Large-Scale Preparation and Labelling Reactions of Deuterated Silanes

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Abstract

A catalytic synthesis of the deuterated silanes $SiEt_3D$, $SiMe_2PhD$ and $SiPh_2D_2$, is reported that allows their facile generation in a 3-4 gram scale, utilizing D_2 (0.5 bar) as the hydrogen isotope source and low catalyst loadings (0.01 mol %). The catalyst precursor is the rhodium (III) complex **1**, that contains a (η^5-C_5Me_5)Rh cation stabilised by coordination to a cyclometallated phoshine $PMeXyl_2$ (Xyl = 2,6-$C_6H_3Me_2$). The same complex is also an active catalyst for the hydrosilylation of the C=O and C≡N bonds of various ketones, aldehydes and α,β-unsaturated nitriles. Hence, combination of these two properties permits development of a simple and proficient one-flask, two-step procedure, for the deuterosilylation of these substrates.

Introduction

The growing demand for deuterium- and tritium-labelled compounds stimulates the search for fast, selective, catalytic methods that allow efficient isotopic incorporation.[1] In general, ^{2}H- and ^{3}H-labelled molecules can be prepared by the same basic procedures. In addition to H/D (or H/T) exchange at carbon centres,[2,3] a convenient labelling practice is reduction of C-X multiple bonds (X = C, N, O) with a hydride

source such as a metal hydride derived from boron, aluminium or tin.[2a,4,5] However, use of these reagents, while common, encounters substantial limitations by the chemistry required (particularly for T-labelling) and by the generation of considerable amounts of waste products.

Hydrosilanes, $SiR_{4-n}H_n$ (n = 1-3), are an extraordinarily important class of reagents for chemical synthesis.[6-12] They are air and moisture stable, and are viewed as environmentally friendly reductants, therefore representing suitable alternatives to the more toxic tin derivatives. Metal catalysed hydrosilylation is a very important industrial and laboratory method,[7-10] widely employed in chemical synthesis (Figure 1) for the reduction of C-X (X = C, N, O) multiple bonds. Furthermore, hydrosilanes can also be utilized for the catalytic reduction of carbon-halogen bonds, including unreactive C-F bonds.[11,12]

Deuterated and tritiated commonly used silanes, like for instance $SiEt_3D$ and $SiEt_3T$, or $SiPh_2D_2$ and $SiPh_2T_2$, would therefore offer significant advantages in the solution of chemical and biochemical problems with the use of hydrogen isotopes. Thus, catalytic deutero- and tritio-silylations will reduce C-O and C-N multiple bonds placing the label at carbon, while simultaneously protecting the resulting alcohol or amine moieties, allowing further multistep synthesis or the direct introduction of a second D or T label. Despite this great potential, deuterated and tritiated silanes have been hardly exploited as isotopic labelling reagents. Most probably, this is due to the scarcity of information on catalytic H/D (or H/T) exchanges at silicon centres,[13-15] which leaves reduction of the silicon-halogen bond of halosilanes with $NaBD_4$, $LiAlD_4$, or a similar deuteride agent, as the more commonly used synthesis of deuterated silanes.[2a,16] For tritium, catalytic H/T exchange at carbon[2d,e,3] is preferred over the use of $LiBT_4$, $NaBT_4$ and LiT and

related reagents.[4,5] Indeed, the high potential of tritiated silanes such as $SiEt_3T$ and $SiPh_2T_2$ was advanced by Saljoughian in 2002,[17] but almost ten years later it does not seem to have been accomplished, most likely because of unsolved problems in the preparation of these tritiating reagents[4,5] (see for example reference 5 for difficulties in the preparation of $SiEt_3T$).

We have recently communicated a very efficient, rhodium-catalysed procedure for the synthesis of deuterated and tritiated silanes.[18a,b] Subsequently, the catalytic properties of this system to effect with great efficacy the deutero- and tritio-silylation of a variety of ketones and aldehydes, using $SiEt_3H$ under subatmospheric pressure of D_2 or T_2, have been exploited.[18c] In this contribution we provide details for the synthesis in a several-gram scale of deuterated silanes catalysed by complex **1** (Figure 2), using $SiEt_3D$, $SiMe_2PhD$ and $SiPh_2D_2$ as representative examples. It is most probable that the method can also be applied to the large scale synthesis of corresponding tritiated silanes with high specific activity. Nevertheless, the lack of facilities in our laboratories to achieve such a goal has limited our work to the preparation of $SiEt_3T$ and tritiated complex **1**, in both cases with low specific activity.[18] In view of the efficacy of our method, microwave enhancement[1b,19] of the labelling procedure has not been considered.

Results and Discussion

Catalytic Synthesis of $SiEt_3D$, $SiMe_2PhD$ and $SiPh_2D_2$.

Figure 2 contains a general representation of the synthesis of deuterosilanes catalysed by compound **1**. As already noted,[18a] this catalytic procedure is based on the following considerations: (a) there is no observable reaction between **1** and H_2 or $SiEt_3H$, but exposure of solutions of **1** to D_2 yields $\mathbf{1(D_{11})^+}$, as a consequence of fast

exchange involving all sp^3-hybridised C-H bonds of the phosphine xylyl groups; (b) treatment of $\mathbf{1(D_{11})^+}$ with an excess of $SiEt_3H$ exchanges the label and affords $SiEt_3D$. We have taken profit of this reactivity to effect the deuteration of some common hydrosilane reagents, namely $SiEt_3H$, $SiMe_2PhH$ and $SiPh_2H_2$ in a large scale (3-4 g). In all probability, this synthesis can be scaled-up further and can also be applied to other tertiary or secondary silanes, and even to primary silanes.[18a] As a general precaution, water must be thoroughly excluded, for compound **1** catalyses also with high efficiency the production of H_2 from H_2O and hydrosilanes.[20]

