Silylated Cyclohexadienes in Radical Chain Hydrosilylations

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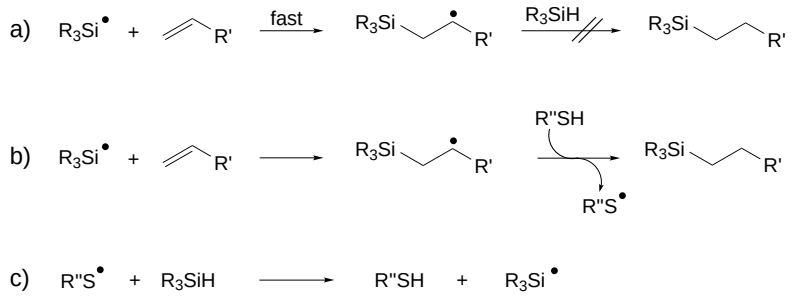
Dedicated to Professor *Dieter Seebach* on the occasion of his 65th birthday

A new method for the mild radical hydrosilylation of alkenes and alkynes is described. Silylated cyclohexadienes that can be readily prepared on large scale are used as radical hydrosilylating reagents. Non-activated alkenes and alkynes are hydrosilylated in high yields. The reaction can be combined with C–C bond formation, as demonstrated for the preparation of silylated cycloalkanes from the corresponding dienes. Furthermore, radical hydrosilylations in combination with β-fragmentation reactions for the synthesis of allylsilanes and hydrosilylations of aldehydes and ketones providing protected alcohols can be readily performed by this strategy.

1. Introduction. – The radical chain hydrosilylation of alkenes in the presence of simple trialkylsilanes in an inefficient reaction and, therefore, rarely used in preparative synthesis. It is well-known that the addition of a silyl radical to an alkene is a fast process [1][2]. However, the subsequent reduction of the resulting β-silylalkyl radical with a trialkylsilane is a slow reaction at ambient temperatures (*Scheme 1*,*a*). This inefficient reduction generally leads to chain termination. Therefore, there are not many procedures known for successful radical chain hydrosilylations. By using more reactive silanes, however, the reduction of the β-silylalkyl radical should be feasible. Indeed, tris(trimethylsilyl)silane [3], with its more reactive Si–H bond compared to regular trialkyl silanes, has been successfully used in radical hydrosilylation reactions [4–6]. Moreover, the surface modification of porous silicon that contains reactive Si–H bonds has also been achieved *via* radical hydrosilylation reactions [7].

Scheme 1

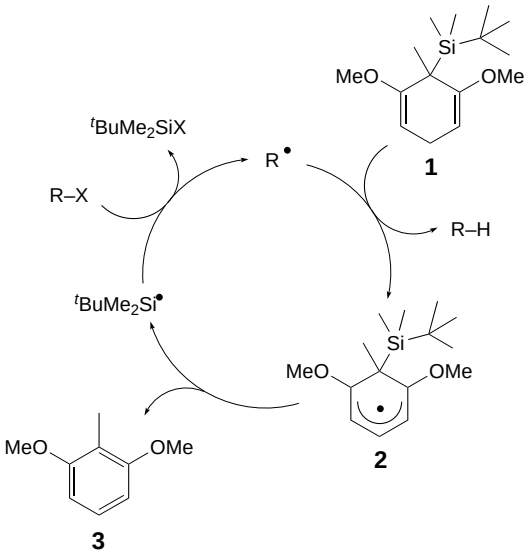


[1]) Part of the Ph.D. Thesis of *S. A.*

In elegant work, *Roberts* showed that the radical hydrosilylation with non-activated trialkylsilanes can be conducted in the presence of thiols as polarity-reversal catalysts [8]. Here, the direct abstraction of H from the silane by the β-silylalkyl radical is replaced by a H-transfer reaction from a thiol (*Scheme 1*,*b*). The thiyl radical generated is then reduced by the silane to provide the chain-carrying silyl radical along with the thiol (*Scheme 1*,*c*). Both types of H-transfer reactions benefit from favorable polar effects. *Matsumoto* and *Ito* generated silyl radical by selective Si–B bond homolysis of bis(diisopropylamino)organosilylboranes and used them in non-chain radical hydrosilylation reactions [9].

Recently, we introduced silylated cyclohexadienes as new Sn-free radical reducing reagents [10]. Various typical radical reactions, *e.g.*, dehalogenations, deselenations, deoxygenations, and intermolecular additions were performed with the aid of these new reagents. The cyclohexadiene CH_2 moiety acts as the H donor in these radical chain reactions [11]. Reduction of a radical R$^{\bullet}$ with reagent **1** affords a cyclohexadienyl radical **2** (*Scheme 2*). Re-aromatization of the latter provides the corresponding silyl radical, which is able to propagate the chain by reaction with the starting halide, xanthate, or phenyl selenide R–X. As a by-product, the methylated resorcin diether **3** is formed. In a preliminary communication, we reported the successful application of silylated cyclohexadienes of type **1** in hydrosilylation reactions [12]. The silyl radical formed in the re-aromatization of **2** is allowed to react with an alkene to form a β-silylalkyl radical that is subsequently reduced with the cyclohexadiene **1** to yield **2** and the corresponding hydrosilylation product.

Scheme 2

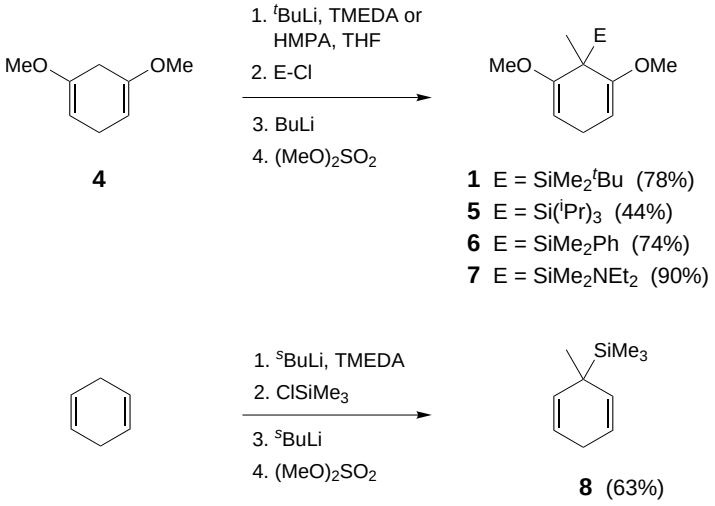


The hydrosilylation of alkenes can formally be regarded as a *transfer-hydrosilylation* since the reagent is transformed into the corresponding arene in a reverse hydrosilylation process. Here, we present in full detail our results on the radical

hydrosilylation of various unsaturated substrates with the aid of silylated cyclohexadienes.

2. Results and Discussion. – *Hydrosilylations of Alkenes.* The reagents **1** and **5**–**7** can be readily prepared from cyclohexadiene **4** [13] in a one-pot procedure (*Scheme 3*). The regioselective metallation [14] of **4** is accomplished with ^{t}BuLi in tetrahydrofurane (THF) with either hexamethylphosphortriamide (HMPA) or the nontoxic *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) as an additive at −78°. Silylation with the commercially available chlorosilanes $ClSiMe_2(^tBu)$, $ClSiMe_2Ph$, $ClSi(^iPr)_3$ or with $ClSiMe_2(NEt_2)$ [15] provided the corresponding silylated cyclohexadienes that, again, underwent metalation upon BuLi addition. Methylation with dimethyl sulfate provided the reagents **1** and **5**–**7** in moderate to high yields (44–90%). Reagent **8** was prepared analogously, starting from cyclohexa-1,4-diene treated with ^{s}BuLi and TMEDA (63%) [16]. The trimethylsilyl derivative prepared from cyclohexadiene **4** (not shown) is not stable and was, therefore, not used in radical hydrosilylation reactions.

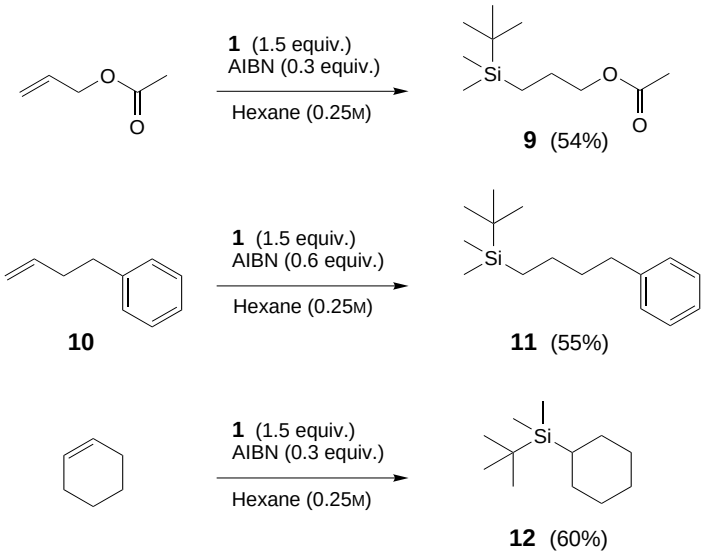
Scheme 3



The radical hydrosilylation of non-activated C=C bonds in the presence of cyclohexadiene **1** was studied first. From our previous work, we knew that hexane is the solvent of choice to perform radical chain reactions with tin hydride substituents of type **1** [10]. We were pleased to find that the hydrosilylation of allyl acetate with reagent **1** worked well in hexane (0.25M) when α,α-azoisobutyronitrile (AIBN) was used as an initiator (sealed tube, 80–85°) (*Scheme 4*). Best results were obtained with 1.5 equiv. of **1** and 0.3 equiv. of AIBN. Under these conditions, the silylated product **9** was isolated in 54% yield. Under analogous conditions, compound **10** was hydrosilylated to afford the tetraalkylsilane **11** in 55% yield. Our method is not restricted to the hydrosilylation of terminal C=C bonds, as demonstrated by the transformation of cyclohexene to the silylated cyclohexane derivative **12** (60%). However, the hydrosilylation of tetrasub-

stituted alkenes failed. Tetramethylethene (2,3-dimethylbut-2-ene), *e.g.*, was recovered almost quantitatively.

