

Electronic Supplementary Information

Si-H activation of Hydrosilanes leading to Hydrido Silyl and Bis(silyl) Nickel Complexes

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Experimental Details

General Considerations

All reactions and subsequent manipulations involving organometallic reagents were performed under a nitrogen or argon atmosphere using standard Schlenk techniques as reported previously.^{S1} Elemental analyses were performed in the microanalytical laboratory of the author's department. NMR spectra were recorded on a Bruker AMX 300 and a Bruker AV 400 at 298 K or on a Bruker DRX-300, Bruker Avance 400 and a Bruker Avance 500 at 296 K. ¹³C NMR spectra are broad-band proton-decoupled ¹³C{¹H}. NMR data are listed in parts per million (ppm) and are reported relative to Tetramethylsilane. Coupling constants are quoted in hertz. Spectra are referenced internally to residual protio-solvent resonances (¹H: C₆D₆, 7.15 ppm, DMSO-*d*₆, 2.50 ppm, toluene-*d*₈ 2.09 ppm) or natural-abundance carbon resonances (¹³C: C₆D₆, 128.0 ppm; DMSO-*d*₆, 39.4 ppm). Infrared spectra were recorded as KBr pellets on a Bruker IFS 28 or on a Nicolet 380 FT-IR and are reported in cm⁻¹. Compound **1** was prepared as previously reported.^{S2} The silanes were purchased from ABCR and used without any further purification.

Synthesis of [Ni(ⁱPr₂Im)₂(SiH₂Ph)₂] **2**

Phenylsilane (250 μL, 2.00 mmol) was added to a suspension of [Ni₂(ⁱPr₂Im)₄(COD)] (420 mg, 0.50 mmol) in 20 mL THF. Immediately after addition of the silane gas evolution (hydrogen) became recognizable. After 15 minutes of stirring at room temperature all volatiles were removed *in vacuo* and the remaining solid was suspended in 20 mL hexane. The undissolved product was filtered off and dried *in vacuo* to afford 390 mg (67 %) of an orange powder. Single crystals suitable for X-ray crystal structure analysis were obtained from saturated diethylether solutions of the compound at -40°C. C₃₀H₄₆N₄NiSi₂ [577.58 g/mol]: Calcd. (found): C 62.38 (62.05), H 8.03 (8.14), N 9.70 (9.46). IR (KBr [cm⁻¹]): 456 (w), 531 (w), 569 (w), 628 (vw), 678 (s), 698 (s), 731 (s), 787 (s), 879 (w), 958 (s), 991 (vw), 1019 (m), 1062 (w), 1096 (m), 1128 (m), 1215 (s), 1258 (w), 1292 (m), 1323 (w), 1367 (m), 1389 (s), 1406 (s), 1416 (s), 1425 (m), 1443 (w), 1464 (m), 1477 (w), 1542 (w), 1559 (w), 1580 (w), 1647 (w), 1985 (vs, br, ν_{SiH}), 2035 (s, br, ν_{SiH}), 2868 (m), 2930 (m), 2970 (s), 3058 (m), 3097 (w), 3130 (m), 3161 (m). ¹H-NMR (400 MHz, 25°C, DMSO-*d*₆): δ/ppm = 0.77 (d, 12 H, ³J_{HH} = 6.4 Hz, ⁱPr-CH₃), 1.15 (d, 12 H, ³J_{HH} = 6.4 Hz, ⁱPr-CH₃), 3.97 (s, 4 H, SiH), 4.49 (sept, 4 H, ³J_{HH} = 6.7 Hz, ⁱPr-CH), 7.13 (m, 6 H, aryl-*H*_{m,p}), 7.27 (s, 4 H, CHCH), 7.43 (m, 4 H, aryl-*H*_o). ¹³C{¹H}-NMR (100 MHz, 25°C, DMSO-*d*₆): δ/ppm = 22.0 (ⁱPr-CH₃), 22.8 (ⁱPr-CH₃), 51.1 (ⁱPr-CH), 117.4 (CHCH), 126.1 (aryl-C_p), 126.70 (aryl-C_m), 134.8 (aryl-C_o), 143.8 (aryl-C_i), 190.1 (NCN). ²⁹Si-NMR (79 MHz, 25°C, DMSO-*d*₆): δ/ppm = -29.1 (t, ¹J_{Si,H} = 149.9 Hz)

