (t, *C*$H_2$$CH_2$Si), 32.8 (d, C(1), C(3)), 29.7 (t, C(4), C(8), C(9), C(10)), 28.2 (d, C(5), C(7)), 7.6 (q, *C*H_3-CH_2), 3.3 (t, *C*$H_2$$CH_3$), 2.4 (t, CH_2*C*H_2Si). EI-MS: *m*/*z* (%) = 421 (3, M^+), 393 (3), 319 (10), 275 (45), 247 (28), 217 (6), 187 (4), 143 (12),115 (100), 87 (4), 59 (2). Anal. Calcd for $C_{26}H_{52}$-Si_2 (420.87): C, 74.13; H, 12.45. Found: C, 74.07; H, 12.34.

Table 1, entry 1: according to general procedure 1, from **1** (10 mg, 5.3×10^{-5} mol), $Pt_2Cl_4(CH_2CH_2)_2$ (0.03 mg, 5.3×10^{-8} mol), and Et_3SiH (13 mg, 11.6×10^{-5} mol). After 10 min at room temperature the mixture was shown by GC to contain **2** and **3** in a ratio of 97/3, which were isolated by chromatography. FC (hexane) gave **2** (14.7 mg, 91%) along with **3** (0.6 mg, 3%).

Table 1, entry 2: according to general procedure 1, from **1** (10 mg, 5.3×10^{-5} mol), $Pt_2Cl_4(CH_2CH_2)_2$ (0.03 mg, 5.3×10^{-8} mol), and Et_3SiH (13 mg, 11.6×10^{-5} mol). After 24 h at reflux the mixture was shown by GC to contain **2** and **3** in a ratio of 85/15, which were isolated by chromatography. FC (hexane) gave **2** (12.6 mg, 78%) along with **3** (3 mg, 14%).

Table 1, entry 3: according to general procedure 1, from **1** (10 mg, 5.3×10^{-5} mol), $Pt(acac)_2$ (0.02 mg, 5.3×10^{-8} mol), and Et_3SiH (13 mg, 11.6×10^{-5} mol). After 24 h at reflux the mixture was shown by GC to contain **2** and **3** in a ratio of 90/10, which were isolated by chromatography. FC (hexane) gave **2** (13 mg, 80%) along with **3** (2 mg, 9%).

Table 1, entry 4: according to general procedure 1, from **1** (10 mg, 5.3×10^{-5} mol), $[Pt(PPh_3)(C_6H_6)]_n$ (1 mL, 5.3×10^{-5} mol/L), and Et_3SiH (13 mg, 11.6×10^{-5} mol). After 24 h at reflux the mixture was shown by GC to contain **2** and **3** in a ratio of 91/9, which were isolated by chromatography. FC (hexane) gave **2** (13.2 mg, 82%) along with **3** (1.8 mg, 8%).

Table 1, entry 5: according to general procedure 1, from **1** (10 mg, 5.3×10^{-5} mol), $Pt(PPh_3)_2(C_6H_6)$ (0.04 mg, 5.3×10^{-8} mol), and Et_3SiH (13 mg, 11.6×10^{-5} mol). After 24 h at reflux the mixture was shown by GC to contain **1**, **2**, and **3** in a ratio of 4/85/11, which were isolated by chromatography. FC (hexane) gave **1** (0.4 mg, 4%) and **2** (12.2 mg, 76%) along with **3** (2.2 mg, 10%).

Table 1, entry 6: according to general procedure 1, from **1** (10 mg, 5.3×10^{-5} mol), $PtCl_2(PPh_3)_2$ (0.04 mg, 5.3×10^{-8} mol), and Et_3SiH (13 mg, 11.6×10^{-5} mol). After 24 h at reflux the mixture was shown by GC to contain **1**, **2**, and **3** in a ratio of 52/47/1, which were isolated by chromatography. FC (hexane) gave **1** (4.7 mg, 47%) and **2** (6.9 mg, 43%) along with **3** (0.2 mg, 1%).

Table 1, entry 7: according to general procedure 1, from **1** (10 mg, 5.3×10^{-5} mol), $Pt(PPh_3)_2(C_2H_4)$ (0.04 mg, 5.3×10^{-8} mol), and Et_3SiH (13 mg, 11.6×10^{-5} mol). After 24 h at reflux the mixture was shown by GC to contain **1**, **2**, and **3** in a ratio of 66/33/1, which were isolated by chromatography. FC (hexane) gave **1** (6 mg, 61%) and **2** (4.9 mg, 30%) along with **3** (0.2 mg, 1%).

Table 1, entry 8: according to general procedure 1, from **1** (10 mg, 5.3×10^{-5} mol), H_2PtCl_6 (0.02 mg, 5.3×10^{-8} mol), and Et_3SiH (13 mg, 11.6×10^{-5} mol). After 24 h at reflux the mixture was shown by GC to contain **1** and **2** in a ratio of 80/20, which were isolated by chromatography. FC (hexane) gave **1** (5.4 mg, 54%) along with **2** (2.2 mg, 14%).

Table 1, entry 9: according to general procedure 1, from **1** (10 mg, 5.3×10^{-5} mol), $Pt(PPh_3)_4$ (0.07 mg, 5.3×10^{-8} mol), and Et_3SiH (13 mg, 11.6×10^{-5} mol). After 24 h at reflux the mixture was shown by GC to contain **1** and **2** in a ratio of 98/2, which were isolated by chromatography. FC (hexane) gave **1** (9 mg, 91%) along with **2** (0.3 mg, 2%).