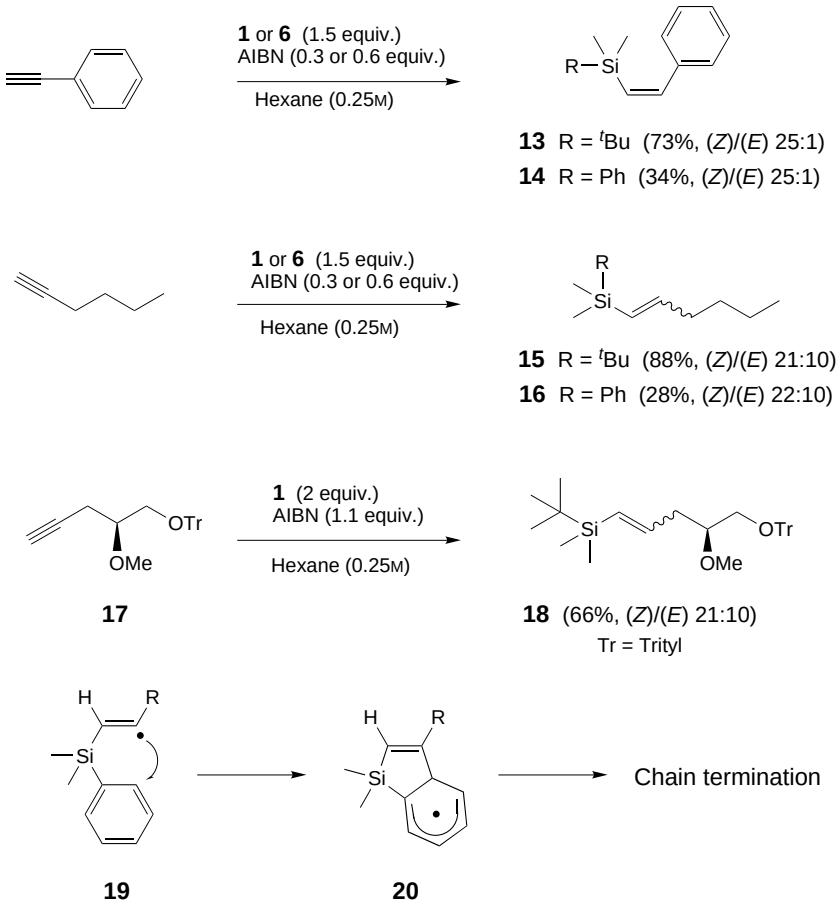
Scheme 4



Hydrosilylations of Alkynes. We next focused on the hydrosilylation of alkynes, which were reacted under the optimized conditions described above (1.5 equiv. of reagent in hexane (0.25M), 0.3 equiv. of AIBN, 80–85°, sealed tube). Hydrosilylation of phenylacetylene with reagent **1** afforded the vinylsilane **13** in 73% yield as a 25:1 mixture of diastereoisomers (*Scheme 5*). An even higher yield (88%) was obtained for **15**, arising from the hydrosilylation of hex-1-yne. However, the stereoselectivity of the reaction dropped markedly ((*Z*)/(*E*) 21:10). It is well-known that Ph-substituted vinyl radicals can be stereoselectively reduced [17]. These π-type vinyl radicals are linear, and the stereoselectivity of the reduction is determined by the size of the substituent in β-position. However, alkyl-substituted (nonconjugated) vinyl radicals are sp^2-hybridized and invert at very low energy barriers [18]. The product ratio depends on the equilibrium constant of the two interconverting vinyl radicals and on the rate constant of the reduction. In general, lower selectivities are obtained for the reduction of these σ-type vinyl radicals compared to the reduction of Ph-substituted vinyl radicals, as observed in our experiments.

Hydrosilylation of alkyne **17** with reagent **1** provided the vinylsilane **18** in 66% yield. Hydrosilylation of phenylacetylene with reagent **6** (instead of **1**) led to **14** in only 19% yield. Thus, hydrosilylation of phenylacetylene with the (*tert*-butyl)dimethylsilyl reagent **1** is much more efficient than with the phenyl(dimethyl)silyl-derived reagent **6**. We believe that the vinyl radical **19**, formed after phenyl(dimethyl)silyl radical addition, reacts with the Ph substituent at the Si-atom to afford the cyclohexadienyl radical **20** (*Scheme 5*). The latter is rather stable and, thus, cannot propagate the chain reaction. Indeed, with 0.6 equiv. of AIBN, the yield of **14** could be slightly increased to 34%. However, further

Scheme 5



increase of the initiator concentration (0.9 equiv.) does not lead to higher yields. A similar result was obtained for the hydrosilylation of hex-1-yne with cyclohexadiene **6**. The vinyl silane **16** was isolated in 28% yield upon adding 0.6 equiv. of AIBN.

Hydrosilylations can also be performed without AIBN by using O_2 (air) as an initiator. Thus, reaction of phenylacetylene with reagent **1** in hexane under an atmosphere of O_2 provided **13** in 55% yield (reflux, 24 h). Attempted room-temperature hydrosilylation with Et_3B/O_2, however, failed.

Hydrosilylation/Cyclization. The hydrosilylation/cyclization of dienes in the presence of transition-metal catalysts is a well-studied reaction [19]. From an ecological point of view, however, it would be favorable if one had not to rely on transition metals. We, therefore, tested our reagents in the hydrosilylation of dienes **21**–**25** and **31** (*cf. Scheme 6* and the *Table*).

Reaction of diene **21** with reagent **1** afforded product **26** in 80% yield as a 43 : 10 mixture of diastereoisomers. The initially formed β-silylalkyl radical undergoes a 5-*exo*-

Scheme 6

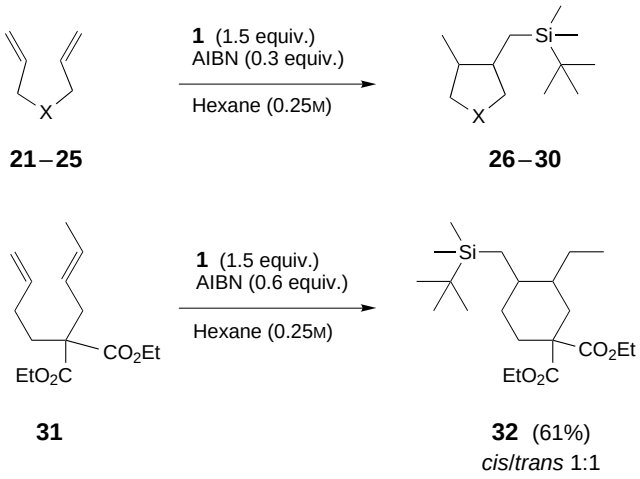
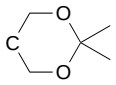


Table. *Hydrosilylation/Cyclization of Various Dienes*

X	Starting material	Yield [%]	Product	*cis*/*trans*
$C(CO_2Et)_2$	**21**	80	**26**	43 : 10
O	**22**	71	**27**	25 : 10
N–Ts	**23**[a])	76	**28**	20 : 10
$C(CH_2OH)_2$	**24**[b])	62	**29**	23 : 10
	**25**	72	**30**	26 : 10

[a]) The reaction was complete in 7 h. [b]) 3 Equiv. of **6** and 0.6 equiv. of AIBN were used.

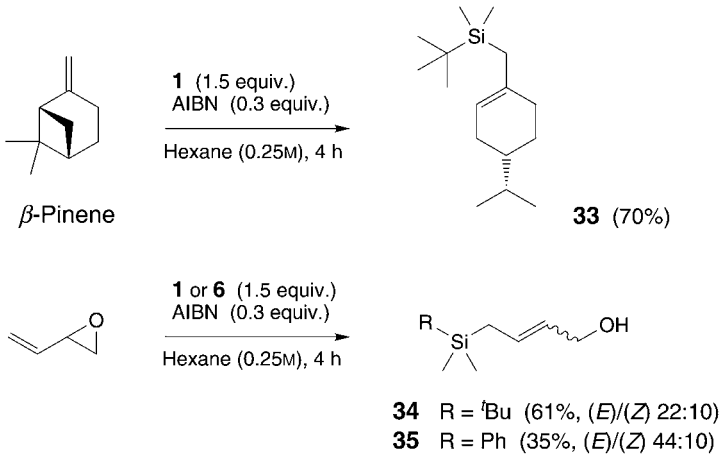
cyclization to a primary radical that is reduced by **1** to the five-membered ring of **26**. The isomer ratio was determined by gas chromatography (GC). The assignment of the relative configuration is based on comparison of the ^{1}H-NMR data with literature values [20]. All compounds were identified in this way. The formation of the *cis*-compound as the major isomer is in accordance with the *Beckwith–Houk* model for 5-*exo*-cyclizations [21]. Similarly, the diallyl ether **22** was readily transformed into the furan derivative **27** in 71% yield, with a diastereoisomer ratio (dr) of 25 : 10. The tosylated pyrrolidine **28** was obtained in 76% yield from sulfonamide **23** (dr 20 : 10). The hydrosilylation of diol **24** did not go to completion under standard conditions. However, with 3 equiv. of **1** and 0.6 equiv. of AIBN product **29** was obtained in 62% yield (dr 23 : 10). Hydrosilylation of acetal **25** led to the cyclization product **30** in 72% yield (dr 26 : 10).

We have previously shown that reagent **1** reduces primary C-radicals about 55 times slower than Bu_3SnH does [10]. This should allow us to study *slow* radical chain

reactions. For instance, the hydrosilylation/cyclization of diene **31** worked well, and the product **32** was isolated in 61% yield (dr 1:1). The silyl radical addition occurs highly regioselectively at the less-hindered terminal C=C bond and is followed by a rather slow 6-*exo*-cyclization. The product of a mono hydrosilylation was not observed.

Since the reduction of the initially formed β-silylalkyl radical with reagent **1** is a slow process, it should be possible to combine it with other radical reactions, *e.g.*, β-fragmentations. This would directly lead to allylsilanes – highly versatile carbon nucleophiles in organic synthesis [22]. We, therefore, studied the hydrosilylation of β-pinene. The expected product **33** was isolated in 70% yield (*Scheme 7*). Hydrosilylation can also be combined with the cleavage of a carbon–heteroatom bond, as shown for the transformation of vinyloxirane to the corresponding allyl alcohol **34** (61%) (*Scheme 7*). A lower yield (35%) was obtained for the analogous reaction performed with reagent **6** leading to **35**.

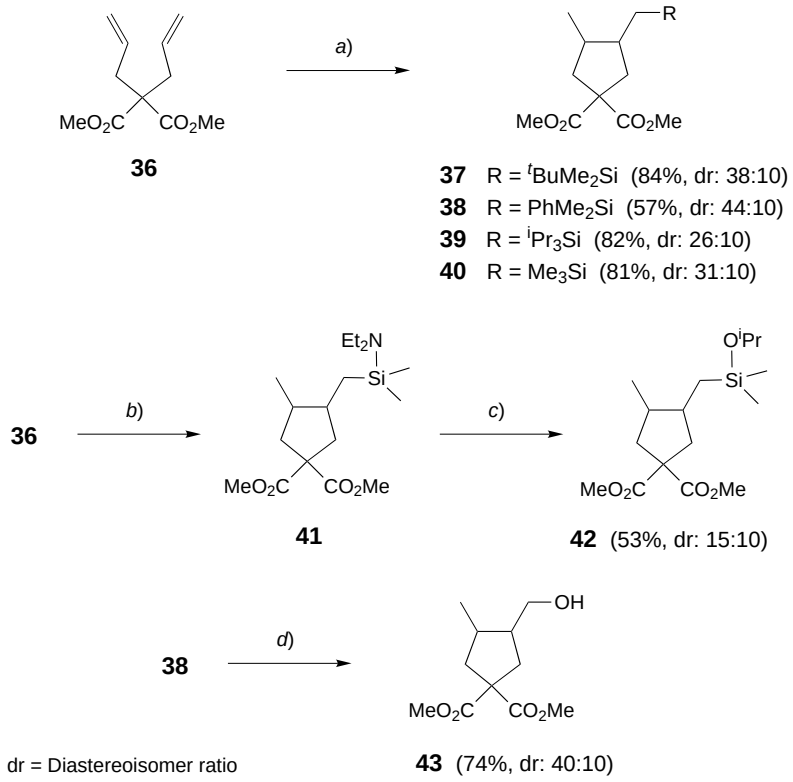
Scheme 7



Our synthetic strategy for the preparation of hydrosilylating reagents basically allows the introduction of any silyl group (*cf. Scheme 3*). To demonstrate this potential, the hydrosilylation/cyclization of diene **36** was studied with the Si reagents **1** and **5**–**8** (*Scheme 8*). It turned out that the nature of the silyl group influences the outcome of the reaction. With the standard reagent **1**, under typical conditions (1.5 equiv. of Si reagent, 0.3 equiv. of AIBN, hexane (0.25M)), the cyclization product **37** was obtained in 84% yield (dr 38:10). The reaction with the phenyl(dimethyl)silyl-derived reagent **6** was less efficient and led to **38** in 57% yield (dr 44:10). Reaction of **36** with the bulky triisopropylsilyl derivative **5** provided the hydrosilylation/cyclization product **39** in only 44% yield (dr 38:10). Finally, with reagent **8**, lacking the methoxy substituents, the hydrosilylation/cyclization of **36** could not be accomplished, and the cyclopentane dicarboxylate **40** was not observed at all. However, we found that the hydrosilylation/cyclization reaction of **36** with reagents **5** and **8** works well at 140° in the presence of di(*tert*-butyl) peroxide as the initiator. The reactions were conducted in hexane in sealed tubes. Under these modified conditions, compound **39** was obtained in 82%

yield, but with a slightly lower selectivity (dr 26:10). The corresponding reaction with the trimethylsilyl derivative **8** at 140° provided **40** in 81% yield as a 31:10 mixture of diastereoisomers.

