Electronic Supplementary Material (ESI) for ChemComm.


Supporting Information for

# Synthesis of Hydrosilanes via Lewis-Base-Catalyzed Reduction of Alkoxysilane by $NaBH_4$

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## Experimental details and compound characterization data

### General considerations

All manipulations were performed under a nitrogen atmosphere using Schlenk techniques or a glove box. Hexane, $C_6H_6$, toluene, THF and $CH_2Cl_2$ were purified by a solvent purification system (MBraun SPS-800 or Glass Contour Ultimate Solvent System). $C_6D_6$ was dried over sodium benzophenone ketyl and distilled. $Me_2PhSiO$*i*Pr (**1c-*i*Pr**)[1], $Me_2PhSiOPh$ (**1c-Ph**)[2], $MePh_2SiOMe$ (**1d**)[1], $Me_2$(*t*Bu)SiOMe (**1g**)[3] and *i*$Pr_3SiOMe$ (**1h**)[4] were prepared according to the literature procedures. $NaBH_4$ granular (99.99% trace metals basis) was purchased from Sigma-Aldrich Co. LLC. and used without purification. All other reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. $^1H$, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra ($^1H$, 600 MHz; $^{11}B$, 193 MHz; $^{13}C$, 151 MHz; $^{29}Si$, 119 MHz) were recorded using a Bruker AVANCE 600 spectrometer. Chemical shifts are reported in $\delta$ (ppm) and are referenced to the residual solvent signals for $^1H$ and $^{13}C$, and to boron trifluoride diethyl ether complex (0.0 ppm) for $^{11}B$ and to trimethyl(phenyl)silane (–4.7 ppm) for $^{29}Si$.

### Synthesis of $Me_2PhSiO$*t*Bu (1-*t*Bu)

To a hexane solution (10 mL) of *t*BuOH (0.87 g, 12 mmol), was added $Me_2PhSiCl$ (2.0 g, 12 mmol) and $NEt_3$ (1.2 g, 12 mmol). The reaction mixture was stirred at room temperature for 24 h. The solution was filtered, and the resulting solid was washed with hexane (20 mL). The filtrate and washings were combined. Fractional distillation was performed to give $Me_2PhSiO$*t*Bu (**1-*t*Bu**) (0.79 g, 3.8 mmol, 32%).

### Catalytic reduction of alkoxysilane with $BH_3$·thf

A typical procedure (Table 1, entry 11) is as follows. A vial was charged with a THF solution (0.3 mL) of $Me_2$(*n*Oct)SiOMe (**1a**) (41 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and mesitylene (6.0 mg, 0.050 mmol) as an internal standard. To the solution was added 1 M $BH_3$·thf THF solution (0.20 mL, 0.20 mmol) at room temperature, and then the solution was stirred for 24 h. The reaction mixture was analyzed by $^1H$ NMR to determine the conversion of **1a** (0.18 mmol, 91%) and the NMR yield of $Me_2$(*n*Oct)SiH (**2a**) (0.18 mmol, 91%).

### Catalytic reduction of alkoxysilane with $NaBH_4$

#### Determination of NMR yield

Typical procedure 1 (Table 2, entry 8) is as follows. A micro tube (diameter: φ8, length: 50 mm, volume: 1 mL) was charged with a $C_6D_6$ suspension (0.05 mL) of $NaBH_4$ (7.6 mg, 0.20 mmol),

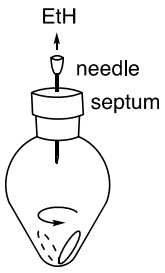
which is pre-grinded in a motar, *n*Oct$_4$NBr (5.6 mg, 0.010 mmol), Me$_2$(*n*Oct)SiOMe (**1a**) (41 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and mesitylene (6.0 mg, 0.050 mmol) as an internal standard. After EtBr (22 mg, 0.20 mmol) was added, the solution was stirred at room temperature for 24 h (a magnetic stirrer bar: φ1.5 × 8 mm, rotating speed: 1,500 rpm). The resulting solution was analyzed by $^1$H NMR to determine the conversion of **1a** (0.19 mmol, 93%) and the NMR yield of Me$_2$(*n*Oct)SiH (**2a**) (0.19 mmol, 93%).

**Determination of isolated yield**

Typical procedure 2 (Table 2, entry 8) is as follows. A 3 mL conical vial was charged with a $C_6H_6$ suspension (0.5 mL) of $NaBH_4$ (76 mg, 2.0 mmol), which is pre-grinded in a motar, (*n*Oct)$_4$NBr (56 mg, 0.10 mmol), Me$_2$(*n*Oct)SiOMe (**1a**) (410 mg, 2.0 mmol) and HMPA (18 mg, 0.10 mmol). EtBr (220 mg, 2.0 mmol) was added at room temperature, and then the solution was stirred at room temperature for 24 h (a magnetic stirrer bar: φ1.5 × 8 mm, rotating speed: 1,500 rpm). The solution was diluted with hexane (20 mL) and filtered through a silica gel pad (eluent: hexane (100 mL)). The volatiles were removed *in vacuo* to give Me$_2$(*n*Oct)SiH (**2a**) as a colourless liquid (319 mg, 1.9 mmol, 93%).

