Tailor-Made Silylating Agents for Efficient Surface Modification

Philippe Schneider, Roland Cloux, Klára Fóti, Ervin sz. Kováts*
Laboratoire de Chimie technique de l'Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

N-Silyldimethylamines are efficient silylating agents for the chemical surface modification of hydroxylated silicon dioxide preparations. The synthesis of chloro(5-X-3,3-dimethylpentyl)-dimethylsilanes and their conversion to the corresponding (dimethylamino) silanes are described, where X is a methoxy, methoxymethoxy, cyano or dimethylamino group. The bulky substituent forms a two stage protecting layer at the surface. The second stage hinders the access of nucleophiles to the silicon atom resulting an enhanced hydrolytic stability.

The adsorption properties of MO_2-type oxide surfaces covered by a dense layer of substituents, as depicted in the Figure, are mainly determined by the nature of the groups exposed at its surface and not by the underlying matrix. For the simplest example, a (3,3-dimethylbutyl)dimethylsiloxy (DMB) monolayer doubly shields the surface.[1,2] The space requirement of the *tert*-butyl "umbrella" of the DMB-substituent is only slightly smaller than that of its methylene-dimethylsiloxy base. Therefore, at dense surface coverage, determined by the van der Waals diameter of the base of the substituent, the protective *tert*-butyl layer will also be nearly compact. Access of reagents to the silicon atom in the base layer will be sterically hindered, resulting in an enhanced chemical stability. Also the layer will be more resistant in contact with mixtures containing nucleophilic species, their attack at the silicon atom being the first step of the solvolytic detachment of siloxy substituents.[3] Surfaces covered by a dense (5-X-3,3-dimethylpentyl)dimethylsiloxy (DMP-X) layer exhibit the same advantages concerning both efficient shielding and hydrolytic stability.[4] The underlying matrix is protected by the same configuration of the tailor-made substituent as for the DMB-layer. Surfaces properties will only be determined by the nature of the substituent group X, i.e. the polar group exposed.

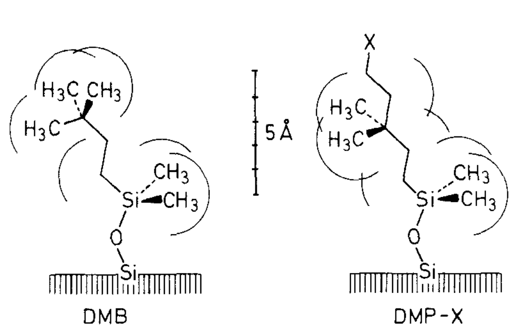
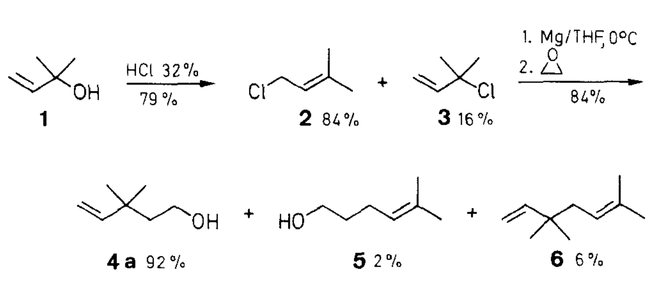


Figure. Van der Waals space requirement of the dimethyl (3,3-dimethylbutyl)siloxy (DMB) and (5-substituted-3,3-dimethylpentyl)dimethylsiloxy (DMP-X) layers.

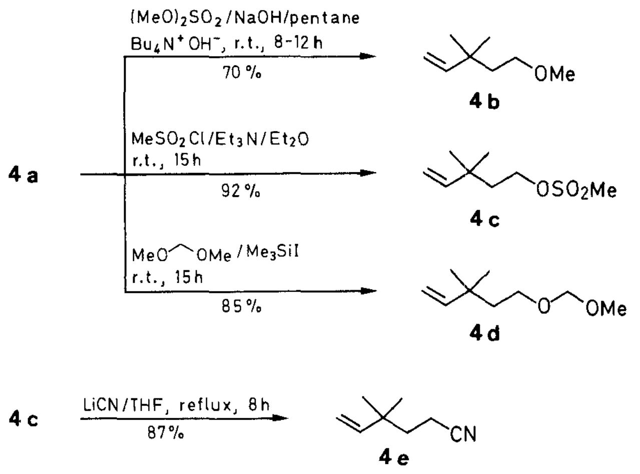
We report here on the synthesis of the dimethylamino-functionalized silylating agents for the chemical modification of silicon dioxide preparations by dense DMP-X monolayers, where X = methoxy, methoxymethoxy, cyano or dimethylamino. For the silylation of titanium(IV) dioxide and zirconium dioxide powders, the corresponding silanols are needed. The dimethylamino derivatives can easily be transformed into silanols by filtering on a wet silica gel column.[5]