Scheme 8



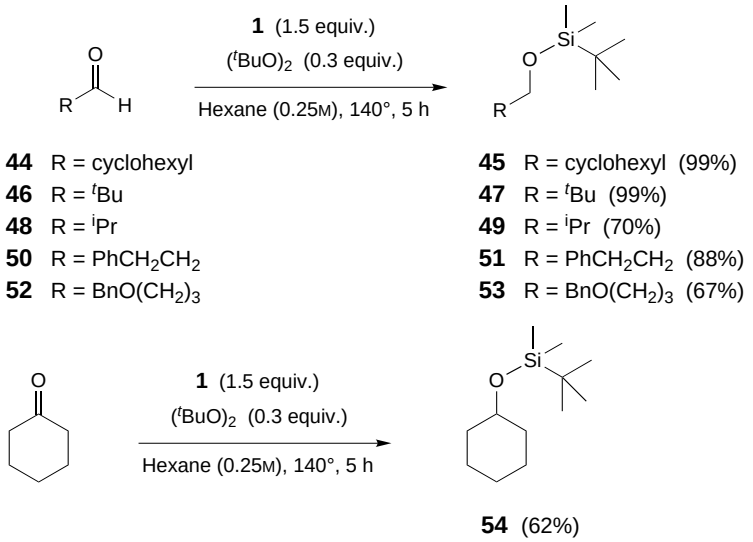
a) **1**, **5**, **6**, or **8** (1.5–2.2 equiv.), AIBN (0.3–0.9 equiv.) or $(^tBuO)_2$ (0.5 equiv.), hexane (0.25M). *b*) **7** (1.5 equiv.), AIBN (0.3 equiv.), hexane (0.25M). *c*) ^{i}PrOH, NH_4Cl. *d*) $Hg(OAc)_2$, AcOOH.

Reagent **7** is an interesting compound, since such aminosilanes can be regarded both as electrophilic and radical silylation reagents. The hydrosilylation of diene **36** with **7**, under standard conditions, provided **41** in a clean reaction (*Scheme 8*). However, it was difficult to isolate the product. We, therefore, treated the crude reaction mixture with ^{i}PrOH in the presence of NH_4Cl [23], which afforded the silylether **42** in 53% yield (dr 15:10).

The phenyl(dimethyl)silyl reagent **6** is synthetically very useful, because the corresponding hydrosilylation products can be easily converted to alcohols by *Tamao–Fleming* oxidation [24]. The cyclization product **38**, *e.g.*, was oxidized to the alcohol **43** in 73% yield [25]. Formally, the above hydrosilylation process can, thus, be regarded as a radical *anti-Markovnikov* hydration.

Hydrosilylation of C=C Bonds. Finally, we studied the radical hydrosilylation of various aldehydes in the presence of **1** [26]. With AIBN as the initiator at 80° in hexane,

Scheme 9



low yields of the corresponding hydrosilylation products were obtained. However, at 140° in sealed tubes and in the presence of $(^t\text{BuO})_2$, all reactions went to completion, and the desired *tert*-butyldimethylsilyl- (TBDMS) protected alcohols were isolated in high yields (*Scheme 9*). Cyclohexanecarbaldehyde (**44**) and pivalaldehyde (**46**) were quantitatively converted to the corresponding silyl ether **45** and **47**. Hydrosilylation of isobutyraldehyde (**48**) afforded **49** in 70% yield. Thereby, some product was lost during the purification process (volatile compound). Attempted hydrosilylations of benzaldehyde failed. Under standard conditions (1.5 equiv. of **1**, 0.3 of $(^t\text{BuO})_2$, 140°), the starting material was mostly recovered. The benzylic radical generated upon addition of the silyl radical is obviously too stable to be reduced by reagent **1**. Somewhat lower yields were obtained for the reductions of the aliphatic aldehydes **50** and **52** leading to **51** (88%) and **53** (67%), respectively. Here, the addition of the silyl radical to the Ph group, a process that would lead to chain termination, probably competes with the desired hydrosilylation. Finally, it should be pointed out that our hydrosilylation method is not restricted to aldehydes. Cyclohexanone, *e.g.*, was converted to the silyl ether **54** in 62% yield.

3. Conclusions. – We have presented a new method for the radical hydrosilylation of alkenes, alkynes, aldehydes, and ketones with the aid of silylated cyclohexadienes. The reaction can formally be regarded as a *transfer-hydrosilylation*, since the reagent is transformed into the corresponding arene by a reverse hydrosilylation reaction, a process not known so far. The synthesis of the silylated cyclohexadiene reagent is straightforward and allows the variation of the silyl group. Various unsaturated substrates are efficiently hydrosilylated with these new reagents in an environmentally benign process. In the hydrosilylation of acetylenes, high stereoselectivities can be

obtained. The hydrosilylation of hepta-1,6-diene derivatives leads to silylated cyclopentanes. Thus, our new method nicely complements hydrosilylation/cyclization reactions performed with (toxic) transition metal catalysts. Vinyl-substituted cyclopropanes and vinyl oxirane are transformed into allyl silanes, useful nucleophiles in synthetic organic chemistry. In addition, the radical hydrosilylation of aldehydes can also be efficiently achieved with our new reagent.

We thank the *Swiss National Science Foundation* (2100-055280.98/1) for funding our work.

Experimental Part

General. Solvents were purified by standard methods. Air- and moisture-sensitive compounds were handled under Ar gas using *Schlenk* techniques. TLC: *Merck* silica gel *60* F_{254} plates; UV detection or staining with a soln. of $KMnO_4$ (1.5 g) in 1M NaOH (333 ml) or with a soln. of $Ce(SO_4)_2 \cdot H_2O$ (10 g), phosphormolybdic acid hydrate (25 g), conc. H_2SO_4 (60 ml), and H_2O (940 ml), followed by heating. FC: *Merck* or *Fluka* silica gel *60* (40–63 μm) at *ca*. 0.4 bar. GC: *Hewlett Packard 5890* chromatograph using *Hewlett Packard HP-5* or *Supelco μ-DEX-120* columns. M.p.: *Büchi 510* apparatus; uncorrected. IR: *Perkin Elmer 782* or *Bruker IFS-200* spectrophotometer, in cm^{-1}. ^1H- and ^{13}C-NMR: *Bruker AMX-500*, *AMX-400*, *AC-300*, or *Varian Gemini 300*. Chemical shifts δ in ppm rel. to $SiMe_4$ as internal standard, *J* in Hz.

General Procedure 1 (*GP 1*) *for the Synthesis of Si Reagents* **1**, **6**, *and* **7**. 1,5-Dimethoxycyclohex-1,4-diene (**4**) [13] was dissolved in THF. The soln. was cooled to *ca*. −70°. After addition of *t*BuLi and stirring for 10 min, HMPA (hexamethylphosphortriamide) or TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) was added. The resulting red or orange soln. was stirred for 60 min at −70°. A soln. of the chlorosilane in THF was slowly added. The soln. was stirred at −50 to −70° for 60 min before BuLi was added. After stirring for another 60 min at the same temp., $(MeO)_2SO_2$ was added. The cooling bath was removed and the mixture was allowed to warm to r.t. Pentane was added, followed by H_2O. The org. layer was separated, washed with H_2O and brine, and dried ($MgSO_4$). The crude products were purified by FC, distillation, or recrystallization.

*(*tert*-Butyl)(2,6-dimethoxy-1-methylcyclohexa-2,5-dienyl)dimethylsilane* (**1**). Prepared according to *GP 1* from **4** (21 g, 0.15 mol) in THF (450 ml), *t*BuLi (94 ml, 1.76M in pentane, 0.165 mol), TMEDA (24.7 ml, 0.165 mol), *t*BuMe$_2$SiCl (24.9 g, 0.165 mol) in THF (30 ml), BuLi (102.5 ml, 1.61M in hexane, 0.165 mol), and $(MeO)_2SO_2$ (15.7 ml, 0.165 mol). Distillation (1.2 mbar, 85°) and recrystallization (MeOH) afforded **1** (31.46 g, 78%). M.p. 32–33°. IR ($CHCl_3$): 2934*s*, 2855*s*, 1677*s*, 1643*w*, 1464*m*, 1344*m*, 1127*s*, 1076*m*, 977*w*. ^1H-NMR (500 MHz, $CDCl_3$): 4.46 (*t*, *J* = 3.7, 2 CH); 3.45 (*s*, 2 MeO); 2.83–2.82 (*m*, CH_2); 1.32 (*s*, Me); 0.85 (*s*, *t*Bu); 0.00 (*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 158.9 (C_q); 88.4 (CH); 53.7 (Me); 35.7 (C_q); 27.3 (Me); 24.5 (CH_2); 19.8 (Me); 19.3 (C_q); −4.9 (Me). EI-MS: 268.2 (15, M^+), 253.1 (7, $[M - Me]^+$), 179.1 (4), 153.1 (29), 152.1 (55), 138.1 (9), 122.1 (21), 121.1 (12), 107.0 (19), 91.0 (11), 89.0 (20), 73.0 (100), 59.0 (16). Anal. calc. for $C_{15}H_{28}O_2Si$ (268.47): C 67.11, H 10.51; found: C 67.16, H 10.69.

