Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Si–H Activation at $(NHC)_2Ni^0$ Leading to Hydrido Silyl and Bis(silyl) Complexes: A Versatile Tool for Catalytic Si–H/D Exchange, Acceptorless Dehydrogenative Coupling of Hydrosilanes, and Hydrogenation of Disilanes to Hydrosilanes

David Schmidt, [a] Thomas Zell, [b] Thomas Schaub [c] and Udo Radius*[a]

[a] Dr. David Schmidt, Prof. Dr. Udo Radius, Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg. Am Hubland, 97074 Würzburg, Germany. E-mail: u.radius@uni-wuerzburg.de

[b] Dr. Thomas Zell, Department of Organic Chemistry, Weizmann Institute of Science, 76100 Rehovot, Israel.

[c] Dr. Thomas Schaub, BASF SE, GCB/H–M313, 67056 Ludwigshafen (Germany)

The Supporting Information contents:

1. General Considerations.

All reactions and subsequent manipulations involving organometallic reagents were performed under nitrogen or argon atmosphere using standard Schlenk techniques as reported previously.[S1] NMR spectra were recorded, if not noted otherwise, on Bruker DRX-300, Bruker Avance 200, Bruker Avance 400, or Bruker Avance 500 spectrometers at 298 K. NMR experiments at variable temperature were conducted on Bruker Avance 200 or Bruker Avance 500 spectrometers and the temperatures were calibrated using a Bruker calibration sample. ^{13}C NMR spectra were broad-band proton-decoupled (^{13}C{^{1}H}). NMR data are listed in parts per million (ppm) and are reported relative to Tetramethylsilane. Coupling constants are quoted in hertz (Hz). Spectra are referenced internally to residual protio-solvent resonances (^{1}H: C_6D_5H, 7.15 ppm, CHD_2-C_6D_5: 2.09 ppm) or natural-abundance carbon resonances (^{13}C: C_6D_6, 128.0 ppm). Elemental analyses were performed in the microanalytical laboratory of the authors' department with an Elementar vario micro cube. GC and GC/MS analyses were conducted on a HP G1800A GCD System (70 eV) and Varian 450-GC/320-MS (70 eV), respectively. Infrared spectra were recorded on a Nicolet 380 FT-IR spectrometer as KBr pellets, as solids by using an ATR unit, or in solution using a cell for measurement and are reported in cm^{-1}. GPC analysis was performed on a SECucrity GPC (1260 infinity, Agilant technology, column: PSS SDV 5µ Guard, PSS SDV 5µ 100A, PSS SDV 5µ 1000A, column temperature: 35°C, concentration 1 mg ml^{-1}, injection volume 25 mL, flow 1 ml min^{-1}, solvent: tetrahydrofuran, dried over sodium/benzophenone and degassed, molecular weight was measured relative to monodisperse polystyrene standards). MALDI-TOF mass spectra were recorded on a Bruker Daltonics spectrometer. Compound **1**[S2] and **2-3**[S3] were prepared as reported previously. The silanes were prepared from $LiAlH_4$ reduction of the corresponding chloro silanes or purchased from ABCR and used without any further purification. *Caution*: $AlCl_xH_{3-x}$ catalyzes the rearrangement of phenyl silanes to SiH_4. Before isolation of the pure material all aluminum chlorides have to be removed from the reaction mixture. [S4]

2. Synthesis of the nickel complexes.

Synthesis of *cis*-[Ni(*i*Pr$_2$Im)$_2$(SiMePh$_2$)(H)] (*cis*-5). The synthesis and full characterization of this compound have been described earlier.[S3] NMR spectroscopy: **^{1}H NMR** (400 MHz, -60 °C, toluene-d_8): δ/ppm = -8.95 (s, 1 H, Ni*H*), 0.78 (d, 6 H, *i*Pr-C*H*$_3$), 0.79 (s, 3 H, SiC*H*$_3$), 0.94 (m, 12 H, *i*Pr-C*H*$_3$), 0.99 (d, 6 H, $^3J_{HH}$ = 5.6 Hz, *i*Pr-C*H*$_3$), 5.12 (m, 2 H, *i*Pr-C*H*), 5.12 (m, 2 H, *i*Pr-C*H*), 6.38 (s, 2 H, C*H*C*H*), 6.38 (s, 2 H, C*H*C*H*) 7.26 (m, 2 H, aryl-*H*p), 7.37 (m, 4 H, aryl-*H*), 8.13 (m, 4 H, aryl-*H*). **^{1}H NMR** (400 MHz, 23 °C, C$_6$D$_6$): δ/ppm = - 9.20 (s, 1 H, Ni*H*), 0.76 (s, 3 H, SiC*H*$_3$), 0.99 (d, 24 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-C*H*$_3$), 5.12 (sept, 4 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-C*H*), 6.38 (s, 4 H, C*H*C*H*), 7.20 (m, 2 H, aryl-*H*$_p$), 7.32 (m, 4 H, aryl-*H*), 8.06 (m, 4 H, aryl- *H*). **^{13}C{^{1}H} NMR** (100 MHz, 23 °C, C$_6$D$_6$): δ/ppm = 4.8 (Si*C*H$_3$), 23.0 (*i*Pr-*C*H$_3$), 51.4 (*i*Pr-*C*H), 115.0 (N*CC*N), 126.1 (aryl-*C*$_p$), 127.1 (aryl-*C*$_{tert}$), 136.7 (aryl-*C*$_{tert}$), 152.1 (aryl-*C*$_i$), 198.0 (N*C*N). **^{29}Si{^{1}H} NMR** (79 MHz, 23 °C, C$_6$D$_6$): δ/ppm = -8.8.

Synthesis of *cis*-[Ni(*i*Pr$_2$Im)$_2$(SiMePh$_2$)(D)] *cis*-5-D. Upon storing a solution of ***cis*-2** in *deutero* benzene for 24 hours at room temperature the hydride resonance disappears and quantitative formation of the product is achieved. Heating the sample leads to acceleration of the reaction, however, with the formation of ***trans*-5-D** as "byproduct". **^{1}H NMR** (400 MHz, 23 °C, C$_6$D$_6$): δ/ppm = 0.77 (s, 3 H, SiC*H*$_3$), 0.99 (d, 24 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-C*H*$_3$), 5.12 (sept, 4 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-C*H*), 6.38 (s, 4 H, C*H*C*H*), 7.20 (m, 2 H, aryl-*H*$_p$), 7.32 (m, 4 H, aryl-*H*$_m$), 8.06 (m, 4 H, aryl-*H*$_o$). Note that ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectra are identical to those of the corresponding hydride complex ***cis*-5**.

Synthesis of *trans*-[Ni(*i*Pr$_2$Im)$_2$(SiMePh$_2$)(D)] (*trans*-5-D). Heating a solution of ***cis*-2** in *deutero* benzene or *deutero* toluene to 60 °C for 6 hours leads to quantitative formation of ***trans*-5-D**. **^{1}H NMR** (400 MHz, toluene-d_8): δ/ppm = 0.28 (s, 3 H, SiC*H*$_3$), 1.32 (d, 24 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-C*H*$_3$), 6.24 (sept, 4 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-C*H*), 6.38 (s, 4 H, C*H*C*H*), 7.16 (m, 6 H, aryl-*H*$_{m+p}$), 7.62 (m, 4 H, aryl-*H*$_o$). **^{13}C{^{1}H} NMR** (100 MHz, 23 °C, C$_6$D$_6$): δ/ppm = 2.3 (Si*C*H$_3$), 23.5 (*i*Pr-*C*H$_3$), 51.7 (*i*Pr-*C*H), 115.2 (N*CC*N), 127.4 (aryl-*C*$_{tert}$), 127.5 (aryl-*C*$_{quart}$), 136.7 (aryl-*C*$_{tert}$), 148.0 (aryl-*C*$_{quart}$), 185.7 (N*C*N). **^{29}Si{^{1}H} NMR** (99 MHz, toluene-d_8, 23 °C): δ/ppm = -23.2.

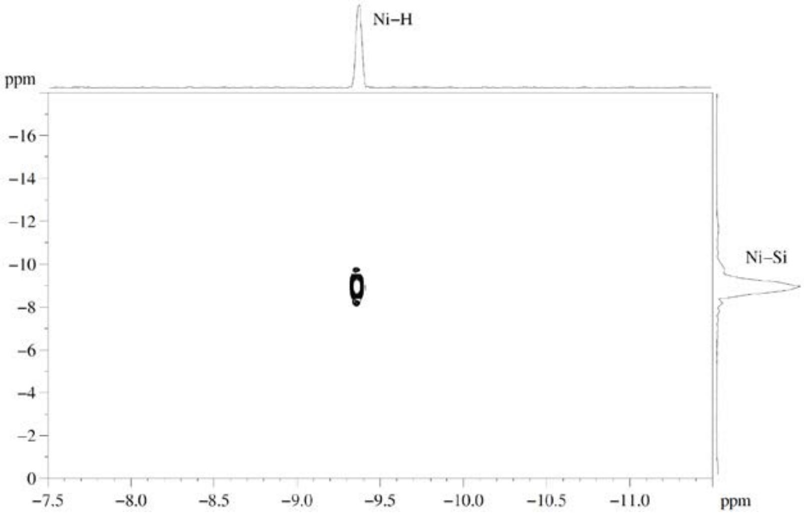


Figure S1. Cross peak between hydride resonance and silicon resonance in the ^{1}H-^{29}Si HMQC NMR spectrum of ***cis*-5** (non deuterated toluene with C_6D_6 capillary).