The key intermediate, 3,3-dimethyl-4-penten-1-ol (**4a**) is obtained by reacting the Grignard reagent prepared from a mixture of the chlorides, 1-chloro-3-methyl-2-butene (**2**) and 2-chloro-2-methyl-3-butene (**3**) with one equivalent of ethylene oxide as shown in Scheme **A**.[6] The chloride **2** is the major compound in the reaction of 2-methyl-3-buten-2-ol (**1**) with 32% hydrochloric acid (**2**/**3** = 84:16). A separation of the isomers is not necessary because **2** and **3** give the same intermediate allylmagnesium compound.[7,8] The latter reacts with ethylene oxide in the absence of catalyst preferentially at the tertiary carbon center to give the expected alcohol **4a** together with its regioisomer **5** and the Würtz compound **6** in a 92:2:6 ratio. The alcohol **4a** is easily isolated by distillation (isolated yield: 77% based on **1**). In the presence of copper(I) halide as catalyst the electrophilic attack is largely favoured at the primary carbon center and the isomer **5** is the main product.[6,9,10]



Scheme **A**

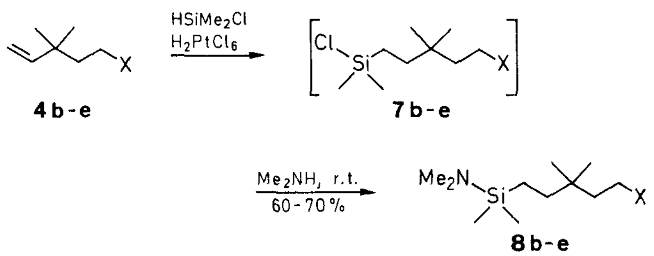
The 1-substituted 3,3-dimethyl-4-pentenes **4b–e**, necessary for the hydrosilylation step are prepared from the alcohol **4a** as shown in Scheme **B**. Reaction with dimethyl sulfate according to Merz's procedure[11] under phase-transfer conditions gives the methoxy derivative **4b** in 70% yield. In order to substitute the hydroxyl function of **4a** by a cyano or a dimethylamino group (Scheme **B**), the alcohol **4a** is first converted to the corresponding methanesulfonate **4c** by reaction with mesyl chloride in diethyl ether in 92% yield. Transetherification of **4a** with dimethoxymethane in the presence of a catalytic amount of iodotrimethylsilane gives **4d** in good yield.[12] Substitution of the methanesulfonate in **4c** by lithium cyanide in refluxing tetrahydrofuran[13] gives the desired nitrile **4e** in 87% yield (Scheme **B**). We did not prepare the corresponding dimethylamino compound, *N*-(3,3-dimethyl-4-pentenyl)-*N*,*N*-dimethyl amine, in order to avoid difficulties encountered in the catalytic hydrosilylation of olefinic amines with Speier's catalyst.[14–16] Therefore, the silyl amine is prepared from the methanesulfonate after hydrosilylation (*vide infra*).



Scheme B

The chloro-(5-X-3,3-dimethylpentyl)dimethylsilanes **7b–e** are prepared from **4b–e** by reacting them with chlorodimethylsilane in the presence of hexachloroplatinic acid as catalyst according to Speier et al.[17] (Scheme **C**). Neither of the chlorosilanes was isolated, because especially the chlorosilane **7b** decomposes during distillation.[18,19] Therefore, the crude reaction mixture is converted to the dimethylamino derivative following the procedure of Szabo et al.[1] Hydrosilylation of the methoxy substituted derivative **4b** with chlorodimethylsilane proceeds smoothly at the boiling temperature of the silane (ca 50 °C) in the presence of hexachloroplatinic acid as catalyst.[12] More severe conditions have to be applied for the hydrosilylation of the olefinic moiety of methanesulfonate **4c** and of nitrile **4e**. The methanesulfonate **4c** is reacted with chlorodimethylsilane at 80 °C in a glass autoclave in the presence of hexachloroplatinic acid without any solvent to give the corresponding chlorosilane **7c**. The nitrile **4e** required a higher temperature of 100 °C in a glass autoclave to give the desired chlorosilane **7e**.