(2,6-Dimethoxy-1-methylcyclohexa-2,5-dienyl)triisopropylsilane (**5**). Cyclohexadiene **4** (4.0 g, 28 mmol) was dissolved in THF (100 ml). The soln. was cooled to *ca*. −70°. After addition of *t*BuLi (20 ml, 1.6M in hexane, 30 mmol) and stirring for 1 h, HMPA (6.0 ml, 33 mmol) was added. The resulting red soln. was stirred for 10 min at −70°. (^{i}Pr)$_3$SiCl (6.68 ml, 30 mmol) was added slowly. The red color of the mixture disappeared. After 5 min, the cooling bath was removed and the mixture was allowed to warm to r.t. Pentane was added, followed by H_2O. The phases were separated, and the org. layer was washed with H_2O (2×) and brine and dried over $MgSO_4$. Removal of the solvent *in vacuo* and distillation (90°, 0.2 mbar) afforded (2,6-dimethoxycyclohexa-2,5-dienyl)triisopropylsilane (7.4 g, 25 mmol, 89%) as a colorless oil. The crude product (1.20 g, 4.0 mmol) was dissolved in THF (15 ml). The soln. was cooled to *ca*. −20°, BuLi (5 ml, 1.63M in hexane, 8.0 mmol) was added, and stirring was continued for 3 h at −20°. HMPA (1.4 ml, 8.0 mmol) was added, and the resulting orange soln. was stirred for 30 min at −30°. $(MeO)_2SO_2$ (0.76 ml, 8.0 mmol) was added, whereupon the color of the mixture disappeared. After 5 min, the cooling bath was removed and the soln. was allowed to warm to r.t. Pentane was added, followed by H_2O, the org. layer was separated, washed with H_2O (2×) and brine, and dried ($MgSO_4$). Removal of the solvent *in vacuo* and purification by FC (pentane) afforded **5** (605 mg, 49%; 44% over two steps) as a colorless amorphous solid. IR ($CHCl_3$): 2947*s*, 2866*s*, 2831*s*, 1681*s*, 1642*m*, 1581*w*, 1465*s*, 1343*m*, 1128*s*, 980*m*, 882*m*. ^1H-NMR (400 MHz, $CDCl_3$): 4.47 (*t*, *J* = 3.6, 2 CH); 3.47 (*s*, 2 MeO); 2.86–2.83 (*m*, CH_2); 1.44 (*s*, Me); 1.26–1.06 (*m*, 3 Me_2CH); 1.09 (*d*, *J* = 6.6, 3 Me_2CH). ^{13}C-NMR (100 MHz, $CDCl_3$): 159.3 (C_q); 88.4

(CH); 53.5 (Me); 24.9 (CH_2); 21.8 (CH); 19.6 (Me); 13.0 (CH). EI-MS: 310.3 (24, M^+), 294.2 (5, $[M-Me]^+$), 267.2 (12), 251.2 (16), 195.1 (10), 157.2 (41), 153.1 (20), 152.1 (100), 115.1 (47), 87.1 (11). Anal. calc. for $C_{18}H_{34}O_2Si$ (310.55): C 69.62, H 11.03; found: C 69.43, H 11.16.

(2,6-Dimethoxy-1-methylcyclohexa-2,5-dienyl)(dimethyl)phenylsilane (**6**). Prepared according to *GP 1* from **4** (280 mg, 2 mmol) in THF (7 ml), ^{t}BuLi (1.4 ml, 1.6M in hexane, 2.2 mmol), HMPA (0.42 ml, 2.4 mmol), (chloro)dimethyl(phenyl)silane (0.37 ml, 2.2 mmol) in THF (2 ml), BuLi (1.6 ml, 1.5M in pentane, 2.4 mmol), and $(MeO)_2SO_2$ (0.2 ml, 2.1 mmol). Purification by FC (pentane/Et_2O 20:1) afforded **6** (427 mg, 74%) as a colorless oil. IR ($CHCl_3$): 3068*w*, 2998*m*, 2952*m*, 2903*m*, 2831*m*, 1677*s*, 1643*w*, 1451*m*, 1427*m*, 1346*m*, 1127*s*, 1076*w*, 979*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.42–7.39 (*m*, 2 arom. H); 7.29–7.20 (*m*, 3 arom. H); 4.39 (*dd*, J_1 = 4.6, J_2 = 2.7, 2 CH); 3.31 (*s*, 2 MeO); 2.62 (*dt*, J_1 = 20.3, J_2 = 4.6, 1 H, CH_2); 2.42 (*dt*, J_1 = 20.3, J_2 = 2.7, 1 H, CH_2); 1.28 (*s*, Me); 0.26 (*s*, 2 Me_2Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 157.5 (C_q); 138.6 (C_q); 134.1 (CH); 128.5 (CH); 126.9 (CH); 89.1 (CH); 53.8 (Me); 36.4 (C_q); 24.3 (CH_2); 17.1 (Me); −3.93 (Me). EI-MS: 288.2 (31, M^+), 271.1 (3), 195.1 (15), 180.1 (3), 163.0 (3), 152.1 (50), 135.0 (100), 122.0 (22), 107.0 (28), 91.0 (11), 77.0 (7). Anal. calc. for $C_{17}H_{24}O_2Si$ (288.46): C 70.78, H 8.39; found: C 70.73, H 8.24.

[(2,6-Dimethoxy-1-methylcyclohexa-2,5-dienyl)dimethylsilyl]diethylamine (**7**). Prepared according to *GP 1* with **4** (4.20 g, 30 mmol) in THF (100 ml), ^{t}BuLi (22.3 ml, 1.48M in hexane, 33 mmol), HMPA (5.77 ml, 33 mmol), $(Et_2N)Me_2SiCl$ [15] (5.46 g, 33 mmol), BuLi (20.5 ml, 1.61M in pentane, 33 mmol) and $(MeO)_2SO_2$ (2.85 ml, 30 mmol). Distillation (80°, 1 mbar) afforded **7** (7.63 g, 90%) as a colorless oil. IR (nujol): 2964*s*, 2904*s*, 2868*m*, 2829*s*, 1678*s*, 1345*m*, 1248*m*, 1211*s*, 1177*m*, 1127*s*, 1031*m*, 811*s*, 766*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.52 (*t*, J = 3.4, 2 CH); 3.51 (*s*, 2 MeO); 2.87 (*dd*, $J_1 = J_2$ = 3.4, C=CH−CH_2); 2.81 (*q*, J = 7.0, 2 CH_2N); 1.32 (*s*, Me); 0.99 (*t*, J = 7.0, 2 $MeCH_2$); 0.12 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 158.7 (C_q); 88.2 (CH); 53.9 (Me); 41.0 (CH_2); 38.5 (C_q); 24.5 (CH_2); 17.3 (CH_3); 16.3 (Me); −2.7. EI-MS: 283 (2, M^+), 268 (4), 197 (9), 152 (22), 132 (47), 131 (69), 130 (100), 117 (15), 116 (84), 103 (37), 88 (19), 73 (20), 72 (31), 70 (24), 59 (58), 58 (32), 57 (12). HR-EI-MS: 283.1965 (M^+, $C_{15}H_{29}NO_2Si^+$; calc. 283.1968).

Trimethyl(1-methylcyclohexa-2,5-dienyl)silane (**8**). Cyclohexa-1,4-diene (0.94 ml, 10 mmol) was dissolved in THF (16 ml) and cooled to *ca.* −60°. ^{s}BuLi (8.4 ml, 1.31M in cyclohexane, 11 mmol) was added. The resulting yellow soln. was treated with TMEDA (1.54 ml, 10 mmol). The mixture was allowed to warm to −35° in 2 h. After addition of Me_3SiCl (1.39 ml, 11 mmol), the soln. was stirred for 1 h at r.t. After cooling to −60°, ^{s}BuLi (8.4 ml, 1.31M in cyclohexane, 11 mmol) was added. The mixture was allowed to warm to −40 to −35°. Stirring was continued for 2 h at this temp. before $(MeO)_2SO_2$ (1.04 ml, 11 mmol) was added. After 5 min, the cooling bath was removed, and the mixture was allowed to warm to r.t. H_2O and Et_2O were added. The org. layer was separated, washed with H_2O (2×), sat. NH_4Cl soln., and brine, and dried ($MgSO_4$). Removal of the solvent *in vacuo* and distillation (16 mbar, 53°) afforded **8** (1.04 g, 63%) as a colorless oil. IR ($CHCl_3$): 3008*m*, 2957*s*, 2863*m*, 2821*m*, 1662*w*, 1616*w*, 1461*m*, 1432*m*, 1404*w*, 1366*w*, 1333*w*, 1095*w*, 999*w*, 959*m*, 925*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.58–5.54 (*m*, 2 CH_2CH); 5.48–5.44 (*m*, 2 CH); 2.73–2.55 (*m*, CH_2); 1.09 (*s*, MeC); −0.01 (*s*, Me_3Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 132.37 (CH); 120.80 (CH); 45.83 (C_q); 26.52 (CH_2); 22.61 (Me); −4.72 (Me). EI-MS: 166.2 (<1, M^+), 107.1 (2), 105.1 (2), 93.0 (1), 92.0 (3), 91.0 (2), 79.0 (3), 78.0 (2), 73.0 (21), 59.0 (2), 39.9 (3), 31.9 (29), 27.9 (100), 17.9 (5). Anal. calc. for $C_{10}H_{18}Si$ (166.34): C 72.21, H 10.91; found: C 71.97, H 10.90.

General Procedure 2 (*GP 2*) *for Hydrosilylation Reactions.* In a pressure-stable glass tube, substrate, Si reagent, and radical initiator were dissolved in hexane. After flushing with Ar, the tube was sealed and heated to 80–85°. After cooling down, the solvent was evaporated *in vacuo*, and the crude product was purified by FC. The diastereoisomer ratio of the products was determined by gas chromatography taking samples of the crude mixture.

*3-[(*tert*-Butyl)dimethylsilyl]propyl Acetate* (**9**). Prepared according to *GP 2* from allyl acetate (100 mg, 1 mmol), reagent **1** (400 mg, 1.5 mmol), and AIBN (50 mg, 0.3 mmol) in hexane (4 ml); 4.5 h. FC (pentane/^{t}BuOMe 40:1) afforded **9** (116 mg, 54%) as a colorless oil. IR (nujol): 2953*s*, 2930*s*, 2885*m*, 2857*m*, 1744*s*, 1468*m*, 1363*m*, 1236*s*, 1048*m*, 835*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.02 (*t*, J = 6.96, CH_2O); 2.05 (*s*, MeCO); 1.67–1.56 (*m*, $CH_2CH_2CH_2$); 0.87 (*s*, ^{t}Bu); 0.53–0.47 (*m*, CH_2Si); −0.05 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 171.0 (C_q); 67.68 (CH_2); 26.92 (Me); 23.99 (CH_2); 21.42 (Me); 16.90 (C_q); 8.63 (CH_2); −6.01 (Me). EI-MS: 159.2 (14, $[M-{}^t\text{Bu}]^+$), 118.1 (8), 117.2 (92), 76.0 (7), 75.0 (100), 73.1 (13), 43.0 (14), 28.0 (5). HR-EI-MS: 119.0841 ($[M-{}^t\text{Bu}]^+$, $C_7H_{15}O_2Si^+$; calc. 119.0841).