**Gram scale synthesis of Ph$_2$SiH$_2$ (2k)**

A 10 mL pear shaped flask was charged with a $C_6H_6$ suspension (2.5 mL) of $NaBH_4$ (0.76 g, 20 mmol), which is pre-grinded in a motar, *n*Oct$_4$NBr (280 mg, 0.50 mmol), Ph$_2$Si(OMe)$_2$ (**1k**) (2.4 g, 10 mmol) and HMPA (360 mg, 2.0 mmol) and sealed with a septum equipped with a needle. EtBr (2.2 g, 20 mmol) was added at room temperature, and then the solution was stirred at room temperature for 24 h (a magnetic stirrer bar of φ3 × 10 mm, 1,500 rpm. The solution was diluted with hexane (20 mL) and filtered through a silica gel pad (eluent: hexane (100 mL)). The volatiles were removed *in vacuo* to give Ph$_2$SiH$_2$ (**2k**) as a colorless liquid (1.3 g, 7.3 mmol, 73%).

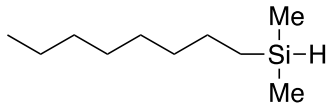



**Compound characterization data**

The products in Table 1 and Table 2, Me$_2$(*n*Oct)SiH (**2a**)[5], Et$_3$SiH (**2b**)[5], Me$_2$PhSiH (**2c**)[5], Me$_2$(C$_6$F$_5$)SiH (**2f**)[6], MeCySiH$_2$ (**3i**)[7], MePhSiH(OMe) (**2j**)[5], MePhSiH$_2$ (**3j**)[5], Ph$_2$SiH(OMe) (**2k**)[5], Ph$_2$SiH$_2$ (**3k**)[5], Me{Cl(CH$_2$)$_3$}SiH$_2$ (**3m**)[8], Me{CF$_3$(CH$_2$)$_2$}SiH$_2$ (**3n**)[9], *n*C$_{12}$H$_{25}$SiH$_3$ (**4p**)[10], CySiH$_3$ (**4q**)[7], and PhSiH$_3$ (**4r**)[5] were identified by comparing their $^1$H NMR data with those previously reported. MeCySiH(OMe) (**2i**) and Cyp$_2$SiH(OMe) (**2l**) were identified by comparing their $^1$H NMR data with those alternatively synthesized by following the reported procedure.[11]

$MePh_2SiH$ (**2d**), $Ph_3SiH$ (**2e**), $Me_2(tBu)SiH$ (**2g**), $iPr_3SiH$ (**2h**) and $n$HexSi$H_3$ (**2o**) were identified by comparing their $^1$H NMR data with commercial sources.

dimethyl(octyl)silane (**2a**)




*Reduction with $BH_3$·thf*

The general procedure was followed with $Me_2$(*n*Oct)SiOMe (**1a**) (41 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and 1 M $BH_3$·thf THF solution (0.20 mL, 0.20 mmol). The resulting solution was analyzed by $^1$H NMR to determine the conversion of **1a** (0.18 mmol, 91%) and the NMR yield of $Me_2$(*n*Oct)SiH (**2a**) (0.18 mmol, 91%).

*Reduction with $NaBH_4$*

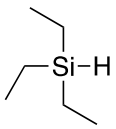
The general procedure 2 was followed with $NaBH_4$ (76 mg, 2.0 mmol), *n*Oct$_4$NBr (56 mg, 0.10 mmol), $Me_2$(*n*Oct)SiOMe (**1a**) (410 mg, 2.0 mmol), HMPA (18 mg, 0.10 mmol) and EtBr (220 mg, 2.0 mmol). The residue was filtered with a silica gel pad (eluent: hexane (100 mL)) to provide **2a** as a colorless liquid in 93% (319 mg).

$^1$H NMR ($C_6D_6$, RT, ppm): δ 0.06 (d, 6H, $^3J_{HH}$ = 3.6 Hz, Si*Me*$_2$), 0.57 (m 2H, SiC*H*$_2$(CH$_2$)$_6$CH$_3$), 0.92 (t, 3H, $^3J_{HH}$ = 7.0 Hz, Si(CH$_2$)$_7$C*H*$_3$), 1.22-1.42 (m, 12H, SiCH$_2$(C*H*$_2$)$_6$CH$_3$)), 4.15 (sep, 1H, $^3J_{HH}$ = 3.6 Hz, Si*H*).

$^{13}$C NMR ($C_6D_6$, RT, ppm): δ –4.3 (s, Si*Me*), 14.3 (s, Si*Oct*), 14.4 (s, Si*Oct*), 23.1 (s, Si*Oct*), 24.8 (s, Si*Oct*), 29.7 (s, Si*Oct*), 29.7 (s, Si*Oct*), 32.3 (s, Si*Oct*), 33.6 (s, Si*Oct*).

$^{29}$Si NMR ($C_6D_6$, RT, ppm): δ –12.8 (s).

triethylsilane (**2b**)




*Reduction with $BH_3$·thf*

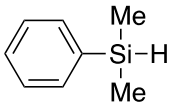
The general procedure was followed with $Et_3SiOMe$ (**1b**) (23 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and 1 M $BH_3$·thf THF solution (0.20 mL, 0.20 mmol). The resulting solution was analyzed by $^1$H NMR to determine the conversion of **1b** (0.16 mmol, 80%) and the NMR yield of $Et_3SiH$ (**2b**) (0.15 mmol, 75%).