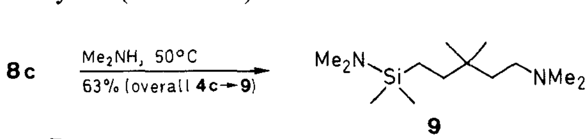
As mentioned already, chlorosilanes **7b–e** are not isolated. In order to prepare the dimethylaminosilanes **8b–e**, the pentane solution of the crude chlorosilanes **7b–e** are reacted with 2.5–3.0 equivalents of anhydrous dimethylamine. After filtration of the dimethylammonium chloride, the aminosilanes **8b–e** are obtained in excellent yields after distillation (Scheme **C**).



4, 7, 8	b	c	d	e
X	OMe	OSO_2Me	OCH_2OMe	CN

Scheme C

Finally, in order to obtain the dimethylamino derivative **9**, the crude methanesulfonate **8c** is reacted with dimethylamine at 50 °C in an autoclave to give **9** in a 63% overall yield (Scheme **D**).



Scheme D

The synthetized dimethylaminosilanes were applied for surface treatment of two surface rehydrated fume silicas. According to the procedure in Ref. 2 fully surface hydrated fume silica samples with specific BET-surface areas of $42.7 \pm 0.6\ m^2 g^{-1}$ and $174 \pm 2\ m^2 g^{-1}$ (hydrated Aerosil 0X50 and Cab-O-Sil-5M) were heated with 20 μmol m^{-2} dimethylaminosilane in a sealed ampoule. Surface coverages attained with **8b**, **8e** and **9** (3.88, 3.95 and 3.89 μmol m^{-2}) were nearly the same as that of a densest DMB-layer [Γ_{sox}(DMB) = 4.00 μmol m^{-2}]. Latter was shown to be the densest possible layer and it had an enhanced hydrolytic stability.[3] In such dense layers, substituents ought to have an upright position similar to that depicted in the Figure due to steric effect enforced by their surrounding neighbours.

Table 1. Compounds **4a–e**, **5**, **8b**, **d**, **e** and **9** Prepared

Product	Yield (%)	Purity[a] (%)	bp (°C)/mbar	$d^{20,b}$ ($g\,cm^{-3}$)	$n_D^{20,c}$	N %[d] calc/found	Molecular Formula[a]
4a	77	99.5	65–66/20	0.913	1.4410	–/–	$C_7H_{14}O$ (114.2)
4b	70	99.9	120–124	0.798	1.4179	–/–	$C_8H_{16}O$ (128.2)
4c	92	99.8	84–85/0.07	1.070	1.4508	–/–	$C_8H_{16}O_3S$ (192.3)
4d	85	99.9	74–75/27	0.866	1.4230	–/–	$C_9H_{18}O_2$ (158.2)
4e	87	98.6	68–70/20	0.838	1.4366	–/–	$C_8H_{13}N$ (123.2)
5	–	98.9	73–74/20	0.890	1.4523	–/–	$C_7H_{14}O$ (114.2)
8b	70	99.5[c]	93–95/9	0.847	1.4415	6.1/6.0	$C_{12}H_{29}NOSi$ (231.5)
8d	69	98.8[c]	95–96/0.5	0.891	1.4414	5.4/4.8	$C_{13}H_{31}NO_2Si$ (261.5)
8e	60	99.6[c]	80–81/0.05	0.879	1.4528	6.2/6.1	$C_{12}H_{26}N_2Si$ (226.4)
9	63	99.5[c]	106–108/7	0.824	1.4475	11.5/11.3	$C_{13}H_{32}N_2Si$ (244.5)

[a] Purity determined by GC. No microanalyses were carried out.
[b] Confidence limit at the 95% confidence level $\Delta_{95} = 0.003\ g\,cm^{-3}$.
[c] $\Delta_{95} = 0.0005$.
[d] Active N determined by titration (see text).

