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(54) Title: DISILANE-, CARBODISILANE-AND OLIGOSILANE CLEAVAGE WITH CLEAVAGE COMPOUND ACTING AS CATALYST AND HYDROGENATION SOURCE

(57) Abstract: The invention relates to a process for the manufacture of monosilanes of formula (I): $\text{Me}_x\text{SiH}_y\text{Cl}_z$ (I), comprising: the step of subjecting a silane substrate (methyldisilanes, methyloligosilanes, or carbodisilanes) to a cleavage reaction of the silicon-silicon bond(s) or the silicon- carbon bonds in silane substrates the reaction involving a cleavage compound selected from a quaternary Group 15 onium compound R_4QX , a heterocyclic amine, a heterocyclic ammonium halide, or a mixture of R_3P and RX . The starting material disilanes to be cleaved has the formula (II): $\text{Me}_m\text{Si}_2\text{H}_n\text{Cl}_o$ (II) The starting material oligosilanes to be cleaved have the general formula (III): $\text{Me}_p\text{Si}_q\text{H}_r\text{Cl}_s$ (II I), The starting material carbodisilanes to be cleaved have the general formula (IV): $(\text{Me}_a\text{SiH}_b\text{Cl}_c)\text{-CH}_2\text{-(Me}_c\text{SiH}_d\text{Cl}_f)$ (IV)



WO 2019/060481 A1

Disilane-, carbodisilane- and oligosilane cleavage with cleavage compounds acting as catalyst and hydrogenation source

TECHNICAL FIELD

5 The present invention relates to the technical field of the production of silane monomers, in particular to the production of mono-, di- and trimethylmonosilanes, starting from disilanes and oligosilanes by a cleavage reaction of the silicon-silicon bond, and from carbodisilanes by silicon-carbon bond cleavage, in each case in the presence of a cleavage compound and optionally a hydrogenation source.

BACKGROUND OF THE INVENTION

Methylchlorosilanes and methylhydrosilanes are highly useful starting materials in synthetic organosilicon chemistry, and therefore constitute an industrially valuable class of compounds. In particular, methylsilanes bearing both chloro- and hydrido substituents
15 constitute attractive starting materials in synthesis due to their bifunctional nature, which means they have functional groups of different reactivities. The chloride ligand is a better leaving group than the hydride group and allows, for instance, the controlled addition of further monomeric or oligomeric siloxane units with retention of the Si-H bond under mild conditions, thereby rendering said chlorohydrosilanes useful as blocking and coupling
20 agents in the synthesis of defined oligo- and polysiloxanes.

Such compounds generally find a wide range of applications, for instance for the manufacture of adhesives, sealants, mouldings, composites and resins for example in the fields of electronics, automotive, construction and many more.

25 The Si-H moieties present in chlorosilanes can be utilized for postsynthesis modifications and functionalisations, for instance for the introduction of organic residues to polyorganosiloxanes or for cross-linking by hydrosilylation reactions, which is desirable in various kinds of compositions containing polyorganosiloxanes.

30 Synthesis of functionalized polysiloxanes starting with transformations via the Si-H bond(s) followed by hydrolysis or alcoholysis of the Si-Cl bond(s) and optionally condensation for the formation of polysiloxanes is also viable.

Although there is a high demand for such bifunctional silanes having both Si-H and Si-Cl
35 bonds, there is no practical, economically reasonable and sustainable industrial process for the synthesis of such building blocks disclosed yet.

The production of methylsilanes by Si-Si-bond cleavage of disilanes has been reported by Lewis and Neely in WO 2013/101618 A1 (US 8,697,901 B2) and WO2013101619A1 (US 8,637,695 B2). In these publications, the hydrochlorinative cleavage of the disilanes of the

5 Direct Process Residue requires the presence of heterocyclic amines or group 15 quaternary onium compounds serving as catalysts, not as reactants. The yields of hydridomonosilanes, in particular of Me_2SiHCl , are comparatively low. The scope of starting materials in above-cited publications is restricted to perchlorinated methyl disilanes.

10 US 5175329A describes a process wherein a mixture of polysilanes and an organotrihalosilane are reacted with hydrogen gas in the presence of a hydrogenolysis catalyst, and a redistribution catalyst, at a temperature of 100° C to 400° C. In one run tetrabutylphosphonium chloride is used as redistribution catalyst. There is no pointer in US 5175329A according to that the redistribution catalyst would participate in the reaction. It is

15 also unlikely that under the conditions of US 5175329A (hydrogen gas/pressure) the redistribution catalyst acts as a hydrogen donor. Moreover, the yields in Me_2SiHCl are very low.

In EP 0574912 B1 (B. Pachaly, A. Schinabeck; 1993) a process for the preparation of

20 methylchlorosilanes from the high-boiling residue from the Direct Process by Si-Si-bond cleavage with hydrogen chloride and a catalyst which remains in the reaction mixture, usually a tertiary amine, is described.

PROBLEM TO BE SOLVED

25 The problem to be solved by the present invention is the provision of a process for the production of monosilanes, in particular methylchloro- and methylhydridomonosilanes, and most preferred hydridosilanes, such as of Me_2SiHCl in particular, by submitting disilanes, oligosilanes and carbodisilanes to cleavage conditions under which the desired products are obtained by Si-Si-bond cleavage, or by Si-C-bond cleavage in case of carbodisilanes acting

30 as substrates. Further, it is the object of present invention to provide a process with improved product yields, product purity, product selectivity of the conversion, convenience of the work-up procedure, ease of handling of the reagents and cost efficiency of the process. The problem to be solved is in particular the provision of such an improved process in which high proportions of methylhydridomonosilanes and methylhydridochloromonosilanes with a high

35 content of hydride substituents can be obtained.

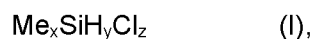
Further, the problem to be solved comprises the provision of a process by which monosilanes such as in particular Me_2SiHCl , Me_2SiH_2 , Me_3SiCl , Me_2SiCl_2 , Me_3SiH , MeSiH_3 , MeSiHCl_2 , MeSiH_2Cl , and MeSiCl_3 can be obtained in high yield from silane substrates, in particular from the residue of the Müller-Rochow Direct Process, the so-called Direct Process Residue (DPR).

According to the present invention, this problem is solved as described in the following.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a process for the production of monosilanes starting from disilanes, carbodisilanes, oligosilanes or mixtures thereof by cleavage of silicon-silicon bonds or carbon-silicon bonds, respectively, and to monosilanes produced by such process.

Subject of the invention is a process for the manufacture of monosilanes of the general formula (I):



wherein

$$x = 0 \text{ to } 3,$$

$$y = 0 \text{ to } 3, \text{ preferably } 1 \text{ to } 3, \text{ more preferably } 1 \text{ or } 2,$$

$$z = 0 \text{ to } 4 \text{ and}$$

$$x + y + z = 4,$$

and mixtures thereof,

comprising:

A) the step of subjecting a silane substrate comprising one or more silanes selected from the group of

a) one or more disilanes of the general formula (II)



wherein

$$m = 0 \text{ to } 6,$$

$$n = 0 \text{ to } 6, \text{ preferably } 0 \text{ to } 4,$$

$$o = 0 \text{ to } 6 \text{ and}$$

$$m + n + o = 6,$$

b) one or more linear or branched oligosilanes of the general formula (III)



wherein

$$q = 3-7$$

$$p = q \text{ to } (2q + 2)$$

$$r, s = 0 \text{ to } (q + 2)$$

$$r + s = (2q + 2) - p$$

and wherein preferably each Si atom bears at least one methyl group, and

c) one or more carbodisilanes of the general formula (IV)



wherein

a, c are independently of each other 1 to 3,

b, d are independently from each other 0 to 2

e, f are independently from each other 0 to 2,

$$a + b + e = 3,$$

$$c + d + f = 3,$$

and mixtures containing compounds of the general formulae (II), (III) and (IV),

to the cleavage reaction of the silicon-silicon bond(s) in the silane substrates of the general formulae (II) and (III) and the silicon-carbon bond(s) of the carbodisilanes of the general formula (IV),

to the reaction with at least one compound (cleavage compound) selected from the group consisting of:

- a quaternary Group 15 onium compound R_4QX , wherein each R is independently a hydrogen or an organyl group, Q is phosphorus, arsenic, antimony or bismuth, and X is a halide selected from the group consisting of F, Cl, Br and I,

- a heterocyclic amine,

- a heterocyclic ammonium halide,

- a mixture of R_3P and RX , wherein R is as defined above, and X is as defined above, and

mixtures of the above-mentioned compounds,

(i) until at least about 50 mol-% of the cleavage compound based on the initial molar amount of the cleavage compound is reacted, and/or

- (ii) until the ratio of the total of the produced monosilanes of the general formula (I) wherein $y = 1$ to 3 is at least about 40 mol-%, preferably at least about 50 mol-%, based on the total molar amount of the monosilanes of the general formula (I), and/or
- (iii) until the ratio of Me_2SiHCl is at least about 20 mol-%, preferably at least about 30 mol-%, based on the total amount of the monosilanes of the general formula (I), and

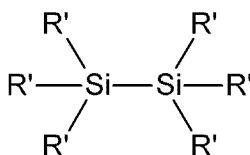
B) optionally a step of separating the resulting monosilanes of the general formula (I).

The cleavage reaction of the silicon-silicon bond(s) and/or the silicon-carbon bond(s) in the silane substrate is preferably carried out in the presence of at least one compound which promotes such bond cleavage and acts as a hydride donor (cleavage compound).

The disilanes of the general formula (II)



can be depicted also by the structural formula:

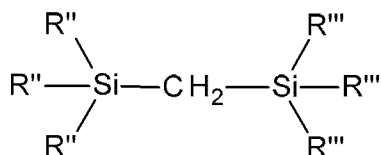


wherein the substituents R' are independently selected from methyl (Me), hydrogen (H) and chlorine (Cl), wherein the number of methyl groups $m = 0$ to 6 , the number of hydrogen atoms $n = 0$ to 6 , and the number of chlorine atoms $o = 0$ to 6 , and the total of $m + n + o = 6$.

The carbodisilanes of the general formula (IV)



can be depicted also by the structural formula:



wherein the substituents R'' are independently selected from methyl (Me), hydrogen (H) and chlorine (Cl), and wherein the substituents R''' are independently selected from methyl (Me), hydrogen (H) and chlorine (Cl), and

5 wherein the number of methyl groups on each silicon atom (a, c) is independently from 1 to 3,

wherein the number of hydrogen atoms on each silicon atom (b, d) is independently from 0 to 2, and

10 wherein the number of chlorine atoms on each silicon atom (e, f) is independently from 0 to 2.

The linear or branched oligosilanes of the general formula (III)



are oligosilanes that have a linear or branched silicon skeleton, wherein $q = 3$ to 7 silicon atoms are bonded to each other by single bonds, and the free valencies of the silicon skeleton are saturated by substituents selected from methyl (Me), hydrogen (H) and chlorine (Cl) with the proviso that the number of methyl groups $p = q$ to $(2q + 2)$, which corresponds to the case where each silicon atom has one methyl group ($p=q$) and the case of permethylated silanes ($p=2q+2$) and which means that there are at least 3 methyl groups up to 16 methyl groups (i.e. in $\text{Si}_7\text{Me}_{16}$) in the silanes; and the number of hydrogen atoms (r) and chlorine atoms (s) are independently of each other 0 to $(q + 2)$, and $r + s = (2q + 2) - p$, wherein q is the number of silicon atoms and p is the number of methyl groups, again with the preferred proviso that each Si atom bears at least one methyl group.

25 In a preferred embodiment of the invention the silane substrate is consisting of one or more silane substrate compounds selected from the group consisting of the disilanes of the general formula (II), linear or branched oligosilanes of the general formula (III) and the carbodisilanes of the general formula (IV).

30 The process of the present invention is characterized inter alia by any of the features (i) to (iii):

(i) The process is run until at least about 50 mol-% of the cleavage compound based on the initial molar amount of the cleavage compound is reacted, and/or

(ii) The process is run until the ratio of the total of the produced monosilanes of the general formula (I) wherein $y = 1$ to 3 is at least about 40 mol-%, preferably at least about 50 mol-%, based on the total molar amount of the monosilanes of the general formula (I).

(iii) The process is run until the ratio of Me_2SiHCl is at least about 20 mol-%, preferably at least about 30 mol-%, based on the total amount of the monosilanes of the general formula (I).

Such features (i) to (iii) are based on the discovery that the cleavage compound under certain conditions also react with the silane substrate and acts as a hydrogen donor in such reaction. In the process of the present invention such features (i) to (iii) can be easily adjusted by setting in particular a suitable reaction time and/or a suitable reaction temperature, and by monitoring the progress of the reaction for example by GC-MS or NMR spectroscopy.

It has been found in particular by the inventors that the cleavage compounds under certain conditions do act as reactants, i.e. they are consumed in the cleavage reactions, and that by virtue of this the amount of the desirable hydridomonosilanes, such as Me_2SiHCl in particular, is significantly increased. Reaction temperature and time are adjusted for a given silane substrate and a given cleavage compound so as to satisfy one or more of the conditions (i) to (iii) above, preferably condition (ii) and/or (iii).

In a preferred embodiment of the process of invention (i) the process is run until at least about 50 mol-% of the cleavage compound based on the initial molar amount of the cleavage compound is reacted.

In a preferred embodiment of the process of invention (ii) the process is run until the ratio of the total of the produced monosilanes of the general formula (I) wherein $y = 1$ to 3 is at least about 40 mol-%, preferably at least about 50 mol-%, based on the total molar amount of the monosilanes of the general formula (I).

In a preferred embodiment of the process of invention (iii) the process is run until the ratio of Me_2SiHCl is at least about 20 mol-%, preferably at least about 30 mol-%, based on the total amount of the monosilanes of the general formula (I).

In the process of the present invention it is possible that one of the features (i) to (iii) is adjusted, or that two of the features (i) to (iii) are adjusted or that preferably all of the features (i) to (iii) are adjusted.

5 In a preferred embodiment of the process according to the invention, the reaction in step A) is carried out for more than about 4 hours, preferably more than about 6 hours, and at a temperature of at least about 200 °C, or the reaction in step A) is carried out for more than about 10 hours preferably more than about 12 hours, at a temperature of more than about 100 °C, preferably more than about 150°C.

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Since the cleavage compound acts as a hydrogen donor, there is no need for any hydrogen gas (H₂) supply to the process different to some of the prior art processes. Accordingly, the process of the present invention is normally carried out without the supply of hydrogen (H₂). This advantageously also avoids the use of high pressure equipment since the process of

15 the present invention can be usually carried out at normal pressure.

In the process of the present invention, one compound of general formula (I) or a mixture of more than one compound of general formula (I) is formed. More preferably, mixtures of more than one compound of the formula (I) are formed.

20

Further preferably, the monosilanes of the general formula (I) formed in the process of the present invention include compounds selected from the group of: MeSiH₂Cl, Me₂SiH₂, Me₂SiHCl, Me₃SiH, Me₃SiCl, MeSiHCl₂, Me₂SiCl₂, MeSiCl₃ and MeSiH₃.

25 The one or more disilanes subjected to the cleavage reaction of the silicon-silicon bond are represented by the general formula (II), wherein m = 0 to 6, and preferably m = 2 to 6.

More preferably, the disilanes subjected to the cleavage reaction of the silicon-silicon bond

30 are represented by the general formula (II) with m = 2 to 6, wherein n = 0. Such disilanes are in particular constituents of the Direct Process Residue (DPR) from the Rochow-Müller Direct Synthesis, for example the methylidisilanes Me₃Si-SiMe₂Cl, ClMe₂Si-SiMe₂Cl, Cl₂MeSi-SiMeCl₂, ClMe₂Si-SiMeCl₂, Me₃Si-SiMeCl₂, which are therefore preferred substrates in the process according to the invention.

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Also preferably, the disilanes subjected to the cleavage reaction of the silicon-silicon bond are represented by the general formula (II) with $m = 2$ to 4 , wherein $n > 0$ and $o > 0$. Such disilanes are partially hydrogenated derivatives in particular of constituents of the Direct Process Residue (DPR) from the Rochow-Müller Direct Synthesis, for example the

5 methylidisilanes $\text{HMe}_2\text{Si-SiMe}_2\text{Cl}$, $\text{H}_2\text{MeSi-SiMeClH}$, HClMeSi-SiMeClH , ClHMeSi-SiMeCl_2 , $\text{H}_2\text{MeSi-SiMeCl}_2$, $\text{HMe}_2\text{Si-SiMeCl}_2$, $\text{ClMe}_2\text{Si-SiMeH}_2$, $\text{HMe}_2\text{Si-SiMeClH}$, $\text{ClMe}_2\text{Si-SiMeClH}$ and $\text{Me}_3\text{Si-SiMeClH}$.

Also preferably, the disilanes subjected to the cleavage reaction of the silicon-silicon bond are represented by the general formula (II) with $m = 2$ to 5 , wherein $n = 1$ to 3 and $o = 0$. Such disilanes are fully hydrogenated derivatives of in particular constituents of the Direct Process Residue (DPR) from the Rochow-Müller Direct Synthesis, for example the

10 methylidisilanes, $\text{HMe}_2\text{Si-SiMe}_2\text{H}$, $\text{H}_2\text{MeSi-SiMeH}_2$, $\text{HMe}_2\text{Si-SiMeH}_2$, $\text{Me}_3\text{Si-SiMeH}_2$ and $\text{Me}_3\text{Si-SiMe}_2\text{H}$.

15 The one or more linear or branched oligosilanes subjected to the cleavage reaction of the silicon-silicon bond are represented by the general formula formula (III), wherein

$$q = 3-7$$

$$p = q \text{ to } (2q + 2)$$

$$r, s = 0 \text{ to } (q + 2)$$

$$r + s = (2q + 2) - p$$

and wherein each Si atom bears at least one methyl group,

and preferably $p = q \text{ to } 2q$.

25 More preferably, the oligosilanes subjected to the cleavage reaction of the silicon-silicon bond are represented by the general formula (III) with $p = q \text{ to } 2q$, wherein $r = 0$. Such oligosilanes are constituents of the Direct Process Residue (DPR) from the Rochow-Müller Direct Synthesis, and include for example the methyloligosilanes $\text{ClMe}_2\text{Si-SiMe}_2\text{-SiMe}_2\text{Cl}$, $\text{ClMe}_2\text{Si-SiMe}_2\text{-SiMe}_2\text{-SiMe}_2\text{Cl}$, $(\text{ClMe}_2\text{Si})_3\text{SiMe}$, $(\text{Cl}_2\text{MeSi})_2\text{SiMeCl}$, $(\text{Cl}_2\text{MeSi})_3\text{SiMe}$, $(\text{Cl}_2\text{MeSi})_2\text{SiMe-SiClMe-SiCl}_2\text{Me}$, $[(\text{Cl}_2\text{MeSi})_2\text{SiMe}]_2$, $[(\text{Cl}_2\text{MeSi})_2\text{SiMe}]_2\text{SiClMe}$, $(\text{Cl}_2\text{MeSi})_2\text{SiMe-SiMe}_2\text{Cl}$, and are therefore preferred substrates in the process according to the invention.

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Also preferably, the oligosilanes subjected to the cleavage reaction of the silicon-silicon bond are represented by the general formula (III) with $p = q \text{ to } 2q$, wherein $r > 0$ and $s > 0$. Such oligosilanes are partially hydrogenated derivatives in particular of constituents of the Direct

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Process Residue (DPR) from the Rochow-Müller Direct Synthesis, for example the methyloligosilane $\text{ClMe}_2\text{Si-SiMe}_2\text{SiMe}_2\text{H}$.

Also preferably, the oligosilanes subjected to the cleavage reaction of the silicon-silicon bond are represented by the general formula (III) with $p = q$ to $2q$, wherein $s = 0$. Such oligosilanes are fully hydrogenated derivatives of constituents in particular of the Direct Process Residue (DPR) from the Rochow-Müller Direct Synthesis, for example the methyloligosilanes $\text{HMe}_2\text{Si-SiMe}_2\text{SiMe}_2\text{H}$, $\text{HMe}_2\text{Si-SiMe}_2\text{-SiMe}_2\text{-SiMe}_2\text{H}$, $(\text{HMe}_2\text{Si})_3\text{SiMe}$, $(\text{H}_2\text{MeSi})_2\text{SiMeH}$, $(\text{H}_2\text{MeSi})_3\text{SiMe}$, $(\text{H}_2\text{MeSi})_2\text{SiMe-SiHMe-SiH}_2\text{Me}$, $[(\text{H}_2\text{MeSi})_2\text{SiMe}]_2$, $[(\text{H}_2\text{MeSi})_2\text{SiMe}]_2\text{SiHMe}$, $(\text{H}_2\text{MeSi})_2\text{SiMe-SiMe}_2\text{H}$.