Table 1, entry 10: according to general procedure 1, from **1** (10 mg, 5.3×10^{-5} mol), $RhCl(PPh_3)_3$ (0.05 mg, 5.3×10^{-8} mol), and Et_3SiH (13 mg, 11.6×10^{-5} mol). After 24 h at reflux the mixture was shown by GC to contain **1**, which was isolated by chromatography. FC (hexane) gave **1** (9.4 mg, 94%).

Table 1, entry 11: according to general procedure 1, from **1** (10 mg, 5.3×10^{-5} mol), $Pt_2Cl_4(CH_2CH_2)_2$ (0.03 mg, 5.3×10^{-8} mol), and Et_3SiH (13 mg, 11.6×10^{-5} mol). After 10 days at reflux the mixture was shown by GC to contain **2** and **3** in a ratio of 50/50, which were isolated by chromatography. FC (hexane) gave **2** (7.4 mg, 45%) along with **3** (10.2 mg, 46%).

Table 1, entry 12: according to general procedure 1, from **1** (10 mg, 5.3×10^{-5} mol), $Pt(acac)_2$ (0.02 mg, 5.3×10^{-8} mol), and Et_3SiH (13 mg, 11.6×10^{-5} mol). After 10 days at reflux the mixture was shown by GC to contain **2** and **3** in a ratio of 50/50, which were isolated by chromatography. FC (hexane) gave **2** (7 mg, 44%) along with **3** (10 mg, 44%).

Table 1, entry 13: according to general procedure 1, from **1** (10 mg, 5.3×10^{-5} mol), $[Pt(PPh_3)(C_6H_6)]_n$ (1 mL, 5.3×10^{-5} mol/L), and Et_3SiH (13 mg, 11.6×10^{-5} mol). After 10 days at reflux the mixture was shown by GC to contain **2** and **3** in a ratio of 52/48, which were isolated by chromatography. FC (hexane) gave **2** (7.3 mg, 45%) along with **3** (9.6 mg, 43%).

General Procedure 2. Formation of Disilacyclic Compounds (Table 2). A mixture of 2,2-divinyladamantane (**1**) (10 mg, 0.053 mmol) and a solution of Zeise's dimer $[Pt_2Cl_4(CH_2CH_2)]$ ([C] = 5.3×10^{-5} mol/L) in 1 mL of dry benzene were placed in 10 mL round-bottomed flask equipped with a

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(43) Corey, J. Y.; Zhu, X.-H.; Bedard, T. C.; Lange, L. D. *Organometallics* **1991**, *10*, 924.
(44) Bacqué, E.; Pillot, J.-P.; Lapouyade, P.; Gerval, P.; Biran, C.; Dunoguès, J. *J. Organomet. Chem.* **1996**, *521*, 99.

magnetic stirring bar, a dry argon inlet, and a reflux condenser. The solution was degassed and stirred at room temperature for 1 h. Disilane compounds (0.064 mmol) were then slowly added, the resulting mixture was stirred for 24 h at reflux under an inert atmosphere, and the reaction was monitored by GC analysis. The solvent was evaporated and the residue filtrated through a short column of silica gel. The selectivity was determined from GC and ^{1}H NMR. For analysis the product was repurified by FC.

Table 2, entry 1: according to general procedure 2, from **1** (100 mg, 5.3×10^{-4} mol), $Pt_2Cl_4(CH_2CH_2)_2$ (0.3 mg, 5.3×10^{-7} mol), and 1,2,3-trimethyl-1,2,3-triphenyltrisilane (**4a**) (231 mg, 6.4×10^{-4} mol). After 24 h at reflux the mixture was shown by GC to contain **5a** which was purified by chromatography. FC (hexane) gave **5a** (246 mg, 84%).