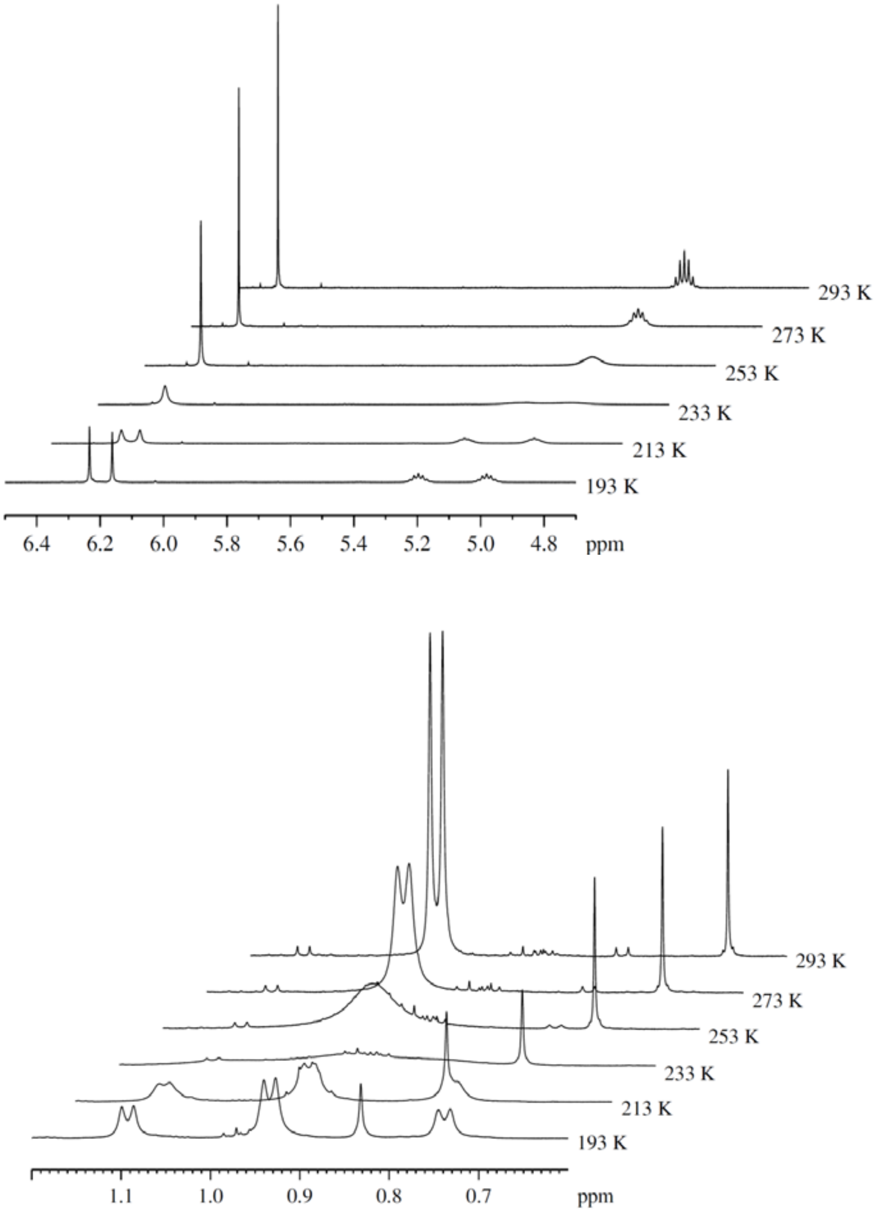


Figure S2. ^{1}H NMR experiment of *cis*-[Ni(*i*Pr$_2$Im)$_2$(SiMePh$_2$)(H)] (***cis*-5**) in toluene-d_8 at variable temperatures. “Freezing” the σ-bond rotation (reversible). Top: Region of the backbone resonances and methine resonances of the *iso*propyl groups. Bottom: Region of the methyl resonances of the *iso*propyl groups and silyl-methyl resonance.

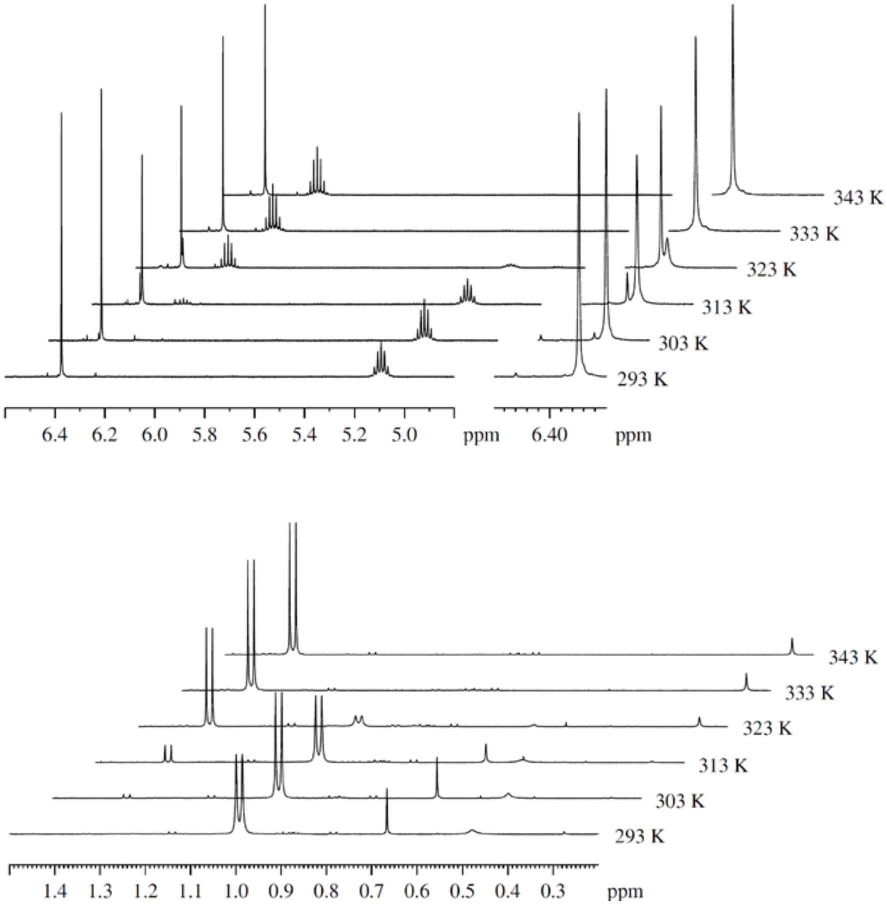


Figure S3. ^{1}H NMR experiment of [Ni(*i*Pr$_2$Im)$_2$(SiMePh$_2$)(H/D)] (***cis*-5**) in toluene-*d*$_8$ at variable temperatures. *Cis*-*trans*-isomerization (irreversible) to give *trans*-[Ni(*i*Pr$_2$Im)$_2$(SiMePh$_2$)(D)] (***trans*-5-D**). Top: Region of the backbone resonances and methine resonances of the *iso*propyl groups. Bottom: Region of the methyl resonances of the *iso*propyl groups and silyl-methyl resonance.

Synthesis of [{(*i*Pr$_2$Im)Ni-μ^2-(HSiPh$_2$)}$_2$] (6). To a suspension of 200 mg complex **1** (240 μmol) in 10 ml toluene 88.5 mg diphenylsilane (90 µl, 480 μmol) were added at room temperature. After stirring the red solution for 24 h at 110 °C, all volatiles were removed *in vacuo* and the residue was suspended in 10 ml hexane. The solid was filtrated and washed twice with 5 ml of hexane to yield 142 mg (75 %) of the red product. Single crystals suitable for X-ray diffraction were obtained by cooling a saturated refluxing solution of complex **6** in C_6D_6 to room temperature. $C_{42}H_{56}N_4Ni_2Si_2$ (790.48): found (calc.) C 63.70 (63.82), H 7.41 (7.14), N 7.66 (7.09). **IR** (KBr): $\tilde{\nu}$ = 424 (s), 451 (vs), 474 (vs), 500 (vs), 567 (m), 629 (s), 681 (vs), 700 (vs), 737 (vs), 850 (m, aryl-$\delta_{=C\text{-}H,oop}$), 879 (m), 994 (s), 1022 (s, aryl-$\delta_{=C\text{-}H,ip}$), 1092 (vs), 1127 (vs, $\nu_{\text{-}Si\text{-}Ph,str}$), 1184 (s), 1216 (vs, NHC-$\gamma_{=C\text{-}}$

$_{H,oop}$), 1297 (vs), 1324 (s), 1367 (vs), 1408 (vs), 1467 (s), 1526 (vs, $\nu_{-Ni\text{-}H\text{-}Si,str}$), 1635 (w, aryl-$\nu_{-C=C,str}$), 2868 (m, $\nu_{-C\text{-}H,str}$), 2932 (s, $\nu_{-C\text{-}H,str}$), 2968 (vs, $\nu_{-C\text{-}H,str}$), 3013 (w, $\nu_{-C\text{-}H,str}$), 3059 (s, $\nu_{-C\text{-}H,str}$), 3131 (w, aryl-$\nu_{=C\text{-}H,str}$), 3160 (m, aryl-$\nu_{=C\text{-}H,str}$). **^{1}H NMR** (500.1 MHz, C_6D_6, 296 K): δ/ppm = -0.84 (s, 2 H, $^{3,4}J_{HH}$ = 2.0 Hz, *cis*-$^{1,2}J_{SiH}$ = 62.5 Hz, *trans*-$^{2}J_{SiH}$ = 20.3 Hz, Ni*H*), 0.89 (d, 24 H, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr-C*H*$_3$), 4.67 (sept, 4 H, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr-C*H*), 6.46 (s, 4 H, C*H*C*H*), 7.17–7.21 (m, 4 H, aryl-C$_{para}$*H*), 7.23–7.27 (m, 8 H, aryl-C*H*), 7.90–7.93 (m, 8 H, aryl-C*H*). **^{13}C{^{1}H} NMR** (50.3 MHz, C_6D_6, 296 K): δ/ppm = 22.8 (*i*Pr-*C*H$_3$), 52.1 (*i*Pr-*C*H), 116.0 (*C*H*C*H), 127.3 (aryl-*C*$_{para}$H), 127.5 (aryl-*C*H), 136.3 (aryl-*C*H), 146.23 (aryl-*C*$_{ipso}$), 192.6 (N*C*N). **^{29}Si{^{1}H} NMR** (39.8 MHz, C_6D_6, 296 K): δ/ppm = 117.6 (*Si*).

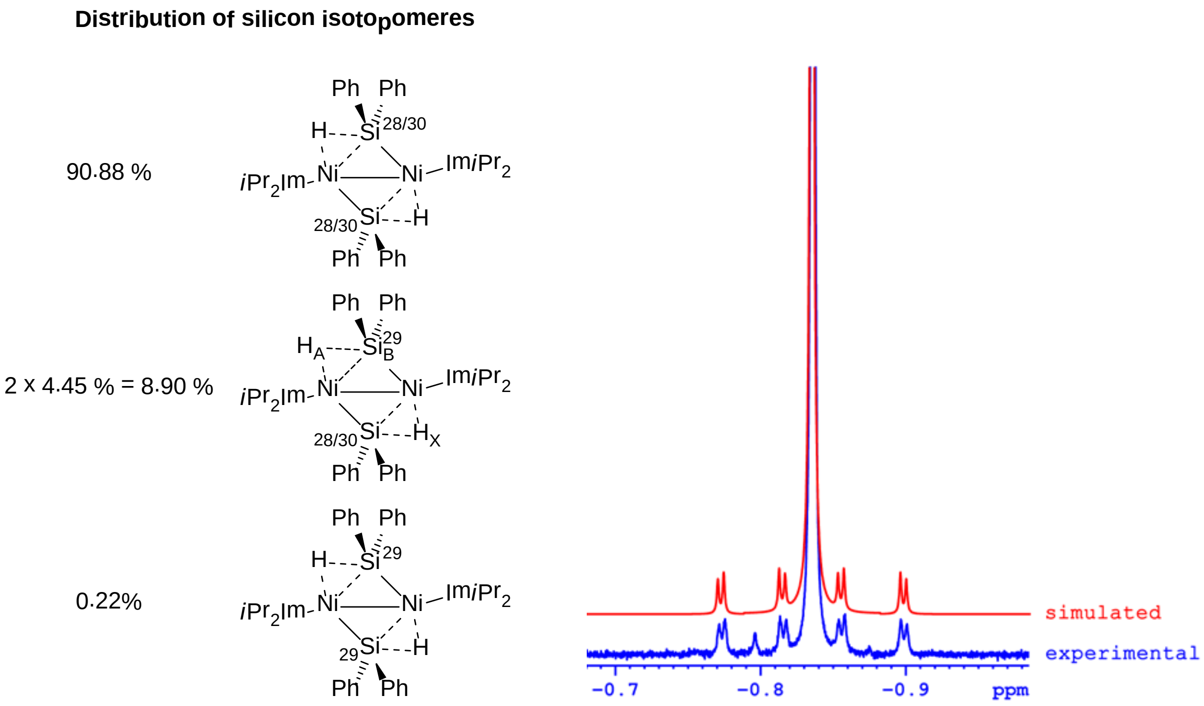


Figure S4: Left: Percentage distribution of all possible silicon isotopomeres of [{(*i*Pr$_2$Im)(H)Ni-μ^2-(SiPh$_2$)}$_2$] **6**. Right: Section (-0.99 to 0.67 ppm) of the experimental (C_6D_6, blue) und calculated (red) ^{1}H NMR spectrum of the hydride resonance of [{(*i*Pr$_2$Im)(H)Ni-μ^2-(SiPh$_2$)}$_2$] (**6**).

