Chiral organometallic reagents. Part 27.[1] The stereochemistry of the carbomagnesiation of a vinylsilane

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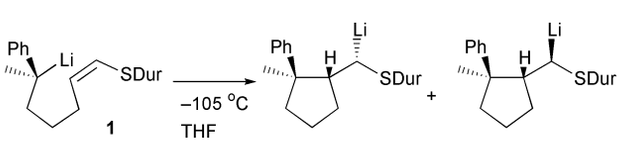
The intramolecular carbomagnesiation of a vinylsilane at 25 °C in THF has been found to proceed in a stereospecific (>95%) *syn*-addition of carbon and magnesium to the double bond. The resulting α-silylalkylmagnesium compounds are not configurationally stable under the reaction conditions. They epimerize with a half-life of 2.7 d at room temperature.

Introduction

The formation and breaking of bonds are fundamental steps in chemistry. For many of the bond forming reactions we know the detailed choreography, *e.g.* for the formation of carbon–heteroatom bonds. Far less is known about the formation of a carbon–metal bond. Prototypical are reactions in which a carbon–lithium bond is being generated. Known processes are the hydrogen–lithium exchange[2,3] (metallation), the halogen–lithium exchange,[4] the tin–lithium exchange reactions[3,5] which, aside from a few exceptions,[6] proceed with retention of configuration. Likewise, a carbon–lithium exchange reaction was found to proceed with retention of configuration.[7]

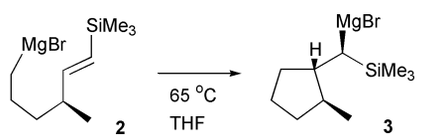
Such statements regarding the stereochemistry of a carbon–lithium bond forming reaction can be made only if the organolithium compound formed is configurationally stable under the reaction conditions, *i.e.* if the observed stereochemical result is under kinetic control. This restricts such studies to organolithium compounds which are configurationally stable at −78 °C up to 0 °C (mainly α-oxygenated or α-amido-substituted organolithium compounds),[8] or to reactions at very low temperature (down to −120 °C) at which only a few reactions proceed. This explains the paucity of the data available.

Another class of reactions, in which carbon–lithium bonds are being formed, is the carbolithiation of alkenes, the addition of an organolithium compound across a C–C-double bond. In a first study on the stereochemistry of such a reaction, we showed that the carbon–lithium bond was formed in a non-stereospecific manner in the intramolecular carbolithiation of the vinyl sulfide **1** at −105 °C [reaction (1)].[9]



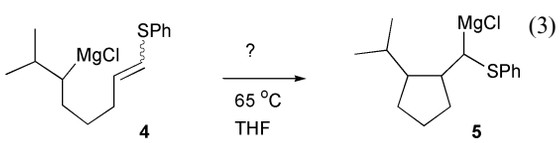
(1)

As generalizations can hardly be drawn from the one and only examined case, we wanted to study the stereochemistry of the related carbomagnesiation of vinyl sulfides. We hoped that the increased configurational stability[1,10] of α-heterosubstituted Grignard reagents would allow us to carry out such studies in a more convenient temperature range. We were encouraged by a study of Utimoto *et al.*,[11] who showed that the following intramolecular carbomagnesiation reaction[12] [reaction (2)] proceeded in refluxing THF.



(2)

In order to study the carbomagnesiation of a vinyl sulfide we generated the precursor system **4** only to find that this system had too many problems, one of which was the lack of chemical stability of the resulting α-phenylthioalkylmagnesium entity above room temperature.



(3)

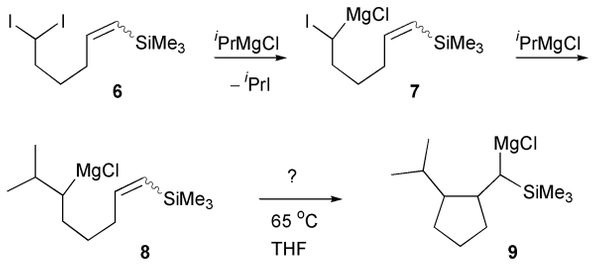
We therefore looked back to the study of Utimoto *et al.* and decided to investigate the stereochemistry of the intramolecular[13] carbomagnesiation of vinylsilanes, *i.e.* the transformation of **8** into **9**. The results are reported in this paper.

Utimoto *et al.* had generated[11] their starting Grignard reagent **2** in a standard fashion by reaction of an alkyl bromide with magnesium metal. This implies the mechanistic uncertainty of the possible formation of radical intermediates, which might undergo a concurrent free radical cyclization to give ultimately the product **3**, however, not by an organometallic carbomagnesiation reaction.[14,15] While this was not a problem in Utimoto's case, we wanted to avoid this potential liability altogether and opted for the generation of our starting Grignard reagent by a carbenoid homologation reaction.[16,17] Reaction of the diiodo compound **6** with isopropylmagnesium chloride should initiate an iodine–magnesium exchange reaction to give **7**, which should react with excess of isopropylmagnesium chloride to give the desired Grignard reagent **8** (Scheme 1). The latter reaction is not suspected to involve free radicals.[18]

Results and discussion

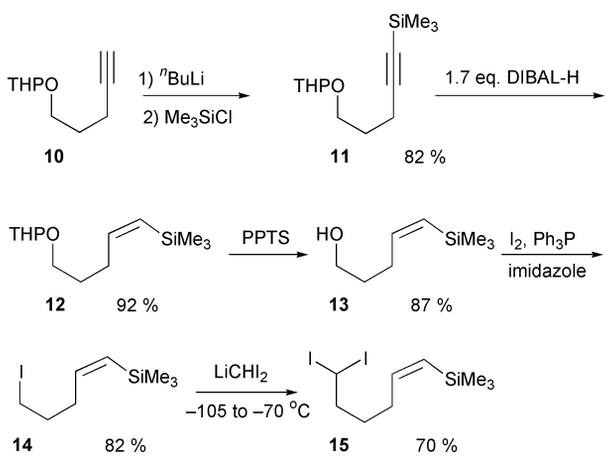
Preparation of the starting materials

A comprehensive study requires both stereoisomers (*E* as well as *Z*) of the vinylsilane substrate **6**. To enter the *Z*-series we started from the known[19] THP-protected pentynol **10**. This was silylated to **11** followed by DIBAL-H reduction, which



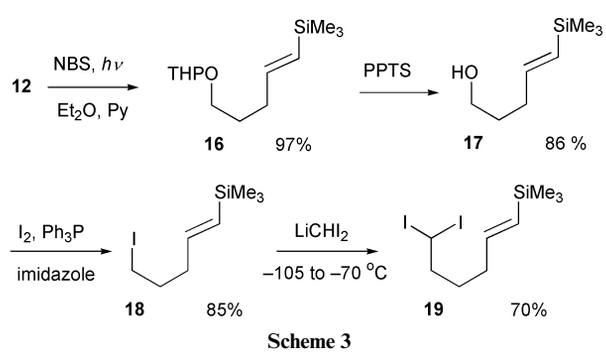
Scheme 1

proceeded only when >1 eq. of DIBAL-H was applied. This furnished 92% of **12** as a 6 : 94 *E*–*Z* mixture. Cleavage of the THP-protecting group could be effected with PPTS without isomerization of the double bond. The alcohol **13** liberated in this manner (87%) was converted to the iodo compound **14** (82%). The required geminal-diiodo function was introduced by nucleophilic substitution with diiodomethyllithium[20] to give **15** as a 6 : 94 *E*–*Z* mixture (Scheme 2).