5a: mixture of 3 stereoisomers, colorless liquid. ^{1}H NMR ($CDCl_3$): δ = 7.6−7.2 (m, 45H, 45 *arom. H*), 2.04−1.97 (m, 12H, C(4)-H_{syn}, C(8)-H_{syn}, C(9)-H_{syn}, C(10)-H_{syn}), 1.83−1.79 (m, 6H, C(1)-*H*, C(3)-*H*), 1.74−1.70 (m, 6H, C(5)-*H*, C(7)-*H*), 1.65−1.61 (m, 6H, C(6)H_2), 1.56−1.51 (m, 12H, CH_2CH$_2$Si), 1.51−1.48 (m, 12H, C(4)-H_{anti}, C(8)-H_{anti}, C(9)-H_{anti}, C(10)-H_{anti}), 0.75−0.70 (m, 12H, CH$_2$CH_2Si), 0.44 (s, 3H, CH_3Si), 0.42 (s, 6H, CH_3Si), 0.40 (s, 3H, CH_3Si), 0.39 (s, 6H, CH_3Si), 0.38 (s, 3H, CH_3Si), 0.35 (s, 3H, CH_3Si), 0.33 (s, 3H, CH_3Si). ^{13}C NMR ($CDCl_3$): δ = 134.2 (s, *C*−Si), 133.3 (d, =*C*H), 133.2 (d, =*C*H), 133.0 (d, =*C*H), 127.9 (d, =*C*H), 127.8 (d, =*C*H), 127.6 (d, =*C*H), 127.4 (d, =*C*H), 127.2 (d, =*C*H), 40.0 (s, C(2)), 38.9 (t, C(6)), 38.8 (t, C(6)), 33.7 (t, C(4), C(8), C(9), C(10)), 33.6 (t, C(4), C(8), C(9), C(10)), 33.5 (t, C(4), C(8), C(9), C(10)), 32.9 (d, C(1), C(3)), 29.8 (d, C(5), C(7)), 29.7 (d, C(5), C(7)), 29.5 (d, C(5), C(7)), 28.4 (t, *C*H$_2$CH$_2$Si), 28.3 (t, *C*H$_2$CH$_2$Si), 8.1 (t, CH$_2$*C*H$_2$Si), 8.0 (t, CH$_2$*C*H$_2$Si), 7.9 (t, CH$_2$*C*H$_2$Si), −7.2 (q, Si*C*H$_3$), −7.3 (q, Si*C*H$_3$), −7.4 (q, Si*C*H$_3$), −7.7 (q, Si*C*H$_3$), −7.8 (q, Si*C*H$_3$), −7.9 (q, Si*C*H$_3$). EI-MS: *m*/*z* (%) = 551 (18, M$^+$), 473 (34), 395 (16), 379 (11), 301 (8), 273 (21), 187 (13), 135 (100), 73 (23), 59 (15). Anal. Calcd for $C_{35}H_{46}Si_3$ (551.0): C, 76.29; H, 8.41. Found: C, 75.98; H, 8.56.

Table 2, entry 2: according to general procedure 2, from **1** (100 mg, 5.3×10^{-4} mol), $Pt_2Cl_4(CH_2CH_2)_2$ (0.3 mg, 5.3×10^{-7} mol), and 1,1,3,3-tetramethyldisilazane (**4b**) (85 mg, 6.4×10^{-4} mol). After 24 h at reflux the mixture was shown by GC to contain **5b** which was purified by chromatography. FC (9:1 hexane/AcOEt) gave **5b** (140 mg, 82%).

5b: colorless liquid. ^{1}H NMR ($CDCl_3$): δ = 2.02 (br d, *J* = 11.9 Hz, 4H, C(4)-H_{syn}, C(8)-H_{syn}, C(9)-H_{syn}, C(10)-H_{syn}), 1.81 (br s, 2H, C(1)-*H*, C(3)-*H*), 1.67 (br s, 2H, C(5)-*H*, C(7)-*H*), 1.64 (br s, 2H, C(6)H_2), 1.62 (m, 4H, CH_2CH$_2$Si), 1.49 (br d, *J* = 11.9 Hz, 4H, C(4)-H_{anti}, C(8)-H_{anti}, C(9)-H_{anti}, C(10)-H_{anti}), 0.33 (m, 4H, CH$_2$CH_2Si), 0.05 (s, 12H, CH_3Si). ^{13}C NMR ($CDCl_3$): δ = 40.5 (s, C(2)), 40.0 (t, C(6)), 33.1 (t, C(4), C(8), C(9), C(10)), 32.9 (d, C(1), C(3)), 28.2 (d, C(5), C(7)), 23.0 (t, *C*H$_2$CH$_2$Si), 8.9 (t, CH$_2$*C*H$_2$Si), 0.2 (q, Si*C*H$_3$). EI-MS: *m*/*z* (%) = 321 (8, M$^+$), 279 (3), 233 (1), 207 (2), 173 (17), 145 (10), 115 (49), 75 (100), 59 (34). Anal. Calcd for $C_{18}H_{35}NSi_2$ (321.65): C, 67.21;H, 10.97; N, 4.35. Found: C, 67.34; H, 11.05; N, 4.21.

Table 2, entry 3: according to general procedure 2, from **1** (100 mg, 5.3×10^{-4} mol), $Pt_2Cl_4(CH_2CH_2)_2$ (0.3 mg, 5.3×10^{-7} mol), and bis(dimethylsilyl)methane (**4c**) (84.3 mg, 6.4×10^{-4} mol). After 24 h at reflux the mixture was shown by GC to contain **5c** and **6c** in a ratio of 83/17, which were isolated by chromatography. FC (hexane) gave **5c** (116 mg, 68%) along with **6c** (46 mg, 14%).

5c: colorless liquid. ^{1}H NMR ($CDCl_3$): δ = 2.02 (br d, *J* = 11.7 Hz, 4H, C(4)-H_{syn}, C(8)-H_{syn}, C(9)-H_{syn}, C(10)-H_{syn}), 1.81 (br s, 2H, C(1)-*H*, C(3)-*H*), 1.66 (br s, 2H, C(5)-*H*, C(7)-*H*), 1.57 (m, 4H, CH_2CH$_2$Si), 1.55 (br s, 2H, C(6)H_2), 1.50 (br d, *J* = 11.7 Hz, 4H, C(4)-H_{anti}, C(8)-H_{anti}, C(9)-H_{anti}, C(10)-H_{anti}), 0.33 (m, 4H, CH$_2$CH_2Si), 0.09 (s, 12H, CH_3Si), −0.23 (s, 2H, SiCH_2-Si). ^{13}C NMR ($CDCl_3$): δ = 40.1 (s, C(2)), 40.0 (t, C(6)), 33.1 (t, C(4), C(8), C(9), C(10)), 32.4 (d, C(1), C(3)), 28.2 (d, C(5), C(7)), 22.7 (t, *C*H$_2$CH$_2$Si), 8.0 (t, CH$_2$*C*H$_2$Si), 0.2 (q, Si*C*H$_3$), −1.66 (t, SiCH_2Si). EI-MS: *m*/*z* (%) = 320 (8, M$^+$), 279 (3), 233 (1), 207 (2), 173 (17), 145 (10), 115 (49), 75 (100), 59 (34). Anal. Calcd for $C_{19}H_{36}Si_2$ (320.66): C, 71.17; H, 11.32. Found: C, 71.10; H, 11.27.