*Reduction with $NaBH_4$*

The general procedure 1 was followed with $NaBH_4$ (7.6 mg, 0.20 mmol), *n*$Oct_4NBr$ (5.6 mg, 0.010 mmol), $Et_3SiOMe$ (**1b**) (23 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and EtBr (22 mg, 0.20 mmol). The resulting solution was analyzed by $^1$H NMR to determine the conversion of **1b** (0.20 mmol, 96%) and the NMR yield of $Et_3SiH$ (**2b**) (0.20 mmol, 96%).

$^1$H NMR ($C_6D_6$, RT, ppm): δ 0.53 (dq, 6H, $^3J_{HH}$ = 3.2 Hz, $^3J_{HH}$ = 7.9 Hz, SiC*H*$_2$CH$_3$), 0.90 (s, 9H, Si*t-Bu*), 3.88 (sep, 1H, $^3J_{HH}$ = 3.2 Hz, Si*H*).

dimethyl(phenyl)silane (**2c**)




*Reduction with $BH_3$·thf*

The general procedure was followed with $Me_2PhSiOMe$ (**1c**) (33 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and 1 M $BH_3$·thf THF solution (0.20 mL, 0.20 mmol). The resulting solution was analyzed by $^1$H NMR to determine the conversion of **1c** (0.18 mmol, 91%) and the NMR yield of $Me_2PhSiH$ (**2c**) (0.18 mmol, 88%).

*Reduction with $NaBH_4$*

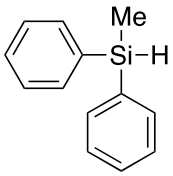
The residue was filtered with a silica gel pad (eluent: pentane (100 mL)) to provide **2c** as a colorless liquid in 83% (226 mg).

$^1$H NMR ($C_6D_6$, RT, ppm): δ 0.21 (d, 6H, $^3J_{HH}$ = 3.8 Hz, Si*Me*$_2$), 4.63 (sept, 1H, $^3J_{HH}$ = 3.8 Hz, Si*H*), 7.19 (m, 3H, *m*, *p*-CH), 7.47 (m, 2H, *o*-C*H*).

$^{13}$C NMR ($C_6D_6$, RT, ppm): δ –3.8 (s, Si*Me*), 128.3 (s, Si*Ph*), 129.5 (s, Si*Ph*), 134.3 (s, Si*Ph*), 137.4 (s, Si*Ph*).

$^{29}$Si NMR ($C_6D_6$, RT, ppm): δ –16.7 (s).

methyldiphenylsilane (**2d**)



*Reduction with $BH_3$·thf*

The general procedure was followed with $MePh_2SiOMe$ (**1d**) (46 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and 1 M $BH_3$·thf THF solution (0.20 mL, 0.20 mmol). The resulting solution was analyzed by $^1$H NMR to determine the conversion of **1d** (0.15 mmol, 78%) and the NMR yield of $MePh_2SiH$ (**2d**) (0.15 mmol, 78%).

*Reduction with $NaBH_4$*

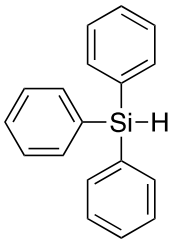
The general procedure 1 was followed with $NaBH_4$ (7.6 mg, 0.2 mmol), *n*$Oct_4NBr$ (5.6 mg, 0.010 mmol), $MePh_2SiOMe$ (**1d**) (46 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and EtBr (22 mg, 0.2 mmol). The resulting solution was analyzed by $^1$H NMR to determine the conversion of **1d** (0.18 mmol, 92%) and the NMR yield of $MePh_2SiH$ (**2d**) (0.18 mmol, 92%).

$^1$H NMR ($C_6D_6$, RT, ppm): δ 0.46 (d, 3H, $^3J_{HH}$ = 3.8 Hz, Si*Me*), 5.14 (q, 2H, $^3J_{HH}$ = 3.8 Hz, Si$H_2$), 7.12-7.20 (m, 3H, *m*,*p*-CH), 7.50 (m, 2H, *o*-C*H*).

$^{13}$C NMR ($C_6D_6$, RT, ppm): δ –5.0 (s, Si*Me*), 128.3 (s, Si*Ph*), 129.6 (s, Si*Ph*), 135.2 (s, Si*Ph*), 135.5 (s, Si*Ph*).

$^{29}$Si NMR ($C_6D_6$, RT, ppm): δ –17.1 (s).

triphenylsilane (**2e**)



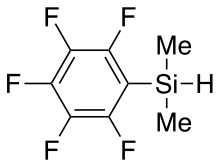

The general procedure 2 was followed with $CH_2Cl_2$ (0.5 mL), $NaBH_4$ (76 mg, 2.0 mmol), *n*$Oct_4NBr$ (56 mg, 0.10 mmol), $Ph_3SiOMe$ (**1e**) (580 mg, 2.0 mmol), HMPA (72 mg, 0.40 mmol) and EtBr (220 mg, 2.0 mmol). The residue was filtered with a silica gel pad (eluent: toluene (100 mL)) to provide the title compound **2e** as a white solid in 91% (474 mg).

