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Controlled synthesis of cyclosiloxanes by NHC-catalyzed hydrolytic oxidation of dihydrosilanes†

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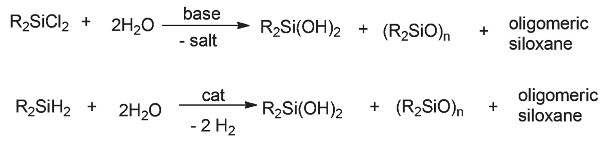
Hydrolytic oxidation of various hydrosilanes in acetonitrile and in the absence of organic solvents catalyzed by an N-heterocyclic carbene organocatalysis is described. The NHC organocatalyst exhibited a very high activity with only 0.1 mol% loading of the catalyst in acetonitrile for aryl-substituted dihydrosilanes to produce hydrogen gas and cyclosiloxanes almost quantitatively in several minutes. The calculated TOF (15 000 h^{-1}) of this organocatalyst is comparable to those of precious metal-based heterogeneous catalysts and much superior to those of the existing homogeneous metal catalysts. The catalytic reaction selectively yielded cyclosiloxanes in high yield without the contamination of silanols. Furthermore, the catalytic reaction can also be furnished under solvent-free conditions at elevated temperatures with 2.5 mol% loading of the NHC in 5–12 hours.

Introduction

Cyclosiloxanes are basic building blocks for the synthesis of various silicon materials that have been applied in both industry and academia.[1] The industrial process for the synthesis of cyclosiloxanes has been largely based on the hydrolysis of chlorosilanes and alkoxylsilanes. However, the hydrolysis required a large amount of bases and high temperatures for the completion with the formation of a number of side products including oligomeric and polymeric silicones and cannot be well controlled (Scheme 1). In recent years, catalytic oxidation of hydrosilanes has become an appealing and selective approach for the production of silanols and siloxanes.[2] Among the known oxidation processes by using various oxidants, hydrolytic oxidation of hydrosilanes with water undoubtedly represents the most economic and environmentally benign process because it produces hydrogen gas as the only by-product. It has been shown that the hydrolytic oxidation of hydrosilanes containing high contents of hydride groups such as $HC(SiH_3)_3$ has been potentially useful as an alternative energy source.[3] Compared to other hazard hydride sources such as lithium aluminum hydrides, which generate hydrogen gas in an uncontrolled manner upon hydrolysis, hydrosilanes are generally stable to water and their hydrolytic oxidation require suitable catalysts.



$$R_2SiCl_2 + 2H_2O \xrightarrow[\text{- salt}]{\text{base}} R_2Si(OH)_2 + (R_2SiO)_n + \text{oligomeric siloxane}$$

$$R_2SiH_2 + 2H_2O \xrightarrow[\text{- 2 }H_2]{\text{cat}} R_2Si(OH)_2 + (R_2SiO)_n + \text{oligomeric siloxane}$$

Scheme 1 Traditional hydrolysis of chlorosilanes *vs.* catalytic hydrolytic oxidation of hydrosilanes.

In recent years, there have been extensive investigations on the catalytic oxidation of hydrosilanes with water catalysed by metal-based catalysts.[2] A number of transition metal-based homogeneous and heterogeneous catalysts, especially those based on precious metals such as gold, rhodium, iridium and ruthenium, have been developed.[2,4–7] However, most of these studies have been concentrated on the hydrolytic oxidation of tertiary hydrosilanes (R_3SiH) for the controlled synthesis of silanols and the hydrolytic oxidation of primary and secondary silanes ($RSiH_3$ and R_2SiH_2) has been much less studied probably due to the complexity of the reactions associated with complex products including silanols, cyclosiloxanes and polymeric materials, which cannot be easily controlled. Thus, the catalysts for the selective formation of a single product are highly desirable.