The one or more carbodisilanes subjected to the cleavage reaction of the silicon-carbon bonds linking the silyl groups with the methylene group are represented by the general formula (IV), wherein

- a, c are independently of each other 1 to 3,
- b, d are independently from each other 0 to 2
- e, f are independently from each other 0 to 2,
- $a + b + e = 3$,
- $c + d + f = 3$,

and preferably $a + c = 2$ to 5.

More preferably, the carbodisilanes subjected to the cleavage reaction of the silicon-carbon bonds are represented by the general formula (IV) with $a + c = 2$ to 5, wherein $b = d = 0$. Such carbodisilanes are constituents of in particular the Direct Process Residue (DPR) from the Rochow-Müller Direct Synthesis, for example the carbodisilanes $\text{Cl}_2\text{MeSi-CH}_2\text{-SiMeCl}_2$, $\text{ClMe}_2\text{Si-CH}_2\text{-SiMeCl}_2$, $\text{ClMe}_2\text{Si-CH}_2\text{-SiMe}_2\text{Cl}$, $\text{Me}_3\text{Si-CH}_2\text{-SiMeCl}_2$ and $\text{Me}_3\text{Si-CH}_2\text{-SiMe}_2\text{Cl}$, and are therefore preferred substrates in the process according to the invention.

Also preferably, the carbodisilanes subjected to the cleavage reaction of the silicon-carbon bonds are represented by the general formula (IV) with $a + c = 2$ to 4, wherein $b + d > 0$ and $e + f > 0$. Such carbodisilanes are partially hydrogenated derivatives of constituents of in particular the Direct Process Residue (DPR) from the Rochow-Müller Direct Synthesis, for example the carbodisilanes $\text{HClMeSi-CH}_2\text{-SiMeClH}$, $\text{HMe}_2\text{Si-CH}_2\text{-SiMeCl}_2$, $\text{HMe}_2\text{Si-CH}_2\text{-SiMe}_2\text{Cl}$, and $\text{Me}_3\text{Si-CH}_2\text{-SiMeClH}$.

Also preferably, the carbodisilanes subjected to the cleavage reaction of the silicon-carbon bonds are represented by the general formula (IV) with $a + c = 2$ to 5, wherein $e + f = 0$. Such

carbodisilanes are fully hydrogenated derivatives of constituents of the Direct Process Residue (DPR) from the Rochow-Müller Direct Synthesis, for example the carbodisilanes $\text{H}_2\text{MeSi-CH}_2\text{-SiMeH}_2$, $\text{HMe}_2\text{Si-CH}_2\text{-SiMeH}_2$, $\text{HMe}_2\text{Si-CH}_2\text{-SiMe}_2\text{H}$, $\text{Me}_3\text{Si-CH}_2\text{-SiMeH}_2$, $\text{Me}_3\text{Si-CH}_2\text{-SiMe}_2\text{H}$.

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The substrates according to the general formulae (II), (III) and (IV) may be submitted to the conditions for cleavage reactions in step A) as single compounds represented by general formulae (II), (III) and (IV), as a mixture of compounds represented by general formulae (II), (III) and (IV) exclusively, or as mixtures comprising one or more compounds represented by

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general formulae (II), (III), or (IV).

Therein, cleavage is the term used to describe the transformation by which disilanes represented by the general formula (II), oligosilanes represented by the general formula (III) and carbodisilanes represented by the general formula (IV) are reacted to produce

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monomeric silanes represented by the general formula (I). In the case of disilanes of the general formula (II) and oligosilanes of the general formula (III), the term "cleavage reaction of the silicon-silicon bond(s)" further indicates that according to the invention, the cleavage of the aforementioned substrates is effected by breaking the bond connecting the silicon atoms of these disilanes and oligosilanes. In the case of carbodisilanes of the general formula (III),

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the term "cleavage reaction of the silicon-carbon bonds" indicates that the cleavage reaction is effected by breaking one or both bonds between the silyl groups of the compounds and the methylene group linking the silyl groups. Such cleavage processes comprise in particular hydrochlorination and hydrogenolysis reactions.

The optional step of separating the resulting monosilanes of the general formula (I) refers to any technical means applied to raise the content of one or more monosilanes according to the general formula (I) in a product mixture, or which results in the separation of single compounds of the formula (I) from a product mixture obtained in step A) of the process according to the invention.

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In a preferred embodiment of the process according to the invention, step A) is carried out by subjecting the silane substrate to the cleavage reaction of the silicon-silicon bond(s) or the silicon-carbon bond(s) in the silane substrate in the presence of at least one compound (cleavage compound) selected from the group consisting of

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- quaternary Group 15 onium compounds R_4QX , wherein each R is independently a hydrogen or an organyl group, Q is phosphorus, arsenic, antimony or bismuth, and X is a

halide selected from the group consisting of F (fluorine), Cl (chlorine), Br (bromine) and I (iodine),

- heterocyclic amines and heterocyclic ammonium halides,
and mixtures of the above-mentioned compounds.

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Preferably mixtures of a) heterocyclic amines and/or heterocyclic ammonium halides and b) quaternary Group 15 onium compounds R_4QX are used.

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In one embodiment, the cleavage compound comprises about 0.01 weight percent to about 99.95 weight percent of a) heterocyclic amines and/or heterocyclic ammonium halides and from about 0.05 weight percent to about 99.9 weight percent of b) quaternary Group 15 onium compounds based on the total weight of components a) and b). In a preferred embodiment, the cleavage compound contains about 5 wt% to about 85 wt% of 2-methylimidazole and about 95 wt% to about 15 wt% of tetra(n-butyl)-phosphonium chloride
15 based on the total weight of the 2-methylimidazole and the tetra(n-butyl)-phosphonium chloride. Advantageously, the weight ratio of a) the heterocyclic amines and/or the heterocyclic ammonium halides relative to b) the-quaternary Group 15 onium compounds is from about 1:9 to about 9:1, more advantageously from about 1:3 to about 3:1. On a molar basis, in certain embodiments, it is desirable to have a molar excess of heterocyclic amines
20 and/or heterocyclic ammonium halides relative to quaternary Group 15 onium compounds. Thus, in the case of tetra(n-butyl)phosphonium chloride and 2-methylimidazole, the molar ratio of the imidazole to the phosphonium chloride can be from about 1.1 to about 100, specifically about 1.5 to about 60 and more specifically about 1.5 to about 20.

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In the sense of the present invention, an organyl group is any organic substituent group, regardless of functional type, having one free valence at a carbon atom.

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Preferably, the quaternary Group 15 onium compound R_4QX is represented by the formula R_4PCl wherein R is independently a hydrogen group or an organyl group, more preferably a hydrogen group, an aromatic group preferably having up to about 30 carbon atoms or an aliphatic hydrocarbon group preferably having up to about 30 carbon atoms.

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Even more preferably, R is independently a hydrogen or an alkyl, cycloalkyl, aryl or alkaryl group having from about 1 to about 30 carbon atoms, preferably about 2 to about 16 carbon atoms. Preferred groups R include methyl, butyl such as n-butyl, iso-butyl, hexyl such as n-hexyl, tetradecyl, such as n-tetradecyl, octyl, such as n-octyl.
Particularly preferred examples of the quaternary 15 onium compound according to the invention are tetra(n-butyl)phosphonium chloride, tetra(n-butyl)phosphonium bromide,

trihexyl(tetradecyl)phosphonium bromide, methyltri(isobutyl)phosphonium bromide, methyltri(isobutyl)phosphonium chloride, tetra(n-octyl)phosphonium chloride, tri(n-butyl)tetradecylphosphonium chloride, and octyltri(n-butyl)phosphonium chloride.

Preferably, the heterocyclic amine according to the invention has at least one nitrogen atom in at least one 4- to 8-membered hydrocarbon ring, wherein the ring atoms adjacent to the nitrogen are carbon or nitrogen, and the hydrocarbon ring or rings are, independently of one another, aromatic or non-aromatic hydrocarbon rings.

More preferably, the heterocyclic amine contains a five-membered ring with 1 to 3 nitrogen atoms.

Even more preferably, the heterocyclic amine is imidazole or a substituted imidazole selected from the group consisting of 1-methylimidazole, 2-methylimidazole, 2-ethylimidazole, 2-isopropyl-imidazole, 4-methylimidazole, 2,4-dimethylimidazole, 2-(2-imidazolyl)imidazole, 2-phenylimidazole, imidazoline, imidazolidine, pyrazole, 3-methylpyrazole, pyrrolidone, N-methylpyrrolidone, 1,3-dimethyl-2-imidazolidone, 1,2,3-triazole, and 1,2,4-triazole.

Preferably, the heterocyclic ammonium halide is derived from a heterocyclic amine having at least one nitrogen atom in at least one 4- to 8-membered hydrocarbon ring, wherein the ring atoms adjacent to the nitrogen are independently carbon or nitrogen atoms, and the hydrocarbon ring or rings are, independently of one another, aromatic or non-aromatic hydrocarbon rings, wherein the halide is fluoride, chloride, bromide.

More preferably, the heterocyclic ammonium halide is derived from a heterocyclic amine with 1 to 3 nitrogen atoms in a five-membered ring, and the halide is fluoride, chloride, bromide or iodide.

Even more preferably, the heterocyclic ammonium halide is 1,2-dimethyl-3-(n-propyl)-imidazolium chloride, 1-ethyl-3-methylimidazolium bromide, 1,2-dimethyl-3-(n-butyl)imidazolium chloride, 1-butyl-3-methyl-imidazolium chloride, 1-(3-cyanopropyl)-3-methylimidazolium chloride, or 1-methylimidazolium chloride.

In another preferred embodiment according to the invention, the quaternary Group 15 onium compound is represented by the formula R_4PCI , wherein R is independently a hydrogen group or an organyl group, more preferably a hydrogen group, an aliphatic hydrocarbon or an aromatic group.

Preferably, R is independently a hydrogen or an alkyl, cycloalkyl, aryl or alkaryl group of about 1 to about 30 carbon atoms, preferably about 2 to about 16 carbon atoms. R include methyl, butyl such as n-butyl, iso-butyl, hexyl such as n-hexyl, tetradecyl, such as n-tetradecyl, octyl, such as n-octyl as substituents.

Particularly preferred examples of the quaternary 15 onium compound according to the invention are tetra(n-butyl)phosphonium chloride, tetra(n-butyl)phosphonium bromide, trihexyl(tetradecyl)phosphonium bromide, methyltri(isobutyl)phosphonium bromide, methyltri(isobutyl)phosphonium chloride, tetra(n-octyl)phosphonium chloride, tri(n-butyl)tetradecylphosphonium chloride, and octyltri(butyl)phosphonium chloride.

In a further preferred embodiment of the process according to the invention, the compounds of the formula R_4PCl are formed *in situ* from compounds of the formulae R_3P and RCI , wherein R is preferably an organyl group as defined above.

Herein, R represents independently a hydrogen or any organyl group as defined above. More preferably, R is independently a hydrogen or an alkyl, cycloalkyl, aryl or alkaryl group from about 1 to about 30 carbon atoms, preferably about 2 to about 16 carbon atoms.

This embodiment comprises in particular also that step A) of the process according to the invention which is carried out with a mixture of a phosphine R_3P , wherein R is as defined above, such as *n*-Bu₃P, and HX, preferably HCl, preferably in an ether solvent.

In another preferred embodiment of the process according to the invention, step A) is carried out by subjecting the silane substrates of the general formulae (II), (III) or (IV) or mixtures thereof to the cleavage reactions of step A) in the presence of a hydrogen halide HX, wherein X is selected from the group consisting of F, Cl, Br and I.

Preferably, the hydrogen halide is HCl.

In a preferred embodiment of the process according to the invention, step A) is carried out in the presence of at least one metal hydride, preferably at least one metal hydride selected from the group of alkali metal hydrides and alkaline earth metal hydrides, more preferably at least one alkali metal hydride, and most preferably lithium hydride.

By the presence of at least one metal hydride in step A), a hydrogenation reaction of the substrates of the general formulae (II), (III) and (IV) or of the products of the general formula (I) also takes place before, during or after the cleavage reaction of the substrates of the general formulae (II), (III) and (IV) under the reaction conditions of step A).

In the sense of the present invention, the term "hydrogenation" refers to the exchange of at least one chloro substituent of a compound by a hydrogen substituent by means of a hydride reagent.

- 5 Preferably, one or more chloro substituents of at least one or more compounds of the general formulae (II), (III) or (IV) submitted to the reaction conditions of step A) are replaced by hydrogen substituents before or during the cleavage reaction by the presence of a metal hydride in reaction step A).
- 10 Also preferably, one or more chloro substituents of at least one or more monosilanes of the general formula (I) obtained in step A) or being part of the substrate mixture are replaced by hydrogen substituents before, during or after the cleavage reaction by the presence of a metal hydride in step A).
- 15 By such hydrogenation reactions, the ratio of hydrogen substituents to chloro substituents in the products of the general formula (I) is increased.

In a further preferred embodiment of the process according to the invention, the silane substrate comprises at least one of the compounds selected from the group consisting of

- 20 Si_2Cl_6 , $\text{Cl}_2\text{MeSi-SiMeClH}$, HClMeSi-SiMeClH , $\text{Cl}_2\text{MeSi-SiMeH}_2$, HClMeSi-SiMeH_2 , $\text{ClMe}_2\text{Si-SiMeClH}$, $\text{Cl}_2\text{MeSi-SiMe}_2\text{H}$, $\text{ClMe}_2\text{Si-SiMeH}_2$, $\text{HMe}_2\text{Si-SiMeClH}$, $\text{ClMe}_2\text{Si-SiMe}_2\text{Cl}$, $\text{Me}_3\text{Si-SiMe}_2\text{Cl}$, $\text{ClMe}_2\text{Si-SiMe}_2\text{H}$, $\text{Me}_3\text{Si-SiMe}_2\text{H}$, $\text{HMe}_2\text{Si-SiMe}_2\text{H}$, $\text{H}_2\text{MeSi-SiMeH}_2$, $\text{HMe}_2\text{Si-SiMeH}_2$, $\text{Cl}_2\text{MeSi-SiMeCl}_2$, $\text{ClMe}_2\text{Si-SiMeCl}_2$, $\text{Me}_3\text{Si-SiMeCl}_2$, $\text{Cl}_2\text{MeSi-CH}_2\text{-SiMeCl}_2$, $\text{ClMe}_2\text{Si-CH}_2\text{-SiMeCl}_2$, $\text{ClMe}_2\text{Si-CH}_2\text{-SiMe}_2\text{Cl}$, $\text{Me}_3\text{Si-CH}_2\text{-SiMeCl}_2$, $\text{Me}_3\text{Si-CH}_2\text{-SiMe}_2\text{Cl}$, $\text{Me}_3\text{Si-CH}_2\text{-SiMe}_3$,
- 25 $\text{ClMe}_2\text{Si-SiMe}_2\text{-SiMe}_2\text{Cl}$, $\text{ClMe}_2\text{Si-SiMe}_2\text{-SiMe}_2\text{-SiMe}_2\text{Cl}$, $(\text{ClMe}_2\text{Si})_3\text{SiMe}$, $\text{ClMe}_2\text{Si-SiMe}_2\text{SiMe}_2\text{H}$, $(\text{Cl}_2\text{MeSi})_2\text{SiMeCl}$, $(\text{Cl}_2\text{MeSi})_3\text{SiMe}$, $(\text{Cl}_2\text{MeSi})_2\text{SiMe-SiClMe-SiCl}_2\text{Me}$, $[(\text{Cl}_2\text{MeSi})_2\text{SiMe}]_2$, $[(\text{Cl}_2\text{MeSi})_2\text{SiMe}]_2\text{SiClMe}$, and $(\text{Cl}_2\text{MeSi})_2\text{SiMe-SiMe}_2\text{Cl}$.

- 30 In another preferred embodiment of the process according to the invention, the molar ratio of the cleavage compound used in step A) to the silane substrate compounds of the general formulae (II), (III) and (IV) is in the range of about 0.0001 to about 100 mol-%, more preferred 0.001 to 50 mol-%, more preferred 0.001 to 25 mol-%, even more preferred 0.01 to 10 mol-%, and most preferably 0.01 to 0.5 mol-% based on the molar amount of the silane substrate compounds. Herein, the molar ratio is defined as n (cleavage reagent in step A)) / n
- 35 (substrates of the general formulae (II), (III) and (IV) in step A).

In another preferred embodiment of the process according to the invention the weight ratio of the cleavage compound used in step A) to the silane substrate compounds of the general formulae (II), (III) and (IV) is in the range of about 0.01 to about 99.95 wt-%, more preferred about 0.1 to about 75 wt-%, more preferred about 0.1 to about 55 wt-%, even more preferred about 1 to about 25 wt-% and most preferably about 2 to about 10 wt-% based on the total weight of the silane substrate.

For the determination of this ratio, all compounds being methyldisilanes of the general formula (II), oligosilanes of the general formula (III) and carbodisilanes of the general formula (IV) submitted to the reaction step (A) are considered, regardless if they are submitted as a part of a mixture comprising other compounds, in particular disilanes and carbodisilanes, which do not fall under the general formulae (II), (III) or (IV).

Process according to any of the previous embodiments, wherein the amount of the metal hydride in step A) in relation to the silane substrate is in the range of about 1 mol-% to about 600 mol-%, preferably about 1 to about 400 mol-%, more preferably about 1 to about 200 mol-%, most preferably about 25 to about 150 mol-%, based on the total molar amount of the chlorine atoms present in silane substrate compounds.

In a preferred embodiment of the process according to the invention the molar ratio of the metal hydride in step A) to the chlorine atoms present in the methyldisilanes of the general formula (II), the oligosilanes (III), or the carbodisilanes of the general formula (IV), or mixtures thereof is in the range of about 1 to about 300 mol-%, more preferred about 10 to about 150 mol-%, even more preferred about 25 to about 100 mol-%, and most preferred about 25 to about 75 mol-% based on the total molar amount of the chlorine atoms present in silane substrate compounds.

In a preferred embodiment of the process according to the invention, the amount of the metal hydride in step A) in relation to the silane substrate is in the range of about 1 mol-% to about 400 mol-%, preferably about 1 to about 200 mol-%, more preferably about 1 to about 100 mol-%, most preferably about 25 to about 50 mol-%, based on the total molar amount of the silane substrate compounds. Herein, the molar ratio is defined as n (metal hydride in step A)) / n (silane substrates of the general formulae (II), (III) and (IV) in step A).

For the determination of this ratio, all compounds being methyldisilanes of the general formula (II), oligosilanes of the general formula (III) and carbodisilanes of the general formula

(IV) submitted to the reaction step (A) are considered, regardless if they are submitted as a part of a mixture comprising other compounds, in particular disilanes and carbodisilanes, which do not fall under the general formulae (II), (III) or (IV).

- 5 In an additional preferred embodiment of the process according to the invention, the silane substrates used in step A) are submitted to a hydrogenation step before the cleavage reaction of the silicon-silicon bond(s) is carried out, wherein chlorine atoms contained in the silane substrates are partially or completely exchanged by hydrogen atoms.
- 10 In the sense of the present invention, the term "hydrogenation" refers to the exchange of at least one chloro substituent of a compound by a hydrogen substituent by means of a hydride reagent.

Preferably, one or more chloro substituents of at least one or more compounds of the
15 general formulae (II), (III) or (IV) which are later submitted to the reaction conditions of step A) are replaced by hydrogen substituents before these silane substrates are submitted to reaction step A).

Also preferably, the hydride reagent used in the hydrogenation step is selected from the
20 group of metal hydrides and organometallic hydride reagents, such as diisobutyl aluminium hydride (DIBAL-H), tributyltin hydride ($n\text{-Bu}_3\text{SnH}$) or sodium bis(2-methoxyethoxy) aluminumhydride.

The term "metal hydrides" in the sense of the present invention comprises complex metal
25 hydrides, such as LiAlH_4 and NaBH_4 .