6c: colorless liquid. ^{1}H NMR ($CDCl_3$): δ = 5.52 (dd, *J* = 18.3 Hz, 11.1 Hz, 1H, C*H*=CH$_2$), 5.13 (dd, *J* = 11.1 Hz, 1.3 Hz, 1H, CH_2=CH cis), 4.84 (dd, *J* = 18.3 Hz, 1.3 Hz, 1H, CH_2=CH trans), 3.32 (m, 1H, Si*H*), 2.05 (br d, *J* = 12.4 Hz, 2H, C(8)-H_{syn}, C(10)-H_{syn}), 2.02 (br d, *J* = 12.4 Hz, 2H, C(8)-H_{syn}, C(10)-H_{syn}), 2.00 (br d, *J* = 12.5 Hz, 2H, C(4)-H_{syn}, C(9)-H_{syn}), 1.99 (br d, *J* = 12.3 Hz, 2H, C(4)-H_{syn}, C(9)-H_{syn}), 1.84 (m, 1H, C(7)-*H*), 1.83 (m, 1H, C(7)-*H*), 1.80 (m, C(5)-*H*), 1.79 (m, C(5)-*H*), 1.71 (br s, 4H, C(1)-*H*, C(3)-*H*), 1.65 (br s, 4H, C(6)H_2), 1.57 (br d, *J* = 12.4 Hz, 2H, C(8)-H_{anti}, C(10)-H_{anti}), 1.54 (br d, *J* = 12.4 Hz, 2H, C(8)-H_{anti}, C(10)-H_{anti}), 1.51 (br d, *J* = 12.5 Hz, 2H, C(4)-H_{anti}, C(9)-H_{anti}), 1.49 (br d, *J* = 12.3 Hz, 2H, (4)-H_{anti}, C(9)-H_{anti}), 1.46 (m, 4H, CH_2CH$_2$Si), 1.43 (m, 2H, CH_2-CH$_2$Si), 0.34 (m, 4H, CH$_2$CH_2Si), 0.30 (m, 2H, CH$_2$CH_2Si), 0.10 (s, 3H, CH_3Si), 0.09 (s, 3H, CH_3Si), 0.08 (s, 6H, CH_3Si), 0.06 (s, 3H, CH_3Si), 0.05 (d, *J* = 3.7 Hz, 6H, CH_3Si), 0.02 (s, 3H, CH_3Si), −0.17 (s, 2H, SiCH_2Si), −0.21 (d, *J* = 4.6 Hz, 2H, SiCH_2Si). ^{13}C NMR ($CDCl_3$): δ = 146.9 (d, *C*H=CH$_2$), 112.7 (t, *C*H$_2$=CH), 45.0 (s, C(2)), 44.9 (s, C(2)), 39.0 (t, C(6)), 34.0 (t, C(4), C(9)), 33.5 (d, C(1), C(3)), 33.0 (d, C(1), C(3)), 32.6 (t, C(8), C(10)), 32.4 (t, C(8), C(10)), 29.8 (t, *C*H$_2$CH$_2$Si), 29.6 (t, *C*H$_2$CH$_2$Si), 29.5 (t, *C*H$_2$CH$_2$Si), 28.4 (d, C(5)), 28.2 (d, C(7)), 27.8 (d, C(7)), 3.4 (t, CH$_2$*C*H$_2$Si), 3.2 (t, CH$_2$*C*H$_2$Si), 3.1 (t, CH$_2$*C*H$_2$Si), 0.29 (q, 6H, *C*H$_3$Si), 0.27 (q, 3H, *C*H$_3$Si), 0.26 (q, 6H, *C*H$_3$Si), 0.24 (q, 3H, *C*H$_3$Si), 0.23 (q, 6H, *C*H$_3$Si), −1.6 (t, 2H, Si*C*H$_2$Si), −1.7 (t, 2H, Si*C*H$_2$Si). CI-MS: *m*/*z* (%) = 641 (9, M$^+$), 582 (15), 506 (4), 478 (11), 344 (34), 316 (13), 258 (10), 186 (35), 173 (71), 158 (40), 133 (100), 79 (24), 59 (6). Anal. Calcd for $C_{38}H_{72}Si_4$ (641.33): C, 71.17; H, 11.32. Found: C, 70.98; H, 11.25.

Table 2, entry 4: according to general procedure 2, from **1** (100 mg, 5.3×10^{-4} mol), $Pt_2Cl_4(CH_2CH_2)_2$ (0.3 mg, 5.3×10^{-7} mol), and 1,1,3,3-tetramethyldisiloxane (**4d**) (85.6 mg, 6.4×10^{-4} mol). After 24 h at reflux the mixture was shown by GC to contain **5d** and **6d** in a ratio of 78/22, which were isolated by chromatography. FC (hexane) gave **5d** (107 mg, 62%) along with **6d** (78 mg, 18%).