Using $SiEt_3H$ as a representative example, 4.2 mg of compound **1** ($3.1x10^{-3}$ mmol) were dissolved in 5 mL of $SiEt_3H$ (31.3 mmol; catalyst concentration 0.01 mol %) in a *ca.* 220 mL flask and stirred at 50 ºC, under 0.5 bar of D_2, for a total time of 16h. Although the H/D exchange is fast at 20 ºC in CH_2Cl_2 solution, heating at 50 ºC permits complete solubilization of the catalyst into the neat silane and hence catalysis performance in the absence of solvent. On the other hand, since an equilibrium between reactants and products in Fig. 2 is established, in order to ensure complete deuteration of the silane (≥99%) in this 5 mL-scale synthesis, the reaction was periodically stopped by cooling at 0 ºC. The flask atmosphere was evacuated by application of vacuum (0.1 bar for *ca*. 20 seconds) and the reaction vessel charged again with 0.5 bar of D_2. This cycle was repeated a total of five times during the global reaction period and the pure $SiEt_3D$ then obtained by trap-to-trap distillation. The same procedure was utilised for the synthesis of $SiMe_2PhD$ and $SiPh_2D_2$. Pure $SiMe_2PhD$ was separated by trap-to-trap distillation too, whereas for $SiPh_2D_2$ a Kugelrohr vacuum distillation apparatus was employed.

The course of the reaction was followed by ^{1}H and $^{29}Si\{^{1}H\}$ NMR spectroscopy and by IR spectroscopy, to monitor the hydrogen isotope exchange. The ^{1}H NMR spectrum of $SiEt_3H$ ($CDCl_3$) exhibits a septet at δ 3.68 ppm that corresponds to the hydrogen atom bonded to silicon. Upon deuteration, this resonance gradually disappears and it is completely absent in the ^{1}H NMR of the final product, which shows instead the corresponding signal in the ^{2}H NMR spectrum. Deuteration of the silane ethyl substituents does not occur. As shown in Fig. 3a, the $^{29}Si\{^{1}H\}$ NMR spectrum of $SiEt_3H$ is a singlet with δ 0.8 ppm, that experiences an isotopic displacement to δ 0.4 ppm ($^{1}J_{Si\text{-}D}$ = 28 Hz) upon deuteration (Fig. 3c). The spectrum of a *ca.* 45:55 mixture of the two isotopologues has been included in Fig. 3b. On the other hand, the IR spectrum of $SiEt_3H$ features a band at *ca.* 2100 cm^{-1} due to ν(Si-H) (Fig. 4) that shifts to about 1530 cm^{-1} in the spectrum of $SiEt_3D$. The relative intensities of these IR bands along the course of the H/D exchange match closely the results obtained from ^{1}H and $^{29}Si\{^{1}H\}$ NMR studies.

Hydro- and Deutero-Silylation of >C=O bonds.

As an extension of previous work from our group in this area,[18b] we have studied the reduction of a common natural product with biological activity, the (R)-camphor molecule, that contains a sterically congested ketone functionality. Reduction of its carbonyl group can give rise to *exo* or *endo* isomers. Entries 3-7 in Table 1 contain the results of this study that encompassed use of $SiEt_3H$, $SiPh_2H_2$, $SiMe_2PhH$, $SiEt_3D$ and $SiMe_2PhD$. For comparative purposes, entries 1 and 2 summarize previous results obtained for acetophenone and $SiEt_3H$ and $SiEt_3D$.[18b] Both $SiEt_3H$ and $SiPh_2H_2$ led to little or no control of diastereoselectivity, although the latter favoured formation of the *exo* product (*ca.* 7:3 ratio of *exo*:*endo*). This selectivity is comparable to that reported

when $RhH(PPh_3)_4$ was used as a catalyst[21a] for this reduction (1.8:1 ratio) but is opposite to catalysis by the iridium cation $[IrH(POCOP)(acetone)]^+$ (POCOP = 2,6-bis(di-*tert*-butylphosphinito)phenyl) that produced an approximate 1:4 ratio of *exo* and *endo* isomers.[21b] Our reaction is less efficient than the latter process, which proceeds quantitatively at 0 ºC.[21b] However, for our system, direct deuterosilylation was achieved by application of the one-flask, two-step procedure described earlier,[18b] that makes use of D_2 as the hydrogen isotope source. Firstly, a dichloromethane solution of catalyst **1** and $SiEt_3H$ (entry 7) or $SiMe_2PhH$ (entry 8) was stirred in the presence of D_2 (0.5 bar) for 2-3 minutes, whereby D-incorporation to $SiEt_3H$ and **1** took place. The gas atmosphere was then replaced by fresh D_2 (0.5 bar) and the process repeated a total of three times, to ensure a D-content in the silane product of ≥99%. Then camphor was added and the mixture stirred at 50 ºC for 24h to yield the isotopically labelled silylborneols in good yields (entries 7 and 8), with diastereoselectivity similar to that observed for the non-labelled product.

In order to analyse competition between the 1,2- and 1,4-addition of the hydrosilane to α,β-unsaturated carbonyl compounds, benzylideneacetone (entries 8-10) and cinnamaldehyde (entries 11-14) were also employed for this study. For the former there was a clear preference for the 1,4-addition with respect to the 1,2- of about 9:1, regardless of the use of $SiEt_3H$ or $SiMe_2PhH$ as the reductant, although the corresponding silyl enols resulted as comparable mixtures of their *Z* and *E* isomers. The more accessible carbonyl group of cinnamaldehyde led to an almost 1:1 ratio of 1,2- and 1,4-addition products, although for the latter reactivity almost only the E isomers of the silyl enols were obtained.