Table 2. Spectral Properties of Compounds **8b**, **d**, **e** and **9**

Product	^1H-NMR ($CDCl_3$/TMS) δ, J(Hz)	MS (EI, 70 eV) m/z (%)
8b	0.02 (s, 6H), 0.5 (m, 2H), 0.86 (s, 6H), 1.2 (m, 2H), 1.51 (t, 2H, J = 7.6), 2.45 (s, 6H), 3.33 (s, 3H), 3.40 (t, 2H, J = 7.6)	218 (M^+, 0.1), 203 (4), 89 (100)
8d	0.02 (s, 6H), 0.5 (m, 2H), 0.87 (s, 6H), 1.2 (m, 2H), 1.53 (t, 2H, J = 7.6), 2.45 (s, 6H), 3.37 (s, 3H), 3.56 (t, 2H, J = 7.6), 4.62 (s, 2H)	233 ($M^+ - CH_3$, 0.6), 171 (8), 89 (100)
8e	0.02 (s, 6H), 0.5 (m, 2H), 0.85 (s, 6H), 1.2 (m, 2H), 1.59 (t, 2H, J = 8.5), 2.25 (t, 2H, J = 8.5), 2.45 (s, 6H)	212 ($M^+ - 1$, 0.1), 198 (14), 89 (100)
9	0.02 (s, 6H), 0.4 (m, 2H), 0.85 (s, 6H), 1.2 (m, 4H), 2.20 (t, 2H, J = 8.5), 2.21 (s, 6H), 2.45 (s, 6H)	245 (M^+, 1.5), 103 (1.4), 58 (100)

Research grade 2-methyl-3-butene-2-ol (**1**), ethylene oxide, THF, Et_3N, $MeSO_2Cl$, HMe_2SiCl, LiH, acetone cyanohydrin, $H_2PtCl_6 \cdot 6\ H_2O$, $(MeO)_2SO_2$, Me_2NH, dimethoxymethane, Me_3SiI, as well as 4Å molecular sieves were purchased from Fluka (Buchs, Switzerland) and used as received. THF was dried over sodium benzophenone ketyl and chlorodimethylsilane was freshly distilled before use. Chlorosilanes **7b–e** were not isolated and not analysed.

GC analyses were performed on a Hewlett-Packard (model 5890A) instrument equipped with a fused silica macrobore capillary column (i.d. = 0.30 mm; length = 25.0 m) with crosslinked methylsilicone as stationary phase. Retention indexes I_T were calculated from isothermal chromatograms made at the temperature T/°C. IR spectra were recorded on a Perkin-Elmer 684 spectrophotometer. ^1H-NMR spectra were recorded at 80 MHz on a Bruker WP80 spectrometer. Safety glass autoclaves were from Ciba-Geigy (Basel, Switzerland).

Determination of active nitrogen in dimethylaminosilanes **8b–e** and **9** was made by mixing the dimethylaminosilanes (~ 1.5 mmol) with 0.1 M HCl (20.0 mL) and titrating the excess acid with methyl red as indicator. The result is given as N% in Table 1.

The purity of dimethylaminosilanes was determined by dissolving **8b–e** and **9** (~ 10 mg) in anhydrous MeOH (100 µL) and heating to 60°C for 10 min to give the corresponding methoxysilanes in quantitative yield. The mixture is then analysed by GC.

1-Chloro-3-methyl-2-butene (2) and 2-Chloro-2-methyl-3-butene (3):
In a 1 L round bottom flask, HCl 37% (250 mL, 3 mol) is diluted with H_2O (35 mL). To the well-stirred aq acid is added 2-methyl-3-butene-2-ol (**1**; 86.1 g, 1 mol) in one portion and the mixture is stirred for 15 min at r.t. (longer reaction times result in a dramatic drop of the yield). The lower acidic layer is separated and the organic phase is washed successively with H_2O (100 mL), sat. aq $NaHCO_3$ (100 mL) and sat. aq NaCl (100 mL). The organic phase is then dried over 4Å molecular sieves (10 g) and is decanted when clear (1.5 h with occasional shaking). Distillation using a 15 cm Vigreux column at 50–64°C/200 mbar gives a colorless liquid containing **2**/**3** = 84:16 and 5% nonidentified impurities (GC/60°C); yield: 83 g (79%). This mixture of **2** + **3** is used directly in the next reaction step. Distillation of a small sample resulted in pure isomer **2** (purity 98%).

^1H-NMR ($CDCl_3$/TMS): δ = 1.74 (d, 3H, J = 1.0, CH_3), 1.77 (br s, 3H, CH_3), 4.09 (d, 2H, J = 7.8, CH_2Cl), 5.45 (t with fine structure, 1H, J = 7.8, =CH).