More preferably, the hydride reagent used for the partial or complete reduction of substrate compounds of the general formulae (II), (III) or (IV) is tributyltin hydride ($n\text{-Bu}_3\text{SnH}$), even
30 more preferably tributyltin hydride ($n\text{-Bu}_3\text{SnH}$) in combination with tetraphenylphosphonium chloride (Ph_4PCl) as catalyst, and most preferably tributyltin with Ph_4PCl as catalyst in diglyme as solvent.

By submitting the substrates of the general formulae (II), (III) or (IV) to such hydrogenation reactions before step A) is conducted, the ratio of hydrogen substituents to chloro
35 substituents in the products of the general formula (I) is increased.

In a further preferred embodiment of the process according to the invention, the hydrogenation of the silane substrates prior to step A) is carried out with a hydride donor selected from the group of metal hydrides, preferably complex metal hydrides and organometallic hydride reagents such as LiAlH_4 , $n\text{-Bu}_3\text{SnH}$, NaBH_4 , $i\text{-Bu}_2\text{AlH}$ or sodium bis(2-methoxyethoxy)aluminumhydride.

According to the invention, the term hydride donor refers to any compound which is capable of donating at least one hydride anion used in a hydrogenation reaction of substrates of the general formulae (I), (II), (III) or (IV) which bear at least one chloro substituent.

In the sense of present invention, the term metal hydride refers to any hydride donor containing at least one metal atom or metal ion.

The term "complex metal hydrides" according to the invention refers to metal salts wherein the anions contain hydrides. Typically, complex metal hydrides contain more than one type of metal or metalloid. As there is neither a standard definition of a metalloid nor complete agreement on the elements appropriately classified as such, in the sense of present invention the term "metalloid" comprises the elements boron, silicon, germanium, arsenic, antimony, tellurium, carbon, aluminum, selenium, polonium, and astatine.

The term "organometallic hydride reagent" refers to compounds that contain bonds between carbon and metal atoms, and which are capable of donating at least one hydride anion used in a hydrogenation reaction of substrates of the general formulae (I), (II), (III) or (IV) which bear at least one chloro substituent.

In another preferred embodiment of the process according to the invention, step A) is carried out in the presence of an organic solvent, more preferably a high-boiling ether compound, even more preferably a high-boiling ether compound being diglyme or tetraglyme, most preferably diglyme.

According to the present invention, the term "organic solvent" refers to any organic compound which is in liquid state at room temperature, and which is suitable as a medium for conducting the cleavage reactions of step A) therein. Accordingly, the organic solvent is preferably inert to the cleavage reagents according to present invention, and to hydrogenation reagents such as metal hydrides under reaction conditions. Furthermore, the

starting materials of the general formulae (II), (III) and (IV) and the products of the general formula (I) are preferably soluble in the organic solvent or fully miscible, respectively.

Preferably, the organic solvent is selected from optionally substituted, preferably unsubstituted linear or cyclic aliphatic hydrocarbons, aromatic hydrocarbons or ether compounds, without being limited thereto.

Herein, the term "ether compound" shall mean any organic compound containing an ether group $-O-$, in particular of formula R_1-O-R_2 , wherein R_1 and R_2 , are independently selected from an organyl group R preferably having up to 20 carbon atoms and optionally one or more hetero atoms.

The organyl group R is selected from optionally substituted, preferably unsubstituted, alkyl, aryl, alkenyl, alkynyl, alkaryl, aralkyl, aralkenyl, aralkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, cycloaralkyl, cycloaralkenyl, cycloaralkynyl, alkoxy, aryloxy, and organosiloxy (cyclic and acyclic) groups, preferably alkyl, alkenyl and aryl groups.

Preferably, R_1 and R_2 , are substituted or unsubstituted linear or branched alkyl groups or aryl groups, which may have further heteroatoms such as oxygen, nitrogen, or sulfur. In the case of cyclic ether compounds, R_1 and R_2 can constitute together an optionally substituted alkylene or arylene group, which may have further heteroatoms such as oxygen, nitrogen, or sulfur.

The ether compounds can be symmetrical or asymmetrical with respect to the substituents at the ether group $-O-$.

The term "ether compound" also comprises linear ether compounds in which more than one ether group may be included, forming a di-, tri-, oligo- or polyether compound, wherein R_1 and R_2 constitute organyl groups when they are terminal groups of the compounds, and alkylene or arylene groups when they are internal groups. Herein, a terminal group is defined as any group being linked to one oxygen atom which is part of an ether group, while an internal group is defined as any group linked to two oxygen atoms being a constituent of ether groups.

Preferred examples of such compounds are dimethoxy ethane, glycol diethers (glymes), in particular diglyme or tetraglyme, without being limited thereto.

In the sense of the present invention, the term "high-boiling ether compound" is defined as an ether compound according to above definition with a boiling point at about 1 bar (ambient pressure) of preferably at least about 70 °C, more preferably at least about 85 °C, even more preferably at least about 100 °C, and most preferably at least about 120 °C.

The application of high-boiling ethers in the present invention is favourable as it facilitates separation of the desired products of the general formula (I) from the reaction mixture containing the solvent and residual starting materials. The products of the general formula (I) in general have lower boiling points than the starting materials, and the boiling points of these products are also lower than the boiling point of high-boiling ethers of above definition. For instance, the boiling points of selected representative products of the general formula (I) are about 35 °C (Me_2SiHCl), about 41 °C (MeSiHCl_2) or about 57 °C (Me_3SiCl), while representative higher-boiling ether compound diglyme has a boiling point of about 162 °C, and the boiling point of a mixture of methylchlorodisilanes principally consisting of isomers of trimethyltrichlorodisilane and dimethyltetrachlorodisilanes, which are respective substrates of the general formula (II) is about 151-158 °C. Application of higher-boiling ether compounds as solvents allows to utilize higher reaction temperatures and simplifies separation of the desired products from the reaction mixture by distillation.

In a preferred embodiment of the process according to the invention, step A) is carried out in the presence of at least one compound of the formula R_4PCl .

Herein, R is independently a hydrogen group or an organyl group, more preferably a hydrogen group, an aromatic group or an aliphatic hydrocarbon group.

Even more preferably, R is independently a hydrogen or an alkyl, cycloalkyl, aryl or alkaryl group of from 1 to 30 carbon atoms. R preferably includes alkyl having up to 16 carbon atoms such as methyl, butyl such as n-butyl, iso-butyl, hexyl such as n-hexyl, tetradecyl, such as n-tetradecyl, octyl, such as n-octyl.

Preferably, the amount of the at least one compound of the formula R_4PCl is in the range of about 0.01 to about 99.95 wt-%, more preferred about 0.1 to about 75 wt-%, more preferred about 0.1 to about 55 wt-%, even more preferred about 1 to about 25 wt-% and most preferably about 2 to about 10 wt-% based on the total weight of the silane substrate.

The term "weight-%" relates to the total weight of substrates of the general formulae (II), (III) and (IV) present in step A).

Compounds of the formula R_4PCl are suitable cleavage compounds, acting as catalysts for the disilane cleavage and as hydrogen source, as they are able to cleave partially or fully hydrogenated disilanes at room temperature, highly methylated disilanes at room temperature to about 140 °C without major decomposition reactions, wherein oligosilanes are

formed as side-products. At higher temperatures, for instance about 180 to about 220 °C and/or longer reaction times it was found that they react with the silane substrates such as disilanes, oligosilanes and carbodisilanes under formation of H-silanes. In particular, when $n\text{-Bu}_4\text{PCl}$ is used, H-silanes are generated by decomposition of $n\text{-Bu}_4\text{PCl}$ to $n\text{-Bu}_3\text{P}$ and formally butyl chloride with subsequent formation of 1-butene and HCl.

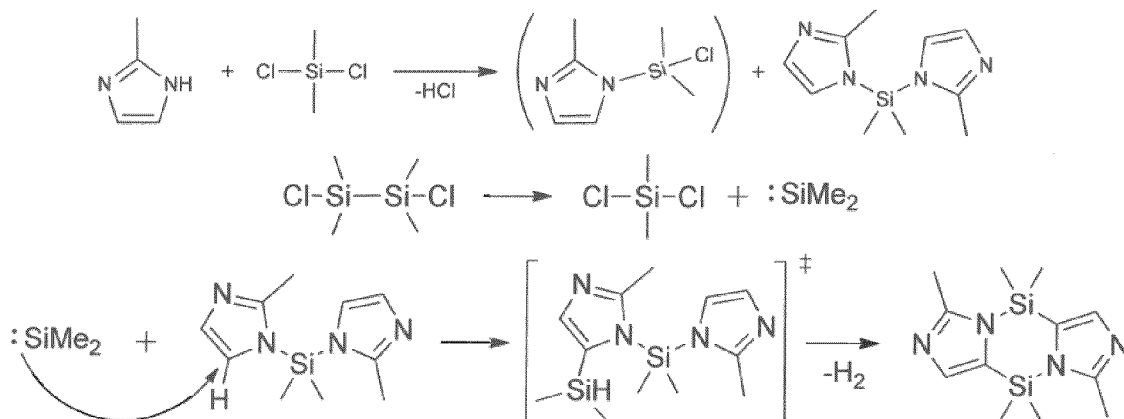
In another preferred embodiment of the process according to the invention, step A) is carried out in the presence of at least one cleavage compound of the formula R_4PCl and at least one methylimidazole.

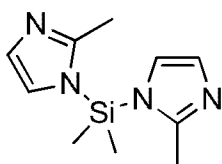
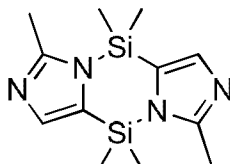
Preferably, each of the cleavage compounds is applied in an amount of about 0.01 to about 99.95 wt-%, more preferred about 0.1 to about 75 wt-%, more preferred about 0.1 to about 55 wt-%, even more preferred about 1 to about 25 wt-% and most preferably about 2 to about 10 wt-% is based on the total weight of the silane substrate.

Preferably, about equal weight amounts of at least one compound of the formula R_4PCl and at least one methylimidazole are applied as cleavage reagent in step A).

Also preferably, the at least one methylimidazole is selected from the group of consisting of 1-methylimidazole, 2-methylimidazole, 4-methylimidazole and 2,4-dimethylimidazole, most preferably it is 2-methylimidazole.

It was found that methylimidazole under certain conditions also act as a reactant in the cleavage reaction. In particular, in the reaction of 2-methylimidazole and $\text{ClMe}_2\text{Si-SiMe}_2\text{Cl}$, 2-methylimidazole reacted with Me_2SiCl_2 to compound **1** (140-160°C) (see equation below). This molecule reacts at higher temperatures ($\geq 200^\circ\text{C}$) to compound **2**, which could be characterized by X-ray diffraction, spectroscopic and microanalytical methods:



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These results explain why high amounts of Me_2SiHCl are obtained using 2-methylimidazole in the cleavage reaction of step A).

Further preferably, the at least one compound of the formula R_4PCI is selected from the group consisting of tetra(*n*-butyl)phosphonium chloride, methyltri(isobutyl)phosphonium chloride, tetra(*n*-octyl)phosphonium chloride, tri(*n*-butyl)tetradecylphosphonium chloride and octyltri(butyl)phosphonium chloride, most preferably it is tetra(*n*-butyl)phosphonium chloride (*n*- Bu_4PCI).

In yet another preferred embodiment of the process, step A) is carried out in the presence of *n*- Bu_4PCI .

Preferably, *n*- Bu_4PCI is applied in an amount of about 0.01 to about 99.95 wt-%, more preferred about 0.1 to about 75 wt-%, more preferred about 0.1 to about 55 wt-%, even more preferred about 1 to about 25 wt-% and most preferably about 2 to about 10 wt-% is based on the total weight of the silane substrate.

In a further preferred embodiment of the process according to the invention, step A) is carried out in the presence of *n*- Bu_4PCI and 2-methylimidazole.

Preferably, each of the cleavage compounds is applied in an amount of about 0.01 to about 99.95 wt-%, more preferred about 0.1 to about 75 wt-%, more preferred about 0.1 to about 55 wt-%, even more preferred about 1 to about 25 wt-% and most preferably about 2 to about 10 wt-% is based on the total weight of the silane substrate.

Generally preferably, about equal weight amounts of *n*- Bu_4PCI and 2-methylimidazole are applied as cleavage reagent in step A).

In another preferred embodiment of the process according to the invention, step A) is carried out in the presence of at least one compound of the formula $R_4\text{PCI}$ and at least one metal hydride, preferably lithium hydride.

- 5 Preferably, the amount of the at least one metal hydride is in the range of about 1 mol-% to about 600 mol-%, preferably about 1 to about 400 mol-%, more preferably about 1 to about 200 mol-%, most preferably about 25 to about 150 mol-%, based on the total molar amount of the chlorine atoms present in silane substrate compounds, while the amount of the at least one compound of the formula $R_4\text{PCI}$ is in the range from about 0.01 to about 99.95 weight-%, more preferably from about 0.1 to about 60 weight-%, even more preferably from about 1 to about 25 weight-%, and most preferably from about 1 to about 5 weight-% based on the total amount of the silane substrate.

- 15 By the presence of at least one metal hydride in step A), the substrates of the general formulae (II), (III) and (IV) are partially or completely hydrogenated before or during the cleavage reaction takes place.

- 20 The resulting partially or fully hydrogenated substrates of the general formulae (II), (III) and (IV) are more readily cleavable by cleavage reagents of the formula RPCl_4 than their analogues prior to hydrogenation. Accordingly, lower reaction temperatures can be applied for cleavage, and the percentage of hydrogen substituents in the resulting silanes of the general formula (I) is increased by such reaction conditions. The content of hydrogen substituents in the products of the general formula (I) is also increased by hydrogenation of cleavage products of the general formula (I) bearing chloro substituents, which is effected by the presence of a metal hydride in step A).

In yet another preferred embodiment of the process according to the invention step A) is carried out in the presence of $n\text{-Bu}_4\text{PCI}$ and lithium hydride.

- 30 Herein, the presence of $n\text{-Bu}_4\text{PCI}$ does not preclude the presence of further cleavage reagents in the reaction mixture of step A), and the presence of lithium hydride does not preclude the presence of further hydrogenation reagents in the reaction mixture of step A).

- 35 In a preferred embodiment of the process according to the invention, step A) is carried out in the presence of about 1 to about 200, preferably about 5 to about 100 mol-% $n\text{-Bu}_4\text{PCI}$ in relation to the amount of the silane substrate compounds of the general formulae (II), (III)

and (IV) and about 1 to about 600 mol-%, preferably about 1 to about 400 mol-% LiH in relation to the chlorine atoms present in the silane substrate compounds of the general formulae (II), (III) and (IV).

5 Herein, the term "amount of silane substrate compounds" refers to the combined molar amounts of all disilanes of the general formula (II), oligosilanes of the general formula (III) or carbodisilanes of the general formula (IV). In the determination of the molar amount these compounds are considered regardless if they are submitted as a part of a mixture comprising other silane compounds, in particular disilanes and carbodisilanes, which do not fall under
10 the general formulae (II), (III) or (IV).

Preferably, the amount of lithium hydride is in the range of from about 1 to about 600 mol-%, more preferably from about 10 to about 350, even more preferably from about 25 to about 200, and most preferably from about 25 to about 100 mol-% based on the molar amount of
15 the chlorine atoms present in the silane substrate compounds of the general formulae (II), (III) and (IV), while the amount of *n*-Bu₄PCl is preferably in the range from about 0.01 to about 99.95 wt-% more preferably from about 0.1 to about 60 wt-%, even more preferably from about 1 to about 25 wt-%, and most preferably from about 1 to about 10 wt-% based on the total weight of the silane substrate.

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In a further preferred embodiment of the process according to the invention, step A) is conducted at a temperature of about 0 °C to about 300 °C, more preferably 20 °C to 280 °C. More preferably the temperature is at least about 100 °C, more preferably at least about 150 °C, more preferably at least 200 °C and most preferably at least 220 °C.

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The reaction time is preferably at least about 4 hours, more preferably at least about 6 hours, more preferably at least about 8 hours and most preferably at least about 10 hours.

Reaction temperature and reaction time of the cleavage reaction are suitably selected for a
30 certain silane substrate and cleavage compound such that at least one of the following parameters is met:

- (i) until at least about 50 mol-% of the cleavage compound based on the initial molar amount of the cleavage compound is reacted, and/or

- (ii) until the ratio of the total of the produced monosilanes of the general formula (I) wherein $y = 1$ to 3 is at least about 40 mol-%, preferably at least about 50 mol-%, based on the total molar amount of the monosilanes of the general formula (I), and/or
- (iii) until the ratio of Me_2SiHCl is at least about 20 mol-%, preferably at least about 30 mol-%, based on the total amount of the monosilanes of the general formula (I).

According to the invention, the reaction temperature in step A) is the temperature of the reaction mixture, i.e. the temperature measured inside the reaction vessel in which the reaction is conducted.

In another preferred embodiment of the process according to the invention, step A) is carried out using at least one quaternary Group 15 onium compound represented by the formula R_4QX , wherein each R is independently a hydrogen or an organyl group, Q is phosphorus, arsenic, antimony or bismuth, and X is a halide selected from the group consisting of F, Cl, Br and I, at a temperature of about 0 °C to about 300 °C, more preferably about 20 °C to about 220 °C, and even more preferably at about 80 to about 160 °C.

In yet another preferred embodiment of the process according to the invention, step A) is carried out using at least one compound selected from heterocyclic amines and heterocyclic ammonium halides as cleavage compound, at a temperature of about 0 °C to about 300 °C, more preferably about 20 °C to about 220 °C, even more preferably at about 100 to about 220 °C, and most preferably at about 140 °C to about 220 °C.

In still another preferred embodiment of the process according to the invention, step A) is carried out using at least one quaternary Group 15 onium compound represented by the formula R_4QX , wherein each R is independently a hydrogen or an organyl group, Q is phosphorus, arsenic, antimony or bismuth, and X is a halide selected from the group consisting of F, Cl, Br and I, and at least one compound selected from heterocyclic amines and heterocyclic ammonium halides as cleavage compound, at a temperature of about 0 °C to about 300 °C, more preferably about 50 °C to about 220 °C, even more preferably at about 100 to about 200 °C, and most preferably at about 120 °C to about 180 °C.

Herein, the reaction temperature in step A) according to the invention is the temperature of the reaction mixture, i.e. the temperature measured inside the reaction vessel in which the reaction is conducted.

Preferably, the reaction vessel can be an ampoule, a sealed tube, a flask or any kind of chemical reactor, without being limited thereto.

Further preferably, the reaction step A) is carried out in a suitably sized reactor made of materials, such as glass or Hastelloy C, which are resistant to corrosion by chlorides. A means of vigorous agitation is provided to disperse or dissolve the cleavage reagent or mixtures of cleavage reagent and metal hydride in the solvent.

In another preferred embodiment of the process according to the invention, step A) is conducted at a pressure of about 0.1 bar to about 30 bar, more preferably at about 1 bar to about 20 bar, most preferably at about 1 bar to about 10 bar.

The indicated pressure ranges refer to the pressure measured inside the reaction vessel used when conducting reaction step A).

In yet another preferred embodiment of the process according to the invention in the step A) the weight ratio of the silane substrates to the organic solvent is in the range of about 1 to about 100 wt-%, more preferably in the range of about 10 to about 80 wt-%, even more preferably about 20 to about 60 wt-%, most preferably about 30 to about 50 wt-% based on the weight of the organic solvent and silane substrate.

In a preferred embodiment of the process according to the invention in the step A) the weight ratio of the cleavage compound to the organic solvent is in the range of about 0.01 to about 100 wt-%, more preferably in the range of about 0.1 to about 50 wt-%, even more preferably about 0.5 to about 20 wt-%, most preferably about 1 to about 10 wt-% based on the weight of the organic solvent and cleavage compound.

Step A) can be done also solvent free. In this case the weight-percentages of the silane substrates to the organic solvent and of the cleavage compound to the organic solvent as indicated before amount to about 100 wt-%.

In a further preferred embodiment of the process according to the invention, the monosilanes of the formula (I) are selected from the group consisting of Me_2SiHCl , Me_2SiH_2 , Me_3SiCl , Me_2SiCl_2 , Me_3SiH , MeSiH_3 , MeSiHCl_2 , MeSiH_2Cl , and MeSiCl_3 .