N-Heterocyclic carbenes have emerged as environmentally benign, efficient and cheap metal-free organocatalysts. The use of NHCs as catalysts for silane transformations such as the silylation of CO_2 and other unsaturated substrates has been reported.[8] We have recently shown that NHCs could efficiently catalyze the dehydrogenative coupling of hydrosilanes with various alcohols.[9a] The organocatalytic oxidation of tertiary silanes with H_2O_2 to silanols has also been reported.[9b] Herein,

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we report on the hydrolytic oxidation of secondary hydrosilanes with water for the selective formation of hydrogen gas and cyclosiloxanes by using an N-heterocyclic carbene as the catalyst. NHC catalysis can be carried out either in organic solvents or under solvent free-conditions with high efficiency and selectivity. Remarkably, the clean and selective formation of cyclosiloxanes can be furnished in acetonitrile in several minutes with only 0.1 mol% loadings of the NHC.

Results and discussion

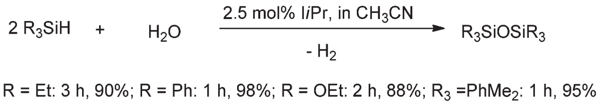
In order to examine the feasibility of the NHC-catalyzed hydrolytic oxidation of hydrosilanes, the oxidation of the selected tertiary silanes Et_3SiH, $PhMe_2SiH$, Ph_3SiH and $(EtO)_3SiH$ has been investigated in THF and acetonitrile at room temperature using 2.5 mol% loading of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (I*i*Pr). The reactions in THF proved to be relatively slow to yield a mixture containing the corresponding silanol and siloxane. For example, the hydrolysis of Ph_3SiH in THF using an excess of water at 0 °C for 3 h yielded Ph_3SiOH and $Ph_3SiOSiPh_3$ in the molar ratio of 7 : 3 based on the NMR analysis, and a complete conversion of Ph_3SiOH into $Ph_3SiOSiPh_3$ was observed in 5 h (Table S1 in the ESI†), indicating the NHCs may also promote the Si–O coupling of the silanol with the hydrosilane. In contrast, the reactions in acetonitrile were much faster and a complete conversion was observed in 2 h at 0 °C. Thus, the reactions of these silanes with water catalyzed by a 2.5% mol loading of I*i*Pr were conducted in CH_3CN at room temperature, and the results are summarized in Table 1. All of the reactions exclusively resulted in the formation of the corresponding siloxanes in 1–3 hours. The hydrolytic oxidation of an alkoxylsilane (Table 1, entry 4) led to the formation of the corresponding alkoxylsiloxane in high yield (88%) while the alkoxyl groups remained intact. The selective formation of siloxanes by the catalytic hydrolytic oxidation of tertiary hydrosilanes has not been reported previously (Scheme 2).[2a]

The selective hydrolytic oxidation of dihydrosilanes is of great interest in that it may present an atom-economical and practical route for the production of cyclosiloxanes. To optimize the conditions for the hydrolytic oxidation of secondary hydrosilanes, the hydrolysis of Ph_2SiH_2 was carried out in acetonitrile with different loadings of I*i*Pr at room temperature (Scheme 3). The results are given in Table 2. The reaction was monitored by the collection of hydrogen gas by water displacement in a graduated cylinder. All of the reactions catalysed by 0.1–2.5% mol% (entries 1–5) of I*i*Pr are almost complete in several minutes. It is noted that the reaction catalysed by 0.1 mol% of I*i*Pr gradually released hydrogen gas in 4 min and the product cyclosiloxane $(Ph_2SiO)_4$ can be isolated in high yield. It appeared that the hydrogen release rate is noticeably slowed down by the increase of the amount of water. For example, the hydrolysis of Ph_2SiH_2 with three equivalents of water was complete in 12 min under the same conditions. There is no reaction observed in the absence of the NHC (entry 6) (Scheme 4).

Table 1 Optimization of the reaction conditions for the hydrolytic oxidation of Ph_2SiH_2

Entry	Loading of I*i*Pr (%)	Time (min)	**Ph$_2$-D$_4$** yield (%)
1	2.5	2	91
2	1.5	2.5	90
3	1.0	2.5	90
4	0.5	2.5	92
5	0.1	4	92
6	0	120	0

Conditions: Ph_2SiH_2 (5 mmol), 1 mL of 5.0 M H_2O in CH_3CN, isolated yield.