Synthesis of [Ni(ⁱPr₂Im)₂(SiHPh₂)₂] 3

Diphenylsilane (222 μ L, 1.20 mmol) was added to a suspension of [Ni₂(ⁱPr₂Im)₄(COD)] (168 mg, 0.20 mmol) in 10 mL toluene. The reaction mixture was stirred about 7 hours at room temperature. All volatiles were removed *in vacuo* and the remaining solid was suspended in 7 mL hexane. The product was filtered off and dried *in vacuo* to afford 240 mg (82 %) of an orange colored powder. C₄₂H₅₄N₄NiSi₂ [729.77 g/mol]: Calcd. (found): C 69.12 (68.88), H 7.46 (7.43), N 7.68 (7.74). IR (KBr [cm⁻¹]): 417 (m), 458 (w), 485 (s), 570 (vw), 675 (s), 712 (s), 757 (w), 861 (s), 1017 (w), 1087 (m), 1124 (m), 1211 (vs), 1260 (w), 1294 (m), 1369 (m), 1389 (s), 1404 (s), 1424 (m), 1464 (w), 1580 (vw), 2037 (m, br, ν_{SiH}), 2930 (w), 2973 (m), 3041 (m), 3131 (w). ¹H-NMR (300 MHz, 23°C, C₆D₆): δ /ppm = 0.62 (br, 24 H, ⁱPr-CH₃), 4.63 (sept, 4 H, ³J_{HH} = 6.1 Hz, ⁱPr-CH), 5.96 (s, 2 H, SiH) 6.31 (s, 4 H, CHCH), 7.14 (m, 12 H, aryl-H), 7.82 (m, 8 H, aryl-H). ¹H-NMR (500 MHz, -60°C, toluene-*d*₈): δ /ppm = 0.33 (d, br, 12 H, ³J_{HH} = 6.2 Hz, ⁱPr-CH₃), 0.74 (br, 12 H, ⁱPr-CH₃), 4.48 (sept, 4 H, ³J_{HH} = 6.5 Hz, ⁱPr-CH), 6.19 (s, 4 H, CHCH), 6.25 (s, 2 H, SiH, ¹J_{SiH} = 167.9 Hz), 7.17 (m, 12 H, aryl-H), 7.84 (br, 8 H, aryl-H). ¹³C{¹H}-NMR (75 MHz, 23°C, C₆D₆): δ /ppm = 22.8 (ⁱPr-CH₃), 51.6 (ⁱPr-CH), 116.7 (NCCN), 126.5 (aryl-C_p), 127.3 (aryl-C_{tert}), 136.2 (aryl-C_{tert}), 146.9 (aryl-C_i), 192.7 (NCN). ²⁹Si{¹H}-NMR (60 MHz, 23°C, C₆D₆): δ /ppm = 4.74.

Synthesis of [Ni(ⁱPr₂Im)₂(SiPh₃)(H)] 4

[Ni₂(ⁱPr₂Im)₄(COD)] (168 mg, 0.20 mmol) and Triphenylsilane (105 mg, 0.40 mmol) were suspended in 10 mL toluene. The yellow solution was stirred at room temperature for one hour. All volatiles were then removed *in vacuo* and the remaining solid was suspended in 10 mL hexane. The product was filtered off, washed with 5 mL hexane and dried *in vacuo* to afford 243 mg (97 %) of a yellow powder. C₃₆H₄₈N₄NiSi [623.57 g/mol]: Calcd. (found): C 69.34 (69.19), H 7.76 (7.69), N 8.98 (8.74). IR (KBr [cm⁻¹]): 403 (w), 471 (w), 512 (m), 618 (w), 669 (w), 701 (m), 745 (w), 806 (w), 881 (vw), 985 (s), 1122 (vs), 1185 (s), 1212 (s), 1242 (vs), 1308 (s), 1368 (w), 1390 (w), 1426 (w), 1460 (w), 1508 (vw), 1561 (vw), 1618 (w), 1638 (w), 1821 (vw, ν_{NiH}), 2024 (vw), 2344 (vw), 2359 (vw), 2871 (vw), 2929 (vw), 2970 (w), 3062 (vw). ¹H-NMR (300 MHz, C₆D₆): δ /ppm = -9.81 (s, 1 H, NiH), 0.93 (d, 24 H, ³J_{HH} = 6.8 Hz, ⁱPr-CH₃), 5.15 (sept, 4 H, ³J_{HH} = 6.8 Hz, ⁱPr-CH), 6.38 (s, 4 H, CHCH), 7.19 (m, 3 H, aryl-H_p), 7.25 (m, 6 H, aryl-H), 7.86 (m, 6 H, aryl-H). ¹³C{¹H}-NMR (75 MHz, 23°C, C₆D₆): δ /ppm = 23.0 (ⁱPr-CH₃), 51.6 (ⁱPr-CH), 115.4 (NCCN), 126.2 (aryl-C_p), 127.0 (aryl-C_{tert}), 136.8 (aryl-C_{tert}), 149.7 (aryl-C_i), 196.8 (NCN). ²⁹Si{¹H}-NMR (60 MHz, 23°C, C₆D₆): δ /ppm = -5.7.