Preferably, the methylmonosilanes of the formula (I) are selected from the group consisting of Me_2SiHCl , MeSiHCl_2 , MeSiH_2Cl , Me_3SiCl , Me_3SiH , Me_2SiH_2 , MeSiH_3 and Me_2SiCl_2 .

In yet another preferred embodiment of the process according to the invention, the
 5 monosilanes of the formula (I) are selected from the group consisting of Me_2SiHCl , Me_3SiCl , and MeSiHCl_2 .

In a preferred embodiment of the process according to the invention, dimethylchloromonosilane Me_2SiHCl is formed by submitting a substrate selected from the
 10 group consisting of $\text{ClMe}_2\text{Si-SiMe}_2\text{Cl}$, $\text{ClMe}_2\text{Si-SiMeCl}_2$, $\text{Me}_3\text{Si-SiMe}_2\text{Cl}$, $\text{HMe}_2\text{Si-SiMe}_2\text{H}$, $\text{HMe}_2\text{Si-SiMeH}_2$, $\text{Me}_3\text{Si-SiMe}_2\text{H}$, $\text{ClMe}_2\text{Si-SiMe}_2\text{H}$, $\text{ClMe}_2\text{Si-SiMeH}_2$, $\text{HMe}_2\text{Si-SiMeCl}_2$, $\text{ClMe}_2\text{Si-CH}_2\text{-SiMeCl}_2$, $\text{Cl}_2\text{MeSi-CH}_2\text{-SiMeCl}_2$, $\text{ClMe}_2\text{Si-CH}_2\text{-SiMe}_2\text{Cl}$, $\text{Me}_3\text{Si-CH}_2\text{-SiMe}_2\text{Cl}$, $\text{ClMe}_2\text{Si-SiMe}_2\text{-SiMe}_2\text{Cl}$, $\text{ClMe}_2\text{Si-SiMe}_2\text{-SiMe}_2\text{-SiMe}_2\text{Cl}$ or $(\text{ClMe}_2\text{Si})_3\text{SiMe}$ to the cleavage reactions of step A).

15

Therein, each of the above-stated substrates may be submitted to the reaction conditions as single substrate, in a mixture with other compounds of the above-stated compounds, or in a mixture with other substrates of the general formulae (II), (III) or (IV).

20 In another preferred embodiment of the process according to the invention, trimethylchlorosilane Me_3SiCl is formed by submitting a substrate selected from the group consisting of $\text{Me}_3\text{Si-SiMe}_2\text{Cl}$, $\text{Me}_3\text{Si-SiMeCl}_2$, $\text{Me}_3\text{Si-SiMe}_2\text{H}$, $\text{Me}_3\text{Si-CH}_2\text{-SiMe}_2\text{Cl}$, $\text{ClMe}_2\text{Si-CH}_2\text{-SiMe}_2\text{Cl}$, $\text{ClMe}_2\text{Si-CH}_2\text{-SiMeCl}_2$, $\text{Me}_3\text{Si-CH}_2\text{-SiMe}_3$ or $\text{Me}_3\text{Si-CH}_2\text{-SiMeCl}_2$ to the cleavage reactions of step A).

25

Therein, each of the above-stated substrates may be submitted to the reaction conditions as single substrate, in a mixture with other compounds of the above-stated compounds, or in a mixture with other substrates of the general formulae (II), (III) or (IV).

30 In a further preferred embodiment of the process according to the invention, methyldichloromonosilane MeSiHCl_2 is formed by submitting a substrate selected from the group consisting of $\text{Cl}_2\text{MeSi-SiMeCl}_2$, $\text{Cl}_2\text{MeSi-SiMe}_2\text{Cl}$, $\text{Cl}_2\text{MeSi-SiMe}_3$, HCiMeSi-SiMeH_2 , HCiMeSi-SiMeClH , HCiMeSi-SiMeCl_2 , $\text{Cl}_2\text{MeSi-SiMeH}_2$, $\text{ClHMeSi-SiMe}_2\text{Cl}$, $\text{Cl}_2\text{MeSi-SiMe}_2\text{H}$, $\text{ClHMeSi-SiMe}_2\text{H}$, $\text{Cl}_2\text{MeSi-CH}_2\text{-SiMeCl}_2$, $\text{ClMe}_2\text{Si-CH}_2\text{-SiMeCl}_2$, $\text{Me}_3\text{Si-CH}_2\text{-SiMeCl}_2$,
 35 $(\text{Cl}_2\text{MeSi})_2\text{SiMeCl}$, $(\text{Cl}_2\text{MeSi})_3\text{SiMe}$, $(\text{Cl}_2\text{MeSi})_2\text{SiMe-SiClMe-SiCl}_2\text{Me}$, $[(\text{Cl}_2\text{MeSi})_2\text{SiMe}]_2$, $[(\text{Cl}_2\text{MeSi})_2\text{SiMe}]_2\text{SiClMe}$ or $(\text{Cl}_2\text{MeSi})_2\text{SiMe-SiMe}_2\text{Cl}$ to the cleavage reactions of step A).

Therein, each of the above-stated substrates may be submitted to the reaction conditions as single substrate, in a mixture with other compounds of the above-stated compounds, or in a mixture with other substrates of the general formula (II), (III) or (IV).

5

In a preferred embodiment of the process according to the invention, the step B) of separating the resulting monosilanes of the formula (I) is carried out by distillation, low temperature condensation, or a combination thereof.

- 10 The term "distillation" in the sense of the present invention relates to any process for separating components or substances from a liquid mixture by selective evaporation and condensation. Therein, distillation may result in practically complete separation of the constituents of a mixture, thus leading to the isolation of nearly pure compounds, or it may be a partial separation that increases the concentration of selected constituents of the mixture in
15 the distillate when compared to the mixture submitted to distillation.

Preferably, the distillation processes which may constitute separation step B) can be simple distillation, fractional distillation, vacuum distillation, short path distillation or any other kind of distillation known to the skilled person.

20

Also preferably, the step B) of separating the monosilanes of the formula (I) according to the invention can comprise one or more batch distillation steps, or can comprise a continuous distillation process.

- 25 Further preferably, the term "low temperature condensation" may comprise separation or enrichment of one or more compounds of the general formula (I) from the reaction mixture by volatilization from the reaction vessel and condensation as a liquid and/or solid in a refrigerated vessel from which it can be subsequently recovered by distillation, or by solution in an ether solvent. Alternatively, the monosilanes can be absorbed in an ether solvent
30 contained in a refrigerated vessel.

In a further preferred embodiment of the process according to the invention, the hydrogenation of the silane substrates prior to step A) is carried out using $n\text{-Bu}_3\text{SnH}$ for partial hydrogenation, or LiAlH_4 for complete hydrogenation.

35

In another preferred embodiment of the process according to the invention, the silane substrates comprising the silane substrate compounds of the general formulae (II), (III), and (IV), and the mixtures thereof are residues of the Rochow-Müller Direct Process (DPR).

- 5 The primary commercial method to prepare alkylhalosilanes and arylhalosilanes is through the Rochow-Müller Direct Process (also called Direct Synthesis or Direct Reaction), in which copper-activated silicon is reacted with the corresponding organohalide, in particular methyl chloride, in a gas-solid or slurry-phase reactor. Gaseous products and unreacted organohalide, along with fine particulates, are continuously removed from the reactor. Hot
- 10 effluent exiting from the reactor comprises a mixture of copper, metal halides, silicon, silicides, carbon, gaseous organohalide, organohalosilanes, organohalodisilanes, carbodisilanes and hydrocarbons. Typically this mixture is first subjected to gas-solid separation in cyclones and filters. Then the gaseous mixture and ultrafine solids are condensed in a settler or slurry tank from which the organohalide, organohalosilanes,
- 15 hydrocarbons and a portion of organohalodisilanes and carbodisilanes are evaporated and sent to fractional distillation to recover the organohalosilane monomers. The solids accumulated in the settler along with the less volatile silicon-containing compounds are purged periodically and sent to waste disposal or to secondary treatment. Organohalodisilanes and carbodisilanes left in the post-distillation residues are also fed to
- 20 hydrochlorination. Organohalodisilanes, organohalopolysilanes and carbodisilanes, related siloxanes and hydrocarbons, either in the post-distillation residues or in the slurry purged from the reactor, boil above organohalosilane monomers. Collectively they are referred to as Direct Process Residue (DPR). The terms higher boilers, high-boiling residue and disilane fraction are also used interchangeably with DPR.
- 25 By the process according to the invention, disilanes, in particular, methylchlorodisilanes of the general formula (II), oligosilanes of the general formula (III) and carbodisilanes of the general formula (IV), which are constituents of the side-products of the Rochow-Müller Direct Process (DPR), can be transformed to monosilanes of the general formula (I) via cleavage reactions, optionally involving hydrogenation of the substrates of the formulae (II), (III), and
- 30 (IV) or the products (I).

In yet another preferred embodiment of the process according to the invention, the process is performed under inert conditions.

- 35 In the sense of present invention, the term "performed under inert conditions" means that the process is partially or completely carried out under the exclusion of surrounding air, in

particular of moisture and oxygen. In order to exclude ambient air from the reaction mixture and the reaction products, closed reaction vessels, reduced pressure and/or inert gases, in particular nitrogen or argon, or combinations of such means may be used.

5 Preferred embodiments of the invention:

In the following the preferred embodiments of the invention are shown:

1. Process for the manufacture of monosilanes of the general formula (I):



10 wherein

$$x = 0 \text{ to } 3,$$

$$y = 0 \text{ to } 3, \text{ preferably } 1 \text{ to } 3, \text{ more preferably } 1 \text{ or } 2,$$

$$z = 0 \text{ to } 4 \text{ and}$$

$$x + y + z = 4,$$

15 and mixtures thereof,

comprising:

A) the step of subjecting a silane substrate comprising one or more silane substrate compounds selected from the group of

a) one or more disilanes of the general formula (II)



wherein

$$m = 0 \text{ to } 6,$$

$$n = 0 \text{ to } 6, \text{ preferably } 0 \text{ to } 4,$$

$$o = 0 \text{ to } 6 \text{ and}$$

25 $m + n + o = 6,$

b) one or more linear or branched oligosilanes of the general formula (III)



wherein

$$q = 3 \text{ to } 7$$

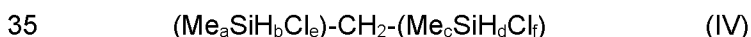
30 $p = q \text{ to } (2q + 2)$

$$r, s = 0 \text{ to } (q + 2)$$

$$r + s = (2q + 2) - p$$

and wherein each Si atom preferably bears at least one methyl group, and

c) one or more carbodisilanes of the general formula (IV)



wherein

a, c are independently of each other 1 to 3,

b, d are independently from each other 0 to 2

e, f are independently from each other 0 to 2,

$a + b + e = 3$,

$c + d + f = 3$,

and mixtures containing compounds of the general formulae (II), (III) and (IV),

to the cleavage reaction of the silicon-silicon bond(s) in the silane substrates of the general formulae (II) and (III) and the silicon-carbon bond(s) of the carbodisilanes of the general formula (IV),

to the reaction with at least one compound (cleavage compound) selected from the group consisting of:

- a quaternary Group 15 onium compound R_4QX , wherein each R is independently a hydrogen or an organyl group, Q is phosphorus, arsenic, antimony or bismuth, and X is a halide selected from the group consisting of F, Cl, Br and I,

- a heterocyclic amine,

- a heterocyclic ammonium halide,

- a mixture of R_3P and RX , wherein R is as defined above, and X is as defined above, and

mixtures of the above-mentioned compounds,

- (i) until at least about 50 mol-% of the cleavage compound based on the initial molar amount of the cleavage compound is reacted, and/or

- (ii) until the ratio of the total of the produced monosilanes of the general formula (I) wherein $y = 1$ to 3 is at least about 40 mol-%, preferably at least about 50 mol-%, based on the total molar amount of the monosilanes of the general formula (I), and/or

- (iii) until the ratio of Me_2SiHCl is at least about 20 mol-%, preferably at least about 30 mol-%, based on the total amount of the monosilanes of the general formula (I), and

B) optionally a step of separating the resulting monosilanes of the general formula (I).

2. Process according to embodiment 1, wherein the reaction in step A) is carried out for more than about 4 hours and at a temperature of at least about 200 °C, or the reaction in step A) is carried out for more than about 10 hours preferably, at a temperature of more than about 100 °C.

3. Process according to embodiments 1 or 2, which is carried out without the supply of hydrogen (H_2).

4. Process according to any of embodiments 1 to 3, wherein the silane substrate is consisting of one or more silane substrate compounds selected from the group consisting of the disilanes of the general formula (II), linear or branched oligosilanes of the general formula (III) and the carbodisilanes of the general formula (IV).

5. Process according to any of the previous embodiments, wherein the quaternary Group 15 onium compound is represented by the formula R_4PCl , wherein R is independently a hydrogen group or an organyl group, more preferably a hydrogen group, an aromatic group or an aliphatic hydrocarbon group.

6. Process according to embodiment 5, wherein the compounds of formula R_4PCl are formed *in situ* from compounds of formula R_3P and RCI .

7. Process according to any of the previous embodiments, wherein step A) is carried out by subjecting the silane substrate to the cleavage reaction of step A) in the presence of a hydrogen halide HX , wherein X is selected from the group consisting of F, Cl, Br and I.

8. Process according to any of the previous embodiments, wherein step A) is carried out in the presence of at least one metal hydride, preferably at least one metal hydride selected from the group of alkali metal hydrides and alkaline earth metal hydrides, more preferably at least one alkali metal hydride, and most preferably lithium hydride.

9. Process according to any of the previous embodiments, wherein the silane substrate, comprises at least one of the compounds selected from the group consisting of Si_2Cl_6 , $Cl_2MeSi-SiMeClH$, $HClMeSi-SiMeClH$, $Cl_2MeSi-SiMeH_2$, $HClMeSi-SiMeH_2$, $ClMe_2Si-SiMeClH$, $Cl_2MeSi-SiMe_2H$, $ClMe_2Si-SiMeH_2$, $HMe_2Si-SiMeClH$, $ClMe_2Si-SiMe_2Cl$, $Me_3Si-SiMe_2Cl$, $ClMe_2Si-SiMe_2H$, $Me_3Si-SiMe_2H$, $HMe_2Si-SiMe_2H$, $H_2MeSi-SiMeH_2$, $HMe_2Si-SiMeH_2$, $Cl_2MeSi-SiMeCl_2$, $ClMe_2Si-SiMeCl_2$, $Me_3Si-SiMeCl_2$, $Cl_2MeSi-CH_2-SiMeCl_2$, $ClMe_2Si-CH_2-SiMeCl_2$, $ClMe_2Si-CH_2-SiMe_2Cl$, $Me_3Si-CH_2-SiMeCl_2$, $Me_3Si-CH_2-SiMe_2Cl$, $Me_3Si-CH_2-SiMe_3$, $ClMe_2Si-SiMe_2-SiMe_2Cl$, $ClMe_2Si-SiMe_2-SiMe_2-SiMe_2Cl$, $(ClMe_2Si)_3SiMe$, $ClMe_2Si-SiMe_2-SiMe_2H$, $(Cl_2MeSi)_2SiMeCl$, $(Cl_2MeSi)_3SiMe$, $(Cl_2MeSi)_2SiMe-SiClMe-SiCl_2Me$, $[(Cl_2MeSi)_2SiMe]_2$, $[(Cl_2MeSi)_2SiMe]_2SiClMe$, and $(Cl_2MeSi)_2SiMe-SiMe_2Cl$, and mixtures thereof.

10. Process according to any of the previous embodiments, wherein the molar ratio of the cleavage compound used in step A) to the silane substrate compounds of the general formulae (II), (III) and (IV) is in the range of about 0.0001 to about 100 mol-%, more preferred 0.001 to 50 mol-%, more preferred 0.001 to 25 mol-%, even more preferred 0.01 to 10 mol-%, and most preferably 0.01 to 0.5 mol-% based on the molar amount of the silane substrate compounds.

11. Process according to any of the previous embodiments, wherein the weight ratio of the cleavage compound used in step A) to the silane substrate is in the range of about 0.01

to about 99.95 wt-%, more preferred about 0.1 to about 75 wt-%, more preferred about 0.1 to about 55 wt-%, even more preferred about 1 to about 25 wt-% and most preferably about 2 to about 10 wt-% is based on the total weight of the silane substrate.

12. Process according to any of the previous embodiments, wherein the amount of the metal hydride in step A) in relation to the silane substrate compounds of the general formulae (II), (III) and (IV) is in the range of about 1 mol-% to about 600 mol-%, preferably about 1 to about 400 mol-%, more preferably about 1 to about 200 mol-%, most preferably about 25 to about 150 mol-%, based on the total molar amount of the chlorine atoms present in silane substrate compounds.

13. Process according to any of the previous embodiments, wherein the silane substrates used in step A) are submitted to a hydrogenation step before the cleavage reaction of the silicon-silicon bond(s) in the silane substrates of the general formulae (II) and (III) and/or the silicon-carbon bond(s) of the carbodisilanes of the general formula (IV) is carried out, wherein chlorine atoms contained in the silane substrates are partially or completely exchanged by hydrogen atoms.

14. Process according to any of the previous embodiments, wherein the hydrogenation of the silane substrates prior to step A) is carried out with a hydride donor selected from the group of metal hydrides, preferably complex metal hydrides and organometallic hydride reagents such as LiAlH_4 , $n\text{-Bu}_3\text{SnH}$, NaBH_4 , $i\text{-Bu}_2\text{AlH}$ or sodium bis(2-methoxyethoxy) aluminumhydride.

15. Process according to any of the previous embodiments, wherein step A) is carried out in the presence of an organic solvent, preferably an high-boiling ether compound, more preferably diglyme or tetraglyme, most preferably diglyme.

16. Process according to the previous embodiments, wherein step A) is carried out in the presence of at least one compound of the formula R_4PCl .

17. Process according to the previous embodiments, wherein step A) is carried out in the presence of at least one compound of the formula R_4PCl and at least one methylimidazole.

18. Process according to any of the previous embodiments, wherein step A) is carried out in the presence of $n\text{-Bu}_4\text{PCl}$.

19. Process according to any of the previous embodiments, wherein step A) is carried out in the presence of $n\text{-Bu}_4\text{PCl}$ and 2-methylimidazole.

20. Process according to the previous embodiments, wherein step A) is carried out in the presence of at least one compound of the formula R_4PCl and at least one metal hydride, preferably lithium hydride.

21. Process according to any of the previous embodiments, wherein step A) is carried out in the presence of $n\text{-Bu}_4\text{PCl}$ and lithium hydride.

22. Process according to any of the previous embodiments, wherein step A) is carried out in the presence of about 0.01 to about 99.95 wt-%, more preferred about 0.1 to about 75 wt-%, more preferred about 0.1 to about 55 wt-%, even more preferred about 1 to about 25 wt-% and most preferably about 2 to about 10 wt-% n-Bu₄PCl wherein the weight percentage
5 wt-% is based on the total weight of the silane substrate and about 1 mol-% to about 600 mol-%, preferably about 1 to about 400 mol-%, more preferably about 1 to about 200 mol-%, most preferably about 25 to about 150 mol-% LiH based on the total molar amount of the chlorine atoms present in silane substrate compounds.

23. Process according to any of the previous embodiments, wherein the step A) is
10 conducted at a temperature of about 0 °C to about 300 °C, preferably at about 20 °C to about 220 °C.

24. Process according to any of the previous embodiments, wherein step A) is carried out using at least one cleavage compound selected from quaternary Group 15 onium compounds represented by the formula R₄QX, wherein each R is independently a hydrogen
15 or an organyl group, Q is phosphorus, arsenic, antimony or bismuth, and X is a halide selected from the group consisting of F, Cl, Br and I, at a temperature of about 0 °C to about 300 °C, more preferably about 20 °C to about 220 °C, and even more preferably at about 80 to about 160 °C.

25. Process according to any of the previous embodiments, wherein step A) is carried out
20 using at least one cleavage compound selected from heterocyclic amines and heterocyclic ammonium halides, at a temperature of about 0 °C to about 300 °C, more preferably about 20 °C to about 250 °C, even more preferably at about 100 to about 220 °C, and most preferably at about 140 °C to about 220 °C.