$^1$H NMR ($C_6D_6$, RT, ppm): δ 5.71 (s, 1H, Si*H*), 7.09-7.19 (m, 9H, *m*,*p*-CH), 7.59 (m, 6H, *o*-C*H*).

$^{13}$C NMR ($C_6D_6$, RT, ppm): δ 128.4 (s, Si*Ph*), 130.0 (s, Si*Ph*), 133.7 (s, Si*Ph*), 136.2 (s, Si*Ph*).

$^{29}$Si NMR ($C_6D_6$, RT, ppm): δ –17.5 (s).

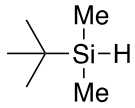
dimethyl(pentafluorophenyl)silane (**2f**)



The general procedure 1 was followed with $NaBH_4$ (7.6 mg, 0.20 mmol), *n*$Oct_4NBr$ (5.6 mg, 0.010 mmol), $Me_2(C_6F_5)SiOEt$ (**1f-Et**) (54 mg, 0.20 mmol), HMPA (7.2 mg, 0.040 mmol) and EtBr (22 mg, 0.20 mmol). The resulting solution was analyzed by $^1$H NMR to determine the conversion of **1f-Et** (0.19 mmol, 95%) and the NMR yield of $Me_2(C_6F_5)SiH$ (**2f**) (0.14 mmol, 69%).

$^1$H NMR ($C_6D_6$, RT, ppm): δ 0.15 (dt, 6H, $^3J_{HH}$ = 3.9 Hz, $^5J_{CF}$ = 0.8 Hz, Si*Me*$_2$), 4.57 (ep, 1H, $^3J_{HH}$ = 3.9 Hz, Si*H*).

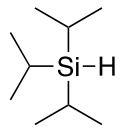
*tert*-butyldimethylsilane (**2g**)



The general procedure 1 was followed with $NaBH_4$ (15.2 mg, 0.40 mmol), *n*$Oct_4NBr$ (5.6 mg, 0.010 mmol), $Me_2$(*t*Bu)SiOMe (**1g**) (29 mg, 0.20 mmol), HMPA (36 mg, 0.20 mmol) and EtBr (44 mg, 0.40 mmol). The resulting solution was analyzed by $^1$H NMR to determine the conversion of **1g** (0.17 mmol, 85%) and the NMR yield of $Me_2$(*t*Bu)SiH (**2g**) (0.13 mmol, 64%).

$^1$H NMR ($C_6D_6$, RT, ppm): δ –0.02 (d, 6H, $^3J_{HH}$ = 3.7 Hz, Si*Me*$_2$), 0.96 (t, 9H, $^3J_{HH}$ = 7.9 Hz, $SiCH_2CH_3$), 3.87 (sep, 1H, $^3J_{HH}$ = 3.7 Hz, Si*H*).

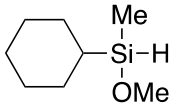
triisopropylsilane (**2h**)



The general procedure 1 was followed with $NaBH_4$ (15.2 mg, 0.40 mmol), *n*$Oct_4NBr$ (5.6 mg, 0.010 mmol), $^i$$Pr_3SiOMe$ (**1h**) (38 mg, 0.20 mmol), HMPA (36 mg, 0.20 mmol) and EtBr (44 mg, 0.40 mmol). The resulting solution was analyzed by $^1$H NMR to determine the conversion of **1h** (0.12 mmol, 58%) and the NMR yield of $^i$$Pr_3SiH$ (**2h**) (0.064 mmol, 32%).

$^1$H NMR ($C_6D_6$, RT, ppm): δ 0.95-1.05 (m, 3H, $^3J_{HH}$ = 3.7 Hz, $SiCH(CH_3)_2$), 1.07 (d, 18H, $^3J_{HH}$ = 6.5 Hz, $SiCH(CH_3)_2$), 3.59 (q, 1H, $^3J_{HH}$ = 2.2 Hz, Si*H*).

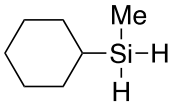
cyclohexyl(methoxy)methylsilane (**2i**)



The general procedure 1 was followed with $NaBH_4$ (15.2 mg, 0.40 mmol), *n*$Oct_4NBr$ (5.6 mg, 0.010 mmol), $MeCySi(OMe)_2$ (**1i**) (38 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and EtBr (44 mg, 0.40 mmol). The resulting solution was analyzed by $^1$H NMR to determine the conversion of **1i** (0.16 mmol, 81%) and the NMR yield of MeCySiH(OMe) (**2i**) (0.010 mmol, 5%) and $MeCySiH_2$ (**3i**) (0.15 mmol, 76%).

