Supplementary Information

Stable Nickel complexes of a Siliconoid/Silylene Hybrid Ligand: Competent Hydrosilylation Catalysts for Terminal Alkenes

Luisa Giarrana,[a] Dennis Welterlich,[a] Michael Zimmer,[a] Bernd Morgenstern[b] and David Scheschkewitz*[a]

M. Sc. L. Giarrana, M. Sc. D. Welterlich, Dr. M. Zimmer, Prof. Dr. D. Scheschkewitz − Krupp-Chair for General and Inorganic Chemistry, Saarland University, 66123 Saarbrücken, Germany

Dr. B. Morgenstern – Service Center X-ray Diffraction, Saarland University, 66123 Saarbrücken, Germany

E-Mail: david.scheschkewitz@uni-saarland.de

Institute and/or researcher X usernames: @scheschkewitz @LuisaGiarrana

Supplementary Information

Table of Contents

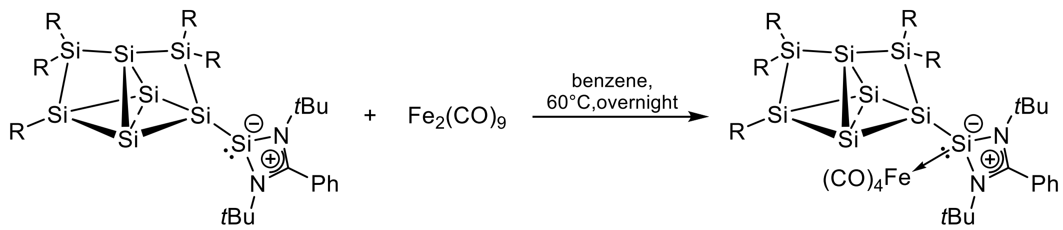
Supplementary Information

1 Experimental Procedures

All manipulations were carried out under a protective atmosphere of argon, by using a glovebox or standard Schlenk techniques. Solvents were dried and degassed by reflux over sodium/benzophenone under argon. [D$_6$]-benzene (C_6D_6) was dried over potassium mirror and distilled under argon prior to use. Si_7Li siliconoid,[1] chloro silylene[2,3] and siliconoid hybrid Si_7NHSi **1**[4] were prepared following the literature protocols while transition metal precursors, triphenyl phosphine and diphenyl silane were used as commercially purchased (under inert gas) and stored in a glove box. NMR spectra were recorded on a Bruker Avance III 300 and a Bruker Avance IV 400 NMR spectrometer (^{1}H = 300.13/ 400.13 MHz, ^{13}C = 75.47/ 100.61 MHz, ^{29}Si = 59.63/ 79.49 MHz). The ^{1}H and ^{13}C{1H} NMR spectra were referenced to the residual proton and natural abundance ^{13}C resonances of the deuterated solvent and chemical shifts were reported relative to $SiMe_4$ (C_6D_6: δ^1H = 7.16 ppm and δ^{13}C = 128.06 ppm, toluene-d_8 δ^1H = 7.09, 7.01, 6.97, 2.08 ppm and δ^{13}C = 137.48, 128.87, 127.96, 125.13, 20.43 ppm). Solid-state NMR data were collected from a Bruker Avance III 400 WB. UV-Vis spectra were recorded on a Shimadzu UV-2600 spectrometer in quartz cells with a path length of 0.1 cm. Elemental analyses were performed on an elemental analyzer Leco CHN-900. Mass spectrometry was measured on a Bruker SolariX 7 Tesla MALDI/ESI/APPI FTICR imaging MS. Melting points were determined under argon in NMR tubes and are uncorrected. The molten samples were examined by NMR spectroscopy to confirm whether decomposition had occurred upon melting. Crystallographic data of the structures reported in this paper has been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

2 Preparation, data and spectra

2.1 Preparation of $Fe(CO)_4$ siliconoid/silylene complex 2



1 **2**

M [g/mol] = 1472.79 1640.67

To Si_7 siliconoid/silylene **1**[4] (100 mg, 0.0679 mmol, 1.0 eq.) added diiron (0) nonacarbonyl $Fe_2(CO)_9$ (27.7 mg, 0.0747 mmol, 1.1 eq.) and 1.0 mL benzene. The brown solution was heated to 60°C and stirred overnight. After cooling to ambient temperature, all volatiles were removed under reduced pressure, and the compound was dried thoroughly. The resulting solid was extracted from 3.0 mL pentane, washed two times with approximately 0.5 mL pentane. Afterwards the solution was concentrated under reduced pressure and at room temperature for crystallization. The title compound **2** was isolated in 46% yield (51.5 mg, 0.0314 mmol).