Scheme 2

To obtain the *E*-isomer the double bond in the (*Z*)-vinylsilane **12** was isomerised[21] to give a 96 : 4 mixture of **16** and **12**. This mixture was subjected to the same reaction sequence eventually providing the diiodo compound **19** as a 96 : 4 *E*–*Z* mixture (Scheme 3).



Scheme 3

Next, we tested the generation of the starting Grignard reagents **21** and **23** from the diiodoalkanes **19** and **15** (Scheme 4). The iodine–magnesium exchange reaction was initiated by treatment of **19** with three equivalents of isopropylmagnesium chloride at −78 °C. This generated first the yellow color of the α-iodoalkyl-iodine ate-complex intermediate,[22] which disappeared quickly (*ca.* 3 min) due to the presence of excess Grignard reagent. On slowly warming to room temperature, the α-iodoalkylmagnesium chloride **7** generated at this stage reacted with the remaining isopropyl Grignard reagent to give the secondary Grignard **21**. This was established by quenching the reaction mixture with methanol.

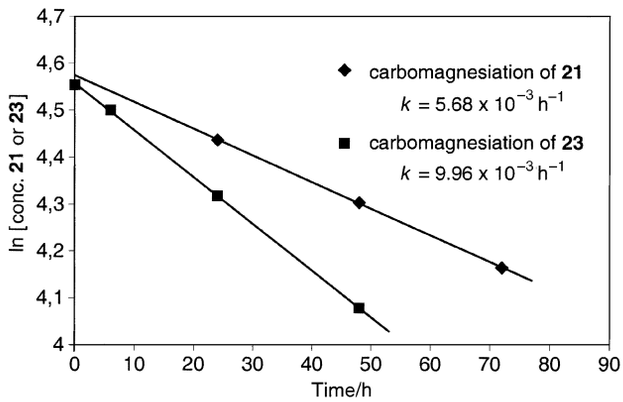
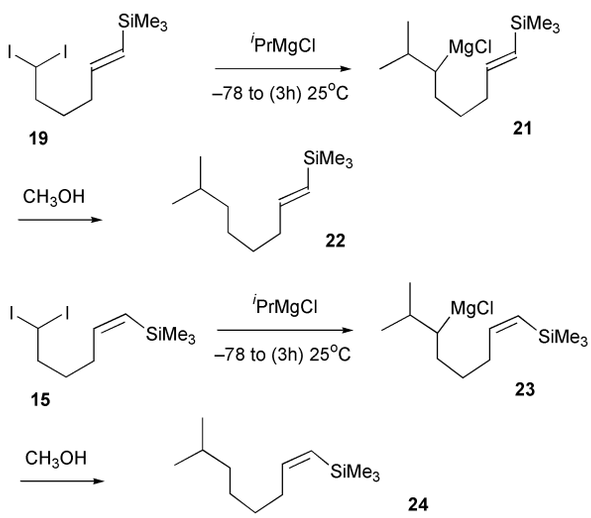


Fig. 1 Determination of the first order rate constants for the intramolecular carbomagnesiation of **21** and **23**.

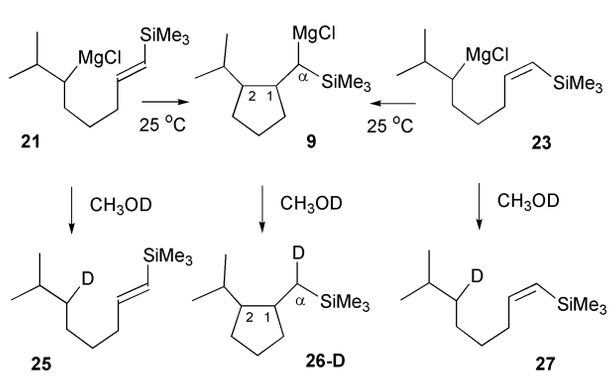


Scheme 4

Thus, starting with **19** (*E* : *Z* = 96 : 4) this reaction sequence led to compound **22** (95%) as a 96 : 4 *E*–*Z* mixture. The stereoisomeric starting material **15** (*E* : *Z* = 6 : 94) furnished likewise 95% of **24** as a 6 : 94 *E*–*Z* mixture. This showed that the starting Grignard reagents **21** and **23** can be generated in high yield.

The carbomagnesiation reaction

While the carbomagnesiation reaction of **21** and **23** to **9** did not occur to a significant extent over three hours at 25 °C, the cyclization of both Grignard reagents **21** or **23** to **9** could be effected by longer reaction times (1–3 d) (Scheme 5). This



Scheme 5

became evident after quenching with [*O*-^{2}H]methanol to give increasing amounts of the deuterated products **26-D**, *cf.* the data in Table 1 (entries 1–8). A plot of ln [**21**] or [**23**] *versus* time (*cf.* Fig. 1) shows that the carbomagnesiation reaction

Table 1 Results of the intramolecular carbomagnesiation reactions

Entry	**21** : **23** E : Z	Temp./°C	Time/h	Product **26-D** Yield (%)	α : β	Products **25**, **27** Yield (%)	Ratio **25** : **27**
1	96 : 4	25	3	0	—	95	96 : 4
2	96 : 4	25	24	15	85 : 15	79	96 : 4
3	96 : 4	25	48	22	75 : 25	69	96 : 4
4	96 : 4	25	72	33	64 : 36	60	96 : 4
5	6 : 94	25	3	0	—	95	6 : 94
6	6 : 94	25	6	4	n.d.[a]	90	6 : 94
7	6 : 94	25	24	17	n.d.[a]	75	6 : 94
8	6 : 94	25	48	40	10 : 90	59	6 : 94
9	6 : 94	65	6	16	n.d.[a]	76	39 : 61
10	6 : 94	65	24	50	20 : 80	23	66 : 34
11	6 : 94	65	48	50	20 : 80	26	75 : 25
12	96 : 4	65	48	80	20 : 80	13	72 : 28