Synthesis of *cis*-[Ni(*i*Pr$_2$Im)$_2$(H)(SiMes$_2$H)] (*cis*-7). To a suspension of 200 mg complex **1** (240 µmol) in 10 ml toluene 129 mg dimesitylsilane (480 µmol) were added at room temperature. After stirring the yellow suspension for 16 h at room temperature, all volatiles were removed *in vacuo* and the residue was suspended in 10 ml hexane. The solid was filtrated and washed twice with 5 ml of hexane to yield 116 mg (56 %) of the yellow product. Single crystals suitable for X-ray diffraction were obtained by cooling a saturated solution of complex ***cis*-7** in toluene to -30 °C. $C_{36}H_{56}N_4NiSi$ (631.64): found (calc.) C 68.46 (68.45), H 8.91 (8.94), N 8.48 (8.87). **IR** (KBr): $\tilde{\nu}$ = 421 (s), 545 (w), 566 (w), 592 (w), 608 (w), 681 (s), 707 (s), 756 (m), 844 (s, aryl-$\delta_{=C\text{-}H,oop}$), 868 (s), 926 (w), 991 (w), 1017 (s, aryl-$\delta_{=C\text{-}H,ip}$), 1057 (w), 1079 (w), 1098 (w), 1131 (m, $\nu_{\text{-}Si\text{-}Ph,str}$), 1213 (vs, NHC-$\gamma_{=C\text{-}H,oop}$), 1281 (s), 1322 (w), 1367 (vs), 1400 (vs), 1462 (s), 1518 (w), 1599 (w, aryl-$\nu_{\text{-}C=C,str}$), 1856 (m, $\nu_{\text{-}Ni\text{-}H,str}$), 1977 (s, $\nu_{\text{-}Si\text{-}H,str}$), 2648 (vw, $\nu_{\text{-}C\text{-}H,str}$), 2724 (w, $\nu_{\text{-}C\text{-}H,str}$), 2917 (vs, $\nu_{\text{-}C\text{-}H,str}$), 2969 (vs, $\nu_{\text{-}C\text{-}H,str}$), 3124 (w, aryl-$\nu_{=C\text{-}H,str}$). **IR** (toluene): $\tilde{\nu}$ = 1217 (w, NHC-$\gamma_{=C\text{-}H,oop}$), 1279 (m), 2000 (s, $\nu_{\text{-}Ni\text{-}H,str}$), 2150 (m, $\nu_{\text{-}Si\text{-}H,str}$). **^{1}H NMR** (500.1 MHz, C_6D_6, 296 K): δ/ppm = -1.86 (s_{br}, 2 H, Si*H*, Ni*H*), 0.98 (d, 24 H, $^3J_{\text{HH}}$ = 6.8 Hz, *i*Pr-C*H*$_3$), 2.27 (s, 6 H, aryl-C$_{para}$C*H*$_3$), 2.88 (s, 12 H, aryl-C$_{ortho}$C*H*$_3$), 5.13 (sept, 4 H, $^3J_{\text{HH}}$ = 6.8 Hz, *i*Pr-C*H*), 6.37 (s, 4 H, C*H*C*H*), 6.94 (s, 4 H, aryl-C$_{meta}$*H*). **^{13}C{^{1}H} NMR** (50.3 MHz, C_6D_6, 296 K): δ/ppm = 21.4 (aryl-C$_{para}$*C*H$_3$), 23.0 (*i*Pr-*C*H$_3$), 24.9 (aryl-C$_{ortho}$*C*H$_3$), 51.5 (*i*Pr-*C*H), 115.2 (*C*H*C*H), 128.5 (aryl-*C*), 134.9 (aryl-*C*), 143.3 (aryl-*C*), 144.0 (aryl-*C*), 197.8 (N*C*N). **^{29}Si{^{1}H} NMR** (39.8 MHz, C_6D_6, 296 K): δ/ppm = -45.3 (*Si*). **^{29}Si NMR** (39.8 MHz, C_6D_6, 296 K): δ/ppm = -45.3 (t, $^{1,2}J_{\text{SiH}}$ = 74.7 Hz, *Si*).

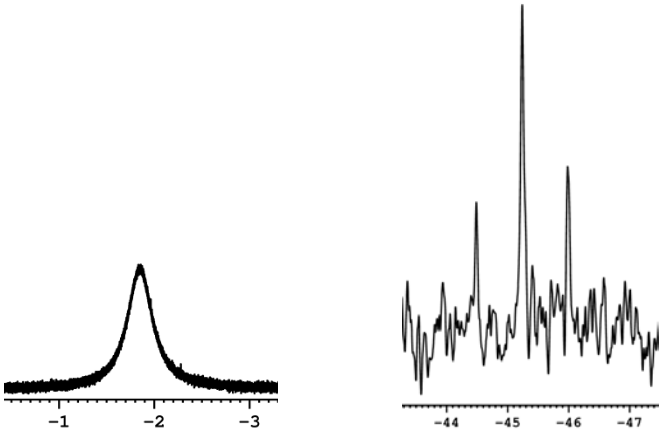
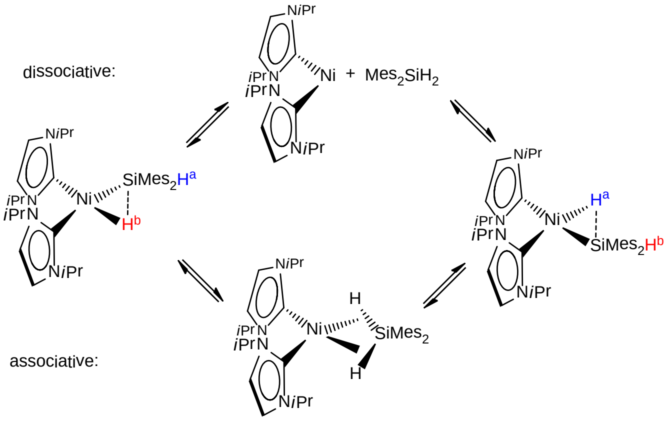


Figure S5: Section (-3.30 to -0.40 ppm) of the ^{1}H NMR spectrum of the hydride resonance of *cis*-[(*i*Pr$_2$Im)$_2$Ni(H)(SiMes$_2$H)] (***cis*-7**) in C_6D_6 (left). Section (-47.5 to 43.3 ppm) of the proton coupled ^{29}Si NMR spectrum (δ_{Si} = -45.3 ppm) of *cis*-[(*i*Pr$_2$Im)$_2$Ni(H)(SiMes$_2$H)] (***cis*-7**) in C_6D_6.

The dynamic behavior of **cis-7** can be explained with an isomerization process, which is responsible for a scrambling of the Si–H protons H^a and H^b (see Scheme S1) and which should be fast on the NMR time scale. This could either be explained by a dissociative process via reductive elimination of dimesityl silane with formation of the Si–H^a bond and consecutive insertion of

{Ni(NHC)$_2$} into the Si–H^b bond, or by an associative process via formation of an intermediate or transition state, which involves two Ni-σ(Si–H) bonds to both Si–H^a and Si–H^b (see Scheme S1).



Scheme S1. Postulated mechanisms for the isomerization of *cis*-[Ni(iPr$_2$Im)$_2$(H)(SiMes$_2$H)] ***cis*-7** in solution. Top: dissociative pathway *via* reductive elimination/oxidative addition. Bottom: associative pathway with formation of a σ-(Si–H) complex.

Synthesis of *cis*-[Ni(*i*Pr$_2$Im)$_2$(H)(Si*t*Bu$_2$Cl)] (*cis*-8). To a suspension of 200 mg complex **1** (240 µmol) in 10 ml toluene 85.8 mg di-*tert*-butylchlorosilane (97 µl, 480 µmol) were added at room temperature. After stirring the orange solution for 3 h at room temperature, all volatiles were removed *in vacuo* and the residue was suspended in 10 ml hexane. The solid was filtrated and washed twice with 3 ml of hexane to yield 194 mg (74 %) of the yellow product. $C_{26}H_{51}ClN_4NiSi$ (541.94): found (calc.) C 57.50 (57.62), H 9.43 (9.49), N 10.31 (10.34). **IR** (KBr): $\tilde{\nu}$ = 447 (s), 477 (vs), 569 (s), 593 (w), 630 (m), 674 (m), 690 (s), 717 (s), 814 (s), 879 (w), 933 (vw), 991 (w), 1015 (m), 1080 (w), 1130 (m), 1217 (vs, NHC-$\gamma_{=C\text{-}H,oop}$), 1285 (s), 1322 (w), 1368 (vs), 1403 (vs), 1466 (s), 1538 (w), 1814 (m, $\nu_{\text{-}Ni\text{-}H,str}$), 2841 (vs, $\nu_{\text{-}C\text{-}H,str}$), 2877 (vs, $\nu_{\text{-}C\text{-}H,str}$), 2972 (vs, $\nu_{\text{-}C\text{-}H,str}$), 3097 (w, $\nu_{\text{-}C\text{-}H,str}$), 3131 (m, $\nu_{\text{-}C\text{-}H,str}$), 3165 (w, $\nu_{\text{-}C\text{-}H,str}$). **^{1}H NMR** (200.1 MHz, C_6D_6, 296 K): δ/ppm = -11.18 (s, 1 H, $^{1,2}J_{\text{SiH}}$ = 20.2 Hz, Si*H*), 1.12 (d$_{\text{br}}$, 24 H, $^3J_{\text{HH}}$ = 6.7 Hz, *i*Pr-C*H*$_3$), 1.66 (s, 18 H, $^3J_{\text{SiH}}$ = 5.7 Hz, *t*Bu-C*H*$_3$), 5.38 (sept, 4 H, $^3J_{\text{HH}}$ = 6.7 Hz, *i*Pr-C*H*), 6.39 (s, 4 H, C*H*C*H*). **^{13}C{^{1}H} NMR** (50.3 MHz, C_6D_6, 296 K): δ/ppm = 23.5 (*t*Bu-*C*), 26.6 (*i*Pr-*C*H$_3$), 27.5 (*i*Pr-*C*H$_3$), 31.2 (*t*Bu-*C*H$_3$), 51.3 (*i*Pr-*C*H), 115.6 (*C*H*C*H), 195.2 (N*C*N). **^{29}Si{^{1}H} NMR** (39.8 MHz, C_6D_6, 296 K): δ/ppm = 59.3 (*Si*).