*(*tert*-Butyl)dimethyl(4-phenylbutyl)silane* (**11**). Prepared according to *GP 2* from (but-3-enyl)benzene (**10**) [27] (132 mg, 1 mmol), **1** (407 mg, 1.5 mmol), and AIBN (50 mg, 0.3 mmol) in hexane (4 ml); 4 h. Additional AIBN (50 mg, 0.3 mmol) was added. The soln. was stirred for another 4 h at 90°. FC (pentane) afforded **11** (136 mg, 55%) as a colorless oil. IR (nujol): 2952*s*, 2927*s*, 2882*m*, 2855*s*, 1466*m*, 1251*s*, 830*s*, 803*m*, 746*m*, 698*s*.

^{1}H-NMR (300 MHz, $CDCl_3$): 7.25–7.19 (*m*, 2 arom. H); 7.15–7.14 (*m*, 3 arom. H); 2.63–2.58 (*m*, PhCH_2); 1.69–1.59 (*m*, CH_2); 1.41–1.30 (*m*, CH_2); 0.86 (*s*, ^{t}Bu); 0.56–0.51 (*m*, CH_2Si); −0.09 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 143.3 (C_q); 128.8 (CH); 128.6 (CH); 125.9 (CH); 36.1 (CH_2); 36.1 (CH_2); 27.0 (Me); 24.5 (CH_2); 17.0 (C_q); 12.7 (CH_2); −5.9 (Me). EI-MS: 233.2 (<1, $[M-Me]^+$), 192.1 (18), 191.2 (100, $[M-{}^t\text{Bu}]^+$), 189.1 (18), 187.2 (9), 135.2 (8), 91.1 (12), 87.0 (21), 73.1 (40), 59.1 (65), 28.0 (13). HR-EI-MS: 191.1262 ($[M-{}^t\text{Bu}]^+$, $C_{12}H_{19}Si^+$; calc. 191.1256).

*(*tert*-Butyl)(cyclohexyl)dimethylsilane* (**12**). Prepared according to *GP 2* from cyclohexene (82 mg, 1 mmol), **1** (400 mg, 1.5 mmol), and AIBN (50 mg, 0.3 mmol) in hexane (4 ml); 15 h. FC (pentane) afforded **12** (119 mg, 60%) as a colorless oil. IR (nujol): 2955*s*, 2926*s*, 2852*s*, 1471*m*, 1446*m*, 1362*w*, 1254*m*, 1247*m*, 1097*w*, 888*w*, 850*m*, 827*m*, 799*m*, 765*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.80–1.68 (*m*, 5 H, CH_2); 1.32–1.11 (*m*, 5 H, CH_2); 0.92 (*s*, ^{t}Bu); 0.81–0.73 (*m*, CHSi); −0.08 (*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 28.92 (CH_2); 28.55 (CH_2); 27.55 (Me); 27.18 (CH_2); 24.22 (CH); 17.50 (C_q); −7.54 (Me). EI-MS: 198.4 (4, M^+), 142.5 (15), 141.4 (86), 113.3 (8), 99.2 (7), 81.3 (48), 74.2 (5), 73.2 (62), 60.2 (7), 59.2 (100), 28.0 (11). HR-EI-MS: 198.1795 (M^+, $C_{12}H_{26}Si^+$; calc. 198.1804).

*(*tert*-Butyl)(dimethyl)[(Z)-2-phenylethenyl]silane* (**13**). Prepared according to *GP 2* from phenylacetylene (102 mg, 1 mmol), **1** (400 mg, 1.5 mmol), and AIBN (50 mg, 0.3 mmol) in hexane (4 ml); 4 h. FC (pentane) afforded **13** (159 mg, 73%) as a colorless oil. Diastereoisomer ratio: (*Z*)/(*E*) 25:1. IR (nujol): 2953*m*, 2926*s*, 2855*m*, 1591*w*, 1572*w*, 1492*w*, 1463*m*, 1251*m*, 824*s*, 777*m*, 699*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.48 (*d*, *J* = 15.2, Si−CH=C*H*); 7.32–7.21 (*m*, 5 arom. H); 5.87 (*d*, *J* = 15.2, Si−C*H*=CH); 0.91 (*s*, ^{t}Bu); −0.07 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 147.7 (CH); 140.3 (C_q); 129.8 (CH); 128.1 (CH); 127.8 (CH); 127.2 (CH); 26.5 (Me); 22.4 (C_q); −4.4 (Me). EI-MS: 203 (<1, $[M-Me]^+$), 162 (28), 161 (100, $[M-{}^t\text{Bu}]^+$), 146 (9), 145 (77), 135 (31), 73 (21), 59 (59). HR-EI-MS: 203.1249 ($[M-Me]^+$, $C_{13}H_{19}Si^+$; calc. 203.1256), 161.0782 ($[M-{}^t\text{Bu}]^+$, $C_{10}H_{13}Si^+$; calc. 161.0787).

(Z)-Dimethyl(phenyl)(2-phenylethenyl)silane (**14**). Prepared according to *GP 2* from phenylacetylene (102 mg, 1.0 mmol), **6** (432 mg, 1.5 mmol), and AIBN (50 mg, 0.3 mmol) in hexane (4 ml); overnight. FC (pentane) afforded **14** (80 mg, 34%) as a colorless oil. Diastereoisomer ratio: (*Z*)/(*E*) 25:1. The spectroscopic data are in agreement with those reported in [28].

*(*tert*-Butyl)(hex-1-enyl)(dimethyl)silane* (**15**). Prepared according to *GP 2* from hex-1-yne (112 µl, 1 mmol), reagent **1** (400 mg, 1.5 mmol), and AIBN (50 mg, 0.3 mmol) in hexane (4 ml); 4.5 h. FC (pentane) afforded **15** (174 mg, 88%) as a colorless oil. Diastereoisomer ratio: (*Z*)/(*E*) 21:10. The NMR-data for the (*Z*)-isomer are in agreement with those reported in [29]. ^{1}H-NMR (300 MHz, $CDCl_3$): (*E*)-**15**: 6.04 (*dt*, J_1 = 18.6, J_2 = 6.1, Si−CH=C*H*); 5.61 (br. *d*, *J* = 18.5, Si−C*H*=CH), 2.13 (*dt*, $J_1 = J_2$ = 6.2, CH_2−CH=CH); 1.38–1.23 (*m*, 2 CH_2); 0.95–0.85 (*m*, $MeCH_2$); 0.87 (*s*, ^{t}Bu); 0.00 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): (*E*)-**15**: 148.8 (CH); 126.6 (CH); 36.7 (CH_2); 31.1 (CH_2); 26.4 (Me); 22.3 (CH_2); 16.9 (C_q); 14.1 (Me); −6.0 (Me).

Dimethyl(hex-1-enyl)(phenyl)silane (**16**). Prepared according to *GP 2* from hex-1-yne (112 µl, 1 mmol), **6** (432 mg, 1.5 mmol), and AIBN (50 mg, 0.3 mmol) in hexane (4 ml); overnight. FC (pentane) afforded **16** (66 mg, 28%) as a colorless oil. Diastereoisomer ratio: (*Z*)/(*E*) 22:10. The spectroscopic data are in agreement with those reported in [30].

*(*tert*-Butyl)[(4S)-4-ethoxy-5-(triphenylmethoxy)pent-1-enyl]dimethylsilane* (**18**). Prepared according to *GP 2* from *4-methoxy-5-(triphenylmethoxy)-1-pentyne* (**17**)[2]) (89.0 mg, 0.25 mmol), reagent **1** (133 mg, 0.50 mmol), and AIBN (25 mg, 0.15 mmol) in hexane (1.5 ml); overnight. After cooling to r.t., the mixture was treated with additional AIBN (25 mg, 0.15 mmol) and stirred for another 24 h at 80–85°. FC (pentane/Et_2O/Et_3N 100:2:1) afforded **18** (78.2 mg, 66%) as a colorless oil. Diastereoisomer ratio: (*Z*)/(*E*) 21:10. IR (nujol): 2952*s*, 2927*s*, 2881*m*, 2855*m*, 1449*m*, 1076*m*, 827*s*, 775*s*, 705*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): (*Z*)-**18**: 7.49–7.46 (*m*, 6 arom. H); 7.33–7.21 (*m*, 9 arom. H); 6.34 (*dt*, J_1 = 14.3, J_2 = 7.3, CH_2−C*H*=CH); 5.54 (*d*, *J* = 14.3, CH=C*H*Si); 3.42 (*s*, MeO); 3.42–3.34 (*m*, CHO); 3.16–3.12 (*m*, CH_2O); 2.41–2.36 (*m*, CH_2−CH=CH); 0.87 (*s*, ^{t}Bu); 0.05 (*s*, Me_2Si); (*E*)-**18**: 7.49–7.46 (*m*, 6 arom. H); 7.33–7.21 (*m*, 9 arom. H); 5.95 (*dt*, J_1 = 18.5, J_2 = 6.8, CH_2−C*H*=CH); 5.65 (*d*, *J* = 18.6, CH=C*H*Si); 3.43 (*s*, MeO); 3.42–3.34 (*m*, CHO); 3.16–3.12 (*m*, CH_2O); 2.41–2.36 (*m*, CH_2−CH=CH); 0.81 (*s*, ^{t}Bu); −0.05 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): (*Z*)-**18**: 145.4 (CH); 144.1 (C_q); 128.2 (CH); 128.7 (CH); 127.7 (CH); 126.9 (CH); 86.6 (C_q); 80.8 (CH); 65.4 (CH_2); 58.0 (Me); 36.0 (CH_2); 26.4 (Me); 16.8 (C_q); −4.2 (Me). ^{13}C-NMR (75 MHz, $CDCl_3$): (*E*)-**18**: 142.7 (CH); 144.1 (C_q); 129.9 (CH); 128.7 (CH); 127.7 (CH); 126.9 (CH); 86.5 (C_q); 80.4 (CH); 65.1 (CH_2); 58.0 (Me); 39.4 (CH_2);

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[2]) Kindly provided by *H. Wehlan* and *U. Koert*.

26.4 (Me); 16.8 (C_q); −6.1 (Me). EI-MS: 287 (4), 244 (9), 243 (45), 184 (37), 147 (32), 115 (11), 99 (19), 98 (100), 87 (10), 81 (20), 73 (53). HR-ESI-MS: 495.2710 ($[M+Na]^+$, $C_{31}H_{40}NaO_2Si^+$; calc. 495.2695).