Less reactive carbonyl species like esters and amides were also investigated. Reactions of several tertiary and secondary silanes with esters ethylbenzoate and ethylbutyrate were unsuccessful, even after prolonged heating at 60 ºC. Similarly, hydrosilylation of benzamide and *N*,*N*-dimethylacetamide proved fruitless. Nevertheless, a positive consequence of these results is that selective reduction of the ketone functionality in α-ketoesters and α-ketoamides should be feasible. In accord with expectations, $SiEt_3H$ added chemoselectively to the keto carbonyl group of ethyl pyruvate (entry 16) to give the corresponding silyl ethers. Thus, compound **1** seems to be a good candidate for the selective hydrosilylation of aldehydes and ketones in the presence of the less reactive ester and amide functional groups.

Hydro- and Deutero-Silylation of C-N multiple bonds.

Reaction of N-benzylidene aniline with 2.2 equiv. of $SiEt_3H$ at 50 ºC for 2h, in the presence of 1 mol % concentration of **1**, gave the expected silylamine product in quantitative yield (Table 2, entry 1). Using the procedure described above for direct deuterations, the D-isotopologue was generated also quantitatively. In this case, to ensure full deuterosilylation we employed a non-optimised time of 12h.

Imine hydrosilylation catalysed by **1** is very sensitive to steric hindrance around the C=N bond. Thus, hydrosilylation of the bulkier aldimine *N*-benzyliden-*t*-butylamine (entry 3), and ketimine (*E*)-*N*-(1-phenylethylidene)aniline (entry 4), occurred with low conversion and in the former case with partial formation of the opposite regioselectivity product (entry 3).

Whereas well-known procedures are available for the hydrosilylation of C=X bonds (X = C, N, O),[7-10] hydrosilylation of C≡N bonds remains comparatively unexplored

because the cyano group behaves as inert under common hydrosilylation conditions.[7e,22] Murai and co-workers used $Co_2(CO)_8$ as catalyst for the reduction of nitriles by $SiMe_3H$ to *N*,*N*-disilylamines.[23a] Subsequently, a heterogeneous, Rh-catalysed process for the hydrosilylation of aromatic aldehydes was developed,[23b] and more recently Gutsulyak and Nikonov have reported a very convenient method for the selective mono- and di-silylation of nitriles, by action of a Ru catalyst.[23c]

Whereas acetonitrile (Table 2, entry 2) underwent only partial conversion in the presence of **1** and $SiEt_3H$ (<40%, 50 ºC, 24h), and benzonitrile remained unaltered even under somewhat more forcing conditions (entry 6), α,β-unsaturated nitriles experienced facile hydrosilylation to produce vinylamines protected with two silyl groups (entries 7-9). This observation, that finds scarce literature precedent,[23a,b] allowed isolation of vinyl bis(silylamines) as stable molecules. The parent vinylamines are usually unstable and decompose gradually even at low temperatures.[24] Use of this method permitted also facile D-labelling of the amine resulting from the double deuterosilylation of cinnamonitrile (entry 8 of Table 2 and Figure 5). At variance with previous reports,[23a,b] other possible products of this reaction, like the protected aliphatic amine, or the also protected allylic amine were not observed (Figure 5). Moreover, the double hydrosilylation of cinnamaldehyde by **1** is highly selective and gives exclusively the *E* isomer.

Conclusions

In summary, we have described a large-scale synthesis (3-4 g) of the D-isotopologues of three common and widely used hydrosilanes, namely $SiEt_3D$, $SiMe_2PhD$ and $SiPh_2D_2$. The simplicity of the process and its generality, along with the stability of the catalyst in air and its recyclability, make our system attractive for practical use. Extension of this

procedure to the preparation of the tritium analogues with high specific activity should be feasible too, but it has not been attempted due to our lack of suitable experimental facilities. We have also developed some labelling reactions of the deuterated silanes with their application to the catalytic deuterosilylation of some organic molecules containing C=O, C=N and C≡N bonds.

Experimental

General

All operations were performed under an argon atmosphere using standard Schlenk techniques, employing dry solvents and glassware. HRMS data were obtained using a Jeol JMS-SX 102A mass spectrometer at the Analytical Services of the Universidad de Sevilla (CITIUS). Infrared spectra were recorded on Bruker Vector 22 spectrometer. The NMR instruments used were Bruker DRX-500, DRX-400 and DRX-300 spectrometers. Spectra were referenced to external $SiMe_4$ (δ 0 ppm) using the residual proton solvent peaks as internal standards (^{1}H NMR experiments), or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments). Spectral assignments were made by routine one- and two-dimensional NMR experiments where appropiate. Catalyst **1** was prepared as previously described.[18a] All substrates were purchased from commercial sources and were distilled under vacuum from $CaCl_2$ or $MgSO_4$ before use. Silanes were purchased from commercial sources and used without further purification. $PMeXyl_2$ (Xyl = 2,6-$C_6H_3Me_2$) was prepared from PCl_3, MeMgBr and XylMgBr.[25a] The rhodium dimer and $ZnCp^*_2$ were also obtained by published procedures.[25b,c] $NaBAr_F$ can either be prepared[25d] or obtained from commercial sources.