Similar to ***cis*-5**, one set of resonances was detected in the ^{1}H and ^{13}C{^{1}H} NMR spectra for the NHC ligands of ***cis*-8**, which split into two distinct sets of resonances at lower temperatures (see Figure S6).

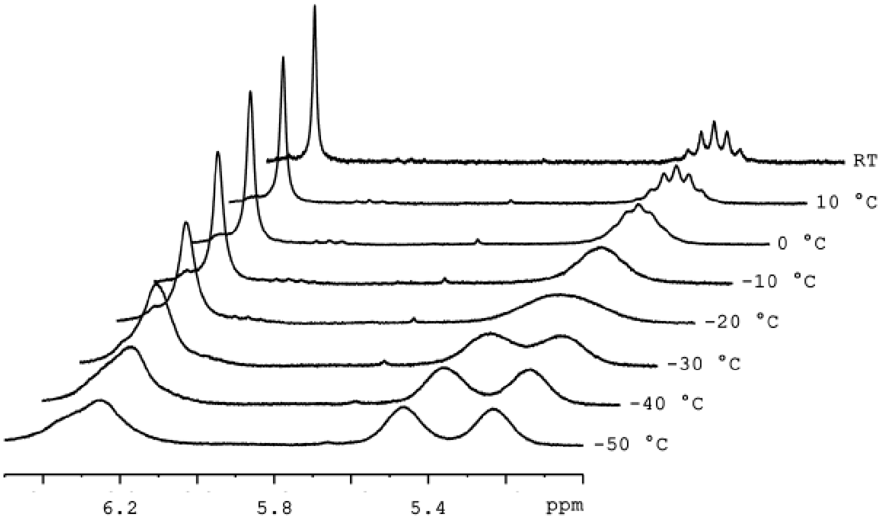


Figure S6: ^{1}H NMR of *cis*-[Ni(*i*Pr$_2$Im)$_2$(H)(Si*t*Bu$_2$Cl)] ***cis*-8** in toluene-*d$_8$* at variable temperatures. "Freezing" the σ-bond rotation (reversible). Region of the backbone and the methine resonances of the *iso*propyl groups.

Synthesis of *cis*-[Ni(*i*Pr$_2$Im)$_2$(SiHMe$_2$)$_2$] (*cis*-9). About 2.00 g dimethylsilane (33.2 mmol) were passed into a suspension of 168 mg complex **1** (200 µmol) in 20 ml toluene at room temperature. After stirring the orange solution for 12 h at room temperature, all volatiles were removed *in vacuo* and the residue was suspended in 7 ml hexane. The solid was filtrated to yield 105 mg (54 %) of the yellow product. Single crystals suitable for X-ray diffraction were obtained by cooling a saturated solution of complex ***cis*-9** in Et$_2$O to -30 °C. $C_{22}H_{46}ClN_4NiSi_2$ (481.49): found (calc.) C 54.74 (54.88), H 9.54 (9.63), N 11.32 (11.64). **IR** (KBr): $\tilde{\nu}$ = 369 (w), 570 (w), 622 (m), 653 (m), 675 (m), 696 (m), 717 (m), 895 (s), 1015 (m), 1129 (m), 1212 (vs, NHC-$\gamma_{=C\text{-}H,oop}$), 1287 (m), 1367 (s), 1403 (s), 1466 (m), 1978 (s, $\nu_{\text{-}Si\text{-}H,str}$), 2877 (m, $\nu_{\text{-}C\text{-}H,str}$), 2930 (s, $\nu_{\text{-}C\text{-}H,str}$), 2972 (s, $\nu_{\text{-}C\text{-}H,str}$), 3120 (w, $\nu_{\text{-}C\text{-}H,str}$), **^{1}H NMR** (300.1 MHz, C$_6$D$_6$, 296 K): δ/ppm = 0.61 (d, 12 H, $^{3}J_{HH}$ = 4.1 Hz, SiC*H*$_3$), 1.04 (br, 24 H, *i*Pr-C*H*$_3$), 4.40 (sept, 2 H, $^{3}J_{HH}$ = 4.1 Hz, Si*H*), 5.10 (sept, 4 H, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr-C*H*), 6.36 (s, 4 H, C*H*C*H*). **^{13}C{^{1}H} NMR** (75.3 MHz, C$_6$D$_6$, 296 K): δ/ppm = 2.4 (Si-*C*H$_3$), 23.0 (*i*Pr-*C*H$_3$), 51.3 (*i*Pr-*C*H), 115.4 (N*CC*N), 197.7 (N*C*N). **^{29}Si{^{1}H} NMR** (60.8 MHz, C$_6$D$_6$, 296 K): δ/ppm = -12.6 (*Si*).

Synthesis of *cis*-[Ni(*i*Pr$_2$Im)$_2$(SiEt$_2$H)$_2$] (*cis*-10). To a suspension of 200 mg complex **1** (240 µmol) in 10 ml toluene 339 mg diethylsilane (498 µl, 3.84 mmol) were added at room temperature. After stirring the orange solution for 2 h at room temperature, the product was crystallized by cooling the reaction mixture to -30 °C to yield 149 mg (58 %) of the orange product. Single crystals suitable for X-ray diffraction were obtained by cooling a saturated solution of complex ***cis-10*** in toluene to -30 °C. $C_{26}H_{54}N_4NiSi_2$ (537.60): found (calc.) C 58.01 (58.09), H 9.86 (10.12), N 10.59 (10.42). **IR** (ATR): $\tilde{\nu}$ = 709 (m), 746 (m), 772 (m), 809 (w), 935 (w), 962 (w), 1003 (m), 1079 (w), 1128 (w), 1213 (vs, NHC-$\gamma_{=C\text{-}H,oop}$), 1287 (w), 1297 (w), 1368 (m), 1390 (m), 1404 (m), 1416 (m), 1437 (w), 1458 (w), 1472 (w), 1666 (vw), 1980 (m, $\nu_{\text{-}Si\text{-}H,str}$), 2872 (m, $\nu_{\text{-}C\text{-}H,str}$), 2914 (m, $\nu_{\text{-}C\text{-}H,str}$), 2935 (m, $\nu_{\text{-}C\text{-}H,str}$), 2968 (m, $\nu_{\text{-}C\text{-}H,str}$). **^{1}H NMR** (500.1 MHz, C_6D_6, 296 K): δ/ppm = 1.03 (d, 24 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-C*H*$_3$), 1.06–1.17 (m, 8 H, C*H*$_2$CH$_3$), 1.50 (t, 12 H, $^3J_{HH}$ = 7.8 Hz, CH$_2$C*H*$_3$), 3.94 (m, 2 H, $^1J_{SiH}$ = 145.1 Hz, Si*H*),5.12 (sept, 4 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-C*H*), 6.33 (C*H*C*H*). **^{13}C{^{1}H} NMR** (125.8 MHz, C_6D_6, 296 K): δ/ppm = 9.3 (*C*H$_2$CH$_3$), 13.1 (CH$_2$*C*H$_3$), 23.2 (*i*Pr-*C*H$_3$), 51.3 (*i*Pr-*C*H), 115.7 (*C*H*C*H), 196.9 (N*C*N). **^{29}Si{^{1}H} NMR** (99.4 MHz, C_6D_6, 296 K): δ/ppm = 7.4 (*Si*).

Synthesis of *cis*-[Ni(*i*Pr$_2$Im)$_2$(SiCyH$_2$)$_2$] (*cis*-11). To a suspension of 200 mg complex **1** (240 µmol) in 10 ml toluene 439 mg cyclohexylsilane (500 µl, 3.84 mmol) were added at room temperature. After stirring the orange solution for 30 min at room temperature, all volatiles were removed *in vacuo* and the residue was suspended in 10 ml hexane. The solid was filtrated and washed twice with 5 ml of hexane to yield 187 mg (63 %) of the orange product. Single crystals suitable for X-ray diffraction were obtained by cooling a saturated solution of complex ***cis-11*** in toluene to -30 °C. $C_{30}H_{58}N_4NiSi_2$ (589.67): found (calc.) C 61.12 (61.11), H 9.74 (9.91), N 9.43 (9.50). **IR** (ATR): $\tilde{\nu}$ = 709 (w), 741 (w), 784 (m), 807 (m), 818 (w), 848 (w), 881 (w), 911 (vw), 963 (s), 992 (m), 1016 (w), 1041 (vw), 1091 (w), 1128 (w), 1164 (vw), 1212 (vs, NHC-$\gamma_{=C\text{-}H,oop}$), 1283 (w), 1366 (m), 1388 (w),1405 (m), 1415 (m), 1437 (w), 1457 (w), 1465 (w), 1472 (w), 1997 (s, br, $\nu_{\text{-}Si\text{-}H,str}$) 2835 (m, $\nu_{\text{-}C\text{-}H,str}$), 2910 (vs, $\nu_{\text{-}C\text{-}H,str}$), 2972 (m, $\nu_{\text{-}C\text{-}H,str}$). **^{1}H NMR** (500.1 MHz, C_6D_6, 296 K): δ/ppm = 1.06 (s$_{br}$, 24 H, *i*Pr-C*H*$_3$), 1.25–1.37 (m, 4 H, C*H*$_2$), 1.41–1.54 (m, 4 H, C*H*$_2$), 1.67–1.78 (m, 4 H, C*H*$_2$), 1.78–1.84 (m, 2 H, SiC*H*), 1.89–1.97 (m, 4 H, C*H*$_2$), 2.30–2.38 (m, 4 H, C*H*$_2$), 3.95 (d, 4 H, $^3J_{HH}$ = 2.7 Hz, $^1J_{SiH}$ = 148.0 Hz, Si*H*$_2$), 5.16 (sept, 4 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-C*H*), 6.35 (C*H*C*H*). **^{13}C{^{1}H} NMR** (125.8 MHz, C_6D_6, 296 K): δ/ppm = 23.3 (*i*Pr-*C*H$_3$), 27.9 (SiCH), 28.0 (*C*H$_2$), 29.5 (*C*H$_2$), 34.5 (*C*H$_2$), 51.5 (*i*Pr-C*H*), 116.0 (*C*H*C*H), 195.7 (N*C*N). **^{29}Si{^{1}H} NMR** (99.4 MHz, C_6D_6, 296 K): δ/ppm = -19.1 (*Si*).