5d: colorless liquid. ^{1}H NMR ($CDCl_3$): δ = 2.02 (br d, *J* = 11.3 Hz, 4H, C(4)-H_{syn}, C(8)-H_{syn}, C(9)-H_{syn}, C(10)-H_{syn}), 1.81 (br s, 2H, C(1)-*H*, C(3)-*H*), 1.66 (br s, 2H, C(5)-*H*, C(7)-*H*), 1.64 (br s, 2H, C(6)H_2), 1.58 (m, 4H, CH_2CH$_2$Si), 1.50 (br d, *J* = 11.3 Hz, 4H, C(4)-H_{anti}, C(8)-H_{anti}, C(9)-H_{anti}, C(10)-H_{anti}), 0.34 (m, 4H, CH$_2$CH_2Si), 0.05 (s, 12H, CH_3Si). ^{13}C NMR ($CDCl_3$): δ = 40.5 (s, C(2)), 40.0 (t, C(6)), 33.0 (t, C(4), C(8), C(9), C(10)), 32.8 (d, C(1), C(3)), 28.1 (d, C(5), C(7)), 23.0 (t, *C*H$_2$CH$_2$Si), 8.8 (t, CH$_2$*C*H$_2$Si), 0.2 (q, Si*C*H$_3$). EI-MS: *m*/*z* (%) = 322 (20, M$^+$), 295 (9), 207 (5), 161 (59), 145 (95), 133 (100), 105 (9), 73 (23), 59 (8). Anal. Calcd for $C_{18}H_{34}OSi_2$ (322.64): C, 67.00; H, 10.62. Found: C, 67.13; H, 10.77.

6d: colorless liquid. ^{1}H NMR ($CDCl_3$): δ = 5.56 (dd, *J* = 18.1 Hz, 11.1 Hz, 2H, C*H*=CH$_2$), 5.13 (dd, *J* = 11.1 Hz, 1.6 Hz, 2H, CH_2=CH cis), 4.85 (dd, *J* = 18.1 Hz, 1.6 Hz, 2H, CH_2=CH trans), 2.05 (br d, *J* = 12.1 Hz, 4H, C(8)-H_{syn}, C(10)-H_{syn}), 2.02 (br d, *J* = 11.3 Hz, 4H, C(4)-H_{syn}, C(8)-H_{syn}, C(9)-H_{syn}, C(10)-H_{syn}), 2.01 (br d, *J* = 12.2 Hz, 4H, C(4)-H_{syn}, C(9)-H_{syn}), 1.82 (br s, 2H, C(1)-*H*, C(3)-*H*), 1.81 (m, 2H, C(7)-*H*), 1.75 (m, 2H, C(5)-*H*), 1.68 (br s, 4H, C(1)-*H*, C(3)-*H*), 1.66 (br s, 2H, C(5)-*H*, C(7)-*H*), 1.64 (br s, 2H, C(6)H_2), 1.62 (br s, 4H, C(6)-H_2), 1.55 (br d, *J* = 12.1 Hz, 4H, C(8)-H_{anti}, C(10)-H_{anti}), 1.51 (br d, *J* = 12.2 Hz, 4H, C(4)-H_{anti}, C(9)-H_{anti}), 1.50 (br d, *J* = 11.3 Hz, 4H, C(4)-H_{anti}, C(8)-H_{anti}, C(9)-H_{anti}, C(10)-H_{anti}), 1.56 (m, 4H, CH_2CH$_2$Si), 1.55 (m, 4H, CH_2CH$_2$Si), 0.38 (m, 4H, CH$_2$CH_2Si), 0.34 (m, 4H, CH$_2$CH_2Si), 0.08 (s, 12H, CH_3Si), 0.05 (s, 12H, CH_3Si). ^{13}C NMR ($CDCl_3$): δ = 146.9 (d, *C*H=CH$_2$), 112.7 (t, *C*H$_2$=CH), 45.3 (s, C(2)), 40.9 (s, C(2)), 40.0 (t, C(6)), 39.1 (t, C(6)), 36.3 (t, C(4), C(9)), 33.9 (d, C(1), C(3)), 33.5 (t, C(8), C(10)), 33.0 (t, C(4), C(8), C(9), C(10)), 32.7 (d, C(1), C(3)),

29.8 (t, CH_2CH_2Si), 28.4 (d, C(5), C(7)), 28.2 (d, C(5)), 27.8 (d, C(7)), 24.5 (t, CH_2CH_2Si), 10.0 (t, CH_2CH_2Si), 9.6 (t, CH_2CH_2-Si), 0.3 (q, CH_3Si), 0.1 (q, CH_3Si). CI-MS: *m/z* (%) = 834 (2, M^+), 644 (8), 578 (7), 510 (5), 481 (27), 453 (18), 381 (10), 367 (8), 321 (40), 173 (71), 133 (100), 79 (24). Anal. Calcd for $C_{50}H_{88}O_2Si_4$ (833.60): C, 72.04; H, 10.64. Found: C, 72.21; H, 10.73.