Synthesis of catalyst 1[18a]

[Figure 6]

Preparation of [(η^5-C_5Me_5)Rh(Cl){PMe(2,6-CH_2(Me)C_6H_3)(2,6-$Me_2C_6H_3$)}] (1-Cl). A solution of $PMe(Xyl)_2$ (131 mg, 0.5 mmol) in 2 mL of THF is added, at -40 ºC, to a solution of $[RhCl(C_2H_4)_2]_2$ (100 mg, 0.25 mmol) in 3 mL of THF. The reaction mixture is stirred for 3 h at this temperature. Then, a solution of $ZnCp_2$* (84 mg, 0.25 mmol) in 1 mL of THF is added and the mixture is stirred for 5 h while allowing the temperature to reach -25 ºC. The solvent is removed under vacuum and the residue extracted with diethyl ether and then evaporated to dryness. The crude is dissolved in 5 mL of CH_2Cl_2 and stirred for 3 h at room temperature. The solvent is removed under vacuum and the crude product washed with pentane to yield complex **1-Cl** as an orange solid in 83% yield. **Anal. Calc.** for $C_{27}H_{35}ClPRh$: C, 61.3; H, 6.7. **Found**: C, 61.2; H, 6.6. ^{1}H, ^{13}C and ^{31}P NMR data can be found in reference 18a.

Synthesis of [(η^5-C_5Me_5)Rh{PMe(2,6-CH_2(Me)C_6H_3)(2,6-$Me_2C_6H_3$)}]$^+BAr_F^-$, (1). To a solid mixture of **1-Cl** (150 mg, 0.28 mmol) and $NaBAr_F$ (252 mg, 0.28 mmol) was added 5 mL of CH_2Cl_2. The reaction mixture was stirred for 10 min at room temperature, after which time the solution was filtered and the solvent evaporated under reduced pressure, to obtain an orange solid (350 mg, 95 %). This complex can be crystallized from a 1:1 mixture of CH_2Cl_2:pentane. **Anal. Calc.** for $C_{59}H_{47}BF_{24}PRh$: C, 52.6; H, 3.5. **Found**: C, 53.0; H, 3.3. ^{1}H, ^{13}C and ^{31}P NMR data can be found in reference 18a.

High-scale synthesis of deuterosilanes

[1-^{2}H]Triethylsilane ($SiEt_3D$). Triethylsilane (5 mL, 31.30 mmol) was added under nitrogen to a pressure vessel (volume *ca*. 220 mL) containing catalyst **1** (4.2 mg, $3.1\cdot10^{-3}$ mmol). The solution was cooled to 0 ºC and nitrogen pumped out. Then the flask was

charged with deuterium (0.5 bar) and the mixture was vigorously stirred at 50 ºC for 16 hours. In order to exchange quantitatively the Si–H bond, the cooling at 0ºC/vacuum (0.1 bar)/D_2 (0.5 bar) process was repeated five times. The solution was transferred to a Young's ampoule and the deuterosilane purified by trap-to-trap distillation to obtain $SiEt_3D$ as a colorless liquid (3.49 g, 96% yield; 99% D incorporation). IR (neat silane): 1530 cm^{-1}. ^1H NMR (500 MHz, C_6D_6, 25 ºC) δ: 0.96 (t, 9 H, $^3J_{HH}$ = 7.9 Hz, $3CH_3$), 0.53 (q, 6 H, $^3J_{HH}$ = 7.9 Hz, $3CH_2$). $^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6) δ: 0.4 (t, $^1J_{SiD}$ = 28 Hz).

[1-^{2}H]Dimethylphenylsilane ($SiMe_2PhD$). The same procedure utilised to deuterate triethylsilane was employed, but using dimethylphenylsilane (5 mL, 32.66 mmol) and catalyst **1** (4.4 mg, $3.2 \cdot 10^{-3}$ mmol). Deuterated dimethylphenylsilane was purified by trap-to-trap distillation and $SiMe_2PhD$ was obtained as a colourless liquid (4.15 g, 93% yield; 99% D incorporation). IR (Neat Silane): 1540 cm^{-1}. ^1H NMR (500 MHz, C_6D_6, 25 ºC) δ: 7.54 (m, 2 H, Ph), 7.28 (m, 3 H, Ph), 0.34 (s, 6 H, $2CH_3$). $^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6) δ: -17.2 (t, $^1J_{SiD}$ = 29 Hz).

[1-$^2H_2$]Diphenylsilane ($SiPh_2D_2$). The same procedure utilised to deuterate triethylsilane was employed, but using diphenylsilane (5 mL, 26.86 mmol) and catalyst **1** (7.3 mg, $5.4 \cdot 10^{-3}$ mmol). Deuterated diphenylsilane was purified by Kugelrohr distillation to obtain $SiPh_2D_2$ as a colourless oil (4.17 g, 84% yield; 99% D incorporation). IR (Nujol): 1550 cm^{-1}. ^1H NMR (500 MHz, C_6D_6, 25 ºC) δ: 7.30 (d, 4 H, $^3J_{HH}$ = 7.8 Hz, *o*-Ph), 6.91 (m, 6 H, *m*,*p*-Ph). $^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6) δ: -33.8 (quintet, $^1J_{SiD}$ = 30 Hz).

Determination of deuterium incorporation. The levels of deuteration exchange were checked by ^1H-NMR, ^{29}Si-NMR and IR spectroscopy. The level of deuteration was monitored by ^1H-NMR spectroscopy. Exchange reactions were considered to be

complete when no integrable ^{1}H signal for the Si–*H* atom could be detected. These results were confirmed by the disappearance of the characteristic signals in the ^{29}Si-NMR and IR spectra. Signals for the hydro- and deuterosilane appear perfectly well resolved in the ^{29}Si NMR spectra due to the isotope effect on the chemical shift (Figure 3). The calculation of the deuterium percentage by ^{29}Si-NMR is totally in accordance with the results obtained from the ^{1}H-NMR analysis. The integration of the bands for ν(Si–H) (*ca.* 2100 cm^{-1}) and ν(Si–D) (*ca.* 1500 cm^{-1}) match up with the results obtained by ^{1}H and ^{29}Si NMR (Figure 4).