$^1$H NMR ($C_6D_6$, RT, ppm): δ 0.10 (d, 3H, $^3J_{HH}$ = 2.9 Hz, Si*Me*), 0.76 (m, 1H, SiC*H*$(CH_2)_5$), 1.14-1.30 (m, 6H, SiCH(C*H*$_2)_5$), 1.62-1.82 (m, 6H, SiCH(C*H*$_2)_5$), 3.33 (s, 3H, O*Me*) 4.61 (qd, 1H, $^3J_{HH}$ = 3.0, 2.9 Hz, Si*H*).

cyclohexyl(methy)lsilane (**3i**)



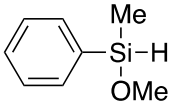
The general procedure 2 was followed with $NaBH_4$ (152 mg, 4.0 mmol), *n*$Oct_4NBr$ (56 mg, 0.10 mmol), $MeCySi(OMe)_2$ (**1i**) (380 mg, 2.0 mmol), HMPA (18 mg, 0.10 mmol) and EtBr (440 mg, 4.0 mmol). The residue was filtered with a silica gel pad (eluent: cold pentane (100 mL)) to provide **3i** as a colorless liquid in 73% (187 mg).

$^1$H NMR ($C_6D_6$, RT, ppm): δ 0.00 (t, 3H, $^3J_{HH}$ = 4.2 Hz, Si*Me*), 0.69 (m, 1H, SiC*H*$(CH_2)_5$), 1.07-1.24 (m, 6H, SiCH(C*H*$_2)_5$), 1.57-1.73 (m, 6H, SiCH(C*H*$_2)_5$), 3.82 (qd, 2H, $^3J_{HH}$ = 2.9, 4.2 Hz, Si*H*).

$^{13}$C NMR ($C_6D_6$, RT, ppm): δ 14.2 (s, Si*Me*), 22.0 (s, Si*Cy*), 27.0 (s, Si*Cy*), 27.9 (s, Si*Cy*), 29.1 (2, Si*Cy*).

$^{29}$Si NMR ($C_6D_6$, RT, ppm): δ –27.1 (s).

methoxy(methyl)phenylsilane (**2j**)

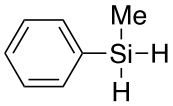


The general procedure 1 was followed with $NaBH_4$ (15.2 mg, 0.40 mmol), *n*$Oct_4NBr$ (5.6 mg, 0.010 mmol), $MePhSi(OMe)_2$ (**1j**) (36 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and EtBr

(44 mg, 0.40 mmol). The resulting solution was analyzed by $^1$H NMR to determine the conversion of **1j** (0.15 mmol, 75%) and the NMR yield of MePhSiH(OMe) (**2j**) (0.010 mmol, 5%) and $MePhSiH_2$ (**3j**) (0.14 mmol, 71%).

$^1$H NMR ($C_6D_6$, RT, ppm): δ 0.32 (t, 3H, $^3J_{HH}$ = 2.9 Hz, Si*Me*)), 3.30 (s, 3H, O*Me*), 5.18 (q, 1H, $^3J_{HH}$ = 2.9 Hz, Si*H*), 7.20 (m, 3H, *m, p*-C*H*), 7.56 (m, 2H, *o*-C*H*).

methyl(phenyl)silane (**3j**)



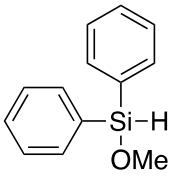

The general procedure 2 was followed with $NaBH_4$ (152 mg, 4.0 mmol), *n*$Oct_4NBr$ (56 mg, 0.10 mmol), $MePhSi(OMe)_2$ (**1j**) (360 mg, 2.0 mmol), HMPA (18 mg, 0.10 mmol) and EtBr (440 mg, 4.0 mmol). The residue was filtered with a silica gel pad (eluent: cold pentane (100 mL)) to provide **3j** as a colorless liquid in 66% (161 mg).

$^1$H NMR ($C_6D_6$, RT, ppm): δ 0.18 (t, 3H, $^3J_{HH}$ = 4.3 Hz, Si*Me*), 4.49 (q, 2H, $^3J_{HH}$ = 4.3 Hz, Si$H_2$), 7.11-7.19 (m, 3H, *m, p*-C*H*), 7.45 (m, 2H, *o*-C*H*).

$^{13}$C NMR ($C_6D_6$, RT, ppm): δ –7.7 (s, Si*Me*), 128.3 (s, Si*Ph*), 129.8 (s, Si*Ph*), 133.4 (s, Si*Ph*), 135.1 (s, Si*Ph*).

$^{29}$Si NMR ($C_6D_6$, RT, ppm): δ –35.5 (s).

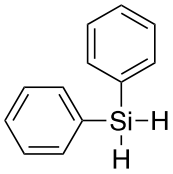
methoxydiphenylsilane (**2k**)




The general procedure 1 was followed with $NaBH_4$ (15.2 mg, 0.40 mmol), *n*$Oct_4NBr$ (5.6 mg, 0.010 mmol), $Ph_2Si(OMe)_2$ (**1k**) (49 mg, 0.20 mmol), HMPA (7.2 mg, 0.040 mmol) and EtBr (44 mg, 0.40 mmol). The resulting solution was analyzed by $^1$H NMR to determine the conversion of **1k** (0.15 mmol, 73%) and the NMR yield of $Ph_2SiH(OMe)$ (**2k**) (0.0060 mmol, 3%) and $Ph_2SiH_2$ (**3k**) (0.14 mmol, 72%).