Synthesis of [Ni(ⁱPr₂Im)₂(SiMePh₂)(H)] 5

Diphenylmethylsilane (160 μ L, 0.80 mmol) was added at room temperature to a suspension of [Ni₂(ⁱPr₂Im)₄(COD)] (168 mg, 0.20 mmol) in 10 mL toluene. The colour of the suspension turned immediately after addition from yellow to red. After 24 hours stirring at room temperature all volatiles were removed *in vacuo* and the remaining oily solid was suspended in 10 mL hexane. The product was filtered off and dried *in vacuo* to afford 204 mg (91 %) of an orange colored powder. Single crystals suitable for X-ray crystal structure analysis were obtained from saturated hexane solutions of the compound at -30°C . C₃₁H₄₆N₄NiSi [561.50 g/mol]: Calcd. (found): C 66.31 (65.37), H 8.26 (8.12), N 9.98 (9.63). IR (KBr [cm⁻¹]): 404 (s), 420 (s), 470 (s), 486 (s), 618 (s), 626 (s), 636 (s), 663 (m), 676 (m), 689 (s), 701 (s), 731 (s), 763 (m), 800 (w), 833 (w), 879 (w), 989 (m), 1017 (m), 1059 (m), 1108 (m), 1128 (m), 1182 (w), 1216 (vs), 1262 (w), 1281 (w), 1294 (w), 1366 (m), 1387 (m), 1401 (m), 1415 (m), 1425 (m), 1459 (w), 1466 (w), 1479 (vw), 1500 (vw), 1508 (vw), 1518 (vw), 1535 (vw), 1561 (vw), 1618 (m), 1638 (m), 1655 (w), 1685 (vw), 1704 (vw), 1719 (vw), 1735 (vw), 1752 (vw), 1763 (vw), 1774 (vw), 1833 (vw, ν_{NiH}), 2118 (vw), 2346 (vw), 2870 (w), 2929 (w), 2970 (w), 3044 (vw), 3058 (w), 3135 (vw), 3161 (vw), 3240 (w). ¹H-NMR (400 MHz, -60°C , toluene-*d*₈): δ /ppm = -8.95 (s, 1 H, NiH), 0.78 (d, 6 H, ⁱPr-CH₃), 0.79 (s, 3 H, SiCH₃), 0.94 (m, 12 H, ⁱPr-CH₃), 0.99 (d, 6 H, ³J_{HH} = 5.6 Hz, ⁱPr-CH₃), 5.12 (m, 2 H, ⁱPr-CH), 5.12 (m, 2 H, ⁱPr-CH) 6.38 (s, 2 H, CHCH), 6.38 (s, 2 H, CHCH) 7.26 (m, 2 H, aryl-H_p), 7.37 (m, 4 H, aryl-H), 8.13 (m, 4 H, aryl-H). ¹H-NMR (400 MHz, C₆D₆): δ /ppm = -9.20 (s, 1 H, NiH), 0.76 (s, 3 H, SiCH₃), 0.99 (d, 24 H, ³J_{HH} = 6.8 Hz, ⁱPr-CH₃), 5.12 (sept, 4 H, ³J_{HH} = 6.8 Hz, ⁱPr-CH), 6.38 (s, 4 H, CHCH), 7.20 (m, 2 H, aryl-H_p), 7.32 (m, 4 H, aryl-H), 8.06 (m, 4 H, aryl-H). ¹³C{¹H}-NMR (100 MHz, 23 $^{\circ}\text{C}$, C₆D₆): δ /ppm = 4.8 (SiCH₃), 23.0 (ⁱPr-CH₃), 51.4 (ⁱPr-CH), 115.0 (NCCN), 126.1 (aryl-C_p), 127.1 (aryl-C_{tert}), 136.7 (aryl-C_{tert}), 152.1 (aryl-C_i), 198.0 (NCN). ²⁹Si{¹H}-NMR (79 MHz, 23 $^{\circ}\text{C}$, C₆D₆): δ /ppm = -8.8.