Table 2, entry 5: according to general procedure 2, from **1** (100 mg, 5.3×10^{-4} mol), $Pt_2Cl_4(CH_2CH_2)_2$ (0.3 mg, 5.3×10^{-7} mol), and 1,1,2,2-tetramethyldisilane (**4e**) (155 mg, 6.4×10^{-4} mol). After 24 h at reflux the mixture was shown by GC to contain **5e** and **6e** in a ratio of 70/30, which were isolated by chromatography. FC (7:3 hexane/AcOEt) gave **5e** (127 mg, 55%) along with **6e** (54 mg, 24%).

5e: single stereoisomer, colorless liquid. ^{1}H NMR ($CDCl_3$): δ = 7.60−7.55 (m, 4H, 2 *arom. H*), 7.40−7.28 (m, 6H, 3 *arom. H*), 2.00 (br d, *J* = 12.0 Hz, 4H, C(4)-H_{syn}, C(8)-H_{syn}, C(9)-H_{syn}, C(10)-H_{syn}), 1.79 (br s, 2H, C(1)-*H*, C(3)-*H*), 1.74 (br s, 2H, C(5)-*H*, C(7)-*H*), 1.65 (br s, 2H, C(6)H_2), 1.59 (m, 4H, CH_2CH_2Si), 1.52 (br d, *J* = 12.0 Hz, 4H, C(4)-H_{anti}, C(8)-H_{anti}, C(9)-H_{anti}, C(10)-H_{anti}), 0.70 (m, 4H, CH_2CH_2Si), 0.36 (s, 6H, CH_3Si). ^{13}C NMR ($CDCl_3$): δ = 134.2 (s, *C*−Si), 133.3 (d, =*C*H), 133.0 (d, =*C*H), 127.8 (d, =*C*H), 127.6 (d, =*C*H), 127.2 (d, =*C*H), 40.1 (s, C(2)), 38.9 (t, C(6)), 33.9 (t, C(4), C(8), C(9), C(10)), 33.0 (d, C(1), C(3)), 29.6 (d, C(5), C(7)), 27.7 (t, CH_2CH_2Si), 8.7 (t, CH_2CH_2Si), −7.4 (q, $SiCH_3$). EI-MS: *m/z* (%) = 430 (34, M^+), 352 (21), 274 (12), 258 (5), 214 (11), 186 (36), 135 (100), 73 (18), 59 (10). Anal. Calcd for $C_{28}H_{38}Si_2$ (430.78): C, 78.07; H, 8.89. Found: C, 77.88; H, 8.76.

6e: single stereoisomer, colorless liquid. ^{1}H NMR ($CDCl_3$): δ = 7.62−7.50 (m, 4H, 4 *arom. H*), 7.39−7.33 (m, 6H, 6 *arom. H*), 5.54 (dd, *J* = 18.1 Hz, 11.3 Hz, 1H, C*H*=CH_2), 5.17 (dd, *J* = 11.3 Hz, 1.5 Hz, 1H, CH_2=CH cis), 4.88 (dd, *J* = 18.1 Hz, 1.5 Hz, 1H, CH_2=CH trans), 3.64 (m, 1H, Si*H*), 2.03 (br d, *J* = 12.0 Hz, 2H, C(8)-H_{syn}, C(10)-H_{syn}), 1.96 (br d, *J* = 12.4 Hz, 2H, C(4)-H_{syn}, C(9)-H_{syn}), 1.80 (m, 1H, C(7)-*H*), 1.79 (m, 1H, C(5)-*H*), 1.72 (br s, 2H, C(1)-*H*, C(3)-*H*), 1.66 (br s, 2H, C(6)-H_2), 1.57 (m, 2H, CH_2CH_2Si), 1.55 (br d, *J* = 12.3 Hz, 2H, C(8)-H_{anti}, C(10)-H_{anti}), 1.52 (br d, *J* = 12.5 Hz, 2H, C(4)-H_{anti}, C(9)-H_{anti}), 0.71 (m, 2H, CH_2CH_2Si), 0.38 (s, 6H, CH_3Si). ^{13}C NMR ($CDCl_3$): δ = 146.7 (d, *C*H=CH_2), 133.3 (d, =*C*H), 133.2 (d, =*C*H), 127.8 (d, =*C*H), 127.7 (d, =*C*H), 127.6 (d, =*C*H), 113.1 (t, CH_2=CH), 45.1 (s, C(2)), 38.9 (t, C(6)), 33.9 (t, C(4), C(9)), 33.4 (d, C(1), C(3)), 32.3 (t, C(8), C(10)), 29.7 (t, CH_2CH_2Si), 29.4 (d, C(5)), 27.7 (d, C(7)), 2.4 (t, CH_2CH_2Si), 8.5 (t, CH_2CH_2-Si), −7.5 (q, $SiCH_3$). CI-MS: *m/z* (%) = 430 (7, M^+), 309 (21), 232 (17), 217 (11), 189 (34), 162 (56), 143 (8), 133 (100), 115 (65), 87 (2), 78 (43), 59 (2). Anal. Calcd for $C_{28}H_{38}Si_2$ (430.78): C, 78.07; H, 8.89. Found: C, 78.11; H, 8.92.