$^1$H NMR ($C_6D_6$, RT, ppm): δ 3.40 (s, 3H, O*Me*), 5.61 (s, 1H, Si*H*), 7.09-7.19 (m, 6H, *m, p*-C*H*), 7.65 (m, 4H, *o*-C*H*).

diphenylsilane (**3k**)



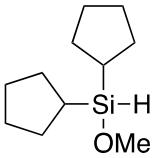
The general procedure 2 was followed with $NaBH_4$ (152 mg, 4.0 mmol), *n*$Oct_4NBr$ (56 mg, 0.10 mmol), $Ph_2Si(OMe)_2$ (**1k**) (490 mg, 2.0 mmol), HMPA (18 mg, 0.10 mmol) and EtBr (440 mg, 4.0 mmol). The residue was filtered with a silica gel pad (eluent: cold pentane (100 mL)) to **3k** as a colorless liquid in 72% (265 mg).

$^1$H NMR ($C_6D_6$, RT, ppm): δ 5.08 (s, 2H, Si*H*), 7.09-7.19 (m, 6H, *m*, *p*-C*H*), 7.51 (m, 4H, *o*-C*H*).

$^{13}$C NMR ($C_6D_6$, RT, ppm): δ 128.4 (s, Si*Ph*), 130.1 (s, Si*Ph*), 131.7 (s, Si*Ph*), 136.0 (s, Si*Ph*).

$^{29}$Si NMR ($C_6D_6$, RT, ppm): δ –33.2 (s).

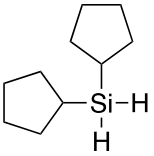
dicyclopentyl(methoxy)silane (**2l**)



The general procedure 1 was followed with $NaBH_4$ (15.2 mg, 0.40 mmol), *n*$Oct_4NBr$ (5.6 mg, 0.010 mmol), $Cyp_2Si(OMe)_2$ (**1l**) (38 mg, 0.20 mmol), HMPA (36 mg, 0.20 mmol) and EtBr (44 mg, 0.40 mmol). The resulting solution was analyzed by $^1$H NMR to determine the conversion of **1l** (0.17 mmol, 86%) and the NMR yield of $Cyp_2SiH(OMe)$ (**2l**) (0.010 mmol, 5%) and $Cyp_2SiH_2$ (**3l**) (0.15 mmol, 77%).

$^1$H NMR ($C_6D_6$, RT, ppm): δ 1.04 (m, 1H, SiC*H*$(CH_2)_4$), 1.36 (m, 2H, SiCH(C*H*$_2)_4$), 1.46 (m, 2H, SiCH(C*H*$_2)_4$), 1.58 (m, 2H, SiCH(C*H*$_2)_4$), 1.80 (m, 2H, SiCH(C*H*$_2)_4$), 3.43 (s, 3H, O*Me*), 4.57 (t, 2H, $^3J_{HH}$ = 2.3 Hz, Si*H*).

dicyclopentylsilane (**3l**)



The general procedure 2 was followed with $NaBH_4$ (152 mg, 4.0 mmol), *n*$Oct_4NBr$ (56 mg, 0.10 mmol), $Cyp_2Si(OMe)_2$ (**1l**) (460 mg, 2.0 mmol), HMPA (360 mg, 2.0 mmol) and EtBr (440 mg,

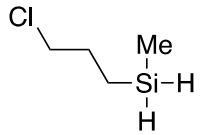
4.0 mmol). The residue was filtered with a silica gel pad (eluent: cold pentane (100 mL)) to provide **3l** as a colorless liquid in 72% (242 mg).

$^{1}$H NMR ($C_6D_6$, RT, ppm): δ 0.99 (m, 1H, SiC*H*$(CH_2)_4$), 1.36 (m, 2H, SiCH(C*H*$_2)_4$), 1.46 (m, 2H, SiCH(C*H*$_2)_4$), 1.58 (m, 2H, SiCH(C*H*$_2)_4$), 1.80 (m, 2H, SiCH(C*H*$_2)_4$), 3.92 (t, 2H, $^{3}J_{HH}$ = 3.2 Hz, Si*H*).

$^{13}$C NMR ($C_6D_6$, RT, ppm): δ 20.8 (s, Si*Cyp*), 27.2 (s, Si*Cyp*), 30.4 (s, Si*Cyp*).

$^{29}$Si NMR ($C_6D_6$, RT, ppm): δ –16.7 (s).

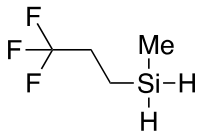
3-chloropropylmethylsilane (**3m**)




The general procedure 1 was followed with $NaBH_4$ (15.2 mg, 0.40 mmol), *n*$Oct_4NBr$ (5.6 mg, 0.010 mmol), Me{$Cl(CH_2)_3$}$Si(OMe)_2$ (**1m**) (37 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and EtBr (44 mg, 0.40 mmol). The resulting solution was analyzed by $^{1}$H NMR to determine the conversion of **1m** (0.16 mmol, 78%) and the NMR yield of Me{$Cl(CH_2)_3$}SiH (**3m**) (0.14 mmol, 70%).