^{1}H NMR (400.13 MHz, C_6D_6, 300 K) δ = 7.640 – 7.616 (m, $C_{10}H_8$), 7.503 (d, $^{3}J_{HH}$ = 7.53 Hz, 1H, ArC-*H*), 7.406 (s, 1H, ArC-*H*), 7.334 (s, 1H, ArC-*H*), 7.264 – 7.240 (m, $C_{10}H_8$), 7.089 – 7.035 (m, 5H, ArC-*H*), 7.012 – 6.995 (m, 2H, ArC-*H*), 6.940 – 6.904 (m, 2H, ArC-*H*), 6.891 (s, 1H, ArC-*H*), 6.816 (m, 1H, ArC-*H*), 6.733 (m, 1H, ArC-*H*), 5.810 (sept, $^{3}J_{HH}$ = 6.62 Hz, 1H, Tip-C*H*(CH_3)$_2$), 4.839 (sept, $^{3}J_{HH}$ = 6.48 Hz, 1H, Tip-C*H*(CH_3)$_2$), 4.668 (sept, $^{3}J_{HH}$ = 6.46 Hz, 1H, Tip-C*H*(CH_3)$_2$), 4.521 (sept, $^{3}J_{HH}$ = 6.46 Hz, 1H, Tip-C*H*(CH_3)$_2$), 3.989 (sept, $^{3}J_{HH}$ = 6.58 Hz, 1H, Tip-C*H*(CH_3)$_2$), 3.881 (sept, $^{3}J_{HH}$ = 6.46 Hz, 1H, Ar-C*H*(CH_3)$_2$), 3.500 (sept, $^{3}J_{HH}$ = 6.49 Hz, 2H, Tip-C*H*(CH_3)$_2$), 3.114 (sept, $^{3}J_{HH}$ = 6.58 Hz, 2H, Tip-C*H*(CH_3)$_2$), 2.907 (sept, $^{3}J_{HH}$ = 6.82 Hz, 1H, Tip-C*H*(CH_3)$_2$), 2.810 (sept, $^{3}J_{HH}$ = 6.82 Hz, 1H, Tip-C*H*(CH_3)$_2$), 2.693 – 2.615 (m, 3H, Tip-C*H*(CH_3)$_2$), 2.225 (t, $^{3}J_{HH}$ = 5.64 Hz, 6H, Tip-CH(CH_3)$_2$), 2.080 (d, $^{3}J_{HH}$ = 6.64 Hz, 3H, Tip-CH(CH_3)$_2$), 1.7202 (d, $^{3}J_{HH}$ = 6.53 Hz, 3H, Tip-CH(CH_3)$_2$), 1.648 (d, $^{3}J_{HH}$ = 6.36 Hz, 3H, Tip-CH(CH_3)$_2$), 1.590 (d, $^{3}J_{HH}$ = 6.53 Hz, 3H, Tip-CH(CH_3)$_2$), 1.554 (d, $^{3}J_{HH}$ = 6.38Hz, 3H, Tip-CH(CH_3)$_2$), 1.512 (d, $^{3}J_{HH}$ = 6.53 Hz, 3H, Tip-CH(CH_3)$_2$), 1.4678 (d, $^{3}J_{HH}$ = 6.69 Hz, 3H, Tip-CH(CH_3)$_2$), 1.4255 (d, $^{3}J_{HH}$ = 6.68 Hz, 3H, Tip-CH(CH_3)$_2$), 1.388 (t, $^{3}J_{HH}$ = 7.40 Hz, 8H, Tip-CH(CH_3)$_2$), 1.319 (t, $^{3}J_{HH}$ = 6.27 Hz, 8H, Tip-CH(CH_3)$_2$), 1.269 – 1.233 (m, hexane), 1.186 (d, $^{3}J_{HH}$ = 6.62 Hz, 6H, Tip-CH(CH_3)$_2$), 1.150 (s, 12H, Si(N(C(CH_3)$_3$))$_2$CPh overlapping with Tip-CH(CH_3)$_2$), 1.129 (s, 5H, Tip-CH(CH_3)$_2$), 1.101 (s, 3H, Tip-CH(CH_3)$_2$), 1.084 (s, 3H, Tip-CH(CH_3)$_2$), 1.067 (t, $^{3}J_{HH}$ = 6.27 Hz, 6H, Tip-CH(CH_3)$_2$), 0.890 (t, hexane), 0.855 (s, 9H, Si(N(C(CH_3)$_3$))$_2$CPh), 0.637 (d, $^{3}J_{HH}$ = 6.62 Hz, 3H, Tip-CH(CH_3)$_2$), 0.578 (dd, $^{3}J_{HH}$ = 9.50 Hz, 6.62 Hz, 6H, Tip-CH(CH_3)$_2$), 0.507 (d, 3H, $^{3}J_{HH}$ = 6.33 Hz, Tip-CH(CH_3)$_2$), 0.3903 (d, 3H, $^{3}J_{HH}$ = 6.33 Hz, Tip-CH(CH_3)$_2$), 0.265 (d, 3H, $^{3}J_{HH}$ = 6.33 Hz, Tip-CH(CH_3)$_2$) ppm.