26. Process according to any of the previous embodiments, wherein step A) is carried out
25 using at least one cleavage compound selected from quaternary Group 15 onium compounds represented by the formula R₄QX, wherein each R is independently a hydrogen or an organyl group, Q is phosphorus, arsenic, antimony or bismuth, and X is a halide selected from the group consisting of F, Cl, Br and I, and at least one cleavage compound selected from heterocyclic amines and heterocyclic ammonium halides, at a temperature of
30 about 0 °C to about 300 °C, more preferably about 50 °C to about 250 °C, even more preferably at about 100 to 220 °C, and most preferably at 150 °C to 220 °C.

27. Process according to any of the previous embodiments, wherein step A) is carried out using at least one cleavage compound selected from quaternary Group 15 onium compounds represented by the formula R₄QX, wherein each R is independently a hydrogen
35 or an organyl group, Q is phosphorus, arsenic, antimony or bismuth, and X is a halide selected from the group consisting of F, Cl, Br and I, and at least one cleavage compound

selected from heterocyclic amines and heterocyclic ammonium halides, at a temperature of about 0 °C to about 300 °C, more preferably about 50 °C to about 220 °C, even more preferably at about 100 to about 200 °C, and most preferably at about 120 °C to about 180 °C.

28. Process according to any of the previous embodiments, wherein the step A) is conducted at a pressure of about 0.1 bar to about 30 bar, more preferably at about 1 bar to about 20 bar, most preferably at about 1 bar to about 10 bar.

29. Process according to any of the previous embodiments, wherein in the step A) the weight ratio of the silane substrate to the organic solvent is in the range of about 1 to about 100 wt-%, more preferably in the range of about 10 to about 80 wt-%, even more preferably about 20 to 60 wt-%, most preferably about 30 to about 50 wt-% based on the weight of the organic solvent and silane substrate.

30. Process according to any of the previous embodiments, wherein in the step A) the weight ratio of the cleavage compound to the organic solvent is in the range of about 0.01 to about 100 wt-%, more preferably in the range of about 0.1 to about 50 wt-%, even more preferably about 0.5 to about 20 wt-%, most preferably about 1 to about 10 wt-% based on the weight of the organic solvent and cleavage compound.

31. Process according to any of the previous embodiments, wherein the monosilanes of the formula (I) are selected from the group consisting of Me_2SiHCl , Me_2SiH_2 , Me_3SiCl , Me_2SiCl_2 , Me_3SiH , MeSiH_3 , MeSiHCl_2 , MeSiH_2Cl , and MeSiCl_3 .

32. Process according to any of the previous embodiments, wherein the monosilanes of the formula (I) are selected from the group consisting of Me_2SiHCl , Me_3SiCl , and MeSiHCl_2 .

33. Process according to any of the previous embodiments, wherein dimethylchloromonosilane Me_2SiHCl is formed by submitting a silane substrate selected from the group consisting of $\text{ClMe}_2\text{Si-SiMe}_2\text{Cl}$, $\text{ClMe}_2\text{Si-SiMeCl}_2$, $\text{Me}_3\text{Si-SiMe}_2\text{Cl}$, $\text{HMe}_2\text{Si-SiMe}_2\text{H}$, $\text{HMe}_2\text{Si-SiMeH}_2$, $\text{Me}_3\text{Si-SiMe}_2\text{H}$, $\text{ClMe}_2\text{Si-SiMe}_2\text{H}$, $\text{ClMe}_2\text{Si-SiMeH}_2$, $\text{HMe}_2\text{Si-SiMeCl}_2$, $\text{Cl}_2\text{MeSi-CH}_2\text{-SiMeCl}_2$, $\text{ClMe}_2\text{Si-CH}_2\text{-SiMeCl}_2$, $\text{ClMe}_2\text{Si-CH}_2\text{-SiMe}_2\text{Cl}$, $\text{Me}_3\text{Si-CH}_2\text{-SiMe}_2\text{Cl}$, $\text{ClMe}_2\text{Si-SiMe}_2\text{-SiMe}_2\text{Cl}$, $\text{ClMe}_2\text{Si-SiMe}_2\text{-SiMe}_2\text{-SiMe}_2\text{Cl}$, $(\text{ClMe}_2\text{Si})_3\text{SiMe}$ and mixtures thereof to the cleavage reactions of step A).

34. Process according to any of the previous embodiments, wherein the trimethylchlorosilane Me_3SiCl is formed by submitting a silane substrate selected from the group consisting of $\text{Me}_3\text{Si-SiMe}_2\text{Cl}$, $\text{Me}_3\text{Si-SiMeCl}_2$, $\text{Me}_3\text{Si-SiMe}_2\text{H}$, $\text{Me}_3\text{Si-CH}_2\text{-SiMe}_2\text{Cl}$, $\text{ClMe}_2\text{Si-CH}_2\text{-SiMe}_2\text{Cl}$, $\text{ClMe}_2\text{Si-CH}_2\text{-SiMeCl}_2$, $\text{Me}_3\text{Si-CH}_2\text{-SiMe}_3$, $\text{Me}_3\text{Si-CH}_2\text{-SiMeCl}_2$ and mixtures thereof to the cleavage reactions of step A).

35. Process according to any of the previous embodiments, wherein the methyldichloromonosilane MeSiHCl_2 is formed by submitting a silane substrate selected from

the group consisting of $\text{Cl}_2\text{MeSi-SiMeCl}_2$, $\text{Cl}_2\text{MeSi-SiMe}_2\text{Cl}$, $\text{Cl}_2\text{MeSi-SiMe}_3$, HClMeSi-SiMeH_2 , HClMeSi-SiMeClH , HClMeSi-SiMeCl_2 , $\text{Cl}_2\text{MeSi-SiMeH}_2$, $\text{ClHMeSi-SiMe}_2\text{Cl}$, $\text{Cl}_2\text{MeSi-SiMe}_2\text{H}$, $\text{ClHMeSi-SiMe}_2\text{H}$, $\text{Cl}_2\text{MeSi-CH}_2\text{-SiMeCl}_2$, $\text{ClMe}_2\text{Si-CH}_2\text{-SiMeCl}_2$, $\text{Me}_3\text{Si-CH}_2\text{-SiMeCl}_2$, $(\text{Cl}_2\text{MeSi})_2\text{SiMeCl}$, $(\text{Cl}_2\text{MeSi})_3\text{SiMe}$, $(\text{Cl}_2\text{MeSi})_2\text{SiMe-SiClMe-SiCl}_2\text{Me}$,
 5 $[(\text{Cl}_2\text{MeSi})_2\text{SiMe}]_2$, $[(\text{Cl}_2\text{MeSi})_2\text{SiMe}]_2\text{SiClMe}$, $(\text{Cl}_2\text{MeSi})_2\text{SiMe-SiMe}_2\text{Cl}$ and mixtures thereof to the cleavage reactions of step A).

36. Process according to any of the previous embodiments, wherein the step of separating the resulting monosilanes of the formula (I) is carried out by distillation, low temperature condensation or a combination thereof.

10 37. Process according to any of the previous embodiments, wherein the hydrogenation of the silane substrates prior to step A) is carried out using $n\text{-Bu}_3\text{SnH}$ for partial hydrogenation and LiAlH_4 for complete hydrogenation.

38. Process according to any of the previous embodiments, wherein the silane substrates of the general formulae (II) and (III), and the carbodisilane substrates of the general formula
 15 (IV), or the mixtures thereof are residues of the Rochow-Müller Direct Process (DPR).

39. Process according to any of the previous embodiments, wherein the process is performed under inert conditions.

40. Monosilanes of the general formula (I) as defined above, as obtainable by the process according to any of the previous embodiments.

20 41. Compositions comprising at least one monosilane of the general formula (I) as defined above, as obtainable by the process according to any of the previous embodiments.

EXAMPLES

The present invention is further illustrated by the following examples, without being limited thereto.

5 General

The first section (Examples 1-14) is directed at detailed investigations of the performance of the cleavage compounds *n*-Bu₄PCl, 2-methylimidazole (2-MIA) and derivatives thereof. In particular, model compounds such as ClMe₂Si-SiMe₂Cl were applied to study the influence of
10 reaction temperature and reaction times. It was demonstrated that both cleavage compounds act as catalysts at lower reaction temperatures, while they act as reaction partners at high temperatures (in particular at about more than 180 °C, in particular at about 220 °C) and thus generate H-silanes (Me₂SiHCl, MeSiHCl₂...) in high yields. At low temperatures, 2-methylimidazole (2-MIA) forms oligosilanes and cleaves these compounds at higher
15 temperatures under decomposition of the cleavage compound. *n*-Bu₄PCl already cleaves disilane substrates at low temperatures, such as r.t. to about 140 °C and also forms oligosilanes. At higher temperatures (about 180 to about 220 °C) H-silanes are formed. By decomposition of *n*-Bu₄PCl to *n*-Bu₃P and formally butyl chloride with subsequent formation of HCl and 1-butene H-silanes are generated.

20 The second section (Examples 15-27) is directed at the hydrogenation of the disilanes/monosilanes and cleavage of hydrogenated disilanes with the cleavage compounds (*n*-Bu₄PCl and 2-MIA). As disilanes form a Si-H-fraction of only about 50 mol% with both of the cleavage compounds, the aim of the experiments of the second section is to obtain higher yields of the H-substituted monosilanes. In the first place, this can be achieved by Cl-
25 H-exchange of the disilanes and subsequent cleavage. Herein, *n*-Bu₄PCl is a suitable catalyst, as it is capable of cleaving partially and fully hydrogenated disilanes to monosilanes to full extent already at room temperature. At this, only a minor amount (about 5mol%) of the catalyst is decomposed in the case of highly methylated and hydrogenated disilanes, as the higher the degree of methylation of the disilanes is, the higher temperatures are required for
30 cleavage.

Identification of products

Products were analyzed by ¹H, ²⁹Si and ¹H-²⁹Si-HSQC NMR spectroscopy. The spectra were recorded on a Bruker AV-500 spectrometer equipped with a Prodigy BBO 500 S1 probe. ¹H-
35 NMR spectra were calibrated to the residual solvent proton resonance ([D₆]benzene δ_H = 7.16 ppm). Product identification was additionally supported by GC-MS analyses and verified

identification of the main products. GC-MS analyses were measured with a Thermo Scientific Trace GC Ultra coupled with an ITQ 900MS mass spectrometer. The stationary phase (Machery-Nagel PERMABOND Silane) had a length of 50 m with an inner diameter of 0.32 mm. 1 μ l of analyte solution was injected, 1/25 thereof was transferred onto the column with a flow rate of 1.7 mL/min carried by Helium gas. The temperature of the column was first kept at 50 °C for 10 minutes. Temperature was then elevated at a rate of 20 °C/min up to 250 °C and held at that temperature for another 20 minutes. After exiting the column, substances were ionized with 70 eV and cationic fragments were measured within a range of 34 – 600 m/z (mass per charge). Product mixtures were diluted with benzene prior to the measurement.

The characteristic ^{29}Si -NMR chemical shifts and coupling constant $^1J\{^{29}\text{Si}-^1\text{H}\}$ for the starting materials and the products formed are listed in Table 1.

Table 1: identification of starting materials and products

No.	compound Si ^A -Si ^B	$\delta^{29}\text{Si}$ [ppm]		$^1J(\text{Si-H})$ [Hz]	
		A	B	A	B
1	$\text{ClMe}_2\text{Si-SiMe}_2\text{Cl}$	17.1		-	
2	$\text{Me}_3\text{Si-SiMe}_2\text{Cl}$	22.5	-18.6	-	
3	$\text{ClMe}_2\text{Si-SiMe}_2\text{H}$	23.0	-39.0	-	
4	$\text{Me}_3\text{Si-SiMe}_2\text{H}$	-19.2	-39.4	-	
5	Me_2SiHCl	11.0		223.3	
6	Me_2SiH_2	-38.1		187.6	
7	Me_3SiCl	30.1		-	
8	Me_2SiCl_2	31.5		-	
9	Me_3SiH	-16.6		182.9	
10	$\text{HMe}_2\text{Si-SiMe}_2\text{H}$	-39.5		177.5	
11	$\text{H}_2\text{MeSi-SiMeH}_2$	-67.8		185.8	
12	$\text{HMe}_2\text{Si-SiMeH}_2$	-39.9	-66.7	180.9	180.5
13	MeSiH_3	-65.5		194.1	
14	$\text{Cl}_2\text{MeSi-SiMeCl}_2$	17.5		-	
15	$\text{ClMe}_2\text{Si-SiMeCl}_2$	15.0	24.6	-	
16	$\text{Me}_3\text{Si-SiMeCl}_2$	34.0	-14.1	-	
17	MeSiHCl_2	10.9		280.2	
18	MeSiH_2Cl	-11.4		229.4	
19	MeSiCl_3	12.3		-	
20	$\text{Cl}_2\text{MeSi-CH}_2\text{-SiMeCl}_2$	26.2		-	
21	$\text{ClMe}_2\text{Si-CH}_2\text{-SiMeCl}_2$	28.1	25.7	-	-
22	$\text{ClMe}_2\text{Si-CH}_2\text{-SiMe}_2\text{Cl}$	28.3		-	

23	Me ₃ Si-CH ₂ -SiMeCl ₂	30.6	-0.5	-	-
24	Me ₃ Si-CH ₂ -SiMe ₂ Cl	30.0	-0.4	-	-
25	Me ₃ Si-CH ₂ -SiMe ₃	-0.5			
26	ClMe ₂ Si-SiMe ₂ -SiMe ₂ Cl	25.4	-43.9	-	
27	ClMe ₂ Si-SiMe ₂ -SiMe ₂ -SiMe ₂ Cl	27.1	-43.2	-	
28	(ClMe ₂ Si) ₃ -SiMe	26.9	-76.2	-	
29	ClMe ₂ Si-SiMe ₂ SiMe ₂ H	27.0	-45.6	-37.8	183.4
30	(Cl ₂ MeSi) ₂ SiMeCl	24.1	-5.3	-	
31	(Cl ₂ MeSi) ₃ SiMe	30.6	-64.3	-	
32	(Cl ₂ MeSi) ₂ SiMe-SiClMe-SiCl ₂ Me	32.3	-64.0	4.5	25.3
33	[(Cl ₂ MeSi) ₂ SiMe] ₂	33.2	-63.2	-	
34	[(Cl ₂ MeSi) ₂ SiMe] ₂ SiClMe	32.1	-60.4	13.1	-
35	(Cl ₂ MeSi) ₂ SiMe-SiMe ₂ Cl	33.9	-66.9	23.8	-
36	Cl ₃ Si-SiCl ₃	-6.5		-	
37	SiCl ₄	-19.0		-	
38	Cl ₂ MeSi-SiMeClH	23.8	-6.7	-	227.4
39	HCiMeSi-SiMeClH	-3.9	-4.3	211.7	-
40	Cl ₂ MeSi-SiMeH ₂	32.1	-61.4	-	196.7
41	HCiMeSi-SiMeH ₂	0.6	-64.7	215.0	203.3
42	ClMe ₂ Si-SiMeClH	17.6	-3.7	-	221.3
43	Cl ₂ MeSi-SiMe ₂ H	33.8	-35.5	-	191.3
44	ClMe ₂ Si-SiMeH ₂	22.6	-64.6	-	195.6
45	HMe ₂ Si-SiMeClH	1.83	-38.2	181.3	198.4

Example 1:

Cleavage reactions of perchlorinated and methylated chlorodisilanes with *n*-Bu₄PCl (5 w%) and 2-methylimidazole (2-MIA, 5 w%) as catalyst in a sealed glass ampoule at 175 °C for 2.5

- 5 h. The starting compounds and reaction products are listed in Table 2.

Table 2 (Reference examples):

products	Cl ₃ Si-SiCl ₃ 1.71 g	Cl ₂ MeSi-SiMeCl ₂ (75mol%) ClMe ₂ Si-SiMeCl ₂ (25mol%) 1.89 g	ClMe ₂ Si-SiMe ₂ Cl 610 mg
SiCl ₄	95mol%	-	-
HSiCl ₃	5mol%	-	-
MeSiCl ₃	-	53mol%	-
MeSiHCl ₂	-	9mol%	-
Me ₂ SiCl ₂	-	38mol%	65mol%
Me ₂ SiHCl	-	traces	5mol%
educts/oligosilanes	-	-	30mol%

For comparison ClMe₂Si-SiMe₂Cl (**1**, 585 mg) reacted at 175 °C with *n*-Bu₄PCl (5 w%) and 2-methylimidazole (2-MIA, 5 w%) as catalyst. Reactions were performed in a sealed NMR tube for 2.5 h, to give mostly the monosilanes Me₂SiCl₂ (51mol%) and small amounts of Me₂SiHCl (4mol%). Additionally, tri- and tetrasilanes Si₃Me₆Cl₂ and Si₄Me₈Cl₂ were formed in a molar ratio of 14mol% to 8mol%. All products formed after 2.5 h reaction time are listed in Table 3. Prolonged heating of the samples for 89 h cleaved the oligosilanes too, finally giving the monosilanes **8** (57mol%), **5** (34mol%) and **7** (7mol%). Disilane **1** remained in the product mixture in small amounts (2mol%) (Table 3).

Table 3

products	reaction time* 2.5 h [mol%]	reaction time 89 h [mol%]
Me ₂ SiCl ₂	51	57
Me ₂ SiHCl	4	34
Me ₃ SiCl	2	7
ClMe ₂ Si-SiMe ₂ Cl	21	2
ClMe ₂ Si-SiMe ₂ -SiMe ₂ Cl	14	-
ClMe ₂ Si-SiMe ₂ -SiMe ₂ -SiMe ₂ Cl	8	-

(*Reference example)

After 89 h reaction time at 175 °C Me₃Si-SiMe₂Cl (**2**) gave **7** (85mol%), Me₃SiH (**9**, 11mol%), and **2** (4mol%), besides traces of different oligosilanes.

Example 2:

A mixture of silanes, composed of compounds listed in Table 4 (13.1 g), Table 5 (14.1 g) and Table 6 (12.5 g), was reacted with the catalyst mixture (*n*-Bu₄PCl 5 w% and 2-MIA 5 w%) in a 250 ml flask, equipped with a thermometer, Vigreux column and a distillation condenser. The reaction mixture was heated to 145 °C while volatile cleavage products were continuously distilled off and collected at -20 °C. After 5 h the reaction was stopped to give monosilanes **19** (44mol%) and **8** (31mol%) as listed in Table 7. The residue mainly consisted of disilanes **1** and **2** and traces of **8**. After 13 h reaction time the resulting product mixture was **19** (36mol%), **8** (33mol%), **17** (29mol%) and **7** (2mol%). The residue mainly consisted of disilanes **1**, **2**, Me₃Si-SiMe₃, and carbodisilanes as well as traces of monosilane **8**.