$^{1}$H NMR ($C_6D_6$, RT, ppm): δ –0.11 (t, 3H, $^{3}J_{HH}$ = 4.2 Hz, Si*Me*$_2$), 0.40 (m, 2H, SiC*H*$_2$$CH_2CH_2Cl$), 1.46 (m, 2H, $SiCH_2$C*H*$_2$$CH_2Cl$), 3.05 (t, 2H, $^{3}J_{HH}$ = 6.8 Hz, $SiCH_2CH_2$C*H*$_2$Cl), 3.77 (sept, 2H, $^{3}J_{HH}$ = 4.2 Hz, Si*H*$_2$).

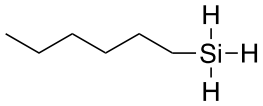
3,3,3-trifluoropropylmethylsilane (**3n**)




The general procedure 1 was followed with $NaBH_4$ (15.2 mg, 0.40 mmol), *n*$Oct_4NBr$ (5.6 mg, 0.010 mmol), Me{$F_3C(CH_2)_2$}$Si(OMe)_2$ (**1n**) (37 mg, 0.20 mmol), HMPA (7.2 mg, 0.040 mmol) and EtBr (44 mg, 0.40 mmol). The resulting solution was analyzed by $^{1}$H NMR to determine the conversion of **1n** (0.16 mmol, 78%) and the NMR yield of Me{$F_3C(CH_2)_2$}SiH (**3n**) (0.13 mmol, 64%).

$^{1}$H NMR ($C_6D_6$, RT, ppm): δ –0.21 (t, 3H, $^{3}J_{HH}$ = 4.1 Hz, Si*Me*$_2$), 0.52 (m, 2H, SiC*H*$_2$$CH_2CF_3$), 1.66 (m, 2H, $SiCH_2$C*H*$_2$$CF_3$), 3.63 (sept, 2H, $^{3}J_{HH}$ = 4.1 Hz, Si*H*$_2$).

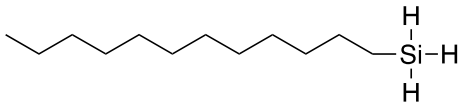
hexylsilane (**4o**)



The general procedure 1 was followed with $NaBH_4$ (22.8 mg, 0.60 mmol), *n*$Oct_4NBr$ (5.6 mg, 0.010 mmol), *n*HexSiOMe (**1o**) (23 mg, 0.20 mmol), HMPA (7.2 mg, 0.040 mmol) and EtBr (65 mg, 6.0 mmol). The resulting solution was analyzed by $^1$H NMR to determine the NMR yield of *n*$HexSiH_3$ (**4o**) (0.13 mmol, 67%).

$^1$H NMR ($C_6D_6$, RT, ppm): δ 0.51-0.56 (m, 2H, $SiCH_2(CH_2)_4CH_3$), 0.86 (t, 3H, $^3J_{HH}$ = 7.2 Hz, $SiCH_2(CH_2)_4CH_3$), 1.12-1.35 (m, 8H, $SiCH_2(CH_2)_4CH_3$), 3.61 (t, 3H, $^3J_{HH}$ = 3.9 Hz, $SiH_3$).

dodecylsilane (**4p**)



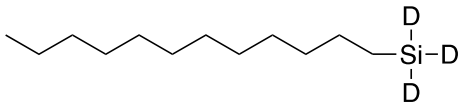
The general procedure 2 was followed with $NaBH_4$ (228 mg, 6.0 mmol), *n*$Oct_4NBr$ (56 mg, 0.10 mmol), *n*$C_{12}H_{25}Si(OMe)_3$ (**1p**) (580 mg, 2.0 mmol), HMPA (72 mg, 0.40 mmol) and EtBr (650 mg, 6.0 mmol). The residue was filtered with a silica gel pad (eluent: cold pentane (100 mL)) to provide **4p** as a colorless liquid in 76% (305 mg).

$^1$H NMR ($C_6D_6$, RT, ppm): δ 0.55 (m, 2H, $SiCH_2(CH_2)_{10}CH_3$), 0.92 (t, 3H, $^3J_{HH}$ = 7.1, $SiCH_2(CH_2)_{10}CH_3$), 1.18-1.38 (m, 20H, $SiCH_2(CH_2)_{10}CH_3$).

$^{13}$C NMR ($C_6D_6$, RT, ppm): δ 6.1 (s, $SiC_{12}H_{25}$), 14.3 (s, $SiC_{12}H_{25}$), 23.1 (s, $SiC_{12}H_{25}$), 26.7 (s, $SiC_{12}H_{25}$), 29.6 (s, $SiC_{12}H_{25}$), 29.8 (s, $SiC_{12}H_{25}$), 29.9 (s, $SiC_{12}H_{25}$), 30.1 (s, $SiC_{12}H_{25}$), 30.1 (s, $SiC_{12}H_{25}$), 30.1 (s, $SiC_{12}H_{25}$), 32.3(s, $SiC_{12}H_{25}$), 32.9 (s, $SiC_{12}H_{25}$).