^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 300 K) δ = 216.79 (s, 4C, *C*O), 167.35 (s, Si(N(C(CH_3)$_3$))$_2$*C*Ph), 155.18, 154.84, 154.75, 153.38, 153.04, 152.61, 151.74, 151.11, 150.20, 149.90, 149.61, 149.40, 141.75, 138.70, 138.11, 137.43, 137.00, 134.01, 131.40 (s, each 1C, Ar-*C*), 130.59, 129.32, 128.89, 128.54, 128.35, (s, each 1C, Ar-C*H*), 128.12, 127.88 (s, each 1C, Ar-*C*), 127.53, 126.02, 124.30 (s, each 1C, Ar-*C*H), 123.30 (d, ^{4}J = 4.83 Hz, Ar-*C*H), 122.68, 122.37, 122.29 (s, each 1C, Ar-*C*H), 122.15 (d, ^{4}J = 4.83 Hz, Ar-*C*H), 121.97, 121.37 (s, each 1C, Ar-*C*H), 55.91, 55.25 (s, Si(N(*C*(CH_3)$_3$))$_2$CPh), 37.53, 37.21, 36.58, 36.37, 35.79, 35.42, 35.34, 34.93, 34.84, 34.77, 34.67, 34.61, 34.52, 34.42, 32.92 (s, each 1C, Tip-CH(*C*H_3)$_2$), 31.92 (s, hexane), 31.80, 31.71 (s, each 3C, Si(N(C(*C*H_3)$_3$))$_2$CPh), 29.15, 28.67, 27.89, 27.84, 27.48, 27.42, 27.16, 26.63, 26.35, 26.27, 25.99, 25.58, 24.87, 24.82, 24.52, 24.45, 24.42, 24.22, 24.15, 24.11, 24.08, 23.99, 23.95, 23.87, 23.80, 23.14 (s, each 1C, Tip-CH(*C*H_3)$_2$), 23.01, 14.32 (s, hexane) ppm.

^{29}Si{^{1}H} NMR (79.49 MHz, C_6D_6, 300 K) δ = 172.7 (s, *Si*(Si(N(C(CH_3)$_3$))$_2$CPh)), 157.1 (s, *Si*Tip), 100.5 (s, Fe*Si*(N(C(CH_3)$_3$))$_2$CPh), 33.6 (s, *Si*Tip$_2$), 5.9 (s, *Si*Tip$_2$), −98.2 (s, *Si* unsubstituted), −198.5 (s, *Si* unsubstituted), −209.0 (s, *Si* unsubstituted) ppm.