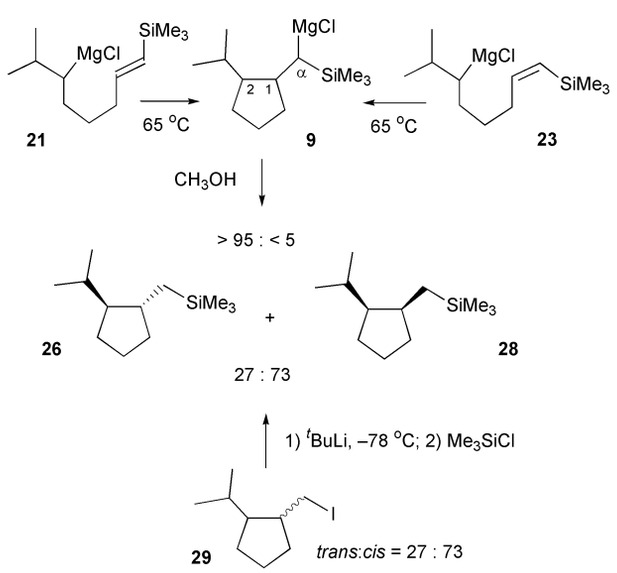
[a] n.d. = not determined.

follows a first order rate law with $k_{21} = 5.66 \times 10^{-3}$ h^{-1} and $k_{23} = 9.96 \times 10^{-3}$ h^{-1}, the cyclization onto the (*Z*)-vinylsilane moiety being the faster one.

Unreacted starting material (**21** or **23**) was quenched to give the deuterated products **25** and **27** (*cf*. Table 1). It is important to note that the formation of either **25** or **27** in these quenching experiments also demonstrates that the Grignard reagents **21** and **23** are constitutionally stable and do not interconvert under the reaction conditions.

The relative configuration of the cyclization products 9

Any discussion of the stereochemistry of the intramolecular carbomagnesiation reaction requires information on the relative configuration at the three stereogenic centers in the cyclization product **9**. In order to generate a larger amount of the cyclization product the carbomagnesiations of either **21** or **23** were carried out for two days in refluxing THF. Quenching with methanol gave in both cases the same cyclopentane derivative **26** (in 80 and 50% yield) as well as the protonation products **22** and **24** (Scheme 6). The disubstituted cyclopentane

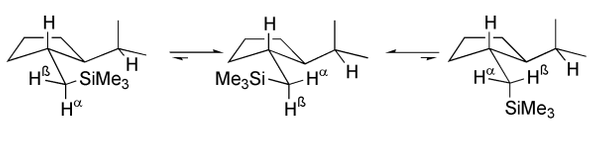


Scheme 6

26 is a single diastereomer. Its relative configuration was established as *trans* with reference to a *cis–trans* mixture made from the iodo compound **29** of known *cis–trans* composition.[23] This is in line with the stereochemistry of a related intramolecular carbomagnesiation reaction.[14]

With the relative configuration at the centers 1 and 2 in **9** established, it remained to determine the relative configuration at the α-position in the deuterated quenching products **26-D**. The relative configuration of **26-D** is considered to be representative of the relative configuration in the immediate cyclization product **9**. ^{2}D-NMR-spectroscopy of the products **26-D** obtained (*cf*. Table 1) showed that two diastereomers α and β were obtained in varying ratios. The α-isomer is characterized by a ^{1}H-decoupled ^{2}H-NMR-signal at $\delta = 0.32$, the β-isomer with one at $\delta = 0.78$ ppm. In undeuterated **26** the two diastereotopic protons appear as two dd's ($J = 14.5$ and 11.3 Hz at $\delta = 0.34$ ppm, and as dd, $J = 14.5$ and 2.9 Hz at 0.78 ppm). It is these coupling constants which allow assignment of the relative configuration of the α- and β-diastereomer of **26** based on the following considerations.

The strong alteration of the vicinal coupling constants (11.3 and 2.9 Hz) indicates[24] that a single conformer at the C^1–C$^\alpha$-bond is populated to >90%. Of the staggered conformations around the C^1–C$^\alpha$-bond in **26**, conformation **26c** cannot be a major contributor to the conformer equilibrium (Scheme 7),



Scheme 7

because it should result in two small vicinal coupling constants. Of the remaining conformers **26a** and **b**, the former is destabilized by a severe steric interaction between the trimethylsilyl and the isopropyl group. Therefore conformation **26b** must be the one that is predominantly populated. Hence, the proton signal at $\delta = 0.32$ ppm can be assigned to H$^\beta$ and the one at $\delta = 0.78$ ppm to H$^\alpha$. This means that of the diastereomers of **26-D** the α-isomer has the deuterium in the position H$^\alpha$ and the β-diastereomer in the position H$^\beta$.

The stereochemistry of the carbomagnesiation reaction

The intramolecular carbomagnesiation of (*E*)-**21** and of the (*Z*)-vinylsilane **23** leads to stereochemical distinct results with regard to α : β diastereomer ratios of **26-D** (*cf*. entries 3 and 8 of Table 1). There is a preference for the (*E*)-silane to lead *via* **30** to α-**26-D** and of the *Z*-isomer **23** to lead *via* **31** to β-**26-D** (Scheme 8), provided that deuteration of the Grignard intermediates occurs with retention of configuration. The α : β diastereomer ratio depends, however, on the reaction time (*cf*. entries 2–4 of Table 1). This suggests that there is a competing epimerisation of the primarily formed α-silylalkyl Grignard intermediates **30** and **31**. A complete epimerisation to **30** and **31** in a ratio of 20 : 80 can be attained when the reaction is carried