The ^1H-NMR of compound **3** is obtained from the spectrum of the mixture by substracting the signals of isomer **2**.

3:
^1H-NMR ($CDCl_3$/TMS): δ = 1.70 (s, 6H, CH_3), 5.06 (dd, 1H, J = 10.0, 0.8, H-4 cis), 5.24 (dd, 1H, J = 17.0, 0.8, H-4 *trans*), 6.12 (dd, 1H, J = 17.0, 10.0, =CH).

3,3-Dimethyl-4-pentene-1-ol (4a):
In a 4-necked round bottom flask equipped with gas inlet, dropping funnel, reflux condenser and mechanical stirrer, Mg turnings (100 g, 4.1 mol) are covered with THF (400 mL). 1,2-Dibromoethane (2.2 g, 11 mmol) is added in order to activate the Mg (15 min). The mixture is cooled to 0°C (ice bath) and a solution of the mixture of chlorides **2** + **3** (218 g, 2.08 mol) in dry THF (350 mL) is added dropwise over 12 h. The mixture is then warmed to r.t., stirred for an additional 8 h and diluted with THF (100 mL). The mixture is now cooled to 0°C and the reflux condenser to – 10°C. Through the gas inlet, a stream of ethylene oxide is introduced near the surface of the stirred mixture. The gas flow is regulated so that all the reagent is consumed and no reflux is observed. After the consumption of 93 g (2.1 mol) of ethylene oxide, the mixture is warmed to r.t., and stirred for 10 h and then refluxed for 3 h. After cooling to r.t., the mixture is decanted from excess Mg into an ice/2.5 M H_2SO_4 mixture (1.2 L). The organic phase is separated and the aqueous layer is extracted with Et_2O (3 × 200 mL). The combined organic phases are washed with brine (3 × 150 mL) and dried (Na_2SO_4). After evaporation of the solvent using a Vigreux column, GC of the residue shows a **4a**/**5**/**6** ratio of 92:2:6. Distillation at 65–66°C/20 mbar furnishes 182 g (77%) of colorless alcohol **4a** of 98.2% purity (**4a**/**5**/**6** = 98.2:0.6:0.1); yield: 182 g (77%); bp 65–66°C/20 mbar (**4a**: I_{60} = 868, **5**: I_{60} = 949, **6**: I_{60} = 902).

^1H-NMR ($CDCl_3$): δ = 1.04 (s, 6H, CH_3), 1.44 (s, 1H, OH), 1.62 (t, 2H, J = 7.2, $C\underline{H}_2CH_2OH$), 3.66 (t, 2H, J = 7.2, $C\underline{H}_2OH$), 4.95 (dd, 1H, J = 10.7 and 1.4, 5-H_{cis}), 4.96 (dd, 1H, J = 17.5 and 1.4, 5-H_{trans}), 5.85 (dd, 1H, J = 17.5, 10.7, =CH).

MS (EI): m/z = 114 (M^+, 0.5), 96 (M – 18, 20), 41 (100).

A sample of isomer **5** is prepared according to Linstrumelle.[10] The same procedure is applied as for the preparation of **4a** but the reaction is carried out at – 30°C in the presence of 10 mol% of CuI as catalyst. The product is distilled at 73–74°C/20 mbar to give the isomer **5** of 98.9% purity (**4a**:**5** = 98.9:0.5 and 0.6% of a non identified compound; GC/60°C).

5:
^1H-NMR ($CDCl_3$/TMS): δ = 1.31 (s, 1H, OH); 1.62 (s + m, 5H, CH_3 + $C\underline{H}_2CH_2OH$), 1.70 (d, 3H, J = 1.0, CH_3), 2.09 (q, 2H, J = 6.9, H_{allyl}), 3.66 (t, 2H, J = 6.3, $C\underline{H}_2OH$), 5.15 (t with fine structure, 1H, J = 6.9, =CH).

On a small scale preparation starting from a mixture of **2** + **3** (1.05 g, 10.0 mmol), the crude mixture is filtered on neutral alumina (Act. III). Elution with pentane affords 0.3 g of diene **6** after removal of the solvent; yield: 0.3 g (22%).