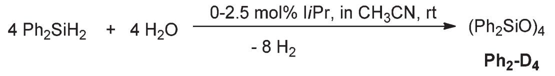


$$2\,R_3SiH + H_2O \xrightarrow[-\,H_2]{2.5\text{ mol\% }I\textit{i}Pr\text{, in }CH_3CN} R_3SiOSiR_3$$

R = Et: 3 h, 90%; R = Ph: 1 h, 98%; R = OEt: 2 h, 88%; R_3 =$PhMe_2$: 1 h, 95%

Scheme 2 Results for the NHC-catalyzed hydrolytic oxidation of tertiary silanes.

Under the optimized conditions with 0.1 mol% of I*i*Pr as the catalyst in acetonitrile, the hydrolytic oxidation of various dihydrosilanes has been studied. The results are summarized in Table 3. The hydrolytic oxidations of Et_2SiH_2 and $(tBu)_2SiH_2$ are much slower than that of phenyl-substituted hydrosilanes at room temperature. The two reactions should be performed at 40 °C for 8 h (entries 7 and 8). In contrast, the hydrolytic reactions of the diaryl-substituted hydrosilanes were complete in several minutes at room temperature to yield the single

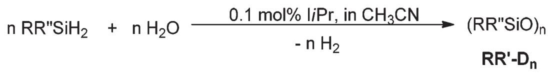


$$4\,Ph_2SiH_2 + 4\,H_2O \xrightarrow[-\,8\,H_2]{0\text{-}2.5\text{ mol\% }I\textit{i}Pr\text{, in }CH_3CN\text{, rt}} \underset{\mathbf{Ph_2\text{-}D_4}}{(Ph_2SiO)_4}$$

Scheme 3 NHC-catalyzed hydrolytic oxidation of Ph_2SiH_2.

Table 2 Results for the hydrolytic oxidation of dihydrosilanes in CH_3CN

Entry	Hydrosilane	*T* (°C)	Time (min)	Product	Yield (%)
1	Ph_2SiH_2	20	5	**D$_4$**	91
2	$PhMeSiH_2$	20	6	**D$_{3-4}$**	92
3	$Ph(CH_2CHCH_2)SiH_2$	20	16	**D$_{3-4}$**	85
4	$Ph(PhCH_2CH)SiH_2$	20	12	**D$_{3-4}$**	88
5	Ph(2-OMePh)SiH_2	20	7	**D$_4$**	92
6	Ph(4-C_2H_3Ph)SiH_2	20	7	**D$_4$**	90
7	tBu_2SiH_2	40	480	**D$_2$**	83
8	Et_2SiH_2	40	480	**D$_{3-5}$**	83



$$n\,RR''SiH_2 + n\,H_2O \xrightarrow[-\,n\,H_2]{0.1\text{ mol\% }I\textit{i}Pr\text{, in }CH_3CN} \underset{\mathbf{RR'\text{-}D_n}}{(RR''SiO)_n}$$

Scheme 4 Hydrolytic oxidation of dihydrosilanes in CH_3CN.

Table 3 Results for the hydrolytic oxidation of dihydrosilanes under solvent-free conditions

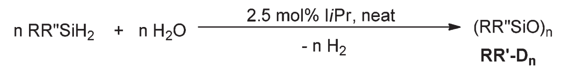
Entry	Hydrosilane	T (°C)	Time (h)	Product	Yield (%)
1	Ph_2SiH_2	90	10	$\mathbf{D_4}$	90
2	$PhMeSiH_2$	60	10	$\mathbf{D_{3-4}}$	98
3	$Ph(CH_2CHCH_2)SiH_2$	60	8	$\mathbf{D_{3-4}}$	95
4	$Ph(PhCH_2CH)SiH_2$	60	5	$\mathbf{D_{3-4}}$	88
5	$Ph(o\text{-}OMePh)SiH_2$	60	12	$\mathbf{D_4}$	95
6	$Ph(p\text{-}C_2H_3Ph)SiH_2$	90	10	$\mathbf{D_4}$	90
7	$t\text{-}Bu_2SiH_2$	60	5	$\mathbf{D_2}$	83
8	Et_2SiH_2	60	6	$\mathbf{D_{3-5}}$	83

Conditions: IiPr (0.041 mmol), hydrosilane (1.6 mmol), H_2O (16 mmol), isolated yield.