General method for the hydrosilylation of C-O and C-N multiple bonds

In a typical experiment, a 2 mL screw-cap glass vial was charged with catalyst **1** (0.7 mg, $0.5x10^{-3}$ mmol), the hydrosilane (1.1 mmol), the organic substrate (0.5 mmol) and CD_2Cl_2 (0.5 mL) in a glovebox. After stirring for 1 hour, the reaction mixture was transferred to a screw-cap NMR tube and the reaction progress checked by ^{1}H-NMR spectroscopy.

General method for the direct deuterosilylation of C-O and C-N multiple bonds.

In a typical experiment, a Young's ampoule was charged with catalyst **1** (0.7 mg, $0.5x10^{-3}$ mmol), triethylsilane (89 μL, 0.55 mmol) and CD_2Cl_2. The solution was cooled to 0 ºC, argon pumped out and replaced by D_2 (0.5 bar). The solution was stirred at room temperature for 10 min, then cooled at 0 ºC, the gas atmosphere pumped out and replace by D_2 (0.5 bar). After repeating this cycle a total of three times, the organic substrate (0.25 mmol) was added and the mixture transferred to a screw-cap NMR tube. The reaction progress was monitored by ^{1}H-NMR spectroscopy.

Characterization of compounds

Hydrosilylation of (*R*)-camphor by hydrosilanes R_nSiH_{4-n} (entries 3-7, table 1). Using the general procedure at 50 ºC, *R*-camphor (0.015 g, 0,1 mmol) was hydrosilylated. Spectroscopic data of the reaction mixture were consistent with previously reported data for these compounds:[26]

^{1}H NMR (500 MHz, CD_2Cl_2):

$SiEt_3H$ (entry 3, table 1; 46 % *endo*, 54 % *exo*): characteristic signals, δ 3.94 (m, 1H, *endo* isomer), 3.57 (dd, $^3J_{HH}$ = 7.9, 3.5 Hz, 1H, *exo* isomer).

$SiPh_2H_2$ (entry 4, table 1; 30 % *endo*, 70 % *exo*): characteristic signals, δ 4.26 (m, 1H, *endo* isomer), 3.85 (dd, $^3J_{HH}$ = 7.8, 3.2 Hz, 1H, *exo* isomer).

$SiMe_2PhH$ (entry 6, table 1; 30 % *endo*, 70 % *exo*): characteristic signals, δ 4.03 (m, 1H, *endo* isomer), 3.65 (dd, $^3J_{HH}$ = 7.5, 3.0 Hz; 1H, *exo* isomer).

Hydrosilylation of benzylideneacetone (entries 8 and 9, table 1). Using the general procedure at 50 ºC, benzylideneacetone (0.015 g, 0,1 mmol) was hydrosilylated. Spectroscopic data of the 1,2- and 1,4-addition products were consistent with previously reported data for these compounds.[27]

^{1}H NMR (400 MHz, CD_2Cl_2):

$SiEt_3H$ (entry 8, table 1): characteristic signals, δ 6.56 (d, $^3J_{HH}$ = 16.0 Hz; =C*H*, 1,2-addition product), 6.27 (dd, $^3J_{HH}$ = 16.0, 6.0 Hz; =C*H*, 1,2-addition product), 4.90 (t, $^3J_{HH}$ = 7.5 Hz, =C*H*, *E*-1,4 addition product), 4.64 (t, $^3J_{HH}$ = 7.0 Hz, =C*H*, *Z*-1,4 addition product), 4.52 (m, C*H*, 1,2 addition product), 3.42 (d, $^3J_{HH}$ = 7.0 Hz, CH_2, *Z*-1,4 addition product), 3.34 (d, $^3J_{HH}$ = 8.0 Hz, CH_2, *E*-1,4 addition product).

$SiMe_2PhH$ (entry 9, table 1): characteristic signals, δ 6.49 (d, $^3J_{HH}$ = 16.0 Hz; =C*H*, 1,2-addition product), 6.25 (dd, $^3J_{HH}$ = 16.0, 6.0 Hz; =C*H*, 1,2-addition product), 4.88 (t, $^3J_{HH}$ = 7.5 Hz, =C*H*, *E*-1,4 addition product), 4.69 (d, $^3J_{HH}$ = 7.0 Hz, =C*H*, *Z*-1,4 addition product), 4.53 (m, C*H*, 1,2 addition product), 3.39 (d, $^3J_{HH}$ = 7.0 Hz, CH_2, *Z*-1,4 addition product), 3.30 (d, $^3J_{HH}$ = 7.5 Hz, CH_2, *E*-1,4 addition product).

Deutero-silylation of benzylideneacetone (entry 10, table 1). Using the general procedure at 25 ºC, benzylideneacetone (0.015 g, 0,1 mmol) was hydrosilylated by [1-^{2}H]-triethylsilane. Spectroscopic data of the non deuterated 1,2-[27a] and 1,4-addition products[27b] were consistent with previously reported data for these compounds.

^{1}H NMR (400 MHz, CD_2Cl_2): characteristic signals, δ 6.53 (d, $^3J_{HH}$ = 16.0 Hz; =C*H*, 1,2-addition product), 6.25 (d, $^3J_{HH}$ = 16.0 Hz; =C*H*, 1,2-addition product), 4.85 (d, $^3J_{HH}$ = 7.5 Hz, =C*H*, *E*-1,4 addition product), 4.61 (d, $^3J_{HH}$ = 7.0 Hz, =C*H*, *Z*-1,4 addition product), 3.36 (bd, $^3J_{HH}$ = 7.0 Hz, CH_2, *Z*-1,4 addition product), 3.29 (bd, $^3J_{HH}$ = 7.5 Hz, CH_2, *E*-1,4 addition product).