6:
^1H-NMR ($CDCl_3$): δ = 0.98 [s, 6H, =C(CH_3)$_2$], 1.60 (br s, 3H, allyl CH_3), 1.72 (d, 3H, J = 1.0, 3H, allyl CH_3), 1.97 (d, 2H, J = 7.6, H_{allyl}), 4.90 (dd, 1H, J = 10.8, 1.5, 7-H_{cis}, 4.92 (dd, 1H, J = 17.5, 1.5, 7-H_{trans}), 5.14 (t with fine structure, 1H, J = 7.6, C=CH), 5.82 (dd, 1H, J = 17.5, 10.8, CH_2=C$\underline{H}$).

1-Methoxy-3,3-dimethyl-4-pentene (4b):
In a 250 mL round bottom flask equipped with a reflux condenser, dropping funnel and an efficient magnetic stirrer, a solution of **4a** (15.0 g, 0.13 mol) in pentane (80 mL) is placed together with a mixture of 45% aq solutions of NaOH (80 mL) and 40% tetrabutylammonium hydroxide (5 mL). The mixture is heated to reflux

under vigorous stirring and dimethyl sulfate (40.3 g, 0.32 mol) is added over a 1 h period. After stirring overnight at r.t. the mixture becomes a thick suspension. 25% aq NH_3 (20 mL) is then added and after stirring for 30 min, the mixture is diluted with H_2O (150 mL) and the organic layer is separated. The aqueous phase is extracted with pentane (2 × 100 mL), the combined organic phases are washed with H_2O (3 × 75 mL), dried (Na_2SO_4) and the solvent is evaporated. Distillation of the residue using a Vigreux column gives **4b** as colorless oil of 99.9% purity (GC, I_{60} = 835); yield: 11.7 g (70%); bp 120–124 °C/960 mbar.

^{1}H-NMR ($CDCl_3$): δ = 1.03 [s, 6H, $(CH_3)_2$], 1.61 (t, 2H, J = 7.5, C$\underline{H}_2$$CH_2O$), 3.31 (s, 3H, OCH_3), 3.36 (t, 2H, J = 7.5, CH_2C$\underline{H}_2$O), 4.92 (dd, 1H, J = 10.7, 1.5, 5-H_{cis}), 4.93 (dd, 1H, J = 17.4, 1.5, 5-H_{trans}), 5.80 (dd, 1H, J = 17.4, 10.7, =CH).

MS (EI): m/z = 113 (M^+ − CH_3, 0.6), 96 (M^+ − CH_3OH, 15), 45 (100).

3,3-Dimethyl-4-pentenyl Methanesulfonate (4c):
In a 1 L round bottom flask equipped with a dropping funnel and an efficient magnetic stirrer is placed a solution of the alcohol **4a** (57.0 g, 500 mmol) and Et_3N (58.0 g, 600 mmol) in Et_2O (500 mL). The mixture is cooled to 0 °C and a solution of $MeSO_2Cl$ (62.0 g, 540 mmol) in Et_2O (250 mL) is added dropwise during 4 h. Stirring at r.t. is maintained for 15 h and the mixture is filtered in a Büchner funnel. The solvent is removed on a rotary evaporator and the residue is distilled using a Vigreux column to give **4c** as colorless viscous oil of 99.1% purity (GC, I_{140} = 1294); yield: 88 g (92%); bp 84–85 °C/0.07 mbar.

^{1}H-NMR ($CDCl_3$): δ = 1.07 [s, 6H, $(CH_3)_2$], 1.79 (t, 2H, J = 7.4, C$\underline{H}_2$$CH_2O$; 2.99 (s, 3H, CH_3SO_2), 4.21 (t, 2H, J = 7.4, CH_2C$\underline{H}_2$O), 4.98 (dd, 1H, J = 17.4, 1.1, 5-H_{trans}), 5.00 (dd, 1H, J = 11.0, 1.1, 5-H_{cis}), 5.77 (dd, 1H, J = 17.4, 11.0, =CH).

MS (DCI, NH_3 positive ions): m/z = 210 (M^+ + NH_4), 113 (M^+ + NH_4 − 97).