Reaction with *o*-bis(dimethylsilyl)benzene (4f): according to general procedure 2, from **1** (100 mg, 5.3×10^{-4} mol), $Pt_2Cl_4(CH_2CH_2)_2$ (0.3 mg, 5.3×10^{-7} mol) and 1,2-bis(dimethylsilyl)benzene (**4f**) (124 mg, 6.4×10^{-4} mol). After 24 h at reflux the mixture was shown by GC to contain **7**, **8**, **9**, and **10** in a ratio of 57/22/8/13, which were isolated by chromatography. FC (hexane) gave **7** (105 mg, 52%) along with **8** (40 mg, 20%), **9** (14 mg, 7%), and **10** (12 mg, 12%).

7: colorless liquid. ^{1}H NMR ($CDCl_3$): δ = 7.56−7.53 (m, 2H, =C*H*), 7.38−7.36 (m, 2H, =C*H*), 1.99 (br d, *J* = 11.9 Hz, 2H, C(8)-H_{syn}, C(10)-H_{syn}), 1.98 (br d, *J* = 12.1 Hz, 2H, C(4)-H_{syn}, C(9)-H_{syn}), 1.94 (m, 1H, C(7)-*H*), 1.99 (m, C(5)-*H*), 1.75 (br s, 2H, C(1)-*H*, C(3)-*H*), 1.72 (br s, 2H, C(6)H_2), 1.67 (br d, *J* = 11.9 Hz, 2H, C(8)-H_{anti}, C(10)-H_{anti}), 1.65 (br d, *J* = 12.1 Hz, 2H, C(4)-H_{anti}, C(9)-H_{anti}), 1.06 (d, *J* = 6.6 Hz, 3H, CH_3-CH), 0.67 (dd, *J* = 12.2 Hz, 8.7, 1H, C*H*CHSi), 0.51 (dd, *J* = 8.7 Hz, 6.6 Hz, 1H, C*H*CH_3), 0.41 (q, 3H, CH_3Si), 0.37 (q, 3H, CH_3Si), 0.35 (q, 3H, CH_3Si), 0.31 (q, 3H, CH_3Si), 0.11 (d, *J* = 12.2 Hz, 1H, SiC*H*Si). ^{13}C NMR ($CDCl_3$): δ = 150.5 (s, *C*Si), 150.0 (s, *C*Si), 131.7 (d, =*C*H), 131.6 (d, =*C*H), 128.7 (d, =*C*H), 128.6 (d, =*C*H), 41.7 (d, C(1)), 37.5 (t, C(6)), 36.5 (t, C(4)), 36.3 (t, C(9)), 36.0 (t, C(8)), 35.9 (t, C(10)), 31.9 (s, C(2)), 28.3 (d, C(3)), 28.1 (d, C(5)), 27.7 (d, C(7)), 25.5 (d, *C*HCHSi), 21.1 (d, *C*HCH_3), 9.4 (q, *C*H_3CH), 3.5 (d, Si*C*HSi), 1.7 (q,*C*H_3Si), 1.6 (q,*C*H_3Si), −0.8 (q,*C*H_3Si), −1.3 (q,*C*H_3Si). CI-MS: *m/z* (%) = 381 (11, M^+), 366 (4), 351(7), 275 (23), 217 (45), 191 (32), 133 (100), 59 (2). Anal. Calcd for $C_{24}H_{36}Si_2$ (380.72): C, 75.72; H, 9.53. Found: C, 75.84; H, 9.65.

8: colorless liquid. ^{1}H NMR ($CDCl_3$): δ = 7.53 (dd, *J* = 5.4 Hz, 3.1, 2H, =C*H*), 7.35 (dd, *J* = 5.4 Hz, 3.1 Hz, 2H, =C*H*), 5.65 (dd, *J* = 18.1 Hz, 11.2 Hz, 1H, C*H*=CH_2), 5.19 (dd, *J* = 11.2 Hz, 1.5 Hz, 1H, CH_2=CH cis), 4.96 (dd, *J* = 18.1 Hz, 1.5 Hz, 1H, CH_2=CH trans), 2.11 (br d, *J* = 11.6 Hz, 2H, C(8)-H_{syn}, C(10)-H_{syn}), 2.07 (br d, *J* = 12.3 Hz, 2H, C(4)-H_{syn}, C(9)-H_{syn}), 1.94 (m, 1H, C(7)-*H*), 1.86 (m, C(5)-*H*), 1.90 (d, *J* = 5.2 Hz, 2H, CH_2CHSi), 1.79 (br s, 2H, C(1)-*H*, C(3)-*H*), 1.67 (br s, 2H, C(6)H_2), 1.62 (br d, *J* = 11.6 Hz, 2H, C(8)-H_{anti}, C(10)-H_{anti}), 1.54 (br d, *J* = 12.3 Hz, 2H, C(4)-H_{anti}, C(9)-H_{anti}), 0.32 (s, 6H, CH_3Si), 0.18 (dd, *J* = 5.2 Hz, 5.2 Hz, 1H, SiC*H*Si), 0.17 (s, 6H, CH_3Si). ^{13}C NMR ($CDCl_3$): δ = 150.5 (s, *C*Si), 150.0 (s, *C*Si), 147.7 (d, *C*H=CH_2), 131.8 (d, =*C*H), 128.5 (d, =*C*H), 113.8 (t,CH_2=CH), 45.4 (s, C(2)), 38.9 (t, C(6)), 34.0 (t, C(4), C(9)), 33.9 (d, C(1), C(3)), 32.9 (t, C(8), C(10)), 32.3(t, CH_2-CHSi), 28.3 (d, C(5)), 28.0 (d, C(7)), 4.8 (d, Si*C*HSi), −0.3 (q, CH_3Si), −1.2 (q, CH_3Si). CI-MS: *m/z* (%) = 381 (17, M^+), 366 (12), 351 (2), 305 (4), 275 (15), 247 (45), 189 (22), 163 (43), 133 (100), 76 (6), 59 (2). Anal. Calcd for $C_{24}H_{36}Si_2$ (380.72): C, 75.72; H, 9.53. Found: C, 75.92; H, 9.69.