¹H-NMR spectrum of 5



Crystallography

Crystals of compound **2** were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to a Stoe-IPDS 1 image plate diffractometer (Mo-K α radiation) equipped with a FTS AirJet low temperature device. Data were collected at 203 K; equivalent reflections were merged and the images were processed with the STOE IPDS software package. Corrections for Lorentz-polarisation effects and absorption were performed and the structures were solved by direct methods. The hydrogen atoms at silicon have been isotropically refined and the other hydrogen atoms were included in calculated positions. Extinction corrections were applied as required. Crystallographic calculations were performed using SHELXS-97 and SHELXL-97.^{S3}

Crystals of compound **5** were immersed in a film of nitrogen cooled perfluoropolyether oil on a glass fiber and transferred to a Bruker APEX diffractometer with a CCD area detector and multi-layer mirror monochromated Mo-K α radiation. The structure was solved using direct methods, refined with the SHELXTL software package^{S3} and expanded using Fourier techniques. All non-hydrogen atoms were

refined anisotropically. The hydrogen atom at nickel has been isotropically refined and the other hydrogen atoms were assigned to idealized positions and were included in structure factors calculations.

Explicit crystallographic information

Compound	$[\text{Ni}(\text{}^i\text{Pr}_2\text{Im})_2(\text{SiH}_2\text{Ph})_2] \mathbf{2} * \text{thf}$
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Empirical formula	(C ₃₀ H ₄₈ N ₄ NiSi ₂) * (C ₄ H ₈ O)
Formula weight (g·mol ⁻¹)	651.72
Temperature (K)	203(2)
Radiation, λ (Å)	Mo K _α 0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	
a (Å)	10.608(2)
b (Å)	10.799(2)
c (Å)	32.098(6)
α (°)	90.00
β (°)	96.47(3)
γ (°)	90.00
Volume (Å ³)	3653.7(13)
Z	4
Density (Mg·m ⁻³)	1.185
Absorption coefficient (mm ⁻¹)	0.627
F(000)	1408
Theta range for collection	3.57 - 26.37
Reflections collected	27454
Independent reflections	7420
Diffractometer	Stoe IPDS 1
Refinement method	Full-matrix least-squares on F ²
Data / parameters / restraints	7420 / 371 / 0
Goodness-of-fit on F ²	1.142
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	R ₁ = 0.0560, wR ₂ = 0.1510
R indices (all data)	R ₁ = 0.0731, wR ₂ = 0.1787
Maximum/minimum residual electron density (e·Å ⁻³)	0.921 / -0.767

Compound	[Ni(ⁱ Pr ₂ Im) ₂ (SiMePh ₂)(H)] 5
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Empirical formula	C ₃₁ H ₄₆ N ₄ NiSi
Formula weight (g·mol ⁻¹)	561.52
Temperature (K)	100(2)
Radiation, λ (Å)	Mo K $_{\alpha}$ 0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	
a (Å)	9.8713(8)
b (Å)	28.291(2)
c (Å)	11.4697(9)
α (°)	90.00
β (°)	105.117(2)
γ (°)	90.00
Volume (Å ³)	3092.3(4)
Z	4
Density (Mg·m ⁻³)	1.206
Absorption coefficient (mm ⁻¹)	0.691
F(000)	1208
Theta range for collection	3.57 - 26.37
Reflections collected	50036
Independent reflections	6568
Diffractometer	Bruker Apex-II CCD
Refinement method	Full-matrix least-squares on F ²
Data / parameters / restraints	6568 / 346 / 0
Goodness-of-fit on F ²	1.049
Final R indices [<i>I</i> > 2 σ (<i>I</i>)]	R ₁ = 0.0268, wR ₂ = 0.0685
R indices (all data)	R ₁ = 0.0303, wR ₂ = 0.0707
Maximum/minimum residual electron density (e·Å ⁻³)	0.819 / -0.268

References

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[S3] G. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.