3,3-Dimethyl-5-methoxymethoxy-1-pentene (4d):
In a 2 L flask equipped with a reflux condenser and magnetic stirrer is placed a solution of the alcohol **4a** (57.1 g, 0.5 mol) in dimethoxymethane (850 mL). Iodotrimethylsilane (1.8 g, 8.8 mmol) is then added and the mixture is stirred at r.t. for 15 h. The brown solution is poured into a mixture of 10% aq $Na_2S_2O_3$ (400 mL) and Et_2O (500 mL). The organic layer is separated and the aqueous phase is extracted with Et_2O (3 × 150 mL). The combined organic phases are washed with H_2O (3 × 250 mL) and dried (Na_2SO_4). After evaporation of the solvent using a Vigreux column, the residue (76.6 g) is dissolved in pentane (100 mL) and filtered on a column of silica gel (400 g) prepared in pentane and eluted with additional pentane (2 L) (to eliminate the unreacted starting alcohol **4a**). After evaporation of the pentane using a Vigreux column the residue is distilled using a smaller Vigreux column with a plug of copper wool at the top, to remove any iodine that may form upon heating; yield: 67.5 g (85%); bp 74–75 °C/27 mbar; 99.9% pure (GC, I_{80} = 1000).

^{1}H-NMR ($CDCl_3$): δ = 1.04 [s, 6H, $(CH_3)_2$], 1.64 (t, 2H, J = 7.0, C$\underline{H}_2$$CH_2O$), 3.36 (s, 3H, OCH_3), 3.51 (t, 2H, J = 7.0, CH_2C$\underline{H}_2$O), 4.60 (s, 2H, OCH_2O), 4.93 (dd, 1H, J = 10.7, 1.4, 5-H_{cis}), 4.93 (dd, 1H, J = 17.4, 1.4, 5-H_{trans}), 5.80 (dd, 1H, J = 17.4, 10.7, =CH).

MS (DCI, NH_3): m/z = 176 (M^+ + NH_4, 100), 159 (M^+ + 1, 22), 127 (20).

1-Cyano-3,3-dimethyl-4-pentene (4e):
In a 500 mL flask equipped with a reflux condenser and a dropping funnel LiH (3.41 g, 0.429 mol) is placed together with anhydrous THF (140 mL) then a solution of acetone cyanohydrin (36.5 g, 0.429 mol) in THF (20 mL) is added dropwise (exothermic reaction). After all the hydride has been consumed, methanesulfonate **4c** (55 g, 0.286 mol) is added in one portion and the mixture is refluxed for 8 h. The dark red mixture is allowed to cool, 2 N aq NaOH (100 mL) is added and the mixture is stirred vigorously (to hydrolyse the unreacted cyanohydrin). The organic layer is washed with aq NaCl (2 × 100 mL). The aqueous phases are combined and extracted with Et_2O (2 × 100 mL). The combined organic extracts are dried (Na_2SO_4), and the solvent evaporated using a 20 cm Vigreux column. Distillation of the residue gives 98.6% pure nitrile **4e** (GC, I_{80} = 969); yield: 30.8 g (87%); bp 68–70 °C/20 mbar.

^{1}H-NMR ($CDCl_3$): δ = 1.04 [s, 6H, $(CH_3)_2$], 1.68 (t with fine structure, 2H, J = 8.0, C$\underline{H}_2$$CH_2CN$), 2.23 (t with fine structure, 2H, J = 8.0, CH_2C$\underline{H}_2$CN), 4.98 (dd, 1H, J = 17.5, 1.1, 5-H_{trans}), 5.04 (dd, 1H, J = 10.8, 1.1, 5-H_{cis}), 5.69 (dd, 1H, J = 17.5, 10.8, =CH).

Chloro(5-methoxy-3,3-dimethylpentyl)dimethylsilane (7b):
In a 50 mL round bottom flask with a reflux condenser, thermometer and magnetic stirrer chlorodimethylsilane (3.90 g, 41 mmol) is placed together with the methoxyalkene **4b** (4.40 g, 34 mmol) and 1% $H_2PtCl_6 \cdot 6H_2O$ in isopropanol (0.15 mL, 0.68 mg Pt). Whilst the reaction mixture is heated to reflux an exothermic reaction takes place within 15 min. The mixture is stirred for a further 3 h at 50 °C, then cooled to r.t. and dissolved in pentane (100 mL). The solution is immediatly used for the preparation of the dimethylaminosilane **8b**.