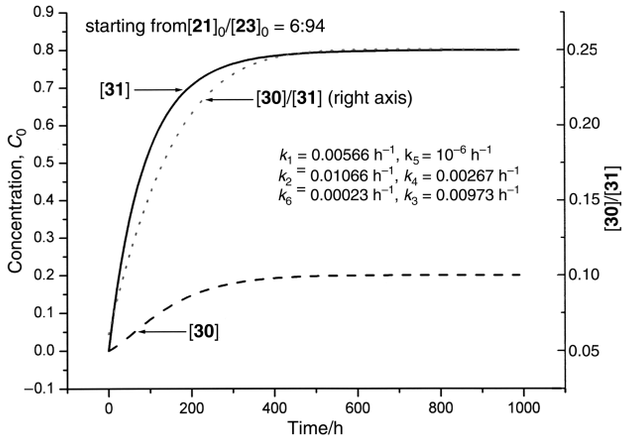
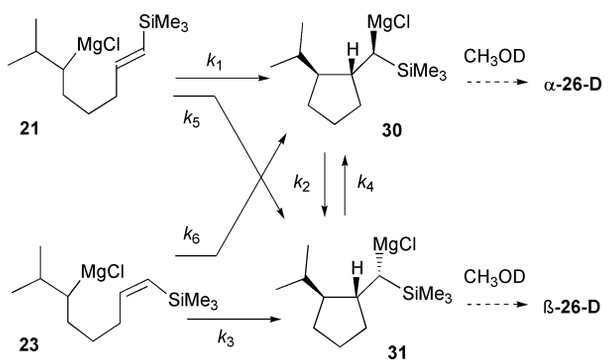


Fig. 2 Calculated concentration (molar fraction) *vs.* time dependence for the cyclization of **23** to **30** and **31**.



Scheme 8

out for two days in refluxing THF (*cf.* entries 11 and 12 of Table 1). The equilibrium value of 20 : 80 is reached using either of the starting materials **21** or **23**.

The results for the carbomagnesiation reaction at room temperature suggest a marked selectivity for the transformation of **21** into **30** and of **23** into **31**. The exact level of the selectivity, *i.e.* the stereochemical course of the carbomagnesiation reaction would become evident if we were able to extract the ratio of the rate constants k_1/k_5 characteristic for the system. The system can be considered as a set of compounds connected to one another by parallel and consecutive first order reactions. The mathematical treatment of such a system has been delineated, *e.g.* by Frost and Pearson.[25] The resulting set of differential equations has been solved analytically to give the time dependence of the concentrations of compounds **21**, **23**, **30** and **31**. The resulting equations could be solved numerically for the individual rate constants with the input of experimentally derived $k_{21} = k_1 + k_5$ and $k_{23} = k_3 + k_6$, the ratio of **21**/**23** at time $t = 0$ (= E/Z), the equilibrium constant k_2/k_4, as well as the reaction times and α : β ratios recorded for two entries in Table 1. Using the data given in entries 4 and 8 of Table 1, the best agreement with the experimental data resulted when k_5 was given a very small negative value of $<10^{-5}$ h^{-1}. Since a negative rate constant has no physical meaning, all that this signals is that k_5 is essentially zero $\pm10^{-5}$ h^{-1}. We therefore arbitrarily set k_5 to $+10^{-6}$ h^{-1}. This then gave the following rate constants: $k_1 = 5.66 \times 10^{-3}$ h^{-1}, $k_2 = 10.6 \times 10^{-3}$ h^{-1}, $k_3 = 9.73 \times 10^{-3}$ h^{-1}, $k_4 = 2.67 \times 10^{-3}$ h^{-1}, $k_6 = 0.23 \times 10^{-3}$ h^{-1}. The calculated variation of concentration of **30** and **31** and of the **30** : **31** ratio with reaction time is shown in Fig. 2 (corresponding to entries 5–8 in Table 1) and in Fig. 3 (corresponding to entries 1–4 in Table 1).

From the above determination of the rate constants it follows that the stereoselectivity of the carbomagnesiation is ≥100 (= k_1/k_5) in the case of **21** and ≥40 (= k_3/k_6) in the case of **23**.[26] Hence, the carbomagnesiation was found to be essentially *syn*-stereospecific. This is in line with the earlier indication by

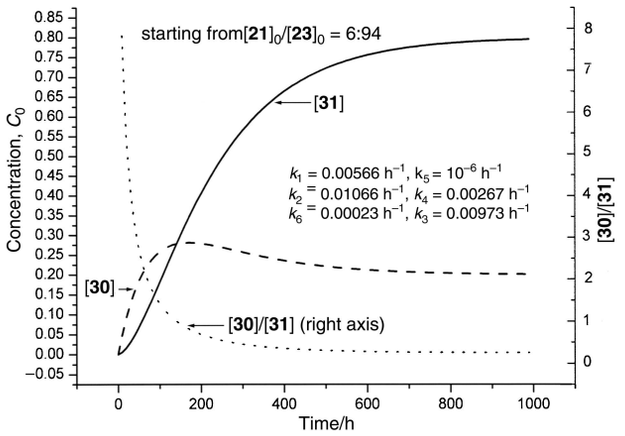
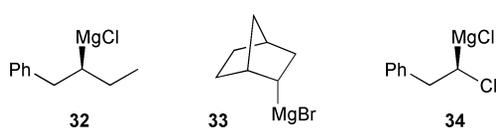


Fig. 3 Calculated concentration (molar fraction) *vs.* time dependence for the cyclization of **21** to **30** and **31**.

Utimoto[11] that the carbomagnesiation of **2** to **3** proceeds as a *syn*-addition. Our results underline the distinct mechanistic scenario of the carbomagnesiation reaction, in contrast to the carbolithiation of **1** which proceeded in a non-stereospecific manner.[9]

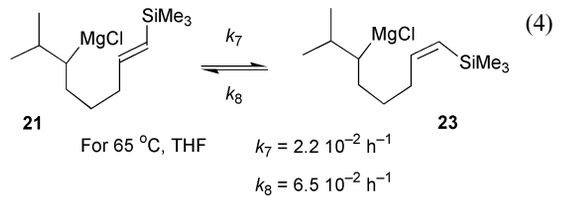
Further aspects

During the above analyses we had determined the rate constant k_2 for the epimerisation of **30** to **31** to be 10.6×10^{-3} h^{-1}. We thereby gained information on the configurational stability of α-silylalkylmagnesium reagents. The epimerisation of **30** occurs with a half life of *ca.* 2.7 d at room temperature in THF. The configurational stability of **30** and **31** is remarkably high[27] compared to the configurational stability of other Grignard reagents. Compound **32** racemizes with $t_{½}$ *ca.* 5 h in a first order process at −10 °C in THF.[18] The related Grignard reagent **33** was reported to epimerize in diethyl ether at room temperature with $t_{½}$ of *ca.* 5 h.[28] The much faster racemization of **34** at



−50 °C probably proceeds by a different mechanism; a halide-promoted process.[1] The configurational stability of the α-silylalkylmagnesium reagents **30** and **31** is, however, not as high as assumed in the previous study by Utimoto *et al.* for the analogous reagent **3**. Utimoto reported that the Grignard reagent **2** cyclized in a stereospecific manner to **3** over 6 h in refluxing THF.[11] According to our results this should have led to considerable epimerisation and would suggest that Utimoto's result is under thermodynamic control, *i.e.* that the epimer equilibrium lies far on the side of **3**. This is, however, at variance with other results reported by Utimoto *et al.*[11] Thus, there remain unresolved discrepancies between Utimoto's and our present study.