Hydrosilylation of cinnamaldehyde (entries 11 and 12, table 1). Using the general procedure at 25 ºC, cinnamaldehyde (13 μL, 0,1 mmol) was hydrosilylated. Spectroscopic data of the 1,2- and *E*-1,4-addition products were consistent with previously reported data for these compounds.[28]

$SiEt_3H$ (entry 11, table 1) ^{1}H NMR (400 MHz, CD_2Cl_2): characteristic signals, δ 6.63 (d, $^3J_{HH}$ = 16.0 Hz; =C*H*, 1,2-addition product), 6.39 (dt, $^3J_{HH}$ = 12.0, 1.2 Hz; =C*H*, *E*-1,4-addition product), 6.33 (dt, $^3J_{HH}$ = 16.0, 5.2 Hz; =C*H*, 1,2-addition product), 5.19 (dt, $^3J_{HH}$ = 12.0, 7.5 Hz; =C*H*, *E*-1,4-addition product), 4.76 (m, =C*H*, *Z*-1,4-addition

product), 4.37 (dd, $^3J_{HH}$ = 5.2, 1.6 Hz; C*H*$_2$, 1,2-addition product), 3.26 (d, $^3J_{HH}$ = 7.5; C*H*$_2$, *E*-1,4-addition product).

SiMe$_2$PhH (entry 12, table 1) ^{1}H NMR (500 MHz, CD_2Cl_2): characteristic signals, δ 6.60 (d, $^3J_{HH}$ = 16.0 Hz; =C*H*, 1,2-addition product), 6.39 (dt, $^3J_{HH}$ = 12.0, 1.2 Hz; =C*H*, *E*-1,4-addition product), 6.32 (dt, $^3J_{HH}$ = 16.0, 5.5 Hz; =C*H*, 1,2-addition product), 5.20 (dt, $^3J_{HH}$ = 12.0, 7.5 Hz; =C*H*, *E*-1,4-addition product), 4.75 (m, =C*H*, *Z*-1,4-addition product), 4.36 (dd, $^3J_{HH}$ = 5.5, 2.0 Hz; C*H*$_2$, 1,2-addition product), 3.20 (d, $^3J_{HH}$ = 7.5; C*H*$_2$, *E*-1,4-addition product).

Deutero-silylation of cinnamaldehyde (entries 13 and 14, table 1). Using the general procedure at 25 ºC, cinnamaldehyde (13 μL, 0,1 mmol) was deuterosilylated Spectroscopic data of the products were consistent with those of the non labeled compounds.

^{1}H NMR (400 MHz, CD_2Cl_2):

SiEt$_3$D (entry 13, table 1): characteristic signals, δ 6.60 (d, $^3J_{HH}$ = 16.0 Hz; =C*H*, 1,2-addition product), 6.39 (dd, $^3J_{HH}$ = 12.0, 1.2 Hz; =C*H*, *E*-1,4-addition product), 6.31 (dd, $^3J_{HH}$ = 16.0, 5.5 Hz; =C*H*, 1,2-addition product), 5.12 (dd, $^3J_{HH}$ = 12.0, 7.5 Hz; =C*H*, *E*-1,4-addition product), 4.70 (m, =C*H*, *Z*-1,4-addition product), 4.32 (bs, C*H*$_2$, 1,2-addition product), 3.21 (bd, $^3J_{HH}$ = 7.5; C*H*$_2$, *E*-1,4-addition product).

SiMe$_2$PhD (entry 14, table 1): characteristic signals, δ 6.60 (d, $^3J_{HH}$ = 16.0 Hz; =C*H*, 1,2-addition product), 6.38 (dd, $^3J_{HH}$ = 12.0, 1.2 Hz; =C*H*, *E*-1,4-addition product), 6.32 (dd, $^3J_{HH}$ = 16.0, 5.5 Hz; =C*H*, 1,2-addition product), 5.19 (dd, $^3J_{HH}$ = 12.0, 7.5 Hz; =C*H*, *E*-1,4-addition product), 4.74 (m, =C*H*, *Z*-1,4-addition product), 4.36 (bs, C*H*$_2$, 1,2-addition product), 3.20 (d, $^3J_{HH}$ = 7.5; C*H*$_2$, *E*-1,4-addition product).

Hydrosilylation of ethyl pyruvate (entry 16, Table 1). Using the general procedure at 50 ºC, ethyl pyruvate (0.012 g, 0,1 mmol) was hydrosilylated by triethylsilane. Spectroscopic data of the reaction mixture were consistent with previously reported data for this compound.[29]

^{1}H NMR (500 MHz, CD_2Cl_2): characteristic signals, δ 4.30 (q, $^3J_{HH}$ = 6.8 Hz, CH_3CH), 4.13 (q, $^3J_{HH}$ = 7.0 Hz, OCH_2CH_3), 1.36 (d, $^3J_{HH}$ = 6.8 Hz, CH_3CH), 1.26 (t, $^3J_{HH}$ = 7.0 Hz, OCH_2CH_3).

Hydrosilylation of N-benzylidene aniline (entry 1, Table 2). Using the general procedure at 50 ºC, N-benzylidene aniline (0.018 g, 0,1 mmol) was hydrosilylated by triethylsilane. Spectroscopic data of the reaction mixture were consistent with previously reported data for this compound.[18a]

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.31 (d, $^3J_{HH}$ = 4.3 Hz, Ph), 7.22 (m, Ph), 7.17 (t, $^3J_{HH}$ = 7.9 Hz, Ph), 6.99 (d, $^3J_{HH}$ = 8.1 Hz, Ph), 6.83 (t, $^3J_{HH}$ = 7.3 Hz, Ph), 4.63 (s, CH_2N), 1.04 (t, $^3J_{HH}$ = 7.8 Hz, $SiCH_2CH_3$), 0.89 (q, $^3J_{HH}$ = 7.8 Hz, $SiCH_2CH_3$).