Table 4

compound	mol%
Me ₂ SiCl ₂	6.8
Me ₃ SiCl	7.1
MeSiCl ₃	12.5
Me ₂ SiHCl	4.3
MeSiHCl ₂	1.4
Me ₅ Si ₂ Cl	3.9
(ClMe ₂ Si) ₂	17.9
(Cl ₂ MeSi) ₂	1.4
Me ₆ Si ₂	0.2
Me ₃ Si-CH ₂ -SiMe ₂ Cl	3.9
(ClMe ₂ Si) ₂ -CH ₂	5.2
(Cl ₂ MeSi) ₂ -CH ₂	14.7
ClMe ₂ Si-CH ₂ -SiMeCl ₂	11.4
Me ₃ Si-CH ₂ -SiMeCl ₂	1.8
Me ₃ Si-CH ₂ -SiMe ₃	7.5

Table 5

starting mixture	mol%
Me ₂ SiCl ₂	7.9
Me ₃ Si-SiMe ₂ Cl	2.0
ClMe ₂ Si-SiMe ₂ Cl	3.5
Cl ₂ MeSi-SiMeCl ₂	49.5
ClMe ₂ Si-SiMeCl ₂	33.7
Me ₃ Si-SiMeCl ₂	3.0
Me ₃ Si-SiMe ₃	0.4

Table 6

starting mixture	mol%
Me ₂ SiCl ₂	12.4
Me ₃ SiCl	2.2
MeSiCl ₃	11.5
Me ₃ Si-SiMe ₂ Cl	16.8
ClMe ₂ Si-SiMe ₂ Cl	22.6
Cl ₂ MeSi-SiMeCl ₂	16.2
ClMe ₂ Si-SiMeCl ₂	7.1
Me ₃ Si-SiMeCl ₂	2.7
Me ₆ Si ₂	2.4
Me ₃ Si-CH ₂ -SiMe ₂ Cl	3.1
(Cl ₂ MeSi) ₂ -CH ₂	0.4
ClMe ₂ Si-CH ₂ -SiMeCl ₂	0.9
Me ₃ Si-CH ₂ -SiMeCl ₂	0.4
Me ₃ Si-CH ₂ -SiMe ₃	1.3

Table 7

reaction time	5 h	13 h
compound	mol%	mol%
MeSiCl ₃	44	36
Me ₂ SiCl ₂	31	33
MeSiHCl ₂	22	29
Me ₃ SiCl	3	2

5

The experiment clearly proved that cleavage of disilanes and carbosilanes becomes increasingly difficult with increasing degree of methylation at the silicon skeletons. Prolonged reaction time accelerated cleavage of disilane **1** that, after 5 h, still dominated over **2** in the residue; after 13 h disilane **2** remained as main component in the reaction residue. H-substituted organosilane **17** was increasingly formed with prolonged reaction times but showed that highly chlorinated disilanes require shorter reaction times/temperatures for cleavage into hydrido substituted monosilanes. In summary, with prolonged reaction times the mixture was transferred into monosilanes nearly quantitatively, only Me₃Si-SiMe₃ remained unreacted. Condensation of the residue at 200 °C in vacuo proved all Si-containing species to be distillable; ³¹P-NMR showed that upon cleavage reaction *n*-Bu₄PCl was in part reacted to give *n*-Bu₃P and traces of *n*-Bu₂PH; unreacted *n*-Bu₄PCl remained in the reaction residue.

10

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Example 3:

Substrate **1** as defined in Table 1 above (260 mg) and the catalyst mixture (*n*-Bu₄PCl, 2-MIA; 7 w% each) were reacted in a sealed NMR tube at 160° C for 25 hours. In a second reaction the mixture was directly heated to 220 °C. The results are listed in Table 8.

Table 8

temperature/time [°C/ h]	160/25	direct heating 220/4
products [mol%]		
Me ₂ SiCl ₂	43.3	36
Me ₃ SiCl	12.8	9
Me ₂ SiHCl	28.7	45
Me ₂ SiH ₂	2.6	7
Me ₃ SiH	-	1
ClMe ₂ Si-SiMe ₂ Cl	7.2	2
trisilane	3.3	-
tetrasilane	2.1	-

Example 4:

Tri- and tetrasilanes as displayed in Table 9 were synthesized from disilane **1** (4.3 g) and 1-MIA (0.5 g) in a 100 ml flask at 165 °C for 3 h.

Table 9

starting mixture	mol%
ClMe ₂ Si-SiMe ₂ -SiMe ₂ Cl	47.1
ClMe ₂ Si-SiMe ₂ -SiMe ₂ -SiMe ₂ Cl	4.7
(ClMe ₂ Si) ₃ -SiMe	5.2
ClMe ₂ Si-SiMe ₂ -SiMe ₂ H	3.3
ClMe ₂ Si-SiMe ₂ Cl	39.7

A mixture of oligosilanes (380 mg) listed in Table 9 was then reacted with the catalyst mixture comparably to the previous Examples (*n*-Bu₄PCl, 2-MIA; 5 w% each) in a sealed NMR tube at different temperatures. The results are shown in Table 10.

Table 10

temperature/time [°C/ h]	160/7*	220/8
products	mol%	mol%
Me ₂ SiCl ₂	21.8	26.8
Me ₃ SiCl	3.1	0.9
Me ₂ SiHCl	7.0	46.6
Me ₂ SiH ₂	-	15.5
ClMe ₂ Si-SiMe ₂ Cl	15.6	5.1
ClMe ₂ Si-SiMe ₂ -SiMe ₂ Cl	19.5	2.4
ClMe ₂ Si-SiMe ₂ -SiMe ₂ -SiMe ₂ Cl	24.4	2.7
(ClMe ₂ Si) ₃ -SiMe	8.2	-
ClMe ₂ Si-SiMe ₂ SiMe ₂ H	0.4	-

(* Reference)

Heating the mixture of oligosilanes to 160 °C for 7 h more tri- and tetrasilanes were formed and no significant cleavage reactions of the oligosilanes were detected. Cleavage of the oligosilanes started at 220 °C/8 h with formation of hydrido silanes and decomposition of *n*-Bu₄PCl to *n*-Bu₃P.

Example 5:

Disilane **1** (523 mg) was admixed with 5 w% of 2-MIA in a sealed NMR tube. Heating of the sample to 140 °C for 23 h showed no significant reaction, after 48 h monomer **8** starts to form, and a lower amount of trisilane **26** and tetrasilane **27** were formed as well in a ratio of 1:0.8:0.2. After 68 h reaction time, 26mol% of monosilanes were formed (**8**, 25mol%; **7**, 1mol%), 28mol% of disilane **1** remained unreacted, trisilane **26** was formed in 30mol%, and the tetrasilane **27** in 16mol%. Additional heating to 220 °C for 21 h lead to significant hydridosilane formation (**5**, 36mol%; **6**, 2mol%). After an overall reaction time of 68 h at 140 °C and 80 h at 220 °C nearly all di- and oligosilanes were decomposed, the products are listed in Table 11. Prolonged reaction times did not change product composition; that may be due to complete decomposition of 2-MIA, because this compound could not been recycled from the reaction mixture. We conclude that 2-MIA was the source for hydrogenation of chlorosilanes obtained from di- and oligosilane splitting at high reaction temperatures.

Table 11

temperature/time [°C/ h]	140/68*	220 /21	220 /80
products	mol%	mol%	mol%
Me ₂ SiCl ₂	25	40	42
Me ₃ SiCl	1	12	13
Me ₂ SiHCl	-	36	35
Me ₂ SiH ₂	-	2	5
ClMe ₂ Si-SiMe ₂ Cl	28	6	-
ClMe ₂ Si-SiMe ₂ -SiMe ₂ Cl	30	3	1
ClMe ₂ Si- SiMe ₂ -SiMe ₂ -SiMe ₂ Cl	16	1	1

(* Reference)

5 Example 6:

Disilane **1** (492 mg) was reacted with *n*-Bu₄PCl (5 w%) at different temperatures and reaction times in a sealed NMR tube. Products formed are listed in Table 12. As demonstrated by Examples 8 and 9, both catalysts react similar at high temperatures. 2-MIA produced oligosilanes faster compared to *n*-Bu₄PCl that subsequently were cleaved, while the phosphonium chloride formed oligosilanes that nearly simultaneously were reacted to monosilanes.

Table 12

temperature/time [°C/ h]	140/68*	160/100*	220/80
products	mol%	mol%	mol%
Me ₂ SiCl ₂	46	52	48
Me ₃ SiCl	15	16	14
Me ₂ SiHCl	5	12	20
Me ₂ SiH ₂	-	-	1
ClMe ₂ Si-SiMe ₂ Cl	17	8	7
ClMe ₂ Si-SiMe ₂ -SiMe ₂ Cl	12	9	8
ClMe ₂ Si- SiMe ₂ -SiMe ₂ -SiMe ₂ Cl	5	3	2

15 (* Reference)

From ³¹P-NMR spectroscopic investigations on the reaction mixture it is concluded that at low temperatures (23 h/140 °C) *n*-Bu₄PCl remained unreacted and acts as a catalyst. At higher

temperatures (160 °C/25 h) *n*-Bu₃P was starting to form besides an unidentified P-containing compound (³¹P-NMR: +23 ppm) that became dominant in the reaction mixture. At prolonged heating (160 °C/75 h to 220 °C/10 h) the *n*-Bu₃P content was increasing but interestingly *n*-Bu₄PCl was recycled under these conditions, the non-identified compound detected at +23 ppm was completely decomposed. Two new signals at -23 and one at -98 ppm demonstrate complex interactions of *n*-Bu₄PCl with the reaction mixture that finally lead to disilane splitting and hydrogen transfer to give hydrido monosilanes.

Example 7:

Disilane **1** (426 mg) was reacted separately with 5 w% of each catalyst (*n*-Bu₄PCl; 2-MIA) in a sealed NMR tube at 220 °C for 21 h, resulting in formation of the product mixtures listed in Table 13. It was shown that under these reaction conditions, hydridosilane formation was favoured with 2-MIA.

Table 13

	2-MIA	<i>n</i> -Bu ₄ PCl
products	mol%	mol%
Me ₂ SiCl ₂	40	49
Me ₃ SiCl	11	15
Me ₂ SiHCl	36	21
Me ₂ SiH ₂	3	1
ClMe ₂ Si-SiMe ₂ Cl	6	7
ClMe ₂ Si-SiMe ₂ -SiMe ₂ Cl	3	6
ClMe ₂ Si-SiMe ₂ -SiMe ₂ -SiMe ₂ Cl	1	1

15mol% of **1** and oligosilanes remained unreacted in case of *n*-Bu₄PCl vs. 10mol% in case of 2-MIA. *n*-Bu₄PCl was nearly completely reacted to give *n*-Bu₃P besides three compounds detected at -23.17, 23.19 and -95.74 ppm. Also 2-MIA was completely decomposed to give a yellow highly viscous liquid. At temperatures < 140 °C 2-MIA acts as disproportionation catalyst, at T> 160 °C it is a reaction partner to form hydridosilanes. Under the same conditions *n*-Bu₄PCl decomposed to give *n*-Bu₃P and 1-but-ene. The hydrogen chloride formed during decomposition of the catalyst acts as cleavage and Si-H forming agent. While the 1-but-ene was identified NMR spectroscopically, no formation of butyl chloride and HCl could be detected.

Example 8

Disilane **1** (302 mg) was reacted with a mixture of *n*-Bu₃P (30 mg) and butyl chloride (14 mg) in a sealed NMR tube at 220 °C for 70 h. Reaction products identified were monosilanes **8** (Me₂SiCl₂ 35mol%), **5** (Me₂SiHCl 30mol%), **7** (Me₃SiCl 13mol%), **9** (Me₃SiH 2mol%) and **6** (Me₂SiH₂ 2mol%). Besides these products, carbodisilane **21** was formed in 18mol%; other carbodisilanes with higher degree of chlorination were detected in traces.

Treating of disilane **1** with solely butyl chloride (without phosphane) under comparable conditions gave no hint to any reaction.

Example 9

20 w% of *n*-Bu₄PCl were admixed with disilane **1** (352 mg) and reacted in a sealed NMR tube at different temperatures. Products obtained are listed in Table 14.

Table 14

	140*	220	direct heating 220
products	mol%	mol%	mol%
Me ₂ SiCl ₂	65	44	44
Me ₃ SiCl	18	16	16
Me ₂ SiHCl	6	30	30
Me ₂ SiH ₂	-	3	3
Me ₃ SiH	-	5	5
ClMe ₂ Si-SiMe ₂ Cl	6	2	2
ClMe ₂ Si-SiMe ₂ -SiMe ₂ Cl	3	-	-
ClMe ₂ Si-SiMe ₂ -SiMe ₂ -SiMe ₂ Cl	2	-	-

(* Reference)

At 140 °C (64 h) monosilanes were already obtained but only 6mol% of hydrosilane **5**, oligosilanes were still present in the mixture (5mol%). Subsequent heating of the sample to 220 °C (24 h) increased the amount of silane **5** to 30mol%. Hydrosilanes **9** and **6** were formed in 5 and 3mol%. Direct heating of **1** (402 mg) with 21 w% of *n*-Bu₄PCl even accelerated conversion and increased Si-H formation in comparison of low temperature reaction (140°C); only traces of disilane or oligosilanes remained unreacted.

Example 10

A mixture of **1** (302 mg) and 2-MIA (14 w%) was heated to 140 °C for 64 h. Monosilane **8** was obtained in 62mol%, **7** in 22mol%, Si-H formation was not detected. Subsequent heating of the sample to 220 °C (64 h) gave silanes **5** in 37mol%, **8** in 40mol%, **7** in 13mol% and **6** in 10mol%. No disilane and oligosilanes remained unreacted; disilane conversion into monosilanes was quantitative. Direct heating of **1** (302 mg) to 220 °C (64 h) with 15 w% 2-MIA even accelerated both conversion and Si-H formation, no di- and oligosilanes remained in the reaction mixture.

Example 11 (starting material)

6 g of a mixture consisting of disilanes **14** (71mol%), **15** (24mol%), **1** (3mol%) and **16** (1mol%), was reacted with 1-methylimidazole (1 g) at 165 °C for 3 hours to give a mixture of oligosilanes listed in Table 15.

Table 15

starting mixture	mol%
(Cl ₂ MeSi) ₂ SiMeCl	4
(Cl ₂ MeSi) ₃ SiMe	54
(Cl ₂ MeSi) ₂ SiMe-SiClMe-SiCl ₂ Me	4
[(Cl ₂ MeSi) ₂ SiMe] ₂	11
[(Cl ₂ MeSi) ₂ SiMe] ₂ -SiClMe	2
(Cl ₂ MeSi) ₂ SiMe-SiMe ₂ Cl	12
Cl ₂ MeSi-SiMeCl ₂	11
Cl ₂ MeSi-SiMe ₂ Cl	2

Example 12

The disilane mixture listed in Example 11 (470 mg) as well as the mixture of oligosilanes (566 mg, Table 15) were reacted with both catalysts (2-MIA and *n*-Bu₄PCl, 5 w% each) in a sealed NMR tube at 220 °C for 17 h. Products obtained are listed in Table 16. It is demonstrated that product formation in both cases is comparable. Cleavage reactions were quantitatively, no di- or oligosilanes remained unreacted.

Table 16

	oligosilane mixture	disilane mixture
compounds	mol%	mol%
Me ₂ SiCl ₂	9	31
Me ₃ SiCl	-	1
MeSiCl ₃	32	47
MeSiHCl ₂	53	21
Me ₂ SiH ₂	6	-

Notably, the oligosilanes produced a significantly higher amount of hydrido silanes (**17**, 53mol%; **6**, 6mol% vs. **17**, 21mol%, no **6**) while the amount of chlorosilane **8** was significantly higher for the disilane mixture. (31mol% vs. 9mol%). In both samples, *n*-Bu₄PCl was completely converted to give *n*-Bu₃P.

Example 13

A mixture of disilanes (490 mg) (Table 6) was reacted with the catalysts (*n*-Bu₄PCl and 2-MIA, 5 w% each) in a sealed NMR tube at 220 °C for 8h. The results are displayed in Table 17.

Table 17

products	mol%
Me ₂ SiCl ₂	54
Me ₃ SiCl	10
Me ₂ SiHCl	33
Me ₂ SiH ₂	3
MeSiCl ₃	-
carbodisilanes	-
disilanes	traces

Example 14A

Reaction of a mixture (1.06 g) of disilanes **1** (95mol%) and **2** (5mol%) with *n*-Bu₄PCl (14 w%) in the presence of HCl in a sealed glass ampoule at 220 °C for 91 h gave monosilanes and unreacted disilane **1** as listed in Table 18A; but-1-ene was detected by ¹H-NMR spectroscopy.

Table 18A

products	mol%
Me ₂ SiCl ₂	59.9
Me ₃ SiCl	11.4
Me ₂ SiHCl	28.7
Me ₂ SiH ₂	traces
MeSiH ₂ Cl	traces
Me ₂ SiH ₂	traces
MeSiH ₃	traces

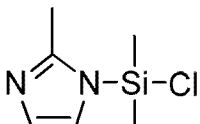
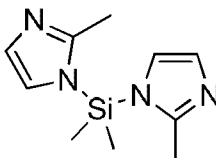
Example 14B:

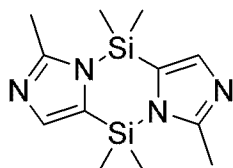
- 5 ClMe₂Si-SiMe₂Cl (4.44 g, 1 eq) was reacted with 2-methylimidazole (1.0 g, 0.5 eq) at 220 °C in a sealed glass ampoule for 67 h. 3.54 g monosilanes were isolated after separation by condensation in vacuo, composition is listed in Table 18B.

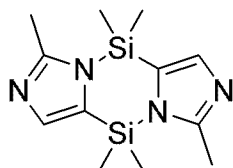
Table 18B

Compound	mol%
Me ₂ SiCl ₂	46.9
Me ₃ SiCl	1.4
Me ₂ SiH ₂	4.8
Me ₂ SiHCl	46.9

10

Additionally, compound  and  were identified by NMR spectroscopy that was formed from the starting reactants with release of HCl at lower reaction temperatures.



- 15 From the high temperature experiment  was isolated in the residue after condensation and was characterized by X-ray diffraction, spectroscopic and microanalytical methods.

Synthesis and cleavage reactions of mixed methylchloro/methylhydrido disilanes

For hydrogenation of methylchlorosilanes tributyltin hydride was used as reducing agent. For the preparation of *n*-Bu₃SnH see: U. Herzog, G. Roewer and U. Pätzold, Katalytische Hydrierung chlorhaltiger Disilane mit Tributylstannan, J. Organomet. Chem 1995,494, 143-147.

Example 15

Disilane **1** (ClMe₂Si-SiMe₂Cl, admixed with 5mol% Me₃Si-SiMe₂Cl **2**) (4.04 g) was reacted in a 1/1 molar ratio with the tin hydride in diglyme and tetraphenylphosphoniumchloride (Ph₄PCl, 3 w%) as catalyst at r.t.. After work up, a mixture of the disilanes **1** (15mol%), **2** (4mol%), **3** (72mol%) and **4** (9mol%) was obtained. 200 mg of those disilanes were subsequently reacted with tetrabutylphosphoniumchloride (*n*-Bu₄PCl, 25 w%) in a sealed NMR tube at 180°C for 9 h. As listed in Table 19, the hydrido disilane **3** was nearly completely cleaved into the monosilanes **5** and **6** that were formed in 68mol% yield. Chlorosilane **7** results from cleavage of the disilane **2**. Unidentified oligosilanes were detected in small amounts.

Table 19

compound	mol%
Me ₂ SiHCl	37
Me ₂ SiH ₂	31
Me ₃ SiCl	14
Me ₂ SiCl ₂	8
Me ₃ SiH	1
educts, oligosilanes	9

Example 16

The mixture of disilanes **1-4** from Example 15 (200 mg) was reacted with 2-methylimidazole (2-MIA, 16 w%) in a sealed NMR tube at 220 °C for 9 h. The amount of chlorosilane **5** was significantly smaller than in Example 15, the main product obtained was dimethylsilane Me₂SiH₂ **6**, followed by Me₃SiCl (**7**, 13.2mol%). Remaining disilanes **2** and **4** were 15.0mol% resp. 8.2mol%. Notably, perhydrogenated disilane **10** was detected in 1.0mol% (Table 20). Prolonged reaction times (69 h) lead to almost quantitative splitting of H-substituted disilanes as well as conversion of tri- and tetrasilanes (**26** and **27**), named in the table as "oligosilanes", into monomers. Products obtained are listed in Table 21 and prove formation of Me₂SiHCl (~40mol%) as main component.

Table 20

compound	mol%
Me ₂ SiHCl	17.1
Me ₂ SiH ₂	31.5
Me ₃ SiCl	13.2
Me ₂ SiCl ₂	8.8
ClMe ₂ Si-SiMe ₂ H	15.0
Me ₃ Si-SiMe ₂ H	8.2
HMe ₂ Si-SiMe ₂ H	1.0
oligosilanes	5.2

Table 21

compound	mol%
Me ₂ SiHCl	39.5
Me ₂ SiH ₂	34.0
Me ₃ SiCl	13.4
Me ₂ SiCl ₂	7.3
ClMe ₂ Si-SiMe ₂ H	5.8

5 Example 17

80 mg of a mixture containing methylhydridodisilanes **11** (85mol%) and **12** (15mol%) were reacted with (*n*-Bu₄PCl, 18 w%) in a sealed NMR tube. Cleavage reaction started already at r.t. and was completed at 50 °C for 62 h. Monosilanes formed were MeSiH₃ (**13**, 75mol%), Me₂SiH₂ (**6**, 18mol%) and Me₂SiHCl (**5**, 7mol%). The catalyst remained nearly unreacted and only traces of *n*-Bu₃P were detected in the ³¹P-NMR spectrum.