There are gratifyingly also consistencies between the two studies: Utimoto noted that the Grignard reagent corresponding to **2** with the vinylsilane moiety in a *Z*-configuration isomerised to the *E*-derivative of **2** under the reaction conditions in refluxing THF. We also noted such an isomerisation between **21** and **23** to occur in refluxing THF (*cf.* entries 9–12 of Table 1) (equilibria 4). The equilibrium position, which lies *ca.* 3 : 1 on the side of the *E*-configured isomer **21**, was reached after almost 48 h. Using the data given for entries 10–12, the isomerisation approaches equilibrium with a rate constant $k_7 + k_8 = 8.7 \times 10^{-2}$ h^{-1}. Thus, the following rate constants can be assigned to this isomerisation. This numerical description of



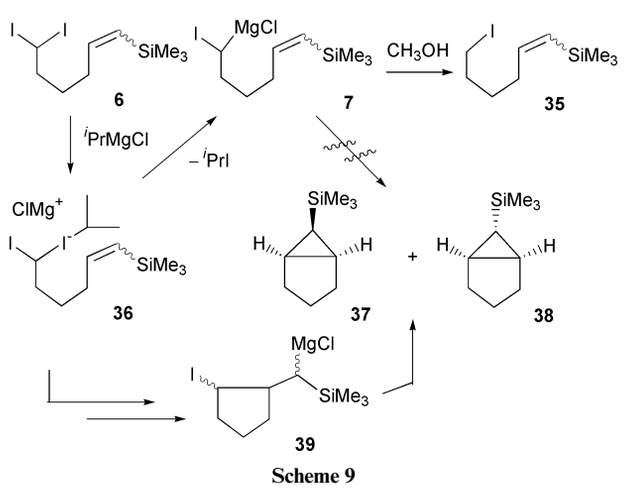
(4)

the isomerisation reaction gives, however, no clue as to the mechanism of this process.

An obvious explanation is that the cyclization of **21** and **23** to **30** and **31** becomes reversible at higher temperatures in THF. However, we are not aware of any precedent for the ring opening of a cyclopentylmethyl to a hexenyl Grignard reagent. In particular, the conversion of an α-silylalkyl Grignard reagent to a secondary alkyl Grignard reagent appears to be thermodynamically uphill and, hence, unlikely.

A further observation was made in the overall reaction that led from the diiodoalkane **6** to the cyclized Grignard reagent **9**. After workup with methanol the NMR spectra did not only reveal the formation of the cyclization products **26** and of the protonation products **22** and **24**, but in practically all experiments further low-intensity NMR-signals were seen at high field: $\delta = -0.60$ (t, $J = 8.7$ Hz) and $\delta = -0.65$ (t, $J = 5.0$ Hz). This indicated the formation of cyclopropylsilanes, albeit in low yield (<1%). We presume that these signals belong to the cyclopropylsilanes **37** and **38** as they match the characteristic NMR data reported for these compounds previously.[29]

The **37** : **38** (*exo* : *endo*) ratio varied from experiment to experiment in the range of 12 : 88 to 50 : 50, but did not depend on the *E* or *Z* geometry of the double bond in **6**. The first thought relates to an intramolecular carbenoid cyclopropanation[30] in the magnesium carbenoid **7**, but it would be hard to accept that this would not occur in a stereospecific manner. To probe this explanation compound **15** was treated with one equivalent of isopropylmagnesium chloride to generate (*Z*)-**7** at −78 °C. After slowly warming to 0 °C a methanol quench provided 96% of the monoiodo compound **35**. Less than 1% of the cyclopropylsilanes **37** and **38** were again formed. It therefore appears that the cyclopropanes are formed prior to and in competition with the generation of the carbenoid **7**. A scenario in which the primarily formed iodine ate-complex **36**[22] undergoes homolysis to initiate a free radical cyclization[31] to lead to the intermediate **39** would account for the non-stereospecific nature of the bicyclization (Scheme 9).



Scheme 9

Experimental

All temperatures quoted are uncorrected. ^{1}H NMR, ^{13}C NMR: Bruker ARX-200, AC-300, ARX-400, AMX-500. Boiling range of petroleum ether: 40–60 °C. Flash chromatography: silica gel Si 60 (40–63 μm; E. Merck KGaA, Darmstadt).

Trimethyl[5-(tetrahydro-2*H*-pyran-2-yloxy)pent-1-ynyl]silane (11)

A solution of *n*-butyllithium (1.43 M in hexane, 4.37 mL, 6.24 mmol) was added dropwise over 20 min at −30 °C into a solution of 5-tetrahydro-2*H*-pyran-2-yloxypent-1-yne (**10**)[19] (1.00 g, 5.94 mmol) in THF (60 mL). The solution was cooled to −50 °C and chlorotrimethylsilane (710 mg, 6.54 mmol) was added over 10 min. After the mixture reached room temperature water (3 mL) was added and the phases were separated. The aqueous phase was extracted with ether (3 × 15 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. Flash chromatography of the residue with pentane–ether = 15 : 1 furnished the product **11** (1.17 g, 82%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.14$ (s, 9 H), 1.48–1.62 (m, 8 H), 2.84 (t, $J = 7.1$ Hz, 2 H), 3.47 (ddd, $J = 9.7$, 6.2, and 6.2 Hz, 1 H, overlaid with m, 1 H), 3.82 (ddd, $J = 9.9$, 6.3, and 6.3 Hz, 1 H, overlaid with m, 1 H), 4.60 (t, $J = 3.4$ Hz, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 0.04$, 16.6, 19.3, 25.4, 28.7, 30.5, 61.9, 65.6, 84.6, 98.5, 106.7. $C_{13}H_{24}O_2Si$ (240.4): Calcd.: C, 64.95; H, 10.06. Found: C, 65.16; H, 10.07%.