*Diethyl 3-{[(*tert*-Butyl)dimethylsilyl]methyl}-4-methylcyclopentane-1,1-dicarboxylate* (**26**; representative example for hydrosilylation/cyclization reactions of dienes; *cf. Table*). Prepared according to *GP 2* from malonate **21** (242 mg, 1 mmol), **1** (400 mg, 1.5 mmol), and AIBN (50 mg, 0.3 mmol) in hexane (4 ml); 4 h. FC (pentane/^{t}BuOMe 30:1) afforded **26** (286 mg, 0.80 mmol, 80%) as a colorless oil. Diastereoisomer ratio: *cis*/*trans* 43:10. IR (nujol): 2954*s*, 2930*s*, 2857*s*, 1732*s*, 1255*s*, 1201*m*, 1179*m*, 1150*m*, 1099*m*, 828*s*, 810*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): *cis*-**26**: 4.19–4.11 (*m*, MeCH_2); 2.38–2.33 (*m*, 2 H, CH_2, CH); 2.10–2.01 (*m*, 3 H, CH_2, CH); 1.87 (*dd*, $J_1=13.4$, $J_2=9.8$, 1 H, CH_2); 1.23 (*t*, $J=7.1$, 2 MeCH_2); 0.85 (*s*, ^{t}Bu); 0.82 (*d*, $J=6.6$, *Me*CH); 0.61 (*dd*, $J_1=14.7$, $J_2=4.5$, 1 H, SiCH_2); 0.42 (*dd*, $J_1=14.7$, $J_2=9.3$, 1 H, SiCH_2); −0.04 (2*s*, 2 MeSi). ^{1}H-NMR (500 MHz, $CDCl_3$): *trans*-**26**: 4.19–4.11 (*m*, 2 MeCH_2); 2.56 (*dd*, $J_1=13.5$, $J_2=6.9$, 1 H, CH_2); 2.49 (*dd*, $J_1=13.4$, $J_2=7.0$, 1 H, CH_2); 1.69–1.62 (*m*, 2 H, CH_2); 1.48–1.35 (*m*, 2 H, CH_2, CH); 1.23 (*t*, $J=7.1$, 2 *Me*CH_2); 0.95 (*d*, $J=6.3$, MeCH); 0.85 (*s*, ^{t}Bu); 0.93–0.85 (*m*, 1 H, SiCH_2); 0.23 (*dd*, $J_1=14.5$, $J_2=11.1$, 1 H, SiCH_2); −0.04 (2*s*, 2 MeSi). ^{13}C-NMR (133 MHz, $CDCl_3$): *cis*-**26**: 173.17 (C_q); 172.17 (C_q); 61.21 (CH_2); 59.00 (C_q); 41.10 (CH_2); 40.67 (CH_2); 39.01 (CH); 37.83 (CH); 26.48 (Me); 16.55 (C_q); 14.87 (Me); 14.02 (Me); 11.98 (CH_2); −5.10 (Me); −5.89 (Me). ^{13}C-NMR (133 MHz, $CDCl_3$): *trans*-**26**: 173.17 (C_q); 172.17 (C_q); 61.21 (CH_2); 58.29 (C_q); 43.54 (CH); 43.69 (CH); 42.90 (CH_2); 41.96 (CH_2); 26.48 (Me); 17.26 (Me); 16.55 (C_q); 15.75 (CH_2); 14.02 (Me); −4.73 (Me); −6.12 (Me). EI-MS: 311.2 (4, $[M-EtO]^+$), 300.3 (21), 299.3 (100, $[M-{}^t\text{Bu}]^+$), 182.1 (6), 181.1 (41), 73.0 (11), 32.0 (6), 28.0 (52). Anal. calc. for $C_{19}H_{36}O_4Si$ (356.57): C 64.00, H 10.18; found: C 63.74, H 10.03.

Diethyl But-2-enyl(but-3-enyl)malonate (**31**). Na (230 mg, 10 mmol) was dissolved in EtOH (7 ml). The soln. was treated with ethyl hex-4-enoate [31] (1.46 g, 6.8 mmol) and stirred for 1 h at r.t. 4-Bromobut-1-ene (1.01 ml, 10 mmol) was added, and the mixture was refluxed overnight. The solvent was removed *in vacuo*, and the residue was dissolved in ^{t}BuOMe. The soln. was washed with sat. NH_4Cl soln. and brine, and dried ($MgSO_4$). Removal of the solvent *in vacuo* and purification by FC (pentane/^{t}BuOMe 25:1) afforded **31** (521 mg, 29%) as a colorless oil. IR (nujol): 3470*w* (br.), 2980*m*, 2937*w*, 1732*s*, 1447*m*, 1385*w*, 1367*w*, 1298*w*, 1266*m*, 1240*m*, 1203*s*, 1134*m*, 1096*w*, 1035*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.86–5.72 (*m*, 1 H, CH_2=C*H*); 5.57–5.45 (*m*, 1 H, CH=CH); 5.30–5.20 (*m*, 1 H, CH=CH); 5.05–4.94 (*m*, CH_2=CH); 4.17 (*q*, $J=7.1$, 2 CH_2O); 2.58 (*d*, $J=7.3$, CH=CHCH_2); 2.02–1.87 (*m*, CH_2CH_2); 1.64 (*d*, $J=6.4$, *Me*CH=CH); 1.24 (*t*, $J=7.1$, 2 MeCH_2). ^{13}C-NMR (125 MHz, $CDCl_3$): 171.7 (C_q); 138.1 (CH_2); 129.9 (CH); 125.1 (CH); 115.3 (CH); 61.4 (CH_2); 57.7 (C_q); 36.2 (CH_2); 31.8 (CH_2); 28.7 (CH_2); 18.4 (Me); 145 (Me). EI-MS: 268.2 (2, M^+), 213.2 (34), 194.2 (31), 167.1 (42), 153.1 (100), 127.1 (25), 125.1 (24), 122.1 (52), 121.2 (40), 107.1 (23), 81.1 (29), 79.1 (24), 55.1 (31), 29.1 (53), 28.0 (37). HR-EI-MS: 268.1687 (M^+, $C_{15}H_{24}O_4^+$; calc. 268.1675).

*Diethyl 4-{[(*tert*-Butyl)dimethylsilyl]methyl}-3-ethylcyclohexane-1,1-dicarboxylate* (**32**). Prepared according to *GP 2* from **31** (110 mg, 1 mmol), **1** (400 mg, 1.5 mmol), and AIBN (50 mg, 0.3 mmol) in hexane (4 ml); 4 h. Additional AIBN (50 mg, 0.3 mmol) was added. The mixture was stirred for another 4 h at 80–85°. FC (pentane/^{t}BuOMe 50:1) afforded *cis*,*trans*-**32** (233 mg, 61%), *ca.* 95% pure, as a colorless oil. Diastereoisomer ratio: *cis*/*trans* 1:1. IR (nujol): 2955*s*, 2932*s*, 2857*s*, 1733*s*, 1464*m*, 1365*w*, 1299*w*, 1247*s*, 1158*m*, 1133*w*, 1096*w*, 1038*w*, 860*w*, 828*m*, 808*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.22–4.13 (*m*, 8 H); 2.41–2.27 (*m*, 2 H); 2.09–2.04 (*m*, 2 H); 1.83–1.58 (*m*, 8 H); 1.40–1.11 (*m*, 20 H); 0.88–0.83 (*m*, 6 H); 0.85 (*s*, ^{t}Bu); 0.83 (*s*, ^{t}Bu); 0.48–0.42 (*m*, 2 H); 0.14–0.06 (*m*, 2 H); −0.04 (*s*, 3 H, $(CH_2)_2$Si); −0.05 (*s*, 3 H, $(CH_2)_2$Si); −0.07 (*s*, 3 H, $(CH_2)_2$Si); −0.10 (*s*, 3 H, $(CH_2)_2$Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 172.8; 171.3; 61.2; 61.0; 60.9; 55.3; 42.3; 40.3; 37.1; 36.1; 32.0; 31.6; 31.3; 30.9; 28.4; 26.5; 26.1; 25.6; 25.5; 16.0; 14.1; 14.0; 11.5; 10.4; −4.0; −4.3; −5.4; −5.8. EI-MS: 369 (<1, $[M-Me]^+$), 327 (66, $[M-{}^t\text{Bu}]^+$), 224 (36), 196 (25), 180 (21), 103 (15), 81 (16), 80 (14), 79 (14), 75 (48), 73 (71), 67 (15), 66 (100), 59 (17), 41 (14), 40 (35). HR-EI-MS: 369.2468 ($[M-Me]^+$, $C_{20}H_{37}O_4Si^+$; calc. 369.2461), 327.1993 ($[M-{}^t\text{Bu}]^+$, $C_{17}H_{31}O_4Si^+$; 327.1992).

*(*tert*-Butyl)[((S)-4-isopropylcyclohex-1-enyl)methyl]dimethylsilane* (**33**). Prepared according to *GP 2* from (−)-(1*S*)-*β*-pinene (136 mg, 1 mmol), **1** (400 mg, 1.5 mmol), and AIBN (50 mg, 0.3 mmol) in hexane (4 ml); 3 h. FC (pentane) afforded **33** (177 mg, 70%) as a colorless oil. IR (nujol): 2954*s*, 2928*s*, 2881*m*, 2856*m*, 1663*w*, 1468*m*, 1437*w*, 1386*w*, 1363*w*, 1250*m*, 1172*m*, 1149*w*, 1007*w*, 828*s*, 807*m*, 746*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.23–5.18 (*m*, C=CH); 2.02–0.82 (*m*, 16 H); 0.87 (*s*, ^{t}Bu); −0.05 (*s*, Me); −0.06 (*s*, Me). ^{13}C-NMR (100 MHz, $CDCl_3$): 135.31 (C_q); 119.07 (CH); 40.15 (CH); 32.35 (CH); 31.97 (CH_2); 29.23 (CH_2); 26.78 (CH_2); 26.48 (Me); 23.15 (CH_2); 20.01 (Me); 19.74 (Me); 16.78 (C_q); −5.53 (Me); −5.89 (Me). EI-MS: 252.6 (9, M^+), 196.4 (15), 195.5 (97, $[M-{}^t\text{Bu}]^+$), 167.4 (11), 139.3 (8), 99.2 (10), 74.2 (8), 73.2 (100), 59.1 (16), 28.0 (14). HR-EI-MS: 252.2277 (M^+, $C_{16}H_{32}Si^+$; calc. 252.2273).

*4-[(*tert*-Butyl)dimethylsilyl]but-4-en-1-ol* (**34**). Prepared according to *GP 2* from 2-vinyloxirane (80.5 µl, 1.0 mmol), reagent **1** (402 mg, 1.5 mmol), and AIBN (50 mg, 0.3 mmol) in pentane (4 ml); 6 h. FC (pentane/Et_2O 8:2) afforded **34** (114 mg, 61%) as a colorless oil. Diastereoisomer ratio: (*E*)/(*Z*) 22:10. IR (nujol): 3343*m* (br.), 2953*s*, 2929*s*, 2883*m*, 2858*s*, 1470*m*, 1404*w*, 1362*w*, 1252*m*, 1154*w*, 1005*m*, 967*m*, 827*s*, 804*m*, 749*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): (*E*)-**34**: 5.75–5.46 (*m*, CH=CH); 4.02 (*d*, *J* = 6.3, CH_2OH); 1.73 (*s*, OH); 1.51 (*d*, *J* = 8.3, CH_2Si); 0.88 (*s*, ^{t}Bu); −0.05 (*s*, Me_2Si). ^{1}H-NMR (300 MHz, $CDCl_3$): (*Z*)-**34**: 5.75–5.46 (*m*, CH=CH); 4.16 (*d*, *J* = 6.6, CH_2OH); 1.73 (*s*, OH); 1.55–1.50 (*m*, CH_2Si); 0.88 (*s*, ^{t}Bu); −0.05 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): (*E*)-**34**: 131.1 (CH); 127.5 (CH); 64.2 (CH_2); 26.5 (Me); 23.5 (C_q); 18.8 (CH_2); −6.5 (Me). EI-MS: 132 (3), 129 (2, $[M - {}^t\text{Bu}]^+$), 76 (7), 75 (100), 73 (32), 54 (5), 40 (8). HR-EI-MS: 129.0726 ($[M - {}^t\text{Bu}]^+$, $C_6H_{13}OSi^+$; calc. 129.0736).