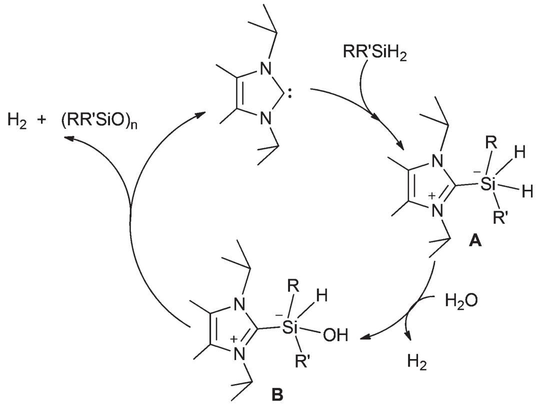
cyclic tetramer D_4 in high yields (entries 1, 5 and 6), indicating that the Lewis acidity of the silicon center has significant effects on the reaction rate. The steric factors of the substituents on the silicon atom have pronounced effects on the ratios of different sizes of cyclosiloxanes (D_3–D_5). The hydrolytic reaction of $(t\mathrm{Bu})_2SiH_2$ yielded the dimer $[(t\mathrm{Bu})_2SiO]_2$ (entry 7) as the only product while a mixture containing D_3–D_5 (entry 8) was obtained in the hydrolytic reaction of Et_2SiH_2, and mixtures of D_3 and D_4 (entries 2–4) were obtained in the hydrolysis of the phenyl–alkenyl-substituted $Ph(CH_2{=}CH)SiH_2$, phenyl–allyl-substituted $Ph(CH_2CH{=}CH_2)SiH_2$ and $PhMeSiH_2$. The mixtures containing the different cyclosiloxanes have been characterized by GC-MS spectroscopy, which indicated that the tetramer D_4 is the major product in all of these cases (for the D_n ratios of the product, see the Experimental section in the ESI†). These results demonstrated that the hydrolytic reaction is viable for the typical alkyl, phenyl, alkenyl and allyl-substituted hydrosilanes. No partial hydrolytic products and polymeric materials were observed in these reactions (Scheme 5).

The hydrolytic oxidation of the dihydrosilanes was also studied under solvent-free conditions. The hydrolysis of Ph_2SiH_2 with 0.1, 1.0 and 2.5 mol% of loadings of IiPr at different temperatures was investigated for the optimization of the reaction conditions. Almost no conversions were obsevered at room temperature, heating the mixture of the 10/1 molar ratio of water/silane with 2.5 mol% of IiPr at 90 °C for 11 h, however, resulted in the formation of the cyclosiloxane $\mathbf{D_4}$ in *ca.* 90% yield; less loading of IiPr (1.0 mol%) led to a low yield (34%). It is noted that the increase of the amount of water accelerated the reaction to some extent but not significantly, indicating that the hydrolysis reaction under solvent-free conditions can be conducted without the strict control of the amount of water. The reaction can be furnished in *ca.* 10 h with the molar ratios of water to a dihydrosilane ranging from 5 to 20. The results for the hydrolytic oxidation of different secondary hydrosilanes are summarized in Table 3. All of the hydrosilanes listed in Table 3 were converted to the corresponding cyclosiloxanes (83–98%) in high yields at elevated temperatures for 5–12 h. The substituents on the silicon atom have no noticeable effects on the reaction rate. This observation is in contrast to that for the hydrolytic reactions of the hydrosilanes in acetonitrile, in which the hydrolytic oxidation of phenyl-substituted hydrosilanes is much faster at ambient temperature than that of the alkyl-substituted Et_2SiH_2. This indicated that acetonitrile played significant roles in the activation of phenyl-substituted hydrosilanes.