(*Z*)-Trimethyl[5-(tetrahydro-2*H*-pyran-2-yloxy)pent-1-enyl]-silane (12)

A solution of DIBAL-H (1.0 M in petroleum ether, 5.8 mL, 5.8 mmol) was added dropwise at 0 °C to a solution of **11** (828 mg, 3.44 mmol) in ether (13 mL). After stirring for 1 h the mixture was held under reflux for 21 h. The solution was cooled to 0 °C. Saturated aqueous NH_4Cl solution (4 mL) was added and the mixture was acidified to pH >5 until the precipitate had dissolved. The phases were separated and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 10 mL). The combined organic phases were dried ($MgSO_4$) and concentrated to leave 767 mg of the crude **12**, which was used as obtained. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.09$ (s, 9 H), 1.45–1.73 (m, 8 H), 2.19 (dt, $J = 7.0$ and 7.0 Hz, 2 H), 3.37 (ddd, $J = 9.5$, 6.3, and 6.3 Hz, 1 H), 3.44–3.51 (m, 1 H), 3.72 (ddd, $J = 9.9$, 6.6, and 6.6 Hz, 1 H), 3.80–3.87 (m, 1 H), 4.54 (t, $J = 3.3$ Hz, 1 H), 5.61 (dt, $J = 13.9$ and 1.1 Hz, 1 H), 6.00 (dt, $J = 13.9$ and 7.5 Hz, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 0.1$, 19.5, 25.4, 29.8, 30.2, 30.6, 62.1, 66.8, 98.6, 129.3, 148.2.

(*Z*)-5-Trimethylsilanylpent-4-en-1-ol (13)

The vinylsilane **12** (767 mg, 3.16 mmol) and pyridinium toluene-*p*-sulfonate (86 mg, 0.34 mmol) were dissolved in ethanol (27 mL), and stirred for 12 h at room temperature and 2 h at 55 °C. The mixture was concentrated and the residue was purified by flash chromatography with pentane–*tert*-butyl methyl ether = 7 : 3 to furnish the alcohol **13** (435 mg, 87%) as a 6 : 94 *E*–*Z* mixture. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.12$ (s, 9 H), 1.66 (tt, $J = 7.0$ and 7.0 Hz, 2 H), 2.22 (dt, $J = 7.3$ and 7.3 Hz, 2 H), 3.20 (br s, 1 H), 3.67 (t, $J = 6.5$ Hz, 2 H), 5.52 (dt, $J = 13.9$ and 1.1 Hz, 1 H), 6.31 (dt, $J = 13.9$ and 7.3 Hz, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 0.1$, 29.7, 32.5, 62.5, 129.4, 146.2. $C_8H_{18}OSi$ (158.3): Calcd.: C, 60.69; H, 11.46. Found: C, 60.42; H, 11.75%.

(*Z*)-(5-Iodopent-1-enyl)trimethylsilane (14)

The alcohol **13** (853 mg, 5.39 mmol) was dissolved in acetonitrile (2.7 mL) and ether (4.4 mL). Triphenylphosphine (1.70 g, 6.47 mmol), imidazole (0.55 g, 8.1 mmol) and iodine (1.37 g, 5.39 mmol) were added sequentially at 0 °C resulting in the formation of a white precipitate. The suspension was stirred for 1 h at room temperature. Aqueous $Na_2S_2O_3$ solution (2 M, 4 mL) was added. The phases were separated and the aqueous phase was extracted with ether (3 × 10 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. Flash chromatography of the residue with pentane furnished **14** (1.23 g, 85%) as a 6 : 94 *E*–*Z* mixture. ^{1}H NMR (400 MHz,

$CDCl_3$): $\delta = 0.13$ (s, 9 H), 1.91 (dt, $J = 7.1$ and 7.1 Hz, 2 H), 2.23 (tt, $J = 7.3$ and 7.3 Hz, 2 H), 3.19 (t, $J = 7.0$ Hz, 2 H), 5.55 (dt, $J = 14.0$ and 1.1 Hz, 1 H), 6.24 (dt, $J = 14.0$ and 7.3 Hz, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 1.0$, 5.5, 29.7, 49.5, 130.8, 146.3. $C_8H_{17}ISi$ (268.2): Calcd.: C, 35.82; H, 6.39. Found: C, 35.61; H, 6.53%.

(*Z*)-(6,6-Diiodohex-1-enyl)trimethylsilane (15)

n-Butyllithium (1.47 M) in hexane (4.82 mL, 7.08 mmol) was added dropwise at −25 °C to a solution of hexamethyldisilazane (1.15 g, 7.1 mmol) in THF (4.8 mL). The brownish solution was allowed to reach 0 °C over 40 min and was then cooled to −110 °C. Diiodomethane (1.90 g, 7.07 mmol) was added over 3 min resulting in the formation of a yellow suspension. The suspension was stirred for 90 min at −105 °C. A solution of **14** (951 mg, 3.54 mmol) in THF (4.5 mL) was added slowly. The mixture was allowed to reach 10 °C over 12 h and was poured into a mixture of saturated aqueous NH_4Cl solution (5 mL), aqueous Na_2SO_3 solution (20%, 5 mL) and ether (10 mL). The phases were separated and the aqueous phase was extracted with ether (2 × 15 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. Flash chromatography of the residue with pentane furnished compound **15** (1.00 g, 70%) as a 6 : 94 *E*–*Z* mixture. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.12$ (s, 9 H), 1.53 (tt, $J = 7.5$ and 7.5 Hz, 2 H), 2.19 (dtd, $J = 7.3$, 7.3, and 1.1 Hz, 2 H), 2.37 (dt, $J = 7.2$ and 7.2 Hz, 2 H), 5.12 (t, $J = 6.4$ Hz, 1 H), 5.54 (dt, $J = 13.9$ and 1.1 Hz, 1 H), 6.26 (dt, $J = 13.9$ and 7.3 Hz, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -25.9$, 0.3, 31.3, 31.7, 47.7, 130.4, 147.4. $C_9H_{18}I_2Si$ (408.1): Calcd.: C, 26.49; H, 4.45. Found: C, 26.32; H, 4.33%.

(*E*)-Trimethyl[5-(tetrahydro-2*H*-pyran-2-yloxy)pent-1-enyl]-silane (16)

N-Bromosuccinimide (25 mg, 0.43 mmol) was added at 0 °C to a solution of **12** (1.77 g, 7.31 mmol) in ether (35 mL) and pyridine (0.61 mL). The solution, contained in a Duran vessel, was irradiated with a Osram-Ultra-Vitalux, 300 W lamp ($\lambda > 300$ nm). After 20 and 40 min further NBS (25 mg each) was added and irradiation was continued for another hour at 0 °C. The solution was washed with hydrochloric acid (2 M, 3 × 7 mL). The organic phase was washed with brine (3 mL) and dried ($MgSO_4$). Concentration of the solution furnished **16** (1.72 g, 97%) as a 96 : 4 *E*–*Z* mixture, which was used as obtained. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.00$ (s, 9 H), 1.42–1.72 (m, 8 H), 2.15 (dt, $J = 7.2$ and 7.2 Hz, 2 H), 3.35 (ddd, $J = 9.5$, 6.3, and 6.3 Hz, 1 H), 3.42–3.49 (m, 1 H), 3.70 (ddd, $J = 9.5$, 6.6, and 6.6 Hz, 1 H), 3.84–3.90 (m, 1 H), 4.56 (t, $J = 3.5$ Hz, 1 H), 5.47 (dt, $J = 18.7$ and 1.3 Hz, 1 H), 6.28 (dt, $J = 18.3$ and 6.2 Hz, 1 H) (*cf*. the data in ref. 32). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -1.3$, 19.4, 25.4, 28.6, 30.6, 33.2, 62.0, 66.8, 98.6, 130.0, 146.3.