9: colorless liquid. ^{1}H NMR ($CDCl_3$): δ = 7.57−7.52 (m, 2H, =C*H*), 7.34−7.29 (m, 2H, =C*H*), 5.653 (dd, *J* = 18.1 Hz, 11.2 Hz, 1H, C*H*=CH_2), 5.14 (dd, *J* = 11.2 Hz, 1.6 Hz, 1H, CH_2=CH cis), 4.84 (dd, *J* = 18.1 Hz, 1.6 Hz, 1H, CH_2=CH trans), 2.102 (br d, *J* = 10.5 Hz, 2H, C(8)-H_{syn}, C(10)-H_{syn}), 1.97 (br d, *J* = 12.7 Hz, 2H, C(4)-H_{syn}, C(9)-H_{syn}), 1.90 (m, 1H, C(7)-*H*), 1.87 (m, C(5)-*H*), 1.78 (br s, 2H, C(1)-*H*, C(3)-*H*), 1.65 (br s, 2H, C(6)H_2), 1.57 (br d, *J* = 10.5 Hz, 2H, C(8)-H_{anti}, C(10)-H_{anti}), 1.52 (br d, *J* = 12.7 Hz, 2H, C(4)-H_{anti}, C(9)-H_{anti}), 1.48 (m, 1H, C*H*Si), 0.68 (m, 2H, CH_2Si), 0.32 (s, 3H, CH_3Si), 0.31 (s, 6H, CH_3Si), 0.30 (s, 3H, CH_3Si). ^{13}C NMR ($CDCl_3$): δ = 150.6 (s, *C*Si), 150.1 (s, *C*Si), 146.9 (d, *C*H=CH_2), 134.5 (d, =*C*H), 134.4 (d, =*C*H), 127.9 (d, =*C*H), 127.8 (d, =*C*H), 112.8 (t,CH_2=CH), 45.2 (s, C(2)), 39.0 (t, C(6)), 34.0 (t, C(4), C(9)), 33.5 (d, C(1), C(3)), 32.4 (t, C(8), C(10)), 28.5 (d, C(5)), 27.8 (d, C(7)), 15.3 (d, *C*HSi), 8.5 (t, *C*H_2Si), −0.8 (q, *C*H_3Si), −2.3 (q, *C*H_3Si). CI-MS: *m/z* (%) = 381 (4, M^+), 365 (25), 349 (12), 317 (6), 305 (18), 261 (28), 247 (18), 192 (32), 185 (13), 158 (76), 136 (17), 133 (100), 76 (43), 59 (11). Anal. Calcd for $C_{24}H_{36}$-Si_2 (380.72): C, 75.72; H, 9.53. Found: C, 75.86; H, 9.61.

10: colorless liquid. ^{1}H NMR ($CDCl_3$): δ = 5.58 (dd, *J* = 18.0 Hz, 11.2 Hz, 1H, C*H*=CH_2), 5.14 (dd, *J* = 11.2 Hz, 1.7 Hz, 1H, CH_2=CH cis), 4.87 (dd, *J* = 18.0 Hz, 1.7 Hz, 1H, CH_2=CH trans), 2.04 (br d, *J* = 12.0 Hz, 4H, C(4)-H_{syn}, C(8)-H_{syn}, C(9)-H_{syn}, C(10)-H_{syn}), 1.81 (br s, 2H, C(1)-*H*, C(3)-*H*), 1.70 (br s, 2H, C(5)-*H*, C(7)-*H*), 1.65 (br s, 2H, C(6)H_2), 1.58 (q, *J* = 7.4 Hz, 2H, CH_2CH_3), 1.55 (br d, *J* = 12.0 Hz, 4H, C(4)-H_{anti}, C(8)-H_{anti}, C(9)-H_{anti}, C(10)-H_{anti}), 0.73 (t, *J* = 7.4 Hz, 3H, CH_3CH_2). ^{13}C NMR ($CDCl_3$): δ = 147.1 (d, *C*H=CH_2), 112.6 (t,CH_2=CH), 44.6 (s, C(2)), 39.2 (t, C(6)), 34.0 (t, C(4), C(9)), 33.7 (d, C(1), C(3)), 32.6 (t, C(8), C(10)), 29.3 (t, CH_2CH_3), 28.6 (d, C(5)), 28.0 (d, C(7)), 6.9 (q, *C*H_3CH_2). CI-MS: *m/z* (%) = 190 (25, M^+), 174 (7), 162 (36), 145 (62), 133 (100), 76 (45), 59 (16). Anal. Calcd for $C_{14}H_{22}$ (190.33): C, 88.35; H, 11.65. Found: C, 88.22; H, 11.60.

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