The mechanism for the hydrolytic oxidation of hydrosilanes catalyzed by the NHC is yet to be investigated. It might be similar to the dehydrogenative coupling of hydrosilanes with alcohols.[9] However, the activation of a hydrosilane by an NHC to from the corresponding hypervalent silicon hydride might also be possible.[8] The significant solvent effects observed in acetonitrile indicated that the catalytic reaction might involve polarized intermediates.[10] Furthermore, the Lewis acidity of silicon centers also shows effects on the reaction rate significantly in acetonitrile. Based on the solvent and substituent effects observed in acetonitrile, the proposed mechanism for the hydrolytic oxidation is given in Scheme 6. The activation of a dihydrosilane by a Lewis basic NHC yielded the NHC-silane adduct **A** featuring the significant zwitterionic character.[8] This activation process could significantly increase the hydride character of the hydrogen atom on the silicon center. The intermediate **A** reacted with a water molecule to yield intermediate **B**, a hypervalent silanol, with the elimination of hydrogen. Intermediate **B** then underwent either intra or intermolecular reaction to from the cyclosiloxane with the elimination of hydrogen gas. Under solvent-free conditions, the same mechanism may be operative, the high loading (2.5%) of the NHC required in this case compared to that in acetonitrile may be due to the stabilization effects of the polar solvent on the zwitterionic intermediates **A** and **B**.



Scheme 5 Hydrolytic oxidation of dihydrosilanes under solvent-free conditions.



Scheme 6 Proposed mechanism for the NHC-catalyzed hydrolytic oxidation of dihydrosilanes.

Summary and conclusions

In summary, we have developed the first efficient and selective organocatalyst for the hydrolytic oxidation of various dihydrosilanes with water for the clean formation of cyclosiloxanes. The catalytic process in acetonitrile for phenyl-substituted hydrosilanes is very fast and produces cyclosiloxanes in several minutes. The reaction can also be furnished under solvent-free conditions to yield cyclosiloxanes at elevated temperatures with a relative low catalyst loading. In all of these reactions, partial hydrolytic products and polymeric siloxanes were not observed. This catalytic system represents one of the highly efficient and selective catalysts for the hydrolytic oxidation of hydrosilanes. This catalytic process is safe and practical without using any hazardous materials, and thus potentially useful for the routine synthesis of cyclosiloxanes. The studies of this catalytic system for the hydrolytic oxidation of trihydrosilanes are currently in progress in our laboratory.

Experimental

Materials and methods

CH_3CN was dried over P_2O_5 and distilled prior to use. Commercial hydrosilanes were purchased from Alfa Aesar and purified by distillation. The N-heterocyclic carbene 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (IiPr) was prepared according to the literature.[11] The other hydrosilanes used in this work were prepared according to the literature[12] or by modified procedures. Elemental analysis was carried out on an Elemental Vario EL analyzer. The ^{1}H, ^{13}C and ^{29}Si spectra were recorded on a Bruker Mercury Plus 400 NMR spectrometer. Chemical shifts are referenced against external Me_4Si (^{1}H, ^{13}C).

General procedure for hydrolytic oxidation in CH_3CN

In a glove box, to a Schlenk tube were added IiPr (0.1%, 0.9 mg, 0.005 mmol) and a hydrosilane (5 mmol). The tube was removed from the glove box and was placed in an oil bath at a specified temperature for a specific time. To this mixture was added 1 mL of CH_3CN containing water (5.0 M of H_2O in CH_3CN) by syringe. In most cases, vigorous evolution of H_2 was noted. The reaction was monitored by thin layer chromatography (TLC). After the reaction was complete, the solvent was removed under vacuum and the product was purified by flash column chromatography on neutral Al_2O_3 using *n*-hexane/ethyl acetate (10 : 1) as an eluent or was washed with *n*-hexane.

General procedure for hydrolytic oxidation under solvent-free conditions

A Schlenk tube was charged with IiPr (2.5%, 0.0074 g, 0.041 mmol) and a hydrosilane (1.6 mmol). The Schlenk tube was placed in an oil bath at a specified temperature and H_2O (16 mmol) was added to the solution by syringe. The mixture was heated to 60 or 90 °C for a specific time. In most cases, vigorous evolution of H_2 was noted. The reaction was monitored by TLC. After the reaction was complete, the product was purified by flash column chromatography on neutral Al_2O_3 using *n*-hexane/ethyl acetate (10 : 1) as an eluent or was washed with *n*-hexane.