$^{29}$Si NMR ($C_6D_6$, RT, ppm): δ –59.4 (s).

dodecylsilane-$d_3$ (**4p-$d_3$**)



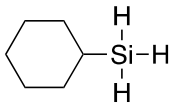
The general procedure 2 was followed with $NaBD_4$ (99 atom% D, 250 mg, 6.0 mmol), *n*$Oct_4NBr$ (56 mg, 0.10 mmol), *n*$C_{12}H_{25}Si(OMe)_3$ (**1p**) (580 mg, 2.0 mmol), HMPA (72 mg, 0.40 mmol) and EtBr (650 mg, 6.0 mmol). The residue was filtered with a silica gel pad (eluent: cold pentane (100 mL)) to provide **4p** as a colorless liquid in 70% (286 mg, 1.4 mmol, 98 atom% D).

$^{1}$H NMR ($C_6D_6$, RT, ppm): δ 0.54 (t, 2H, $^{3}J_{HH}$ = 7.9 Hz, SiC$H_2$($CH_2$)$_{10}$$CH_3$), 0.92 (t, 3H, $^{3}J_{HH}$ = 7.5, $SiCH_2(CH_2)_{10}CH_3$), 1.18-1.38 (m, 20H, $SiCH_2(CH_2)_{10}CH_3$).

$^{13}$C NMR ($C_6D_6$, RT, ppm): δ 5.9 (s, Si$C_{12}H_{25}$), 14.3 (s, Si$C_{12}H_{25}$), 23.1 (s, Si$C_{12}H_{25}$), 26.6 (s, Si$C_{12}H_{25}$), 29.6 (s, Si$C_{12}H_{25}$), 29.8 (s, Si$C_{12}H_{25}$), 30.0 (s, Si$C_{12}H_{25}$), 30.1 (s, Si$C_{12}H_{25}$), 30.1 (s, Si$C_{12}H_{25}$), 30.1 (s, Si$C_{12}H_{25}$), 32.3(s, Si$C_{12}H_{25}$), 32.8 (s, Si$C_{12}H_{25}$).

$^{29}$Si NMR ($C_6D_6$, RT, ppm): δ –60.2 (sept, $^{1}J_{SiD}$ = 29.3 Hz).

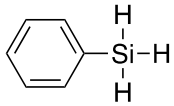
cyclohexylsilane (**4q**)



The general procedure 1 was followed with $NaBH_4$ (22.8 mg, 0.60 mmol), *n*$Oct_4NBr$ (5.6 mg, 0.010 mmol), $CySi(OMe)_3$ (**1q**) (23 mg, 0.20 mmol), HMPA (7.2 mg, 0.040 mmol) and EtBr (65 mg, 6.0 mmol). The resulting solution was analyzed by $^{1}$H NMR to determine the NMR yield of $CySiH_3$ (**4q**) (0.13 mmol, 67%).

$^{1}$H NMR ($C_6D_6$, RT, ppm): δ 0.75 (m, 1H, SiC*H*($CH_2$)$_5$), 1.05-1.18 (m, 5H, ax-C*H*), 1.50-1.66 (m, 5H, eq-C*H*), 3.58 (d, 3H, $^{3}J_{HH}$ = 3.1 Hz, $SiH_3$).

phenylsilane (**4r**)



The general procedure 1 was followed with $NaBH_4$ (22.8 mg, 0.60 mmol), *n*$Oct_4NBr$ (5.6 mg, 0.010 mmol), $PhSi(OMe)_3$ (**1r**) (22 mg, 0.20 mmol), HMPA (7.2 mg, 0.040 mmol) and EtBr (65 mg, 6.0 mmol). The resulting solution was analyzed by $^{1}$H NMR to determine the NMR yield of $PhSiH_3$ (**4r**) (0.10 mmol, 49%).

$^{1}$H NMR ($C_6D_6$, RT, ppm): δ 4.23 (s, 3H, Si*H*), 7.07 (m, 2H, *m*, *p*-C*H*), 7.11 (m, 1H, *p*-C*H*), 7.39 (m, 2H, *o*-C*H*).

**References**


1) L. Horner and J. Mathias, *J. Organomet. Chem.*, 1985, **282**, 155.
2) P. F. Hudrlik and D. K. Minus, *J. Organomet. Chem.*, 1996, **521**, 157.
3) W. J. Leigh, R. Boukherroub and C. Kerst, *J. Am. Chem. Soc.*, 1998, **120**, 9504.
4) R. Savela, W. Zawartka and R. Leino, *Organometallics*, 2012, **31**, 3199.

5) K. Aoyagi, K. Matsumoto, S. Shimada, K. Sato and Y. Nakajima, *Organometallics*, 2019, **38**, 210.
6) A. J. Oliver and W. A. G. Graham, *J. Organomet. Chem.* 1969, **19**, 17.
7) K. G. Penman, W. Kitchin and W. Adcock, *J. Org. Chem.*, 1989, **54**, 5390.
8) A. W. P. Jarvie and R. J. Rowley, *J. Organomet. Chem.*, 1973, **57**, 261.
9) A. Benouargha, D. Boulahia, B. Boutevin, G. Caporiccio, F. Guida-Pietrasanta and A. Ratsimihety, *Phosphourus Sulfur Silicon Relat. Elem.*, 1996, **113**, 79.
10) L. Rosenberg and D. N. Kobus, *J. Organomet. Chem.*, 2003, **685**, 107.
11) J. Ohshita, R. Taketsugu, Y. Nakahara and A. Kunai, *J. Organomet. Chem.*, 2004, **689**, 3258.