With 2-MIA (10 w%) as catalyst monosilane formation started at 180 °C (16 h) and was finished at 220 °C for 90 h to give **13** (82mol%) and **6** (18mol%) quantitatively.

Example 18

- 15 Tetramethyldisilane (80 mg, **10**) was reacted with *n*-Bu₄PCl (54 w%) in a sealed NMR tube and completely cleaved at 180 °C (17 h) to give Me₂SiH₂ (**6**, 87mol%) Me₃SiH (**9**, 7mol%), Me₂SiHCl (**5**, 4mol%) and Me₃SiCl (**7**, 2mol%).

Example 19A (starting material)

- 20 A mixture (1.22 g) of methylchlorodisilanes **14** (72mol%), **15** (23mol%), **1** (3.5mol%) and **16** (1.5mol%) was reacted in a 50 ml flask with *n*-Bu₃SnH in different molar ratios. In sample I about 18mol% of the chloro substituents were replaced by H-substituents, in sample II

37mol% and in sample III 55mol%. The reductions were performed in diglyme (1 ml) with PPh_4Cl (4 w%) as catalyst for 64h at r.t to give the disilane mixtures I to III (Table 22-24).

Table 22

disilanes	mol%
$\text{Cl}_2\text{MeSi-SiMeCl}_2$	33
$\text{ClMe}_2\text{Si-SiMe}_2\text{Cl}$	5
$\text{H}_2\text{MeSi-SiMeCl}_2$	22
ClHMeSi-SiMeCl_2	9
$\text{Cl}_2\text{MeSi-SiMe}_3$	1
$\text{Cl}_2\text{MeSi-SiMe}_2\text{Cl}$	30

5

Table 23

disilanes	mol%
$\text{Cl}_2\text{MeSi-SiMeCl}_2$	8
$\text{ClMe}_2\text{Si-SiMe}_2\text{Cl}$	5
$\text{H}_2\text{MeSi-SiMeCl}_2$	22
ClHMeSi-SiMeCl_2	24
$\text{Cl}_2\text{MeSi-SiMe}_2\text{Cl}$	31
$\text{Cl}_2\text{MeSi-SiMe}_3$	2
$\text{H}_2\text{MeSi-SiHMeCl}$	4
ClHMeSi-SiHMeCl	2
$\text{H}_2\text{MeSi-SiMeH}_2$	2

Table 24

disilane	mol%
$\text{Cl}_2\text{MeSi-SiMeCl}_2$	9
$\text{ClMe}_2\text{Si-SiMe}_2\text{Cl}$	8
$\text{H}_2\text{MeSi-SiMeCl}_2$	39
ClHMeSi-SiMeCl_2	5
$\text{Cl}_2\text{MeSi-SiMe}_2\text{Cl}$	5
$\text{Cl}_2\text{MeSi-SiMe}_3$	2
$\text{H}_2\text{MeSi-SiHMeCl}$	18
ClHMeSi-SiHMeCl	1
$\text{H}_2\text{MeSi-SiMeH}_2$	10
$\text{Me}_3\text{Si-SiMeH}_2$	3

10

Example 19B

Sample I (Table 22) (150 mg) was reacted with *n*-Bu₄PCl (17 w%) in a sealed NMR tube at different temperatures. Product compositions and molar distributions were determined NMR-spectroscopically. The results are listed in Table 25.

5

Table 25

compound	r.t. / 1 h mol%	60 °C / 66 h mol%	220 °C / 23 h mol%
Cl ₂ MeSi-SiMeCl ₂	1.4	-	-
ClMe ₂ Si-SiMeCl ₂	2.4	-	-
ClMe ₂ Si-SiMe ₂ Cl	3.5	3.0	-
Me ₂ SiHCl	5.5	3.6	4.2
Me ₃ SiCl	2.8	1.7	1.8
Me ₂ SiCl ₂	14.6	16.4	28.9
MeSiCl ₃	3.1	8.1	14.9
MeSiHCl ₂	61.2	56.0	15.1
MeSiH ₂ Cl	5.5	6.2	33.0
MeSiH ₃	-	-	2.1
oligosilanes	-	5	-

Sample II (Table 23) (150 mg) was reacted with *n*-Bu₄PCl (19 w%) in a sealed NMR tube at different temperatures. Product compositions and molar distributions were determined NMR-spectroscopically. The results are listed in Table 26.

10

Table 26

compound	r.t. / 1 h mol%	60 °C / 66 h mol%	220 °C / 23 h mol%
Cl ₂ MeSi-SiMeCl ₂	-	-	
ClMe ₂ Si-SiMeCl ₂	-	-	
ClMe ₂ Si-SiMe ₂ Cl	2.7	2.6	-
Me ₂ SiHCl	15.4	10.5	10.4
Me ₃ SiCl	1.5	2.0	1.9
Me ₂ SiCl ₂	12.2	16.1	23.6
MeSiCl ₃	0.8	1.8	4.2
MeSiHCl ₂	37.5	32.9	22.9
MeSiH ₂ Cl	23.7	24.7	27.2
MeSiH ₃	6.2	9.4	9.8
oligosilanes	-	-	-

As concluded from Table 26 disilane cleavage already started at r.t. H-substituted disilanes were already completely cleaved to mainly give the chlorosilanes **17** (61.2mol%), **18** (5.5mol%) and **8** (14.6mol%). Chlorinated methylsilanes require significantly higher temperatures for cleavage. MeSiH₃ (**13**, 2mol%) is only formed at 220 °C, possibly by H-Cl exchange of monomeric species.

Disilanes of sample II were mostly cleaved at r.t. to monomers, only **1** remained unreacted. At 220 °C (23 h) this disilane too was completely converted to monosilanes.

- 10 Sample III (Table 24) (200 mg) was nearly completely reacted with *n*-Bu₄PCl (24 w%) already at 80 °C within 15 min to give the monosilanes as listed in Table 27, only traces of **1** remained uncleaved.

Table 27

compound	80 °C /15 min mol%
Cl ₂ MeSi-SiMeCl ₂	-
ClMe ₂ Si-SiMeCl ₂	-
ClMe ₂ Si-SiMe ₂ Cl	0.6
Me ₂ SiHCl	12.1
Me ₃ SiCl	1.4
Me ₂ SiCl ₂	6.2
MeSiCl ₃	-
MeSiHCl ₂	11.7
MeSiH ₂ Cl	38.0
MeSiH ₃	30.0
oligosilanes	-

- 15 Summarizing the experiments of Example 19B, cleavage reactions with *n*-Bu₄PCl proved that cleavage of disilanes was faster with increasing degree of hydrogenation at the silicon backbone. The cleavage is decelerated with increasing degree of methylation at silicon. In case of silicon chlorination cleavage is accelerated with increasing degree of chlorination at the silicon moiety.

20

Example 20A (Starting Material)

For simulation of a mono- and disilane fraction obtained from the Müller-Rochow-Direct Process, a mixture (1.10 g) of compounds listed in Table 4, (1.19 g) of monosilane **8** and highly chlorinated disilanes listed in Table 5 and (1.07 g) of compounds listed in Table 7 were

mixed and reacted with different molar amounts of *n*-Bu₃SnH (procedure is described in Example 33) to replace 25, 50 and 75mol% of all chlorine substituents at silicon. After reduction, the products were isolated by condensation/distillation to give the product mixtures IV, V and VI listed in Table 28.

5

Table 28

compound	sample IV mol%	sample V mol%	sample VI mol%
ClMe ₂ Si-SiMe ₂ Cl	18	9	7
Me ₂ SiCl ₂	18	20	27
Me ₅ Si ₂ Cl	16	23	28
MeSiCl ₃	13	7	9
H ₂ MeSi-SiMeH ₂	9	18	-
ClMe ₂ Si-SiMeCl ₂	4	-	-
Cl ₂ MeSi-CH ₂ -SiMe ₃	4	2	3
MeSiH ₂ Cl	3	-	-
H ₂ MeSi-SiMeCl ₂	3	3	1
HMe ₂ Si-SiMeH ₂	3	2	1
Me ₃ Si-SiMe ₃	2	5	4
ClMe ₂ Si-CH ₂ -SiMeCl ₂	2	2	6
Me ₃ Si-SiMeCl ₂	1	2	4
HMe ₂ Si-SiMe ₂ H	1	1	2
Cl ₂ MeSi-CH ₂ -SiMeCl ₂	1	3	2
ClMe ₂ Si-CH ₂ -SiMe ₂ Cl	1	2	4
ClMe ₂ Si-CH ₂ -SiMe ₃	1	1	3

Example 20B

Cleavage reactions with mixture IV (280 mg) were performed with *n*-Bu₄PCl (6 w%) in a sealed NMR tube. NMR measurements were taken at r.t., 140 °C (23 h) and 220 °C (16 h).

10 Cleavage reactions already started at r.t. and only traces of Me₃Si-SiMe₃ (~1mol%) remained unreacted at 220 °C (Table 29).

Table 29

compound	r.t. / 1 h mol%	140 °C / 23 h mol%	220 °C / 16 h mol%
ClMe ₂ Si-SiMe ₂ Cl	12.1		-
Me ₂ SiHCl	16.5	20.8	21.6
Me ₃ SiCl	1.1	5.0	11.3
Me ₂ SiCl ₂	10.1	37.5	40.2
MeSiCl ₃	-	-	-
MeSiHCl ₂	16.7	10.2	7.4
MeSiH ₂ Cl	14.4	11.1	11.3
Me ₂ SiH ₂	-	-	1.9
MeSiH ₃	8.8	5.6	2.7
Me ₃ Si-SiMe ₃	0.9	0.6	1.1
Me ₃ Si-SiMe ₂ Cl	7.5	2.8	-
carbodisilanes	11.9	6.4	2.5

In Table 30 the results of the comparable cleavage reactions of samples V and VI are listed.

5

Table 30

compound	sample V			sample VI		
	r.t. / 1 h mol%	140 °C / 23 h mol%	220 °C / 16 h mol%	r.t. / 1 h mol%	140 °C / 23 h mol%	220 °C / 16 h mol%
ClMe ₂ Si-SiMe ₂ Cl	13.1	-	-	18.1	-	-
Me ₂ SiHCl	18.6	36.4	29.7	14.3	29.5	27.3
Me ₃ SiCl	1.6	11.3	17.4	2.6	13.6	22.9
Me ₂ SiCl ₂	11.3	28.9	29.2	15.4	37.8	37.2
MeSiHCl ₂	6.2	1.5	2.0	1.1	0.8	1.2
MeSiH ₂ Cl	6.3	1.6	4.3	0.7	-	2.7
Me ₂ SiH ₂	1.1	2.5	7.2	2.5	1.5	2.3
MeSiH ₃	11.4	5.4	6.9	5.2	2.3	1.7
Me ₃ Si-SiMe ₃	1.3	2.0	1.2	2.0	2.6	1.3
Me ₃ Si-SiMe ₂ Cl	16.9	2.4	-	19.7	1.5	-
carbodisilanes	12.2	8.0	2.1	18.4	10.4	3.4

From cleavage reactions of samples IV – VI it is obvious that with increasing replacement of Cl against H in the methylchlorodisilanes R_nSi₂Cl_{6-n} with Cl≥3, the partial hydrido substituted disilanes were cleaved significantly faster. Cleavage of disilanes with Me≥4 (partial or perhydrogenated) required higher temperatures. At about 140 °C mainly the chlorosilanes 8,

10

7, 5 and 17 were formed. Investigation of the cleavage reactions by ^{31}P -NMR spectroscopy proved the activity of $n\text{-Bu}_4\text{PCl}$ as real catalyst, only at 220 °C and higher, the latter is completely reacted to give $n\text{-Bu}_3\text{P}$, traces of $n\text{-Bu}_2\text{PH}$ and 1-but-ene, and hydrogen chloride. HCl is responsible for the final formation of H/Cl substituted monosilanes.

5

Example 21

In a 50 ml flask, a mixture of disilanes 14 (69mol%), 15 (26mol%), 1 (4mol%) and 16 (1mol%) (244 mg) was reacted with Ph_4PCl (25.3 mg) and LiH (202 mg) in 0.5 mL of diglyme. Already at r.t. 75mol% of monosilanes were formed, with 17 in 40mol%. 25mol% of disilanes remained uncleaved, 10mol% of those were reduced ($\text{SiCl} \rightarrow \text{SiH}$) (Table 31). MeSiH_3 that might have been formed evaporated in the open system due to its low boiling point (-57 °C). That is why the same disilane mixture (122 mg) was reacted with the catalyst/LiH (1 w%/4 w%) in a sealed NMR tube at r.t.. In this case monosilane 13 was detected in 13mol%, 17 was formed in 21mol% and 18 in 33mol% yield.

15

Table 31

compound	mol%
MeSiHCl_2	40
Me_2SiHCl	9
MeSiH_2Cl	10
Me_2SiCl_2	10
Me_3SiCl	2
MeSiCl_3	4
$\text{Cl}_2\text{MeSi-SiMeCl}_2$	4
$\text{ClMe}_2\text{Si-SiMe}_2\text{Cl}$	1
$\text{ClMe}_2\text{Si-SiMeCl}_2$	9
$\text{Me}_3\text{Si-SiMeCl}_2$	1
$\text{MeH}_2\text{Si-SiMeCl}_2$	2
$\text{MeH}_2\text{Si-SiMeHCl}$	6
$\text{HMe}_2\text{Si-SiMeH}_2$	1
$\text{MeH}_2\text{Si-SiMeH}_2$	1

Example 22

A mixture of disilanes 1 (62mol%), 2 (30mol%), 15 (4mol%), and 14 (4mol%) (107 mg) was reacted with the $n\text{-Bu}_4\text{PCl/LiH}$ system (1.3 mg/29.3 mg) and 0.3 ml diglyme as solvent in a sealed NMR tube first at r.t. and then at 200 °C for 23 h. As can be seen from Table 32, under low temperature conditions the disilanes were initially reduced, perhydrogenated

20

disilanes **10** and **4** were formed in 82.6mol% and 17.5mol%; traces of hydrogenated monosilanes Me_2SiH_2 and MeSiH_3 were also detected. At 200 °C all disilanes were completely cleaved.

The ^{31}P -NMR spectrum of the sample proved that $n\text{-Bu}_4\text{PCl}$ was completely reacted to give $n\text{-Bu}_3\text{P}$ and traces of $n\text{-Bu}_2\text{PH}$. Reinvestigations showed that nearly all disilanes were already cleaved at 140 °C.

Table 32

	r.t.	200 °C
compound	mol%	mol%
MeSiHCl_2	-	7.1
Me_2SiH_2	traces	38.3
Me_3SiH	traces	54.6
MeSiH_3	traces	traces
$\text{HMe}_2\text{Si-SiMe}_2\text{H}$	82.6	-
$\text{Me}_3\text{Si-SiMe}_2\text{H}$	17.4	-

Example 23

The mixture of mono- and disilanes from Example 2 (Table 5) (167 mg) was reacted with 73 mol% LiH (15 mg) and $n\text{-Bu}_4\text{PCl}$ (2.9 mg) and 0.3 ml diglyme as solvent in a sealed NMR tube at first at r.t. and subsequently at 140 °C (23 h). The product distribution is listed in Table 33. At 140 °C the amount of dichlorosilane **8** increased significantly from 15mol% to 37mol%, obviously from cleavage of disilane **1** that was still present at r.t.. At 140 °C the amount of **13** is strongly decreased (26mol% → 9mol%), while that of **17** was strongly increased (6mol% → 16mol%). Notably, the catalyst remained unchanged under those conditions (no $n\text{-Bu}_3\text{P}$ formation).

Table 33

	r.t.	140 °C
compound	mol%	mol%
MeSiHCl_2	6	16
Me_2SiHCl	20	10
MeSiH_2Cl	26	23
Me_2SiH_2	2	-
MeSiH_3	26	9
Me_2SiCl_2	15	37
Me_3SiCl	3	3
$\text{ClMe}_2\text{Si-SiMe}_2\text{Cl}$	1	-
$\text{Me}_3\text{Si-SiMe}_2\text{Cl}$	1	2
Me_6Si_2	traces	traces

Example 24

The mixture of mono- and disilanes of Example 2 (Table 6) (97 mg) was reacted with 100 mol% LiH (10 mg) and *n*-Bu₄PCl (3.2 mg) and 0.3 ml diglyme as solvent in a sealed NMR tube, first at r.t. and subsequently at 140 °C (23 h). Product distribution is listed in Table 34.

- 5 In the presence of the catalyst, even the partially- and perhydrogenated methylidisilanes were mostly cleaved at r.t., the perchlorinated methylidisilanes remained unreacted. At 140 °C monosilanes **6**, **13**, and **5** became main products (94mol%), only 3mol% of disilanes **2** and **26** were still detected in the reaction mixture. Upon cleavage reaction, the catalyst was not reacted to give *n*-Bu₃P.

Table 34

	r.t.	140 °C
compound	mol%	mol%
MeSiHCl ₂	2	-
Me ₂ SiHCl	8	11
Me ₂ SiH ₂	9	48
MeSiH ₃	62	35
Me ₃ SiCl	-	3
ClMe ₂ Si-SiMe ₂ Cl	2	-
Me ₃ Si-SiMe ₂ Cl	6	2
HMe ₂ Si-SiMe ₂ Cl	9	-
Me ₆ Si ₂	2	1

Example 25

The mixture of mono-, di- and carbodisilanes from Example 2 (Table 4) (143 mg) was reacted with 100 mol% LiH (15.4) and the catalyst *n*-Bu₄PCl (4.1 mg) and 0.3 ml diglyme as solvent in a sealed NMR tube at r.t. and subsequently at 140 °C (23 h). Product formation is shown in Table 35. Cleavage reactions already started at r.t., 85mol% of monomers were obtained in presence of the catalyst. Increasing the reaction temperature to 140 °C, the amount of Me₂SiH₂ (**6**, 39mol%) was increased significantly by cleavage of mainly disilanes **10**, **3**, **4**, **1**, and **2**. Notably, even the carbodisilanes were reacted to monosilanes, as documented by the high amount of methylsilane (**13**, 59mol%). At r.t., the catalyst remained unchanged but was decomposed at 140°C to give an unknown species besides *n*-Bu₃P.

Table 35

	r.t.	140 °C
compound	mol%	mol%
Me ₂ SiHCl	4	-
Me ₂ SiH ₂	7	39
MeSiH ₃	71	59
ClMe ₂ Si-SiMe ₂ Cl	3	-
Me ₃ Si-SiMe ₂ Cl	4	-
HMe ₂ Si-SiMe ₂ Cl	11	-
Me ₃ Si-SiMe ₂ H	-	2

Example 26

In a 100 ml flask, the mixture of mono- and disilanes (10.6 g) from Example 2 (listed in Table 6) was reacted with n-Bu₄PCl (0.28 g) and LiH (0.8 g, 75 mol%) in 5 mL of diglyme at 130 °C for 5 h. Volatile products formed (3.22 g) were separated by condensation and are listed in Table 36. NMR spectroscopic investigations of the residue proved formation of highly methylated hydrogen substituted disilanes and carbodisilanes but they remained mostly uncleaved. Instead, increasing the reaction temperature to 160 °C (5 h) and characterization of low boiling components (1.03 g) proves significant cleavage of all disilanes and even the carbosilanes to mainly produce the technically very valuable monosilanes MeSiHCl₂ (40mol%) and MeSiH₂Cl (26mol%) (Table 36). In the reaction residue traces of highly methylated disilanes besides small amounts of uncleaved carbodisilanes were identified.