Reactions in CH_3CN and spectroscopic data for the Si–O coupling products

$Et_3SiOSiEt_3$.[13] 3 h at room temperature, colorless oil, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, J = 8.0 Hz, 18H, CH_2CH_3), 0.52 (q, J = 8.0 Hz, 12H, CH_2CH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 6.95 (CH_2CH_3), 6.58 (CH_2CH_3); ^{29}Si NMR (79 MHz, $CDCl_3$): δ 78.8 (s).

$Ph_3SiOSiPh_3$.[14] 1 h at room temperature, white solid, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.49 (m, 12H, C_6H_5), 7.42–7.38 (m, 6H, C_6H_5), 7.31–7.27 (m, 12H, C_6H_5); ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 135.5, 135.2, 129.8, 127.7 (C_6H_5); ^{29}Si NMR (79 MHz, $CDCl_3$): δ −18.6 (s).

$(EtO)_3SiOSi(OEt)_3$.[13] 2 h at room temperature, colourless oil, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.64 (q, J = 7.1 Hz, 12H, CH_2CH_3), 1.20 (t, J = 7.1 Hz, 18H, CH_2CH_3); ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 57.3 (CH_2CH_3), 18.0 (CH_2CH_3); ^{29}Si NMR (79 MHz, $CDCl_3$): δ 8.87 (s).

$PhMe_2SiOSiPhMe_2$.[14] 1 h at room temperature, colorless oil, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62–7.60 (m, 4H, *o*-C_6H_5), 7.43–7.38 (m, 6H, m, *p*-C_6H_5), 0.40 (s, 12H, Me_2); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 140.0, 133.2, 129.4, 127.9, 1.01 (Me_2); ^{29}Si NMR (79 MHz, $CDCl_3$): δ 1.17 (s).

Hydrolysis of diphenylsilane (D_4).[15] 5 min at room temperature, white solid, 91% yield. ^{1}H NMR (400 MHz, C_6D_6): δ 7.71 (d, J = 8 Hz, 16H, C_6H_5), 7.11 (t, J = 8.0 Hz, 8H, *p*-C_6H_5), 7.03 (t, J = 8 Hz, 16H, *m*-C_6H_5); ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 134.5, 134.5, 130.1, 127.7; ^{29}Si NMR (79 MHz, C_6D_6): δ −42.82 (s).

Hydrolysis of di(*tert*)butylsilane ($^{tBu}D_2$). 12 h at 40 °C, white solid, 83% yield. ^{1}H NMR (400 MHz, C_6D_6): δ 1.05 (s, 36H, $C(CH_3)_3$); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 27.3 (*t*Bu), 19.8 (*t*Bu); ^{29}Si NMR (79 MHz, $CDCl_3$): δ −7.19 (s); MS (EI): *m*/*z* 176.1 $[^{tBu}D_2/2 + H_2O]^+$.

Hydrolysis of *o*-methoxy-phenylphenylsilane ($^{OMe}D_4$). 6 min at room temperature, white solid, 92% yield. ^{1}H NMR (400 MHz, C_6D_6): δ 7.92–7.89 (m, 2H), 7.83–7.81 (m, 2H), 7.57–7.54 (m, 4H), 7.50–7.46 (m, 2H), 7.42–7.32 (m, 5H), 7.29–7.27 (m, 2H), 7.25–7.04 (m, 11H), 6.77–6.52 (m, 6H), 6.28–6.22 (m, 2H), 3.37 (s, 3H), 3.30 (s, 3H), 2.98 (s, 3H), 2.84 (s, 3 H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 139.0, 136.9, 134.6, 134.5, 134.3, 133.9, 130.1, 127.7, 125.4, 114.6, 53.9 (O*Me*); ^{29}Si NMR (79 MHz, C_6D_6): δ −42.82 (s); MS (ESI): *m*/*z* 930.2736 $[^{OMe}D_4 + H_2O]^+$.