(*E*)-5-Trimethylsilanylpent-4-en-1-ol (17)

Compound **16** (1.77 g, 7.30 mmol) was allowed to react as described in the preparation of **13** to furnish the alcohol **17** (994 mg, 86%) as a 96 : 4 *E*–*Z* mixture. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.01$ (s, 9 H), 1.61 (tt, $J = 7.0$ and 7.0 Hz, 2 H), 1.78 (br s, 1 H), 2.13 (dt, $J = 7.0$ and 7.0 Hz, 2 H), 3.55 (t, $J = 6.5$ Hz, 2 H), 5.62 (dt, $J = 18.5$ and 1.4 Hz, 1 H), 5.98 (dt, $J = 18.5$ and 6.3 Hz, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -1.3$, 31.4, 32.8, 61.9, 130.2, 146.2. $C_8H_{18}OSi$ (158.3): Calcd.: C, 60.69; H, 11.46. Found: C, 60.48; H, 11.79%.

(*E*)-(5-Iodopent-1-enyl)trimethylsilane (18)

Compound **17** (207 mg, 1.31 mmol) was allowed to react as described in the preparation of **14** to furnish the iodo compound **18** (298 mg, 85%) as a 96 : 4 *E*–*Z* mixture. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.04$ (s, 9 H), 1.94 (dt, $J = 7.0$ and 7.0 Hz, 2 H), 2.23 (tt, $J = 6.4$ and 6.4 Hz, 2 H), 3.18 (t, $J = 7.0$ Hz, 2 H), 5.79 (dt, $J = 18.5$ and 1.3 Hz, 1 H), 5.96 (dt, $J = 18.5$ and 6.0 Hz, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -1.2$, 6.4, 32.3, 37.1, 131.6, 144.3. $C_8H_{17}ISi$ (268.2): Calcd.: C, 35.82; H, 6.39. Found: C, 35.75; H, 6.35%.

(*E*)-(6,6-Diiodohex-1-enyl)trimethylsilane (19)

Diiodomethane (1.32 g, 4.91 mmol) and compound **18** (657 mg, 2.46 mmol) were allowed to react as described in the preparation of **15** to furnish the diiodo compound **19** (0.70 g, 70%) as a 96 : 4 *E*–*Z* mixture. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.05$ (s, 9 H), 1.54 (tt, $J = 7.4$ and 7.4 Hz, 2 H), 2.16 (dtd, $J = 7.0$, 7.0, and 1.3 Hz, 2 H), 2.36 (dt, $J = 7.2$ and 7.2 Hz, 2 H), 5.12 (t, $J = 6.4$ Hz, 1 H), 5.66 (dt, $J = 18.5$ and 1.4 Hz, 1 H), 5.99 (dt, $J = 18.5$ and 6.0 Hz, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -25.9$, −1.2, 30.7, 34.5, 47.6, 131.1, 142.4. $C_9H_{18}I_2Si$ (408.1): Calcd.: C, 26.49; H, 4.45. Found: C, 26.32; H, 4.33%.

(*E*)-Trimethyl(7-methyloct-1-enyl)silane (22)

A solution of the diiodo compound **19** (*E* : *Z* = 96 : 4, 100 mg, 246 μmol) in THF (0.7 mL) was added dropwise at −78 °C to a solution of isopropylmagnesium chloride (1.80 M in ether, 0.42 mL, 0.74 mmol) and THF (0.7 mL). After stirring for 3 min the solution became colourless. The solution was allowed to reach room temperature over 3 h resulting in the formation of a white precipitate. After stirring for 6 h methanol (0.14 mL, 3.5 mmol), saturated aqueous NH_4Cl solution (1 mL), and water (0.5 mL) were added. The phases were separated and the aqueous phase was extracted with ether (3 × 4 mL). The combined organic phases were dried ($MgSO_4$) and carefully concentrated (20 min, 0 °C, 100–150 mbar; 1 min, 0 °C, 30 mbar). The crude product was analysed by ^{1}H NMR spectroscopy and gas chromatography. Flash chromatography with pentane furnished **22** (46 mg, 95%) as a 96 : 4 *E*–*Z* mixture. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.04$ (s, 9 H), 0.85 (d, $J = 6.2$ Hz, 6 H), 1.11–1.21 (m, 2 H), 1.22–1.41 (m, 4 H), 1.44–1.55 (m, 1 H), 2.05 (dt, $J = 7.3$ and 7.3 Hz, 2 H), 5.61 (dt, $J = 18.5$ and 1.5 Hz, 1 H), 6.03 (dt, $J = 18.5$ and 6.3 Hz, 1 H) (*cf*. the data in ref. 33). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -1.2$, 22.6, 26.8, 27.8, 28.9, 36.7, 38.8, 129.5, 147.4. When the reaction was quenched with [*O*-^{2}H]methanol, the mono-deutero-compound **25** was obtained. ^{13}C NMR (50 MHz, $CDCl_3$): as above but 38.4 (t, $J = 18.8$ Hz). ^{2}H NMR (75 MHz, $CDCl_3$): $\delta = 1.19$ (br s). $C_{12}H_{25}DSi$: HRMS (EI): Calcd.: 199.1866. Found: 199.1857.

In the ^{2}H NMR spectra a further signal (10% of intensity) is seen at 1.51 ppm. This is likely to belong to (*E*)-(7-deuterio-7-methyloct-1-enyl)trimethylsilane.[34]

(*Z*)-Trimethyl(7-methyloct-1-enyl)silane (24)

The diiodo alkane **15** (*E* : *Z* = 6 : 94, 100 mg, 245 μmol) was allowed to react as described in the preparation of **22** to furnish the vinylsilane **24** (46 mg, 95%) as a 6 : 94 *E*–*Z* mixture. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.11$ (s, 9 H), 0.86 (d, $J = 6.5$ Hz, 6 H), 1.08–1.19 (m, 2 H), 1.20–1.39 (m, 4 H), 1.45–1.56 (m, 1 H), 2.11 (dt, $J = 7.3$ and 7.3 Hz, 2 H), 5.46 (dt, $J = 14.0$ and 1.3 Hz, 1 H), 6.30 (dt, $J = 14.0$ and 7.3 Hz, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 0.2$, 22.6, 27.1, 27.9, 30.0, 33.6, 38.9, 128.7, 149.3. $C_{12}H_{26}Si$: HRMS (EI) Calcd.: 198.1804. Found: 198.1796.