Deutero-silylation of cinnamaldehyde (entry 2, table 2). Using the general procedure at 25 ºC, N-benzylidene aniline (18 mg, 0,1 mmol) was deuterosilylated by [1-^{2}H]-triethylsilane. Spectroscopic data of the deuterosilylated product were consistent with those of the non labeled compound. ^{1}H-NMR (500 MHz, CD_2Cl_2): δ 7.28 (d, $^3J_{HH}$ = 4.3 Hz, Ph), 7.20 (m, Ph), 7.15 (t, $^3J_{HH}$ = 7.8 Hz, Ph), 6.96 (d, $^3J_{HH}$ = 8.1 Hz, Ph), 6.80 (t, $^3J_{HH}$ = 7.5 Hz, Ph), 4.58 (br. s, CHDN), 1.02 (t, $^3J_{HH}$ = 7.8 Hz), 0.86 (q, $^3J_{HH}$ = 7.8 Hz, 6H).

Hydrosilylation of *N*-benzyliden-*t*-butylamine (entry 3, Table 2). Using the general procedure at 50 ºC, *N*-benzyliden-*t*-butylamine (18 μL, 0,1 mmol) was hydrosilylated

by triethylsilane. ^{1}H NMR (400 MHz, CD_2Cl_2): characteristic signals, δ 4.14 (s, N-C*H*-Si, C-Si isomer), 3.75 (s, C*H*$_2$-NSi, C-N isomer), 1.22 (s, ^{t}Bu, C-Si isomer), 1.19 (s, ^{t}Bu, C-N isomer).

Hydrosilylation of (*E*)-*N*-(1-phenylethylidene)aniline (entry 4, Table 2). Using the general procedure at 50 ºC, ketimine (*E*)-*N*-(1-phenylethylidene)aniline (0.020 mg, 0,1 mmol) was hydrosilylated by triethylsilane. Spectroscopic data of the reaction mixture were consistent with previously reported data for this compound.[30] ^{1}H NMR (300 MHz, CD_2Cl_2): characteristic, δ 6.7 (d, $^{3}J_{HH}$ = 8.2 Hz, N-Ph(*orto*)), 4.52 (q, $^{3}J_{HH}$ = 6.7 Hz, CH_3C*H*-N), 1.62 (d, $^{3}J_{HH}$ = 6.7 Hz, C*H*$_3$CH-N).

Hydrosilylation of (*E*)-*N*-(1-phenylethylidene)aniline (entry 5, Table 2). Using the general procedure at 50 ºC, acetonitrile (5 μL, 0,1 mmol) was hydrosilylated by triethylsilane. ^{1}H NMR (500 MHz, CD_2Cl_2): characteristic signals, δ 2.88 (q, $^{3}J_{HH}$ = 7.4 Hz, CH_3C*H*$_2$N), 0.84 (t, $^{3}J_{HH}$ = 7.4 Hz, C*H*$_3$CH$_2$N).

Hydrosilylation of cinnamonitrile (entry 7, Table 2). Using the general procedure at 50 ºC, cinnamonitrile (0.013 mg, 0,1 mmol) was hydrosilylated by triethylsilane. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.29 (t, $^{3}J_{HH}$ = 7.4 Hz, Ph), 7.19 (m, Ph), 6.05 (d, $^{3}J_{HH}$ = 13.4 Hz, HC=C*H*-N), 5.22 (m, *H*C=CH-N), 3.30 (d, $^{3}J_{HH}$ = 12.9 Hz, C*H*$_2$), 0.96 (t, $^{3}J_{HH}$ = 7.9 Hz, SiCH$_2$C*H*$_3$), 0.67 (q, $^{3}J_{HH}$ = 7.9 Hz, SiC*H*$_2$CH$_3$). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 142.2 (*C*(quat), 135.3 (HC=*C*H-N), 128.6 (*orto*-*C*), 126.0 (*meta*-*C*), 120.4 (*para*-*C*), 37.0 (H*C*=CH-N), 8.3 (Si*C*H$_2$CH$_3$), 5.2 (SiCH$_2$*C*H$_3$).

Deutero-silylation of cinnamonitrile (entry 8, table 2). Using the general procedure at 50 ºC, cinnamonitrile (13 mg, 0,1 mmol) was deuterosilylated by [1-^{2}H]-triethylsilane. Spectroscopic data of the deuterosilylated product were consistent with those of the non

labeled compound. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.30 (t, $^{3}J_{HH}$ = 7.4 Hz, Ph), 7.21 (m, Ph), 5.22 (d, $^{3}J_{HH}$ = 6.7 Hz, *H*C=CH-N), 3.31 (d, $^{3}J_{HH}$ = 6.7 Hz, C*H*$_2$), 0.98 (t, $^{3}J_{HH}$ = 7.9 Hz, SiCH$_2$C*H*$_3$), 0.69 (q, $^{3}J_{HH}$ = 7.9 Hz, SiC*H*$_2$CH$_3$).

Hydrosilylation of ciclohex-1-ene-1-carbonitrle (entry 9, Table 2). Using the general procedure at 80 ºC, ciclohex-1-ene-1-carbonitrle (0.011 mg, 0,1 mmol) was hydrosilylated by triethylsilane. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.64 (s, C=C*H*-N), 2.19 (m, *orto*-C*H*$_2$), 2.05 (m, *orto*-C*H*$_2$), 1.55 (m, *meta,para*-C*H*$_2$), 4.63 (s, C*H*$_2$N), 0.97 (t, $^{3}J_{HH}$ = 7.6 Hz, SiC*H*$_2$CH$_3$), 0.64 (q, $^{3}J_{HH}$ = 7.6 Hz, SiCH$_2$C*H*$_3$). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 136.7 (*C*(quat), 125.4 (C=*C*H-N), 34.2 (*orto-C*), 28.8 (*orto-C*), 28.2 (*meta-C*), 27.6 (*meta-C*), 27.3 (*para-C*), 8.0 (Si*C*H$_2$CH$_3$), 6.2 (SiCH$_2$*C*H$_3$).