Hydrolysis of *p*-vinyl-phenylphenylsilane ($^{p\text{-vinyl}}D_4$). 7 min at room temperature, white solid, 90% yield. ^{1}H NMR (400 MHz, C_6D_6): δ 7.80–7.77 (m, 8H), 7.69–7.65 (m, 8H), 7.13–7.07 (m, 20H), 6.49 (dd, J = 12 Hz, 4H, $CHCH_2$), 5.57 (d, J = 12 Hz, 4H, $CHCH_2$), 5.05 (d, J = 12 Hz, 4H, $CHCH_2$); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 139.0, 136.9, 134.6, 134.5, 134.3, 133.9, 130.1, 127.7, 125.4 ($CHCH_2$), 114.6 ($CHCH_2$); ^{29}Si NMR

(79 MHz, $CDCl_3$): δ −42.9 (s); MS (ESI): *m*/*z* 914.2942 $[^{p\text{-viny}}D_4 + H_2O]^+$.

Hydrolysis of diethylsilane.[16] 12 h at 40 °C, colorless oil, 83% yield. A mixture containing $^{Et}D_3$, $^{Et}D_4$ and $^{Et}D_5$ was obtained, and the ratio of $^{Et}D_3/^{Et}D_4/^{Et}D_5$ = 22/67/11 was estimated by GC-MS. ^1H NMR (400 MHz, C_6D_6): δ 1.10–1.06 (t, *J* = 8 Hz, CH_2CH_3), 0.66–0.64 (q, *J* = 8 Hz, CH_2CH_3). GC-MS: *m*/*z* 481.2 $[D_5 - C_2H_5]^+$, 379.0 $[D_4 - C_2H_5]^+$, 277.0 $[D_3 - C_2H_5]^+$.

Hydrolysis of vinylphenylsilane.[17] 12 min at room temperature, colorless oil, 88% yield. A mixture containing $^{viny}D_3$ and $^{viny}D_4$ was obtained, and the ratio of $^{viny}D_3$ and $^{viny}D_4$ = 5/95 was estimated by GC-MS. ^1H NMR (400 MHz, C_6D_6): δ 7.93–7.62, 7.25–7.02 (C_6H_5), 6.39–5.75 (C_2H_3). MS (EI): *m*/*z* 714.0 $[^{viny}D_5 - C_2H_3]^+$, 565.1 $[^{viny}D_4 - C_2H_3]^+$.

Hydrolysis of allylphenylsilane. 16 min at room temperature. Colorless oil. 85% yield. A mixture containing $^{ally}D_3$ and $^{ally}D_4$ was obtained, and the ratio of $^{ally}D_3$ and $^{ally}D_4$ = 12/88 was estimated by GC-MS. ^1H NMR (400 MHz, C_6D_6): δ 7.90–7.47, 7.29–6.98 (m, C_6H_5), 6.09–5.55 ($CH_2CH{=}CH_2$), 5.15–4.64 ($CH_2CH{=}CH_2$), 2.09–1.69 ($CH_2CH{=}CH_2$). MS (EI): *m*/*z* 649.2 $[^{allyl}D_4]^+$, 607.2 $[^{ally}D_4 - C_3H_5]^+$, 571.2 $[^{ally}D_4 - C_6H_5]^+$, 549.1 $[^{ally}D_4 - C_6H_5 - C_3H_5 + H_2O]^+$, 487.1 $[^{allyl}D_3]^+$, 447.1 $[^{ally}D_3 - C_3H_5]^+$, 409.0 $[^{ally}D_3 - C_6H_5]^+$.

Hydrolysis of methylphenylsilane.[18] 6 min at room temperature, colorless oil, 92% yield. A mixture containing $^{CH_3}D_3$ and $^{CH_3}D_4$ was obtained, and the ratio of $^{CH_3}D_3$ and $^{CH_3}D_4$ = 3/97 was estimated by GC-MS. ^1H NMR (400 MHz, C_6D_6): δ 7.84–7.49, 7.27–7.04 (m, C_6H_5), 0.56–0.26 (*Me*). MS (EI): *m*/*z* 529.2 $[^{CH_3}D_4 - CH_3]^+$, 451.1 $[^{CH_3}D_4 - C_6H_5 - CH_3]^+$, 393.2 $[^{CH_3}D_3 - CH_3]^+$, 315.1 $[^{CH_3}D_3 - C_6H_5 - CH_3]^+$.

Reactions under solvent-free conditions and spectroscopic data for the Si–O coupling products

Data are given in the ESI.†

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