Chloro(5-mesyloxy-3,3-dimethylpentyl)dimethylsilane (7c):
In a 100 mL glass autoclave equipped with a magnetic stirring bar is placed $H_2PtCl_6 \cdot 6H_2O$ (80 mg, 0.18 mmol), mesylate **4c** (48.0 g, 0.25 mol) and chlorodimethylsilane (26.5 g, 0.28 mol). The autoclave is closed and heated in an oil bath to 80 °C. Within a few min the mixture turns to brown. It is stirred for 3.5 h at 80 °C. [The reaction is monitored by ^{1}H-NMR; no signals around δ = 5 (vinyl protons)]. The crude mixture is diluted with pentane (300 mL) and used immediatly for the conversion to the dimethylaminosilane **8c**.

Chloro(3,3-dimethyl-5-methoxymethoxy)pentyldimethylsilane (7d):
To a 100 mL round bottom flask equipped with a reflux condenser, dropping funnel, magnetic stirrer and a thermocouple is placed unsaturated ether **4d** (31.6 g, 0.200 mol) and a 1% solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol (0.1 mL) under an Ar atmosphere. The mixture is heated to 70 °C and chlorodimethylsilane (28.4 g, 0.300 mol) is added dropwise. An exothermic reaction takes place within a few min (the internal temperature raises to 100 °C). The addition rate is adjusted so that the temperature never decreases below 70–75 °C. If the temperature decreases, introduction of chlorodimethylsilane is discontinued until another portion of the catalyst solution (0.1 mL) is added. After complete addition the brown mixture is stirred at 70–75 °C overnight, then cooled to r.t., diluted with pentane (500 mL) and used immediately for the conversion to **8d**.

Chloro(5-cyano-3,3-dimethylpentyl)dimethylsilane (7e):
In a 100 ml all-glass autoclave $H_2PtCl_6 \cdot 6H_2O$ (0.14 g, 0.27 mmol) is placed together with chlorodimethylsilane (4 mL) (for drying and activation of the catalyst) and the mixture is stirred at r.t. in an Ar atmosphere. After 1 h, the orange crystals disappear to give a pale yellow suspension. Solvent is now eliminated at 10^{-1} Torr (30 min) when a dark brown solid remains. To this catalyst are added nitrile **4e** (30.8 g, 0.25 mol) and chlorodimethylsilane (28.4 g, 0.3 mol), the autoclave is closed and heated in an oil bath to 100 °C under vigorous magnetic stirrer. After 3 h at this temperature, the autoclave is cooled to r.t. and the dark brown mixture is diluted with pentane (200 mL). The resulting crude unfiltered mixture is used immediately for the preparation of **8e**.

Dimethylaminosilanes 8b–e; General Procedure:
In an Ar atmosphere the crude reaction mixture of **8b–e** in pentane is placed in a round bottom flask equipped with a reflux condenser cooled to − 10 °C and a dropping funnel with pressure-equalizer. Anhydrous Me_2NH (~ 2.5–3 equivs) is introduced as liquid in the cooled dropping funnel and then is allowed to evaporate slowly into the reaction flask. The mixture is stirred overnight at r.t. and is filtered through a fritted glass funnel under positive Ar pressure. The precipitate is washed with a little more pentane and the solvent is distilled using a Vigreux column (Ar atmosphere). Distillation of the residue under reduced pressure affords the corresponding pure dimethylaminosilane. This procedure is used for the preparation of all dimethylaminosilanes with the exception of **8c**, which is not distilled but the crude filtered mixture is used for the subsequent preparation of **9** (*vide infra*).

N-[(5-Dimethylamino-3,3-dimethylpentyl)dimethylsilyl]-*N,N*-dimethylamine (9):

Crude aminosilane **8c** prepared from chlorosilane **7c** is placed in a stainless steel autoclave equipped with a 100 mL glass tube and a magnetic stirrer, then after cooling to − 70 °C dimethylamine (28.2 g, 0.620 mol) is condensed. The autoclave is closed, heated to 50 °C for 4 d under stirring, cooled again to − 70 °C opened and allowed to warm to r.t. The excess of Me_2NH is evaporated and the residue is diluted with pentane (150 mL) and filtered through a fritted glass funnel under N_2 atmosphere. After evaporation of the solvent, the residue is distilled using a Vigreux column to afford aminosilane **9** as a colorless oil of 98.5 % purity (GC, 140 °C); yield: 48 g (79 % from **4c**); bp 106–108 °C/6.8 mbar. A second distillation gives 99.5 % pure silane **9**; yield: 38.2 g (63 %).

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