Synthesis of *trans*-[Ni(*i*Pr$_2$Im)$_2$(Si(OEt)$_3$)$_2$] (*trans*-12). To a suspension of 200 mg complex **1** (240 µmol) in 10 ml toluene 335 mg triethoxysilane (376 µl, 2.88 mmol) were added at room temperature. After stirring the orange solution for 30 h at 80 °C, all volatiles were removed *in vacuo* and the residue was suspended in 10 ml hexane. The solid was filtrated and washed twice with 5 ml of hexane to yield 187 mg (63 %) of the orange product. Single crystals suitable for X-ray diffraction were obtained by cooling a saturated solution of complex ***trans-12*** in toluene to -30 °C. $C_{30}H_{62}N_4NiO_6Si_2$ (689.70): found (calc.) C 52.34 (52.24), H 9.06 (8.83), N 8.07 (8.14). **IR** (ATR): $\tilde{\nu}$ = 709 (w), 741 (w), 784 (m), 807 (m), 818 (w), 848 (w), 881 (w), 911 (vw), 963 (s), 992 (m), 1016 (w), 1041 (vw), 1091 (w), 1128 (w), 1164 (vw), 1212 (vs, NHC-$\gamma_{=C\text{-}H,oop}$), 1283 (w), 1366 (m), 1388 (w),1405 (m), 1415 (m), 1437 (w), 1457 (w), 1465 (w), 1472 (w), 1997 (s, br, $\nu_{\text{-}Si\text{-}H,str}$) 2835 (m, $\nu_{\text{-}C\text{-}H,str}$), 2910 (vs, $\nu_{\text{-}C\text{-}H,str}$), 2972 (m, $\nu_{\text{-}C\text{-}H,str}$). **^{1}H NMR** (200.1 MHz, C_6D_6, 296 K): δ/ppm = 1.18 (t, 18 H, $^3J_{HH}$ = Hz, CH$_2$C*H*$_3$), 1.50 (d, 24 H, $^3J_{HH}$ = 6.7 Hz, *i*Pr-C*H*$_3$), 3.63 (q, 12 H, $^3J_{HH}$ = 7.0 Hz, C*H*$_2$CH$_3$), 5.22 (sept, 4 H, $^3J_{HH}$ = 6.7 Hz, *i*Pr-C*H*), 6.51 (s, 4 H, C*H*C*H*). **^{13}C{^{1}H} NMR** (50.3 MHz, C_6D_6, 296 K): δ/ppm = 19.1 (CH$_2$*C*H3), 23.3 (^{i}Pr-*C*H$_3$), 51.6 (^{i}Pr-*C*H), 56.5 (*C*H$_2$CH$_3$), 115.4 (*C*H*C*H), 190.3 (N*C*N). **^{29}Si{^{1}H} NMR** (39.8 MHz, C_6D_6, 296 K): δ/ppm = -16.3 (*Si*).

3. Experiments for the 1 catalyzed Si-H/D exchange reaction of triethylsilane with C_6D_6.

Synthesis of $DSiEt_3$ via 1 catalyzed reaction of $HSiEt_3$ with C_6D_6. A NMR tube was charged with complex **1** (30 mg 35.7 µmol, 5.0 mol%), C_6D_6 (1.0 mL) and triethylsilane (114 µL, 714 µmol). No gas evolution was observed after addition. The sample was stored at room temperature upon flame sealing of the NMR tube. A conversion of 44.0% to DSiEt was observed after 44 hours (integration in ^{1}H NMR). Heating the sample for four days to 80 °C led to a conversion of 95.5%.
$DSiEt_3$: EI/MS m/z (%): 117 (5.8) $[M]^+$, 88 (84.8) $[Et_2SiD]^+$, 86 (29.6) $[EtSiC_2H_5]^+$, 60 (100.0) $[EtSiHD]^+$. **^{1}H NMR** (400 MHz, 23 °C, C_6D_6): δ/ppm = 0.53 (quart, 6 H, $^3J_{HH}$ = 7.9 Hz, CH_2), 0.97 (t, 9 H, $^3J_{HH}$ = 7.9 Hz, CH_3). **$^{13}C\{^1H\}$ NMR** (75 MHz, 23 °C, C_6D_6): δ/ppm = 2.8 (CH_2), 8.4 (CH_3). **$^{29}Si\{^1H\}$ NMR** (79 MHz, 23 °C, C_6D_6): δ/ppm = -0.4 (t, $^3J_{SiD}$ = 27.3 Hz).
Compare to **$HSiEt_3$**: **EI/MS** m/z (%): 116 (7,3) $[M]^+$, 87 (89.1) $[Et_2SiH]^+$, 86 (45.4) $[EtSiC_2H_5]^+$, 59 (100.0) $[EtSiH_2]^+$. **^{1}H NMR** (300 MHz, 23 °C, C_6D_6): δ/ppm = 0.54 (dquart, 6 H, $^3J_{HH}$ = 3.2 Hz, $^3J_{HH}$ = 7.9 Hz, CH_2), 0.97 (t, 9 H, $^3J_{HH}$ = 7.9 Hz, CH_3), 3.86 (sept, 1 H, $^3J_{HH}$ = 3.2 Hz, SiH). **$^{13}C\{^1H\}$ NMR** (75 MHz, 23 °C, C_6D_6): δ/ppm = 2.8 (CH_2), 8.4 (CH_3). **$^{29}Si\{^1H\}$ NMR** (79 MHz, 23 °C, C_6D_6): δ/ppm = 0.1 (s).

Procedure for the time depended ^{1}H NMR experiment (2.0 mol% catalyst, 5.0 eq. C_6D_6, 70 °C). A NMR tube was charged with complex **1** (27 mg 32.1 µmol, 2.0 mol%) and C_6D_6 (600 µL). The suspension was frozen with liquid nitrogen, triethylsilane (252 µL, 1578 µmol) was added and also frozen.
The NMR tube was flame sealed and transferred to the spectrometer in the frozen state. The sample was heated to room temperature immediately before the experiment. The results of this experiment are discussed in the article.

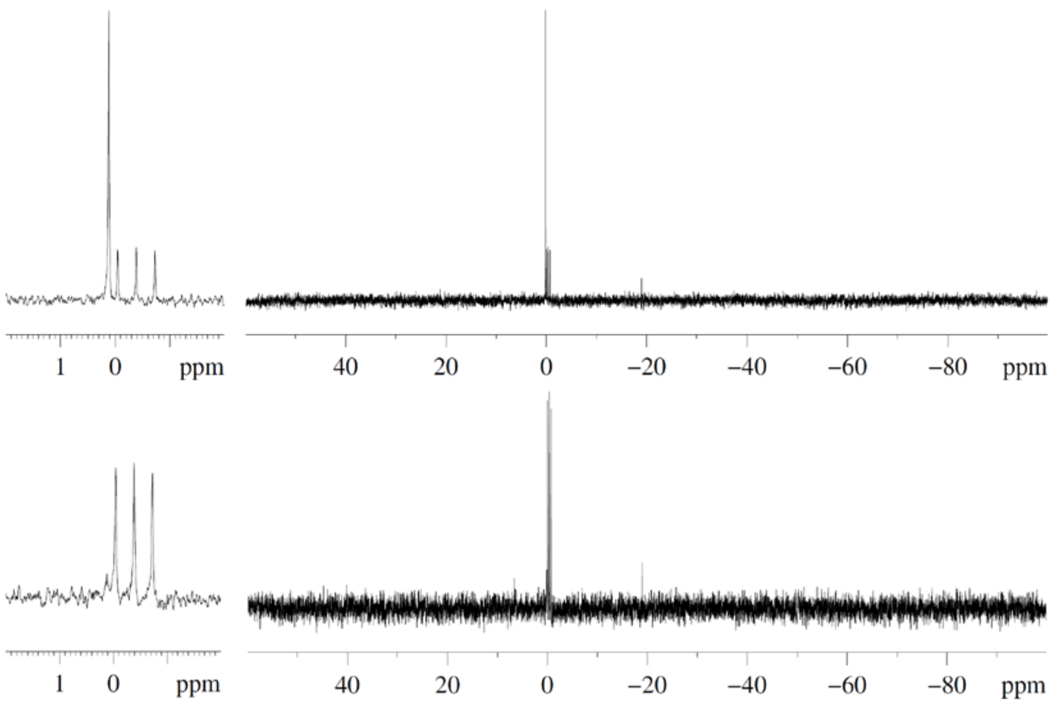


Figure S7. ^{29}Si{^{1}H} NMR spectra of the **1** catalyzed deuteration of triethylsilane (HSiEt$_3$ resonance: singlet; DSiEt resonance: triplet). Upper part: Spectrum taken at an early stage of the catalysis. Lower part: Spectrum taken at a final stage of the catalysis.