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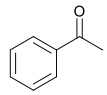
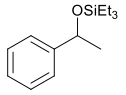
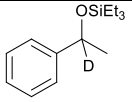
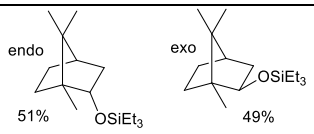
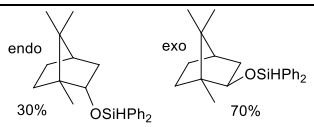
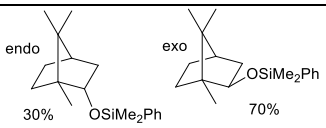
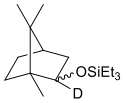
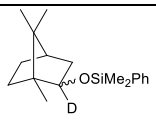
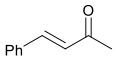
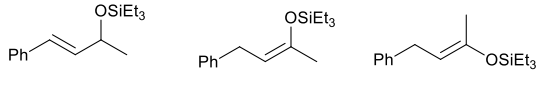
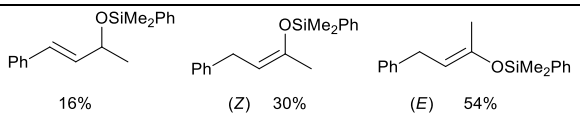
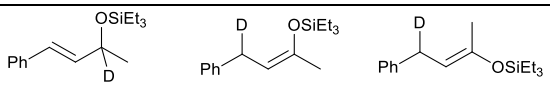
Tables

Table 1. Hydro- and deuterosilylation of C-O double bonds

Entry	Substrate	S/C	Silane	T (ºC)	t (h)	%Conv	Product
1		1000	$SiEt_3H$	25	1	99	
2		200	$DSiEt_3$	25	5	99	
3		200	$SiEt_3H$	50	24	50	
4		200	$SiPh_2H_2$	50	24	70	
5		200	$SiMe_2PhH$	50	40	99	
6		200	$SiEt_3D$	50	40	59	
7		200	$SiMe_2PhD$	50	40	70	
8		200	$SiEt_3H$	25	1	99	
9		200	$SiMe_2PhH$	25	1	99	
10		200	$SiEt_3D$	25	1	99	

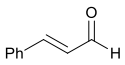
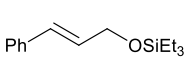
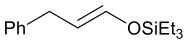
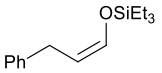
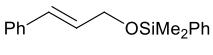
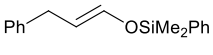
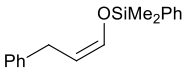
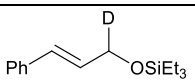
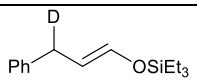
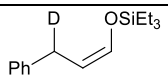
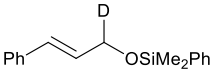
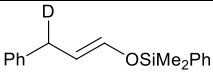
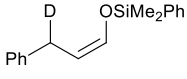
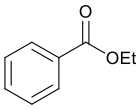
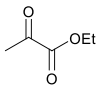
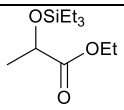
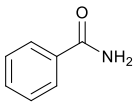
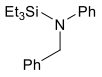
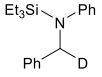
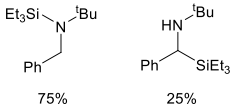
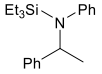
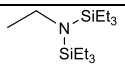
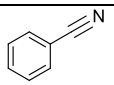
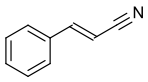
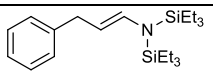
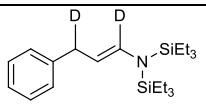
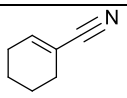
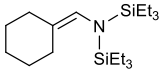
11		200	$SiEt_3H$	25	1	99	 48%	 (*E*) 52%	 (*Z*) < 0,5%
12		200	$SiMe_2PhH$	25	2	99	 50%	 (*E*) 50%	 (*Z*) < 0,5%
13		200	$SiEt_3D$	25	5	99	 48%	 (*E*) 50%	 (*Z*) 2%
14		200	$SiMe_2PhD$	25	5	99	 57%	 (*E*) 34%	 (*Z*) 9%
15		200	$SiEt_3H$	60	48	0	Only minor unidentified products		
16		200	$SiEt_3H$	50	24	99	 < 10% dialkyl ether		
17		100	$SiEt_3H$	60	48	0	No reaction		

Table 2. Hydro- and deuterosilylation of C-N multiple bonds

Entry	Substrate	S/C	Silane	T (°C)	t (h)	%Conv	Product
1		100	$SiEt_3H$	50	2	100	
2		100	$SiEt_3D$	50	12	100	
3		100	$SiEt_3H$	50	24	15	 75% 25%
4		100	$SiEt_3H$	50	24	40	
5	CH_3CN	100	$SiEt_3H$	50	24	38	
6		100	$SiEt_3H$	60	48	0	No reaction
7		100	$SiEt_3H$	50	6	100	
8		100	$SiEt_3D$	50	36	100	
9		100	$SiEt_3H$	80[b]	7	95	

Conditions: Silane (2,2 eq for imines and 3 eq for nitriles), solvent (CD_2Cl_2, 0.5 mL).[b]Solvent $ClCH_2CH_2Cl$.