When the reaction mixture was quenched with [*O*-^{2}H]-methanol the mono-deuterated product **27** was obtained. ^{13}C NMR (50 MHz, $CDCl_3$): as above but 38.5 (t, $J = 18.8$ Hz). ^{2}H NMR (75 MHz, $CDCl_3$): $\delta = 1.19$ (br s). $C_{12}H_{25}DSi$: HRMS (EI): Calcd.: 199.1866. Found: 199.1863.

In the ^{2}H NMR spectrum there was an additional signal at $\delta = 1.51$ (10% of intensity). This is likely to belong (*Z*)-trimethyl(7-deuterio-7-methyloct-1-enyl)silane.[34]

trans-(2-Isopropylcyclopentylmethyl)trimethylsilane (26)

The diiodo alkane **15** (*E* : *Z* = 6 : 94, 100 mg, 245 μmol) was allowed to react as described in the preparation of **22**. The reaction mixture was held for 2 d at 60 °C before being quenched with methanol. Workup as described for **22** furnished a crude product which contained **26** as the major product alongside **22** and **24** in a 75 : 25 ratio. In order to separate **26**, the crude product was taken up in dichloromethane (0.6 mL) and cooled to −78 °C. A solution of bromine (1.00 M in dichloromethane, 0.16 mL, 0.16 mmol) was added dropwise until a yellow colour persisted. The mixture was allowed to reach room temperature and the solvents were carefully removed (20 min, 0 °C, 100–150 mbar; 1 min, 0 °C, 30 mbar). The crude product was purified by flash chromatography with pentane to give compound **26** (25 mg, 50%) as a colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = -0.01$ (s, 9 H), 0.34 (dd, $J = 14.5$ and 11.3 Hz, 1 H), 0.76 (d, $J = 6.8$ Hz, 3 H), 0.78 (dd, $J = 14.5$ and 2.9 Hz, 1 H), 0.89 (d, $J = 6.9$ Hz, 3 H), 0.93–1.85 (m, 9 H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -0.7$, 17.6, 22.4, 23.4, 24.2, 26.7, 29.2, 35.2, 38.6, 55.7. $C_{12}H_{26}Si$: HRMS (EI): Calcd.: 198.1804. Found: 198.1809.

When the reaction mixture was quenched with [*O*-^{2}H]-methanol instead, the resulting **26-D** was obtained as a 20 : 80 mixture of isotopomers. ^{2}H NMR (75 MHz, $CDCl_3$): α-**26-D**: $\delta = 0.78$ (br s); β-**26-D**: $\delta = 0.32$ (br s). $C_{12}H_{25}DSi$: HRMS (EI): Calcd.: 199.1866. Found: 199.1873.

A *cis*–*trans* mixture of **26** was prepared as follows. A solution of *tert*-butyllithium (1.45 M in pentane, 0.35 mL, 0.65 mmol) was added dropwise at −78 °C over 5 min into a solution of 1-iodomethyl-2-isopropylcyclopentane (**29**)[35] (*trans* : *cis* = 27 : 73, 75 mg, 0.23 mmol) in pentane (1.7 mL) and ether (1.1 mL). After 3 min chlorotrimethylsilane (0.22 mL, 1.74 mmol) was added and the mixture was allowed to reach room temperature over 2 h. Saturated aqueous NH_4Cl solution (2 mL) was added and the phases were separated. The aqueous phase was extracted with ether (3 × 4 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. Flash chromatography of the residue with pentane furnished a 27 : 73 mixture of the silanes **26** and **28** (54 mg, 85%). $C_{12}H_{26}Si$: HRMS (EI): Calcd.: 198.1804. Found: 198.1805.

The following NMR signals of **28** were recorded: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.00$ (s, 9 H), 0.19 (dd, $J = 14.5$ and 12.5 Hz, 1 H), 0.46 (dd, $J = 14.6$ and 1.4 Hz, 1 H), 0.87 (d, $J = 6.6$ Hz, 3 H), 0.88 (d, $J = 6.6$ Hz, 3 H), 0.93–1.85 (m, 9 H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -0.7$, 13.8, 21.9, 22.2, 27.4, 29.5, 32.7, 36.2, 53.9.

6-Trimethylsilylbicyclo[3.1.0]hexanes (37 and 38)

In the crude product obtained by the carbomagnesiation of compounds **21** or **23**, as described above in the preparation of **26**, the following additional ^{1}H NMR signals were recorded (400 MHz, $CDCl_3$): $\delta = -0.60$ (t, $J = 8.7$ Hz, 1 H), 0.07 (s, 9 H), corresponding to the literature data[29] for compound **37** and $\delta = -0.65$ (t, $J = 5.0$ Hz, 1 H), −0.10 (s, 9 H), corresponding to the literature data[29] for compound **38**.

(*Z*)-(6-Iodohex-1-enyl)trimethylsilane [(*Z*)-35]

A solution of the diiodo alkane **15** (*E* : *Z* = 6 : 94, 100 mg, 245 μmol) in THF (0.7 mL) was added at −78 °C to a solution of isopropylmagnesium chloride (1.80 M, in ether, 0.42 mL, 0.74 mmol) and THF (0.7 mL). The solution was allowed to reach 0 °C over 3 h resulting in the formation of a white precipitate. Methanol (0.14 mL, 3.5 mmol), saturated aqueous NH_4Cl solution (1 mL), and water (0.5 mL) were added. The phases were separated and the aqueous phase was extracted with ether (3 × 4 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. The crude product was analysed by ^{1}H NMR spectroscopy and by gas chromatography to show the presence of **35** (*E* : *Z* = 6 : 94) and traces (<1%) of **37** and **38**. Flash chromatography of the residue with pentane furnished (*Z*)-**35** (66 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.11$ (s, 9 H), 1.41–1.60 (m, 2 H), 1.79–1.92 (m, 2 H), 2.15 (dt, $J = 7.5$ and 7.5 Hz, 2 H), 3.19 (t, $J = 6.9$ Hz, 2 H), 5.50 (dt, $J = 14.0$ and 1.0 Hz, 1 H), 6.26 (dt, $J = 14.0$ and 6.8 Hz, 1 H) (*cf*. the data given in ref. 36).

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