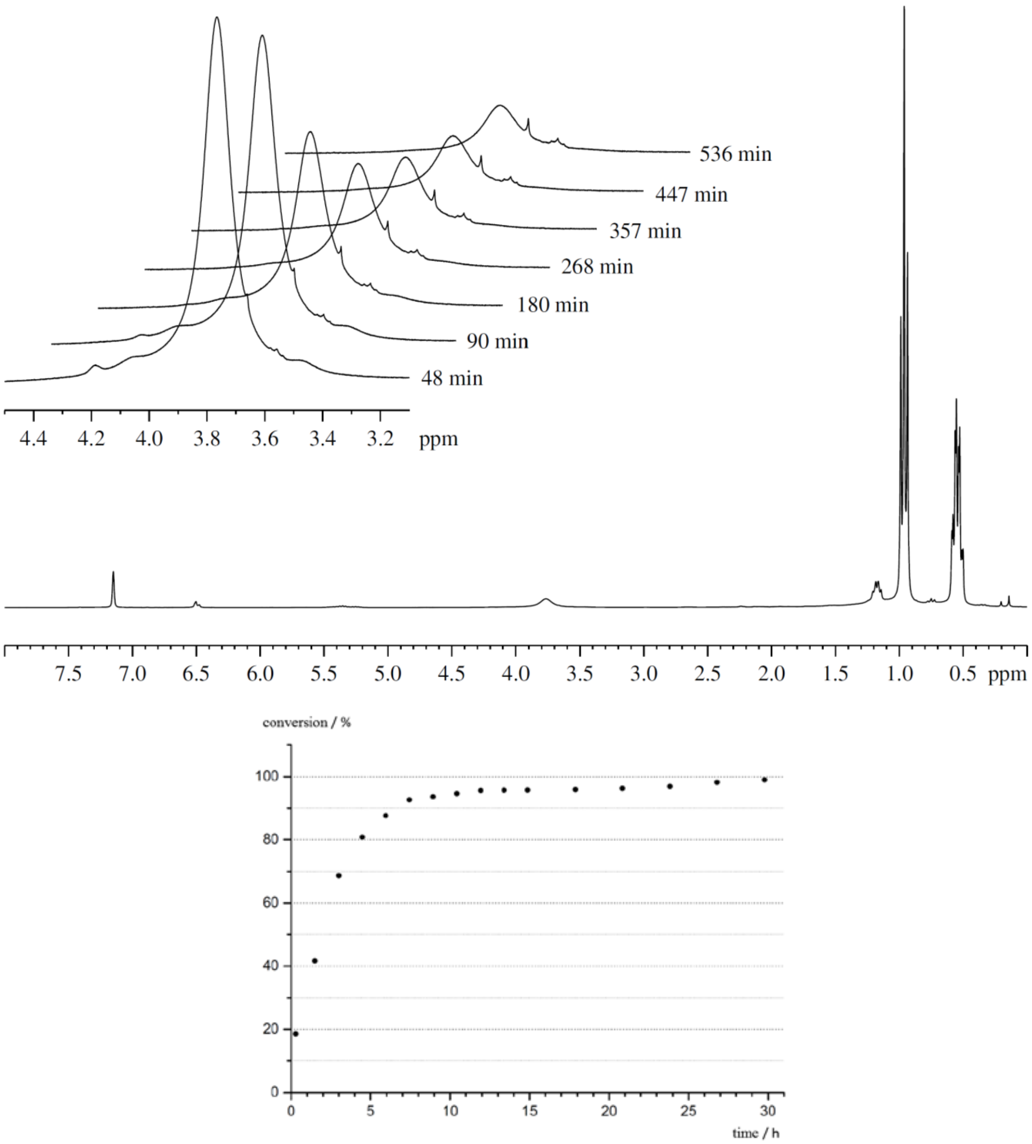


Figure S8. Top: ^{1}H NMR spectrum of the H/D isotope exchange reaction (2.0 mol% catalyst, 5.0 eq. C_6D_6, 70 °C). Time depended decrease of the silyl hydride resonance and overview spectrum (14 min after addition). Bottom: Conversion vs. time plot of the **1** catalyzed deuteration of triethylsilane (from the integration of the Si-*H* resonance vs. the $SiCH_2CH_3$ resonances).

4. Experiments for the 1 catalyzed dehydrocoupling of $PhSiH_3$ and Ph_2SiH_2.

Dehydrogenative coupling of diphenylsilane. 1.49 g diphenylsilane (1.50 ml, 8.08 mmol) was added to 169 mg of complex **1** (202 μmol, 2.5 mol%) at room temperature. Immediately after addition a vigorous hydrogen evolution could be observed, that slowly decreases after 30 minutes but is still observable after several hours. After 8 days a complex mixture of oligo silanes can be obtained as a resinous residue, which crystalizes up on standing. Attempts to chromatography the mixture of products over silica (hexane) failed, due to the similar polarities of the different silanes. In addition to the used diphenylsilane, triphenylsilane and 1,1,2,2-tetraphenyldisilane were detected by GC/MS-analysis. By multinuclear NMR experiments diphenylsilane, 1,1,2,2-tetraphenyldisilane and 1,1,2,2,3,3-hexaphenyltrisilane were identified in a ratio of 1.00 : 0.52 : 0.35 (integration of the Si*H*-resonances). In addition to that resonances for *cis*-$[(i\mathrm{Pr}_2\mathrm{Im})_2\mathrm{Ni}(\mathrm{SiPh}_2\mathrm{H})_2]$ (***cis*-3**) and $[\{(i\mathrm{Pr}_2\mathrm{Im})\mathrm{Ni}\text{-}\mu^2\text{-}(\mathrm{HSiPh}_2)\}_2]$ (**6**) can be observed in the ^{1}H NMR spectra. Single crystals of 1,1,2,2,3,3-hexaphenyltrisilane suitable for X-ray diffraction were grown by storage of a sample enriched with the trimer (see Figure S9). **^{1}H NMR** (200.1 MHz, C_6D_6, 296 K): δ = 5.07 (s, 2 H, SiH_2, diphenylsilane), 5.47 (s, 2 H, Si*H*, 1,1,2,2-tetraphenyldisilane), 5.54 (s, 2 H, Si*H*, 1,1,2,2,3,3-hexaphenyltrisilane). **^{29}Si{^{1}H} NMR** (39.8 MHz, C_6D_6, 296 K): δ = -42.6 (*Si*, 1,1,2,2,3,3-hexaphenyltrisilane), -35.0 (*Si*H, 1,1,2,2-tetraphenyldisilane), -33.7 (*Si*H_2, diphenylsilane), -32.2 (*Si*H, 1,1,2,2,3,3-hexaphenyltrisilane).

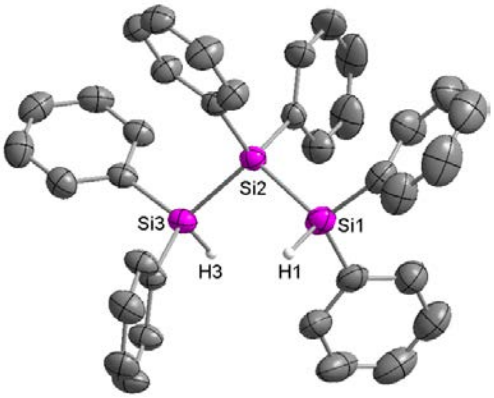


Figure S9. Molecular structure of 1,1,2,2,3,3-hexaphenyltrisilane in the solid state (ellipsoids set at 50% probability level). The hydrogen atoms at the terminal Si atoms have been refined isotropically, all other hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1-Si2 2.3578(7), Si2-Si3 2.3592(7), Si1-H1 1.4420(243), Si3-H3 1.3953(209), Si1-Si2-Si3 107.71(3).

Dehydrogenative coupling of phenylsilane. 439 mg phenylsilane (500 µl, 4.06 mmol) was added to 11.9 mg of [Ni_2(*i*Pr_2Im)$_4$(COD)] **1** (28.4 µmol, 0.7 mol-%) at room temperature. Immediately after addition a vigorous hydrogen evolution could be observed, that slowly decreases after 30 minutes but is still observable after several hours. In the course of the reaction the viscosity of the mixture increases until a waxy solid is obtained after 9 days containing linear and cyclic oligosilanes. The product mixture is analyzed by GPC as well as NMR and IR spectroscopy (Figure S10-S12). **GPC:** M_w = 1119; M_n = 924 ; M_w/M_n = 1.2. **^{1}H NMR** (500.1 MHz, C_6D_6, 296 K): δ = 4.27-4.94 (br, linear oligomeres), 4.94-5.77 (br, cyclic oligomeres) (ratio: 1.00 : 0.61). **IR** (ATR): $\tilde{\nu}$ = 2023-2233 (vs, br, $\nu_{\text{-}Si\text{-}H,str}$). In addition to that, 1,2-diphenyldisilane and 1,2,3-triphenyltrisilane could be detected by GC/MS-analysis next to diphenyl- und triphenylsilane. In the mass spectra (MALDI-TOF; matrix: DCTP; voltage polarity: positive) of the product mixture only cyclic oligosilanes $(SiPhH)_n$ could be detected with $5 \leq n \leq 17$ (and more) as the corresponding K^+-adducts (Figure S13). The most intensive signal can be attributed to the heptamer and octamer, which is in good agreement with the GPC-data.

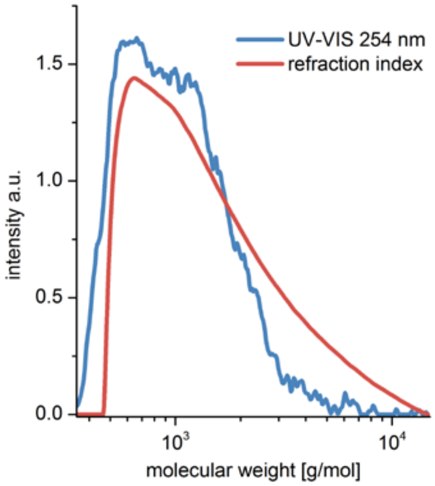


Figure S10. Section of the GPC-trace of the product mixture obtained by catalytic dehydrocoupling of phenylsilane using 0.7 mol% [Ni_2(*i*Pr_2Im)$_4$(COD)] (**1**).

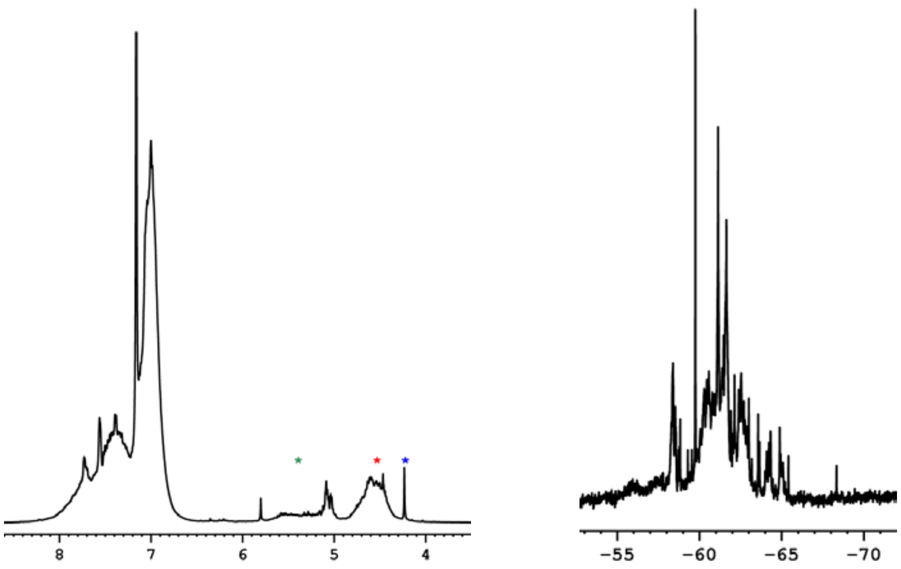


Figure S11. Left: Section of the ^{1}H NMR spectrum (3.5 to 8.5 ppm) of the product mixture obtained by catalytic dehydrocoupling of phenylsilane using 0.7 mol% [Ni$_2$(*i*Pr$_2$Im)$_4$(COD)] (**1**). The resonance marked with a blue asterisk corresponds to phenylsilane. The resonance marked with a red asterisk (4.28 to 4.90 ppm) can be attributed to linear and the one marked with a green asterisk (4.96 to 5.86 ppm) to cyclic oligomers. Right: Section of the ^{29}Si{^{1}H} NMR spectrum (-72 to -53 ppm) of the product mixture obtained by catalytic dehydrocoupling of phenylsilane using 0.7 mol% [Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)] (**1**).