4-[Dimethyl(phenyl)silyl]but-2-en-1-ol (**35**). Prepared according to *GP 2* from 2-ethenyloxirane (95 µl, 1.2 mmol), **6** (514 mg, 1.8 mmol), and AIBN (60 mg, 0.4 mmol) in hexane (4 ml); 5 h. FC (pentane/Et_2O 8:2) afforded **35** (84 mg, 35%) as a colorless oil. Diastereoisomer ratio: (*E*)/(*Z*) 44:10. The NMR-data for the (*E*)-isomer are in agreement with those reported in [32]. ^{1}H-NMR (200 MHz, $CDCl_3$): (*Z*)-**35**: 7.54–7.46 (*m*, 2 arom. H); 7.37–7.33 (*m*, 3 arom. H); 5.75–5.42 (*m*, CH=CH); 3.95 (*d*, *J* = 6.2, CH_2OH); 1.78–1.71 (*m*, CH_2Si); 0.31 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): (*Z*)-**35**: 138.4 (C_q); 133.6 (CH); 129.2 (CH); 128.5 (CH); 127.8 (CH); 126.6 (CH); 58.3 (CH_2); 18.4 (CH_2); −3.4 (Me).

Dimethyl 3-Methyl-4-[(triisopropylsilyl)methyl]cyclopentane-1,1-dicarboxylate (**39**, representative example, *cf. Scheme 8*): Prepared according to *GP 2* from **36** (217 mg, 1.02 mmol), **5** (666 mg, 2.15 mmol), and (^{t}BuO)$_2$ (100 µl, 0.54 mmol) in hexane (4 ml); 6 h, 140°. FC (pentane/^{t}BuOMe 40:1) afforded **39** (311 mg, 0.84 mmol, 82%) as a colorless oil. Diastereoisomer ratio: *cis*/*trans* 26:10. IR (nujol): 2944*s*, 2891*m*, 2866*s*, 1736*s*, 1362*m*, 1435*m*, 1254*s*, 1202*m*, 1153*m*, 882*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): *cis*-**39**: 3.70 (*s*, MeO); 3.69 (*s*, MeO); 2.41 (*dd*, J_1 = 13.1, J_2 = 6.4, 1 H, CH_2); 2.38–2.33 (*m*, 1 H, CH_2); 2.20–2.00 (*m*, 3 H, CH_2, CH); 1.91 (*dd*, J_1 = 13.1, J_2 = 10.4, 1 H, CH_2); 1.11–0.98 (*m*, 3 Me_2CH); 1.03 (br. *s*, 3 Me_2CH); 0.85 (*d*, *J* = 6.9, MeCH); 0.69 (*dd*, J_1 = 15.0, J_2 = 3.5, 1 H, CH_2Si); 0.49 (*dd*, J_1 = 14.9, J_2 = 10.3, 1 H, CH_2Si). ^{1}H-NMR (300 MHz, $CDCl_3$): *trans*-**39**: 3.70 (*s*, MeO); 3.69 (*s*, MeO); 2.62 (*dd*, J_1 = 14.1, J_2 = 8.2, 1 H, CH_2); 2.50 (*dd*, J_1 = 13.6, J_2 = 6.9, 1 H, CH_2); 1.73–1.63 (*m*, 2 H, CH, CH_2); 1.52–1.44 (*m*, 2 H, CH, CH_2); 1.11–0.98 (*m*, Me_2CH); 1.03 (br. *s*, 3 Me_2CH); 0.85 (*d*, *J* = 6.9, *Me*CH); 0.76 (*dd*, J_1 = 15.0, J_2 = 3.4, 1 H, CH_2Si); 0.36 (*dd*, J_1 = 15.0, J_2 = 11.3, CH_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): *cis*-**39**: 173.6 (C_q); 173.4 (C_q); 59.0 (C_q); 52.6 (Me); 41.0 (CH_2); 40.6 (Me); 38.4 (2 CH); 18.8 (Me); 14.8 (Me); 11.4 (CH); 8.9 (CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): *trans*-**39**: 173.6 (C_q); 173.4 (C_q); 58.2 (C_q); 52.6 (Me); 44.1 (CH); 43.2 (CH); 42.0 (2 CH_2); 24.4 (Me); 18.2 (Me); 11.4 (CH); 9.3 (CH_2). EI-MS: 329.1 (8), 328.2 (25), 327.1 (100, $[M - {}^i\text{Pr}]^+$), 325.1 (26), 145.1 (14), 117.1 (16), 75.0 (12), 28.0 (34). HR-EI-MS: 327.1992 ($[M - C_3H_7]^+$, $C_{17}H_{31}O_4Si^+$; calc. 327.1991).

Dimethyl 3-{[(Isopropyloxy)dimethylsilyl]methyl}-4-methylcyclopentane-1,1-dicarboxylate (**42**). Prepared according to *GP 2* from **36** (212 mg, 1.0 mmol), **7** (425 mg, 1.5 mmol), and (^{t}BuO)$_2$ (55 µl, 0.30 mmol) in hexane (4 ml); 4 h, 140°. The solvent was removed *in vacuo*, the residue was dissolved in ^{i}PrOH (2 ml), and the resulting soln. was treated with a cat. amount of NH_4Cl and stirred overnight at r.t. The solvent was removed *in vacuo*, and H_2O and Et_2O were added. The org. phase was separated, washed with brine, and dried ($MgSO_4$). Purification by FC (pentane/Et_2O 40:1) afforded **42** (175 mg, 53%) as a colorless oil. Diastereoisomer ratio: *cis*/*trans* 15:10. IR (nujol): 2956*m*, 2874*w*, 1736*s*, 1436*w*, 1381*w*, 1368*w*, 1253*s*, 1199*m*, 1172*m*, 1126*m*, 1027*s*, 882*m*, 840*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): *cis*-**42**: 3.99–3.93 (*m*, Me_2CH); 3.69 (*s*, 2 MeO); 2.41–2.34 (*m*, 2 H, CH, CH_2); 2.15–2.04 (*m*, 2 H, CH, CH_2); 2.00 (*dd*, J_1 = 13.6, J_2 = 4.2, 1 H, CH_2); 1.91 (*dd*, J_1 = 13.3, J_2 = 9.6, 1 H, CH_2); 1.12 (*d*, *J* = 6.1, Me_2CH); 0.81 (*d*, *J* = 6.6, Me); 0.64 (*dd*, J_1 = 14.6, J_2 = 4.7, 1 H, CH_2Si); 0.51 (*dd*, J_1 = 14.6, J_2 = 9.2, 1 H, CH_2Si); 0.10 (*s*, Me_2Si). ^{1}H-NMR (400 MHz, $CDCl_3$): *trans*-**42**: 3.99–3.93 (*m*, Me_2CH); 3.69 (*s*, 2 MeO); 2.59 (*dd*, J_1 = 13.6, J_2 = 6.7, 1 H, CH_2); 2.48 (*dd*, J_1 = 13.3, J_2 = 6.4, 1 H, CH_2); 1.73–1.64 (*m*, 2 H, CH, CH_2); 1.38–1.15 (*m*, 2 H, CH, CH_2); 1.13 (*d*, *J* = 6.0, Me_2CH); 0.94 (*d*, *J* = 5.9, Me); 0.90–0.82 (*m*, 1 H, CH_2Si); 0.35 (*dd*, J_1 = 15.6, J_2 = 10.8, 1 H, CH_2Si); 0.10 (*s*, Me_2Si). ^{13}C-NMR (100 MHz, $CDCl_3$): *cis*-**42**: 173.40 (C_q); 64.77 (CH); 58.87 (C_q); 52.56 (Me); 43.38 (CH); 42.13 (CH_2); 41.21 (CH_2); 38.13 (CH); 25.78 (Me); 16.92 (CH_2); 14.90 (Me); −0.57 (Me); −0.64 (Me). ^{13}C-NMR (100 MHz, $CDCl_3$): *trans*-**42**: 173.57 (C_q); 64.80 (CH); 58.13 (C_q); 52.56 (Me); 42.69 (CH); 42.69 (CH_2); 40.55 (CH_2); 37.57 (CH); 25.78 (Me); 20.38 (CH_2); 17.14 (Me); −0.81 (Me). EI-MS: 330 (2, M^+), 315 (68), 271 (60), 270 (100), 257 (85), 197 (80), 189 (83), 154 (49), 145 (48), 140 (65), 123 (40), 117 (75), 108 (86), 107 (45), 95 (34), 91 (53), 81 (38), 75 (45), 45 (30). HR-EI-MS: 330.1856 (M^+, $C_{16}H_{30}O_5Si^+$; calc. 330.1863).

Dimethyl 3-(Hydroxymethyl)-4-methylcyclopentane-1,1-dicarboxylate (**43**). Ac_2O (5.4 ml, 57 mmol) was treated with 3 drops of conc. H_2SO_4 and cooled to 0°. To this soln., H_2O_2 (3.60 ml, 35% in H_2O, 42 mmol) was added. The resulting soln. was stirred at r.t. for 30 min. Silane **38** (171 mg, 0.49 mmol) was dissolved in 6 ml of

the above soln. and treated with $Hg(OAc)_2$ (263 mg, 0.79 mmol) [33]. The soln. was stirred for 5 h at r.t. Et_2O (80 ml) was added, the org. phase was separated, washed with sat. $Na_2S_2O_3$ soln., H_2O, $NaHCO_3$ soln., and brine, and dried ($MgSO_4$). Filtration and removal of the solvent *in vacuo* yielded the crude product, which was purified by FC (pentane/^{t}BuOMe 1:1) to afford pure **43** (83 mg, 0.36 mmol, 74%) as a colorless oil. Diastereoisomer ratio: *cis*/*trans* 4:1. The NMR data for the *trans*-isomer are in agreement with those reported in [25]. *cis*-**43**: ^{1}H-NMR (300 MHz, $CDCl_3$): 3.65 (*s*, 2 MeO); 3.60 (*dd*, $J_1 = 11.0$, $J_2 = 5.6$, 1 H, C*H*OH); 3.45 (*dd*, $J_1 = 10.7$, $J_2 = 6.3$, 1 H, CH_2OH); 2.43 (*dd*, $J_1 = 13.4$, $J_2 = 6.8$, 1 H, CH_2); 2.33–2.09 (*m*, 4 H, CH_2, CH); 1.86 (*dd*, $J_1 = 13.4$, $J_2 = 7.3$, 1 H, C–CH_2); 1.81 (br. *s*, 1 H, OH); 0.88 (*d*, $J = 6.8$, *Me*CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 173.9 (C_q); 173.6 (C_q); 63.1 (CH_2); 59.4 (C_q); 53.1 (Me); 53.0 (Me); 44.8 (CH); 42.2 (CH_2); 36.7 (CH_2); 35.6 (CH); 15.1 (Me).

*(*tert*-Butyl)(cyclohexylmethoxy)dimethylsilane* (**45**). Prepared according to *GP 2* from *cyclohexanecarbaldehyde* (**44**; 121 µl, 1 mmol), **1** (400 mg, 1.5 mmol), and (^{t}BuO)$_2$ (55 µl, 0.3 mmol) in hexane (4 ml); 5 h, 140°. FC (pentane/NEt_3 100:1) afforded **45** (225 mg, 99%) as a colorless oil. The spectral data are in agreement with those reported in [34].