Table 36

compound	130 °C/5 h			160 °C/5 h		
	mol%	weight [g]	amount of substance [mol]	mol%	weight [g]	amount of substance [mol]
Me ₂ SiCl ₂	35.2	1.46	0.0113	-	-	-
Me ₃ SiCl	1.4	0.05	0.0005	3.9	0.06	0.0005
MeSiCl ₃	1.8	0.08	0.0006	15.9	0.21	0.0022
Me ₂ SiHCl	16.3	0.49	0.0052	1.9	0.02	0.0003
MeSiHCl ₂	13.7	0.51	0.0044	40.2	0.33	0.0055
MeSiH ₂ Cl	13.7	0.36	0.0044	26.0	0.16	0.0036
Me ₂ SiH ₂	2.1	0.04	0.0007	1.7	0.02	0.0002
MeSiH ₃	15.8	0.23	0.0051	1.3	0.03	0.0002
Me ₃ Si-SiMe ₂ H	-	-	-	5.4	0.10	0.0007
HMe ₂ Si-SiMe ₂ H	-	-	-	3.7	0.10	0.0005
total:	100	3.22	0.0322	100	1.03	0.0137

Example 27

In a 100 ml flask, the mixture of mono- and disilanes from Example 2 as listed in Table 4 was reacted with *n*-Bu₄PCl (0.36 g) and LiH (0.53 g, 51 mol%) in 6 mL of diglyme at 130 °C for 5 h. Volatile products (1.66 g) formed were separated by condensation and are listed in Table 37. Highly methylated hydrogen substituted disilanes and carbodisilanes were formed but remained mostly uncleaved. Reaction at 160 °C for 5 h and condensation of the volatile products formed (0.98 g) were identified as monosilanes, also listed in Table 37. In the reaction residue traces of highly methylated disilanes besides small amounts of uncleaved carbodisilanes were detected.

Table 37

compound	130 °C/5 h			160 °C/5 h		
	mol%	weight [g]	amount of substance [mol]	mol%	weight [g]	amount of substance [mol]
Me ₂ SiCl ₂	19.1	0.41	0.0032	3.1	0.05	0.0004
Me ₃ SiCl	1.1	0.02	0.0002	3.7	0.05	0.0005
MeSiCl ₃	2.9	0.07	0.0005	-	-	-
Me ₂ SiHCl	13.8	0.22	0.0023	38.6	0.45	0.0048
MeSiHCl ₂	22.6	0.43	0.0038	-	-	-
MeSiH ₂ Cl	18.4	0.25	0.0031	3.1	0.03	0.0004
Me ₂ SiH ₂	5.7	0.06	0.0010	24.7	0.18	0.0030
MeSiH ₃	12.6	0.10	0.0021	26.1	0.15	0.0032
Me ₃ Si-SiMe ₂ Cl	2.1	0.06	0.0004	0.4	0.06	0.00004
ClMe ₂ Si-SiMe ₂ Cl	0.4	0.01	0.0001	-	-	-
Me ₃ Si-SiMe ₃	1.3	0.03	0.0002	0.3	0.01	0.000004
total:	100	1.66	0.0322	100	0.98	0.01238

Example 28

The mixture of mono- and disilanes (357 mg) of Example 2 (listed in Table 5) was reacted with *n*-Bu₃P (16 mg) in a diglyme/HCl solution (11.6 M) (molar ratio disilane/HCl 1:1) in a sealed NMR tube at 80 °C for 16.5 h to give monomers in 97.1 mol% (listed in Table 38). Only highly methylated disilanes **1** and **2** were still present. No oligomeric structures could be detected NMR spectroscopically. For this reaction no other hydrogen source was required except HCl that presumably reacted as a silylene trapping agent preventing the silylene insertion into the Si-Si-bond giving oligomeric structures. The main products formed were MeSiCl₃ (39.7 mol%), Me₂SiCl₂ (28.1 mol%) and MeSiHCl₂ (27.6 mol%).

Table 38

compound	mol%
Me ₂ SiCl ₂	28.1
Me ₃ SiCl	1.7
MeSiCl ₃	39.7
MeSiHCl ₂	27.6
ClMe ₂ Si-SiMe ₂ Cl	1.8
Me ₃ Si-SiMe ₂ Cl	1.1

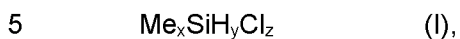
It will be understood that any numerical range recited herein includes all sub-ranges within that range and any combination of the various endpoints of such ranges or sub-ranges, be it
5 described in the examples or anywhere else in the specification.

It will also be understood herein that any of the components of the invention herein as they are described by any specific genus or species detailed in the examples section of the specification, can be used in one embodiment to define an alternative respective definition of any endpoint of a range elsewhere described in the specification with regard to that
10 component, and can thus, in one non-limiting embodiment, be used to supplant such a range endpoint, elsewhere described.

It will be further understood that any compound, material or substance which is expressly or implicitly disclosed in the specification and/or recited in a claim as belonging to a group of structurally, compositionally and/or functionally related compounds, materials or substances
15 includes individual representatives of the group and all combinations thereof.

CLAIMS

1. Process for the manufacture of monosilanes of the general formula (I):



wherein

$x = 0$ to 3 ,

$y = 0$ to 3 , preferably 1 to 3 , more preferably 1 or 2 ,

10 $z = 0$ to 4 and

$x + y + z = 4$,

and mixtures thereof,

comprising:

A) the step of subjecting a silane substrate comprising one or more silane substrate
15 compounds selected from the group of

a) one or more disilanes of the general formula (II)



wherein

$m = 0$ to 6 ,

$n = 0$ to 6 , preferably 0 to 4 ,

$o = 0$ to 6 and

$m + n + o = 6$,

25

b) one or more linear or branched oligosilanes of the general formula (III)



wherein

$q = 3$ to 7

$p = q$ to $(2q + 2)$

$r, s = 0$ to $(q + 2)$

$r + s = (2q + 2) - p$

and wherein each Si atom preferably bears at least one methyl group, and

35

c) one or more carbodisilanes of the general formula (IV)



wherein

a, c are independently of each other 1 to 3,

b, d are independently from each other 0 to 2

e, f are independently from each other 0 to 2,

$a + b + e = 3$,

$c + d + f = 3$,

and mixtures containing compounds of the general formulae (II), (III) and (IV),

to the cleavage reaction of the silicon-silicon bond(s) in the silane substrates of the general formulae (II) and (III) and the silicon-carbon bond(s) of the carbodisilanes of the general formula (IV),

to the reaction with at least one compound (cleavage compound) selected from the group consisting of:

- a quaternary Group 15 onium compound R_4QX , wherein each R is independently a hydrogen or an organyl group, Q is phosphorus, arsenic, antimony or bismuth, and X is a halide selected from the group consisting of F, Cl, Br and I,

- a heterocyclic amine,

- a heterocyclic ammonium halide,

- a mixture of R_3P and RX , wherein R is as defined above, and X is as defined above,

and

mixtures of the above-mentioned compounds,

- (i) until at least about 50 mol-% of the cleavage compound based on the initial molar amount of the cleavage compound is reacted, and/or

- (ii) until the ratio of the total of the produced monosilanes of the general formula (I) wherein $y = 1$ to 3 is at least about 40 mol-%, preferably at least about 50 mol-%, based on the total molar amount of the monosilanes of the general formula (I), and/or

- (iii) until the ratio of Me_2SiHCl is at least about 20 mol-%, preferably at least about 30 mol-%, based on the total amount of the monosilanes of the general formula (I), and

B) optionally a step of separating the resulting monosilanes of the general formula (I).

2. Process according to claim 1, wherein the reaction in step A) is carried out for more than about 4 hours and at a temperature of at least about 200 °C, or the reaction in step A) is carried out for more than about 10 hours preferably, at a temperature of more than about 100 °C.

3. Process according to claims 1 or 2, which is carried out without the supply of hydrogen (H_2).
4. Process according to any of the previous claims, wherein the quaternary Group 15 onium compound is represented by the formula R_4PCl , wherein R is independently a
5 hydrogen group or an organyl group, more preferably a hydrogen group, an aromatic group or an aliphatic hydrocarbon group, optionally step A) is carried out in the presence of at least one compound of the formula R_4PCl , preferably $n-Bu_4PCl$, and optionally at least one methylimidazole.
5. Process according to any of the previous claims, wherein step A) is carried out by
10 subjecting the silane substrate to the cleavage reaction of step A) in the presence of a hydrogen halide HX , wherein X is selected from the group consisting of F, Cl, Br and I.
6. Process according to any of the previous claims, wherein step A) is carried out in the presence of at least one metal hydride, preferably at least one metal hydride selected
15 from the group of alkali metal hydrides and alkaline earth metal hydrides, more preferably at least one alkali metal hydride, and most preferably lithium hydride.
7. Process according to any of the previous claims, wherein the silane substrate, comprises at least one of the compounds selected from the group consisting of
20 Si_2Cl_6 , $Cl_2MeSi-SiMeClH$, $HClMeSi-SiMeClH$, $Cl_2MeSi-SiMeH_2$, $HClMeSi-SiMeH_2$, $ClMe_2Si-SiMeClH$, $Cl_2MeSi-SiMe_2H$, $ClMe_2Si-SiMeH_2$, $HMe_2Si-SiMeClH$, $ClMe_2Si-SiMe_2Cl$, $Me_3Si-SiMe_2Cl$, $ClMe_2Si-SiMe_2H$, $Me_3Si-SiMe_2H$, $HMe_2Si-SiMe_2H$, $H_2MeSi-SiMeH_2$, $HMe_2Si-SiMeH_2$, $Cl_2MeSi-SiMeCl_2$, $ClMe_2Si-SiMeCl_2$, $Me_3Si-SiMeCl_2$, $Cl_2MeSi-CH_2-SiMeCl_2$, $ClMe_2Si-CH_2-SiMeCl_2$, $ClMe_2Si-CH_2-SiMe_2Cl$, $Me_3Si-CH_2-SiMeCl_2$, $Me_3Si-CH_2-SiMe_2Cl$, $Me_3Si-CH_2-SiMe_3$, $ClMe_2Si-SiMe_2-SiMe_2Cl$, $ClMe_2Si-SiMe_2-SiMe_2-SiMe_2Cl$, $(ClMe_2Si)_3SiMe$, $ClMe_2Si-SiMe_2-SiMe_2H$, $(Cl_2MeSi)_2SiMeCl$, $(Cl_2MeSi)_3SiMe$, $(Cl_2MeSi)_2SiMe-SiClMe-SiCl_2Me$, $[(Cl_2MeSi)_2SiMe]_2$, $[(Cl_2MeSi)_2SiMe]_2SiClMe$, and $(Cl_2MeSi)_2SiMe-SiMe_2Cl$, and mixtures thereof.
8. Process according to any of the previous claims, wherein the molar ratio of the cleavage compound used in step A) to the silane substrate compounds of the general formulae (II), (III) and (IV) is in the range of about 0.0001 to about 100 mol-%, more preferred 0.001 to 50 mol-%, more preferred 0.001 to 25 mol-%, even more preferred 0.01 to 10 mol-%, and most preferably 0.01 to 0.5 mol-% based on the molar amount of the silane substrate compounds.
9. Process according to any of the previous claims, wherein the silane substrates used
35 in step A) are submitted to a hydrogenation step before the cleavage reaction of the silicon-silicon bond(s) in the silane substrates of the general formulae (II) and (III)

and/or the silicon-carbon bond(s) of the carbodisilanes of the general formula (IV) is carried out, wherein chlorine atoms contained in the silane substrates are partially or completely exchanged by hydrogen atoms, and preferably the hydride donor selected from the group of metal hydrides, preferably complex metal hydrides and organometallic hydride reagents such as LiAlH_4 , $n\text{-Bu}_3\text{SnH}$, NaBH_4 , $i\text{-Bu}_2\text{AlH}$ or sodium bis(2-methoxyethoxy) aluminumhydride.

10. Process according to any of the previous claims, wherein step A) is carried out in the presence of an organic solvent, preferably a high-boiling ether compound, more preferably diglyme or tetraglyme, most preferably diglyme.

11. Process according to the previous claims, wherein step A) is carried out in the presence of at least one compound of the formula R_4PCl , preferably $n\text{-Bu}_4\text{PCl}$, and at least one metal hydride, preferably lithium hydride.

12. Process according to any of the previous claims, wherein step A) is carried out using at least one cleavage compound selected from quaternary Group 15 onium compounds represented by the formula R_4QX , wherein each R is independently a hydrogen or an organyl group, Q is phosphorus, arsenic, antimony or bismuth, and X is a halide selected from the group consisting of F, Cl, Br and I, and at least one cleavage compound selected from heterocyclic amines and heterocyclic ammonium halides, at a temperature of about 0°C to about 300°C , more preferably about 50°C to about 220°C , even more preferably at about 100°C to about 200°C , and most preferably at about 120°C to about 180°C .

13. Process according to any of the previous claims, wherein the monosilanes of the formula (I) are selected from the group consisting of Me_2SiHCl , Me_2SiH_2 , Me_3SiCl , Me_2SiCl_2 , Me_3SiH , MeSiH_3 , MeSiHCl_2 , MeSiH_2Cl , and MeSiCl_3 , preferably the monosilanes of the formula (I) are selected from the group consisting of Me_2SiHCl , Me_3SiCl , and MeSiHCl_2 .

14. Process according to any of the previous claims, wherein dimethylchloromonosilane Me_2SiHCl is formed by submitting a silane substrate selected from the group consisting of $\text{ClMe}_2\text{Si-SiMe}_2\text{Cl}$, $\text{ClMe}_2\text{Si-SiMeCl}_2$, $\text{Me}_3\text{Si-SiMe}_2\text{Cl}$, $\text{HMe}_2\text{Si-SiMe}_2\text{H}$, $\text{HMe}_2\text{Si-SiMeH}_2$, $\text{Me}_3\text{Si-SiMe}_2\text{H}$, $\text{ClMe}_2\text{Si-SiMe}_2\text{H}$, $\text{ClMe}_2\text{Si-SiMeH}_2$, $\text{HMe}_2\text{Si-SiMeCl}_2$, $\text{Cl}_2\text{MeSi-CH}_2\text{-SiMeCl}_2$, $\text{ClMe}_2\text{Si-CH}_2\text{-SiMeCl}_2$, $\text{ClMe}_2\text{Si-CH}_2\text{-SiMe}_2\text{Cl}$, $\text{Me}_3\text{Si-CH}_2\text{-SiMe}_2\text{Cl}$, $\text{ClMe}_2\text{Si-SiMe}_2\text{-SiMe}_2\text{Cl}$, $\text{ClMe}_2\text{Si-SiMe}_2\text{-SiMe}_2\text{-SiMe}_2\text{Cl}$, $(\text{ClMe}_2\text{Si})_3\text{SiMe}$ and mixtures thereof to the cleavage reactions of step A), and/or

wherein the trimethylchlorosilane Me_3SiCl is formed by submitting a silane substrate selected from the group consisting of $\text{Me}_3\text{Si-SiMe}_2\text{Cl}$, $\text{Me}_3\text{Si-SiMeCl}_2$, $\text{Me}_3\text{Si-SiMe}_2\text{H}$,

Me₃Si-CH₂-SiMe₂Cl, ClMe₂Si-CH₂-SiMe₂Cl, ClMe₂Si-CH₂-SiMeCl₂, Me₃Si-CH₂-SiMe₃,
 Me₃Si-CH₂-SiMeCl₂ and mixtures thereof to the cleavage reactions of step A), and/or
 wherein the methyldichloromonosilane MeSiHCl₂ is formed by submitting a silane
 substrate selected from the group consisting of Cl₂MeSi-SiMeCl₂, Cl₂MeSi-SiMe₂Cl,
 5 Cl₂MeSi-SiMe₃, HCIMeSi-SiMeH₂, HCIMeSi-SiMeClH, HCIMeSi-SiMeCl₂, Cl₂MeSi-
 SiMeH₂, ClHMeSi-SiMe₂Cl, Cl₂MeSi-SiMe₂H, ClHMeSi-SiMe₂H, Cl₂MeSi-CH₂-
 SiMeCl₂, ClMe₂Si-CH₂-SiMeCl₂, Me₃Si-CH₂-SiMeCl₂, (Cl₂MeSi)₂SiMeCl,
 (Cl₂MeSi)₃SiMe, (Cl₂MeSi)₂SiMe-SiClMe-SiCl₂Me, [(Cl₂MeSi)₂SiMe]₂,
 [(Cl₂MeSi)₂SiMe]₂SiClMe, (Cl₂MeSi)₂SiMe-SiMe₂Cl and mixtures thereof to the
 10 cleavage reactions of step A).

15. Process according to any of the previous claims, wherein the silane substrates of the
 general formulae (II) and (III), and the carbodisilane substrates of the general formula
 (IV), or the mixtures thereof are residues of the Rochow-Müller Direct Process (DPR).

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2018/051853

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C07F7/12
 ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013/101619 A1 (MOMENTIVE PERFORMANCE MAT INC [US]) 4 July 2013 (2013-07-04)	1-5, 7-10, 12-15
Y	Process for the manufacture of a monosilane such as MeSiHCl ₂ , comprising the step of subjecting a mixture of carbosilanes and polysilanes comprising amongst them compounds such as ClMe ₂ Si-SiMe ₂ Cl, that are the high-boiling direct process residues (DPR) of the Müller-Rochow process (see [2]-[3], pages 1-2) to a cleavage reaction of the Si-Si bond or Si-C-Si bond (see [5]), where the reaction is catalyzed by cleavage compounds comprising a mixture of phosphonium halide salts of formula R ₄ P ⁺ Hal ⁻ and a heterocyclic amine (e.g. 2-methyl-imidazole, see page 8, [31]). The amount of monosilanes comprising at -/--	6,11



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

18 December 2018

Date of mailing of the international search report

03/01/2019

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2018/051853

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	least one Si-H bond is less than 40 mol % with respect to all monosilanes and the amount of Me₂SiHCl is less than 20% of the total amount of all formula (I) monosilanes (see pages 20-25, tables 2-4, 5A and 5B) -----	
X	WO 2013/101618 A1 (MOMENTIVE PERFORMANCE MAT INC [US]) 4 July 2013 (2013-07-04)	1-5, 7-10, 12-15
Y	Process for the manufacture of a monosilane such as MeSiHCl₂, comprising the step of subjecting a mixture of carbosilanes and polysilanes comprising amongst them compounds such as ClMe₂Si-SiMe₂Cl (see [23]), that constitute the high-boiling direct process residues (DPR) of the Müller-Rochow Process (see [2]-[3], pages 1-2) to a cleavage reaction of the Si-Si bond or Si-C-Si bond (see [4]), where the reaction is catalyzed by cleavage compounds comprising a mixture of phosphonium halide salt of general formula R₄P-Hal and a heterocyclic amine (such as e.g. 2-methyl-imidazole, see page 8, [31]), whereby the amount of monosilanes comprising at least one Si-H bond is less than 40 mol% with respect to all monosilanes and the amount of Me₂SiHCl is less than 20% of the total amount of all formula (I) monosilanes (see pages 20-33, tables 5A-18) -----	6,11
X	US 5 175 329 A (BOKERMAN GARY N [US] ET AL) 29 December 1992 (1992-12-29)	1
A	Cleavage of polysilanes constituting the high-boiling residue of the Müller-Rochow process (see column 2, lines 46-59) by a hydrogenolysis catalyst (complexed metals, see column 4, lines 40-52) and a redistribution catalyst (quaternary phosphonium halides, column 5, lines 15-23) in the presence of hydrogen: examples 1-2 and claim 1 -----	6,11
Y	US 5 922 894 A (CRUM BRUCE ROBERT [US] ET AL) 13 July 1999 (1999-07-13) Cleavage of polysilanes constituting the high-boiling residue of the Müller-Rochow process (see column 4, example 1) by a metal hydride (LiAlH₄) in the presence of hydrogen: examples 1-2 and claim 1 -----	6,11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2018/051853

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2013101619 A1	04-07-2013	CN 104144934 A EP 2797936 A1 JP 6242344 B2 JP 2015509087 A KR 20140117377 A US 2013172593 A1 WO 2013101619 A1	12-11-2014 05-11-2014 06-12-2017 26-03-2015 07-10-2014 04-07-2013 04-07-2013
WO 2013101618 A1	04-07-2013	CN 104136445 A EP 2797935 A1 JP 6242343 B2 JP 2015503563 A KR 20140117375 A US 2013172594 A1 WO 2013101618 A1	05-11-2014 05-11-2014 06-12-2017 02-02-2015 07-10-2014 04-07-2013 04-07-2013
US 5175329 A	29-12-1992	CA 2091513 A1 DE 69316061 D1 DE 69316061 T2 EP 0564109 A1 ES 2113486 T3 JP H069655 A JP 3193513 B2 KR 100257644 B1 US RE35298 E US 5175329 A	04-10-1993 12-02-1998 06-08-1998 06-10-1993 01-05-1998 18-01-1994 30-07-2001 01-06-2000 16-07-1996 29-12-1992
US 5922894 A	13-07-1999	EP 0997467 A2 JP 2000136192 A US 5922894 A	03-05-2000 16-05-2000 13-07-1999