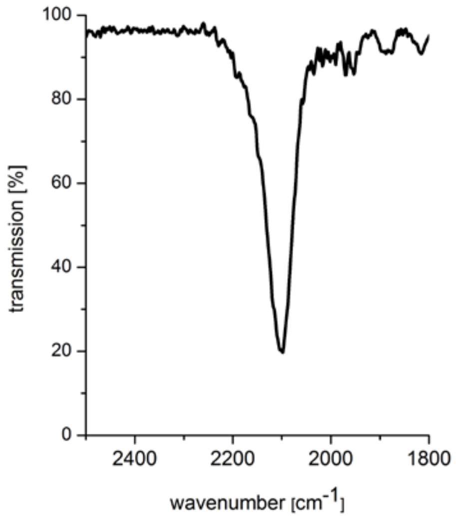
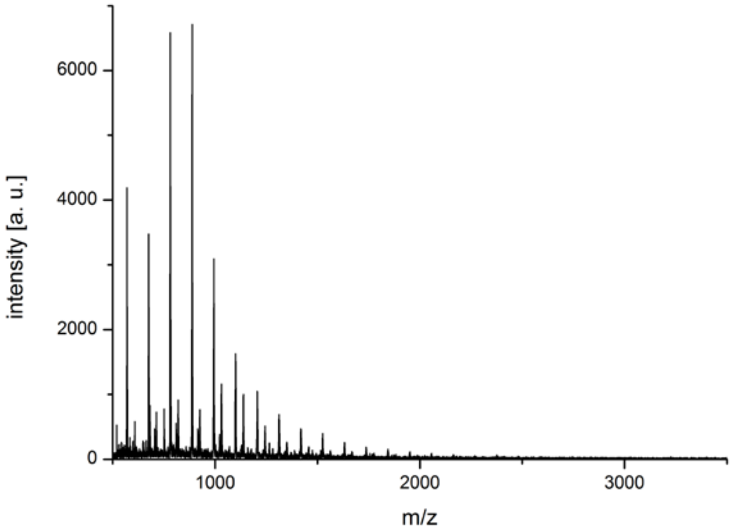


Figure S12: Section of the IR-spectrum (1800 to 2500 cm^{-1}) of the product mixture obtained by catalytic dehydrocoupling of phenylsilane using 0.7 mol% [Ni$_2$(*i*Pr$_2$Im)$_4$(COD)] (**1**).



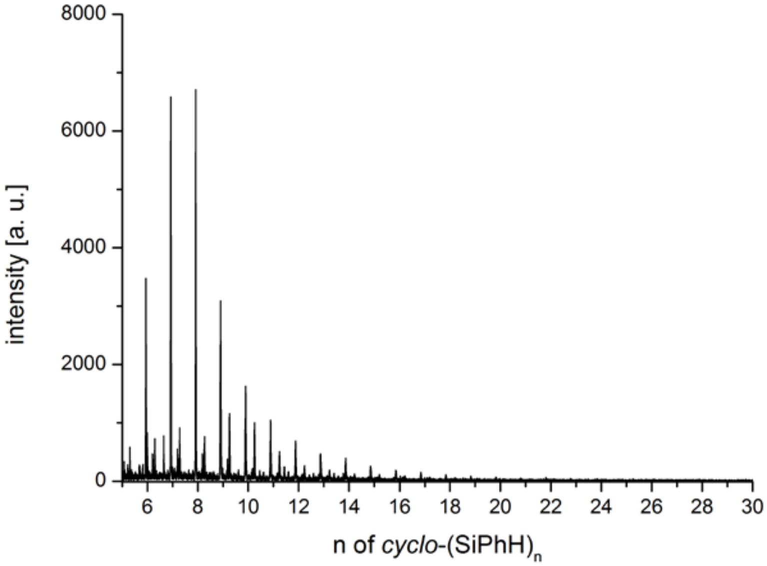


Figure S12: Section of the MALDI-TOF spectrum (matrix: DCTP; voltage polarity: positive) of the product mixture obtained by catalytic dehydrocoupling of phenylsilane using 0.7 mol% [Ni_2(*i*Pr_2Im)$_4$(COD)] (**1**).

5. Hydrogenation of disilanes to hydrosilanes catalyzed by complex 1.

General procedure.

A reaction mixture (suspension or solution) of the corresponding disilane (listed in Table S1) and 5.0 mol% complex **1** in 20 ml toluene were placed in a 120 ml Schlenk tube and pressurized with 1.8 bar H_2. After stirring the resulting mixture for 2 days at room temperature a sample was taken for GC/MS analysis. Afterwards, the solvent was removed under reduced pressure and the residue was suspended in 15 ml hexane. After filtration and removal of the solvent the crude product was purified by column chromatography using hexane as the eluent and analyzed by NMR spectroscopy.

Table S1: Conversion and isolated yields of the hydrogenation of hexaphenyldisilane (Ph_6Si_2), 1,1,2,2-tetraphenyldimethyldisilane ($Ph_4Me_2Si_2$), 1,1,2,2-tetramethyldiphenyldisilane ($Me_4Ph_2Si_2$), and hexamethyldisilane (Me_6Si_2).

Disilane	Conversion estimated by GC/MS [%]	Isolated yield [%]
Ph_6Si_2 (258 mg, 479 μmol)	0	0
$Ph_4Me_2Si_2$ (1.89 g, 4.79 mmol)	100	83
$Me_4Ph_2Si_2$ (1.30 g, 4.79 mmol)	76	43
Me_6Si_2 (702 mg, 4.79 mmol)	0	0

Diphenylmethylsilane as isolated from the reaction.

^{1}H NMR (200.1 MHz, C_6D_6, 296 K): δ = 0.47 (d, 3 H, $^3J_{HH}$ = 3.9 Hz, CH_3), 5.13 (q, 1 H, $^3J_{HH}$ = 3.9 Hz, $^1J_{SiH}$ = 193.1 Hz, Si*H*), 7.09–7.19 (m, 6 H, aryl-C*H*), 7.45–7.56 (m, 4 H, aryl-C*H*). **^{13}C{^{1}H} NMR** (50.3 MHz, C_6D_6, 296 K): δ = -4.8 (*C*H_3), 128.3 (aryl-*C*H), 129.8 (aryl-C_{para}H), 135.2 (aryl-*C*H), 135.6 (aryl-C_{ipso}).

Phenyldimethylsilane as isolated from the reaction.

^{1}H NMR (200.1 MHz, C_6D_6, 296 K): δ = 0.18 (d, 6 H, $^3J_{HH}$ = 3.8 Hz, CH_3), 4.56 (sept, 1 H, $^3J_{HH}$ = 3.8 Hz, $^1J_{SiH}$ = 188.2 Hz, Si*H*), 7.09–7.19 (m, 3 H, aryl-C*H*), 7.35–7.46 (m, 2 H, aryl-C*H*). **^{13}C{^{1}H} NMR** (50.3 MHz, C_6D_6, 296 K): δ = -3.6 (*C*H_3), 128.2 (aryl-*C*H), 129.5 (aryl-C_{para}H), 134.3 (aryl-*C*H), 137.4 (aryl-C_{ipso}).

6. Crystallography

Crystal data collection and processing parameters are given in Table S2. Crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to a Bruker D8 Apex-1 diffractometer with CCD area detector and graphite-monochromated Mo-Kα radiation equipped with an Oxford Cryosystems low-temperature device (**6**, ***cis*-7**, ***cis*-10**, ***cis*-11**, ***trans*-12**, trisilane) or a Stoe-IPDS image plate diffractometer (graphite-monochromated Mo-Kα radiation) equipped with a FTS AirJet low temperature device (***cis*-9**). Data were collected at 173 K (**6**, ***cis*-7**, ***cis*-10**, ***cis*-11**, ***trans*-12**, trisilane) or 203 K (***cis*-9**). The images were processed with the Bruker software packages and equivalent reflections were merged. Corrections for Lorentz-polarization effects and absorption were performed if necessary and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms, and hydrogen atoms located at nickel or silicon were isotropically refined. All other hydrogen atoms were included in calculated positions and refined using a riding model. Extinction corrections were applied as required. Crystallographic calculations were performed using the SHELXTL software package. [S4] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms not located at nickel or silicon were assigned to idealized positions and were included in structure factors calculations.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no.s CCDC 997522-997529. Copies of the data can be obtained free of charge on application to CCDC.

Table S2. Crystallographic Data of *cis*-[Ni(*i*Pr$_2$Im)$_2$(H)(SiPh$_3$)] ***cis*-4**, [{Ni(*i*Pr$_2$Im)(μ^2-SiPh$_2$H)}$_2$] **6**. *cis*-[Ni(*i*Pr$_2$Im)$_2$(H)(SiMes$_2$H)] ***cis*-7**, *cis*-[Ni(*i*Pr$_2$Im)$_2$(SiHMe$_2$)$_2$] ***cis*-9**, *cis*-[Ni(*i*Pr$_2$Im)$_2$(SiEt$_2$H)$_2$] ***cis*-10,** *cis*-[Ni(*i*Pr$_2$Im)$_2$(SiCyH$_2$)$_2$] ***cis*-11,** *trans*-[Ni(*i*Pr$_2$Im)$_2$(Si(OEt)$_3$)$_2$] ***trans*-12,** 1,1,2,2,3,3-Hexaphenyltrisilan.

	***cis*-4**	**6**	***cis*-7**	***cis*-9**
Formula	$C_{36}H_{48}N_4NiSi$	$C_{42}H_{54}N_4Ni_2Si_2$	$C_{36}H_{56}N_4NiSi$ • 0.5 C_7H_8	$C_{22}H_{46}N_4NiSi_2$
Formula weight	623.58	788.49	677.71	481.52
Color, shape	orange, block	red, block	yellow, block	orange, prism
Cryst. size [mm^3]	0.17x0.11x0.09	0.06x0.14x0.29.	0.25x0.22x0.10	0.50x0.30x0.20
Crystal system	Monoclinic	monoclinic	monoclinic	monoclinic
Space group	*Cc*	*P*2$_1$/c	*C*2/c	C2/c
a [Å]	11.8454(8)	10.480(5)	41.417(8)	32.548(7)
b [Å]	18.6420(13)	16.614(7)	11.756(2)	9.6502(19)
c [Å]	16.1698(14)	12.530(6)	16.723(3)	18.368(4)
β [°]	103.264(3)°	106.519(7)	104.22(3)	99.54(3)
Volume [Å^3]	3475.4(5)	2091.9(16)	7893(3)	5689(2)
Z	4	2	4	8
Density [g·cm^{-3}]	1.192	1.252	1.141	1.124
µ [mm^{-1}]	0.622	0.990	0.552	0.780
F (000)	1336	836	2936	2096
θ [°]	2.08 – 26.76	2.03 – 26.32	1.01 – 26.09	2.20 - 25.95
Index	$-14 \leq h \leq 14$, $-23 \leq k \leq 21$, $-20 \leq l \leq 20$	$-12 \leq h \leq 12$, $-20 \leq k \leq 20$, $-15 \leq l \leq 15$	$-50 \leq h \leq 50$, $-14 \leq k \leq 14$, $-20 \leq l \leq 20$	$-37 \leq \mathrm{h} \leq 39$, $-11 \leq \mathrm{k} \leq 11$, $-22 \leq \mathrm{l} \leq 22$
Reflections collected	20197	32458	82571	17280
Indep. Reflections	6715	4191	7787	5357
Observed Reflections [$I>2\sigma$(I)]	6103	3326	6614	4120
R_{int}	0.0446	0.0587	0.0497	0.0448
Restraints	2	0	0	0
Parameters	390	234	434	270
*R*1 / *wR*2 [$I>2\sigma$(I)]	0.0313/0.0622	0.0310/0.0758	0.0373/0.0930	0.0371/0.0872
*R*1 /*wR*2 (all data)	0.0377/0.0644	0.0450/0.0832	0.0463/0.1019	0.0563/0.0952
Largest diff peak and hole [e·Å^{-3}]	0.361/-0.215	0.443/-0.212	0.492/-0.186	0.411/ -0.323
GooF	0.996	1.038	1.056	1.000

Table S2 contd.