*(*tert*-Butyl)[(*tert*-butyl)methoxy]dimethylsilane* (**47**). Prepared according to *GP 2* from *pivalaldehyde* (**46**) (108 µl, 1 mmol), **1** (400 mg, 1.5 mmol), and (^{t}BuO)$_2$ (55 µl, 0.3 mmol) in hexane (4 ml); 5 h, 140°. FC (pentane/Et_2O 100:1) afforded **47** (201 mg, 99%) as a colorless oil. IR (neat): 2955*s*, 2718*w*, 1473*s*, 1362*s*, 1257*s*, 1103*s*, 1029*m*, 1006*m*, 936*w*, 837*s*, 667*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.21 (*s*, CH_2O); 0.90 (*s*, ^{t}Bu); 0.86 (*s*, ^{t}Bu); 0.02 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 73.1 (CH_2); 31.6 (C_q); 26.2 (Me); 25.9 (Me); 22.7 (C_q); –5.5 (Me). EI-MS: 202 (33, M^+), 189 (1), 188 (23), 187 (100), 40 (39). HR-EI-MS: 201.1669 ([M–H]$^+$, $C_{11}H_{25}OSi^+$; calc. 201.1675).

*(*tert*-Butyl)[(isopropyl)methoxy]dimethylsilane* (**49**). Prepared according to *GP 2* from *2-methylpropanal* (**48**, 91 µl, 1 mmol), **1** (400 mg, 1.5 mmol), and (^{t}BuO)$_2$ (55 µl, 0.3 mmol) in hexane (4 ml); 5 h, 140°. FC (pentane/NEt_3 100:1) afforded **47** (131 mg, 70%) as a colorless oil. The spectral data are in agreement with those reported in [35].

*(*tert*-Butyl)dimethyl(3-phenylpropoxy)silane* (**51**). Prepared according to *GP 2* from *3-phenylpropanal* (**50**; 134 mg, 1 mmol), **1** (400 mg, 1.5 mmol), and (^{t}BuO)$_2$ (55 µl, 0.3 mmol) in hexane (4 ml); 5 h, 140°. FC (pentane/Et_3N 100:1) afforded **51** (221 mg, 88%) as a colorless oil. The spectral data are in agreement with those reported in [36].

*[4-(Benzyloxy)butoxy](*tert*-butyl)dimethylsilane* (**53**). Prepared according to *GP 2* from *4-(benzyloxy)butanal* (**52**[3]; 178 mg, 1 mmol), **1** (400 mg, 1.5 mmol), and (^{t}BuO)$_2$ (55 µl, 0.3 mmol) in hexane (4 ml); 5 h, 140°. FC (pentane/Et_2O 100:1) afforded **53** (198 mg, 67%) as a colorless oil. IR (neat): 3030*w*, 2953*s*, 2856*s*, 1472*m*, 1361*m*, 1256*s*, 1203*w*, 1098*s*, 1029*w*, 1006*w*, 836*s*, 775*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.36–7.26 (*m*, 5 arom. H); 4.50 (*s*, CH_2); 3.63 (*t*, $J = 6.3$, CH_2O); 3.49 (*t*, $J = 6.4$, CH_2O); 1.75–1.51 (*m*, 2 CH_2), 0.89 (*s*, ^{t}Bu); 0.04 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.6 (C_q); 128.3 (CH); 127.6 (CH); 127.5 (CH); 72.8 (CH_2); 70.3 (CH_2); 63.0 (CH_2); 29.5 (CH_2); 26.2 (CH_2); 26.0 (Me); 18.3 (C_q); –5.3 (Me). EI-MS: 294 (< 1, M^+), 237 (2), 145 (19), 131 (4), 92 (28), 91 (100), 75 (5), 73 (7), 71 (7). HR-EI-MS: 294.2020 (M^+, $C_{17}H_{30}O_2Si^+$; calc. 294.2015).

*(*tert*-Butyl)(cyclohexyloxy)dimethylsilane* (**54**). Prepared according to *GP 2* from cyclohexanone (98 mg, 1 mmol), **1** (400 mg, 1.5 mmol), and (^{t}BuO)$_2$ (55 µl, 0.3 mmol) in hexane (4 ml); 5 h, 140°. FC (pentane/NEt_3 100:1) afforded **54** (132 mg, 62%) as a colorless oil. The spectral data are in agreement with those reported in [37].

REFERENCES

[1] C. Chatgilialoglu, K. U. Ingold, J. C. Scaiano, *J. Am. Chem. Soc.* **1983**, *105*, 3292.
[2] C. Chatgilialoglu, *Chem. Rev.* **1995**, *95*, 1229.
[3] C. Chatgilialoglu, *Acc. Chem. Res.* **1992**, *25*, 188; C. Chatgilialoglu, C. Ferreri, T. Gimisis, in 'The Chemistry of Organic Silicon Compounds', Eds. S. Rappoport, Y. Apeloig, Wiley, London, 1998, Vol. 2, p. 1539; C. Chatgilialoglu, C. H. Schiesser, in 'The Chemistry of Organic Silicon Compounds', Eds. S. Rappoport, Y. Apeloig, Wiley, London, 2001, Vol. 3, p. 341.
[4] B. Kopping, C. Chatgilialoglu, M. Zehnder, B. Giese, *J. Org. Chem.* **1992**, *57*, 3994.
[5] K. J. Kulicke, C. Chatgilialoglu, B. Kopping, B. Giese, *Helv. Chim. Acta* **1992**, *75*, 935.
[6] K. Miura, K. Oshima, K. Utimoto, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2348.
[7] D. D. M. Wayner, R. A. Wolkow, *J. Chem. Soc., Perkin Trans. 2* **2002**, 23.

[3]) Kindly provided by *M. Bossart*.

[8] B. P. Roberts, *Chem. Soc. Rev.* **1999**, *28*, 25.
[9] A. Matsumoto, Y. Ito, *J. Org. Chem.* **2000**, *65*, 5707.
[10] A. Studer, S. Amrein, *Angew. Chem., Int. Ed*. **2000**, *39*, 3080.
[11] G. Binmore, J. C. Walton, L. Cardellini, *J. Chem. Soc., Chem. Commun*. **1995**, 27; P. A. Baguley, L. V. Jackson, J. C. Walton, *J. Chem. Soc., Perkin Trans. 1* **2002**, 304 and refs. cit. therein.
[12] S. Amrein, A. Timmermann, A. Studer, *Org. Lett*. **2001**, *3*, 2357.
[13] E. Piers, J. R. Grierson, *J. Org. Chem*. **1977**, *42*, 3755.
[14] A. M. Birch, G. Pattenden, *J. Chem. Soc., Perkin Trans 1* **1983**, 1913.
[15] K. Tamao, E. Nakajo, Y. Ito, *Tetrahedron* **1988**, *44*, 3997.
[16] C. W. Roberson, K. A. Woerpel, *Org. Lett*. **2000**, *2*, 621.
[17] B. Giese, *Angew. Chem. Int. Ed*. **1989**, *28*, 969.
[18] R. W. Fessenden, R. H. Shuler, *J. Chem. Phys.* **1963**, *39*, 2147.
[19] Cationic platinum complexes: R. A. Widenhoefer, M. A. DeCarli, *J. Am. Chem. Soc*. **1998**, *120*, 3805; C. N. Stengone, R. A. Widenhoefer, *Tetrahedron Lett*. **1999**, *40*, 1451; N. S. Perch, R. A. Widenhoefer, *J. Am. Chem. Soc*. **1999**, *121*, 6960; T. Pei, R. A. Widenhoefer, *Org. Lett*. **2000**, *2*, 1469; N. S. Perch, T. Pei, R. A. Widenhoefer, *J. Org. Chem*. **2000**, *65*, 3836; X. Wang, H. Chakrapani, C. N. Stengone, R. A. Widenhoefer, *J. Org. Chem*. **2001**, *66*, 1755; Palladium complexes: T. Pei, R. A. Widenhoefer, *J. Org. Chem*. **2001**, *66*, 7639; Neodymium metallocene complexes: S. Onozawa, T. Sakakura, M. Tanaka, *Tetrahedron Lett*. **1994**, *35*, 8177; Yttrium metallocene catalysts: G. A. Molander, *Chemtracts* **1998**, *11*, 237 and refs. cit. therein; G. A. Molander, E. D. Dowdy, in 'Topics in Organometallic Chemistry', Ed. S. Kobayashi, Springer, New York, 1999, Vol. 2, p. 120.
[20] K. Miura, K. Oshima, K. Utimoto, *Bull. Chem. Soc. Jpn*. **1993**, *66*, 2348.
[21] A. L. J. Beckwith, C. H. Schiesser, *Tetrahedron* **1985**, *41*, 3925; D. C. Spellmeyer, K. N. Houk, *J. Org. Chem*. **1987**, *52*, 959.
[22] I. Fleming, A. Barbero, D. Walter, *Chem. Rev.* **1997**, *97*, 2063.
[23] A. G. M. Barrett, J. Head, M. L. Smith, N. S. Stock, A. J. P. White, D. J. Williams, *J. Org. Chem*. **1999**, *64*, 6005.
[24] G. R. Jones, Y. Landais, *Tetrahedron* **1996**, *52*, 7599.
[25] R. A. Widenhoefer, C. N. Stengone, *J. Org. Chem*. **1999**, *64*, 8681.
[26] I. Ojima, in 'The Chemistry of Organic Silicon Compounds', Eds. S. Patai, Z. Rappoport, Wiley, Chichester, 1989, p. 1479.
[27] J. L. Charlton, G. J. Williams, G. N. Lypka, *Can. J. Chem*. **1980**, *58*, 1271.
[28] K. Itami, T. Nokami, Y.-i. Yoshida, *Tetrahedron* **2001**, *57*, 5045.
[29] M. M. Doyle, W. R. Jackson, P. Perlmutter, *Aust. J. Chem*. **1989**, *42*, 1907.
[30] C.-H. Jun, R. H. Crabtree, *J. Organomet. Chem*. **1993**, *447*, 177.
[31] E. N. Eccott, R. P. Linstead, *J. Chem. Soc*. **1929**, 2153; R. Takeuchi, M. Kashio, *J. Am. Chem. Soc*. **1998**, *120*, 8647.
[32] P. Le Ménez, V. Fargeas, I. Berque, J. Poisson, J. Ardisson, J.-Y. Lallemand, A. Pancrazi, *J. Org. Chem*. **1995**, *60*, 3592.
[33] I. Fleming, P. E. J. Sanderson, *Tetrahedron Lett*. **1987**, *28*, 4229.
[34] K. Hattori, H. Sajiki, K. Hirota, *Tetrahedron* **2001**, *57*, 2109.
[35] K. Burgess, W. A. van der Donk, S. A. Westcott, T. B. Marder, R. T. Baker, J. C. Calabrese, *J. Am. Chem. Soc*. **1992**, *114*, 9350.
[36] A. S. Pilcher, P. DeShong, *J. Org. Chem*. **1993**, *58*, 5130.
[37] K. Yamamoto, M. Takemae, *Bull. Chem. Soc. Jpn*. **1989**, *62*, 2111.

Received May 29, 2002