	***cis*-10**	***cis*-11**	***trans*-12**	**trisilane**
Formula	$C_{26}H_{54}N_4NiSi_2$	$C_{30}H_{58}N_4NiSi_2$	$C_{30}H_{62}N_4NiO_6Si_2$	$C_{36}H_{32}Si_3$
Formula weight	537.62	589.69	689.73	548.89
Color, shape	orange, block	orange, block	yellow, block	colorless, plate
Cryst. size [mm^3]	0.48x0.45x0.35	0.35x0.29x0.25	0.20x0.13x0.12	0.18x0.12x0.03
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	*C*2/c	*C*2/c	$P2_1$/n	$P\bar{1}$
a [Å]	36.437(3)	15.655(4)	10.576(2)	9.9470(12)
b [Å]	9.9652(8)	11.439(3)	12.144(2)	10.5252(13)
c [Å]	18.8125(14)	19.648(5)	14.883(3)	16.903(2)
α [°]	90	90	90	102.664(2)
β [°]	111.354(2)	106.741(9)	102.49(3)	98.563(2)
γ [°]	90	90	90	110.928(2)
Volume [Å^3]	6361(8)	3369.3(16)	1866.3(6)	1561.8(3)
Z	8	4	2	2
Density [g·cm^{-3}]	1.123	1.163	1.227	1.167
μ [mm^{-1}]	0.704	0.671	0.627	0.175
F (000)	1288	1288	748	580
θ [°]	2.13 – 26.08	2.16 – 26.16	2.16 – 26.23	2.17 – 24.71
Index	$-44 \leq h \leq 44$, $-12 \leq k \leq 12$, $-23 \leq l \leq 23$	$-19 \leq h \leq 19$, $-14 \leq k \leq 14$, $-22 \leq l \leq 24$	$-13 \leq h \leq 12$, $-15 \leq k \leq 15$, $0 \leq l \leq 18$	$-11 \leq h \leq 11$, $12 \leq k \leq 12$, $0 \leq l \leq 19$
Reflections collected	39789	12233	7173	5327
Indep. Reflections	6304	3332	3736	5327
Observed Reflections [$I>2\sigma(I)$]	5762	2822	3102	4851
R_{int}	0.0291	0.0355	0.0339	0.0725
Restraints	0	0	0	0
Parameters	318	180	203	360
$R1$ / $wR2$ [$I>2\sigma(I)$]	0.0250 / 0.0652	0.0300 / 0.0658	0.0426 / 0.1159	0.0430 / 0.1175
$R1$ /$wR2$ (all data)	0.0383 / 0.0672	0.0384 / 0.0691	0.0574 / 0.1363	0.0465 / 0.1211
Largest diff peak and hole [e·Å^{-3}]	0.421 / -0.202	0.336 / -0.224	0.767 / -0.651	0.437 / -0.215
GooF	1.052	1.026	1.149	1.029

Selected bond lengths and angles for the molecular structures

Figure 1. Molecular structure of *cis*-[Ni(*i*Pr$_2$Im)$_2$(H)(SiPh$_3$)] (***cis*-4**) in the solid state (ellipsoids set at 50% probability level). The hydrogen atom at nickel has been located from the electron density map and refined isotropically, all other hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Ni-C1 1.897(2), Ni-C11 1.935(2), Ni-Si 2.2017(6), Ni-H1 1.44(2), Si-H1 2.0976(1). Selected angles (deg): C1-Ni-C11 102.01(9), C1-Ni-Si 100.34(7), C1-Ni-H1 166.0(9), C11-Ni-H1 91.9(9), C11-Ni-Si 153.32(6), Si-Ni-H1 66.6(9). Selected angles between defined planes (deg): Ni-Si-H1//C1-Ni-C11 16.447(28).

Figure 2. Molecular structure of [{(*i*Pr$_2$Im)Ni-μ^2-(HSiPh$_2$)}$_2$] (**6**) in the solid state (ellipsoids set at 50% probability level). The hydrogen atoms at nickel have been located from the electron density map and isotropically refined, all other hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Ni-C1 1.8941(19), Ni-Si 2.1953(8), Ni-Si‘ 2.2393(9), Ni-Ni 2.5136(12), Ni-H 1.57(2), Si-H 1.62(2). Selected angles (deg): Ni-Si-Ni‘ 69.05(4), Si-Ni-Si‘ 110.95(4), C1-Ni-Si 100.02(6), C1-Ni-Si‘ 149.02(6), C1-Ni-H‘ 102.6(8), C1-Ni-Ni‘ 156.32(6), H‘-Ni-Si‘ 46.5(8), H‘-Si‘-Ni 44.5(8), Selected torsion angles and angles between defined planes (deg): C1-Ni-Ni‘-C1‘ 180.000(201), H‘-Ni-Ni‘-H 180.000(1166), H‘-Ni-Ni‘-C1‘ 1.252(839), Ni-Si-Ni‘//Ni-Si‘-Ni‘ 0.000(28), Si-Ni-Si‘//Si-Ni‘-Si‘ 0.000(38).

Figure 3. Molecular structure of *cis*-[Ni(*i*Pr$_2$Im)$_2$(H)(SiMes$_2$H)] (***cis*-7**) in the solid state (ellipsoids set at 50% probability level). The Ni–H and Si–H hydrogen atoms have been located from the electron density map and have been isotropically refined, all other hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Ni-C1 1.9065(19), Ni-C11 1.9268(18), Ni-Si 2.2199(7), Ni-H2 1.39(2), Si-H2 1.96(2), Si-H1 1.42(2). Selected angles (deg): C1-Ni-C11 104.55(8), H2-Ni-Si 60.9(9), H2-Si-Ni 38.2(6), C11-Ni-H2 90.2(9), C1-Ni-Si 104.30(5), C1-Ni-H2 165.2(9), C11-Ni-Si 150.40(6). Selected angles between defined planes (deg): C1-Ni-C11//Si-Ni-H2 6.757(388).

Figure 4. Molecular structure of *cis*-[Ni(*i*Pr$_2$Im)$_2$(SiMeH$_2$)$_2$] (***cis*-9**) (top), *cis*-[Ni(*i*Pr$_2$Im)$_2$(SiEt$_2$H)$_2$] (***cis*-10**) (middle), and *cis*-[Ni(*i*Pr$_2$Im)$_2$(SiCyH$_2$)$_2$] (***cis*-11**) (bottom) in the solid state (ellipsoids set at 50% probability level). The hydrogen atoms at silicon have been refined isotropically, all other hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): *Cis*-[Ni(*i*Pr$_2$Im)$_2$(SiMeH$_2$)$_2$] (***cis*-9**): Ni-C1 1.928(2), Ni-C11 1.921(2), Ni-Si1 2.2419(10), Ni-Si2 2.2442(8), Si1-Si2 2.9236(12), C1-Ni-C11 100.74(9), Si1-Ni-Si2 81.33(3), C1-Ni-Si1 92.61(7), C11-Ni-Si2 94.80(8), C1-Ni- Si2 152.03(7), C11-Ni-Si1 156.87(7), Ni-Si1-C20 116.96(10), Ni-Si1-C21 112.16(16), Ni-Si2-C22 119.82(11), Ni-Si2-C23 105.45(10), plane C1-Ni-C11//Si1-Ni-Si2 33.657(77). *Cis*-[Ni(*i*Pr$_2$Im)$_2$(SiEt$_2$H)$_2$] (***cis*-10**): Ni-C1 1.9182(13), Ni-C11 1.9306(13), Ni-Si1 2.2588(4), Ni-Si2 2.2661(4), Si1-Si2 3.0501(6), Si1-Ni-Si2 84.763(14), C1-Ni-C11 97.74(5), C1-Ni-Si1 90.66(4), C11-Ni-Si2 90.99(4), C1-Ni-Si2 162.97(4), C11-Ni-Si1 163.42(4), plane C1-Ni-C11//Si1-Ni-Si2 21.797(32). *Cis*-[Ni(*i*Pr$_2$Im)$_2$(SiCyH$_2$)$_2$] (***cis*-11**): Ni-C1 1.9309(16), Ni-Si 2.2491(7), Si-Si‘ 2.8405(9), C1-Ni-C1‘ 102.01(9), Si-Ni-Si‘ 78.32(3), C1-Ni-Si 91.21(5), C1-Ni-Si‘ 162.70(5), plane C1-Ni-C1‘//Si-Ni-Si‘ 17.975(40).

Figure 5. Molecular structure of *trans*-[Ni(*i*Pr$_2$Im)$_2$Ni(Si(OEt)$_3$)$_2$] (***trans*-12**) in the solid state (ellipsoids set at 50% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Ni-C1 1.867(2), Ni-Si 2.2806(8). Selected angles (deg): C1-Ni-Si 88.30(7), C1-Ni-Si‘ 91.70(7), C1-Ni-C1‘ 180.00(4), Si-Ni-Si‘ 180.00(3).

7. References

[S1] J. Attner, U. Radius, *Chem. Eur. J.*, 2001, ***7***, 783.

[S2] (a) T. Schaub, U. Radius, *Chem. Eur. J.*, 2005, **11**, 5024.
(b) Schaub, T.; Backes, M.; Radius, U., *Organometallics*, 2006, **25**, 4196.

[S3] T. Zell, T. Schaub, K. Radacki, U. Radius, *Dalton Trans.*, 2011, 1852

[S4] (a) J. L. Speier, R. E. Zimmerman, *J. Am. Chem. Soc.* **1955**, *77*, 6395. (b) J. P. Banovetz, H. Suzuki, R. M. Waymouth, *Organometallics* **1993**, *12*, 4700. (c) H. Gilman, D. H. Miles, *J. Org. Chem.* **1958**, *23*, 326.

[S5] G. M. Sheldrick, *Acta Crystallogr. A* **2008**, *64*, 112.