Supplementary Information

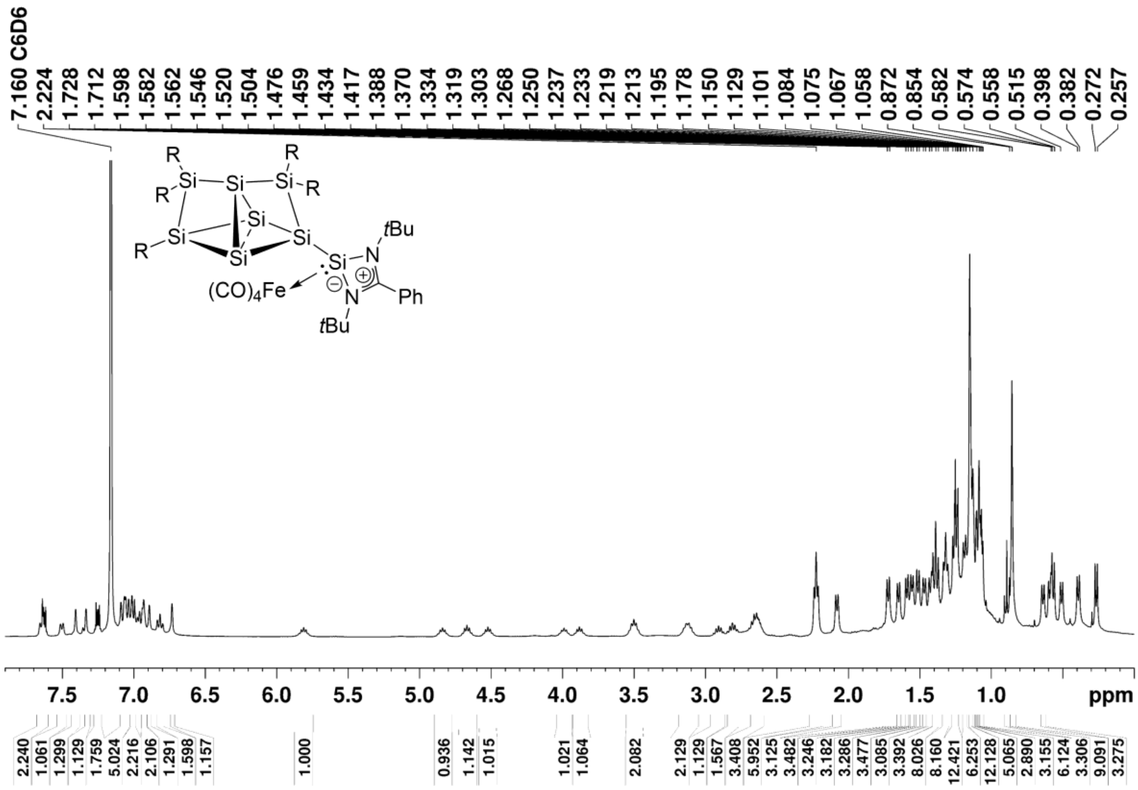
CP-MAS ^{29}Si{^{1}H} NMR (79.53 MHz, 13 KHz, 300 K) δ = 170.6 (s, *Si*(Si(N(C(CH$_3$)$_3$))$_2$CPh)), 164.0 (s, *Si*Tip), 101.1 (s, Fe*Si*(N(C(CH$_3$)$_3$))$_2$CPh), 39.1 (s, *Si*Tip$_2$), 9.9 (s, *Si*Tip$_2$), −88.8 (s, *Si* unsubstituted), −206.9 (s, *Si* unsubstituted), −212.5 (s, *Si* unsubstituted) ppm.

Elemental analysis: calculated for $C_{94}H_{138}N_2FeO_4Si_8$: C 68.82 %, H 8.48 %, N 1.71%; Found: C 68.08 %, H 7.43 %, N 1.31 %. The lower values compared to those calculated are quite common for unsaturated silicon clusters due to incomplete combustion typically attributed to the formation of silicon carbides and/or nitrides. In addition, elemental analysis has come under scrutiny because of highly variable results of bona fide identical samples.[5]

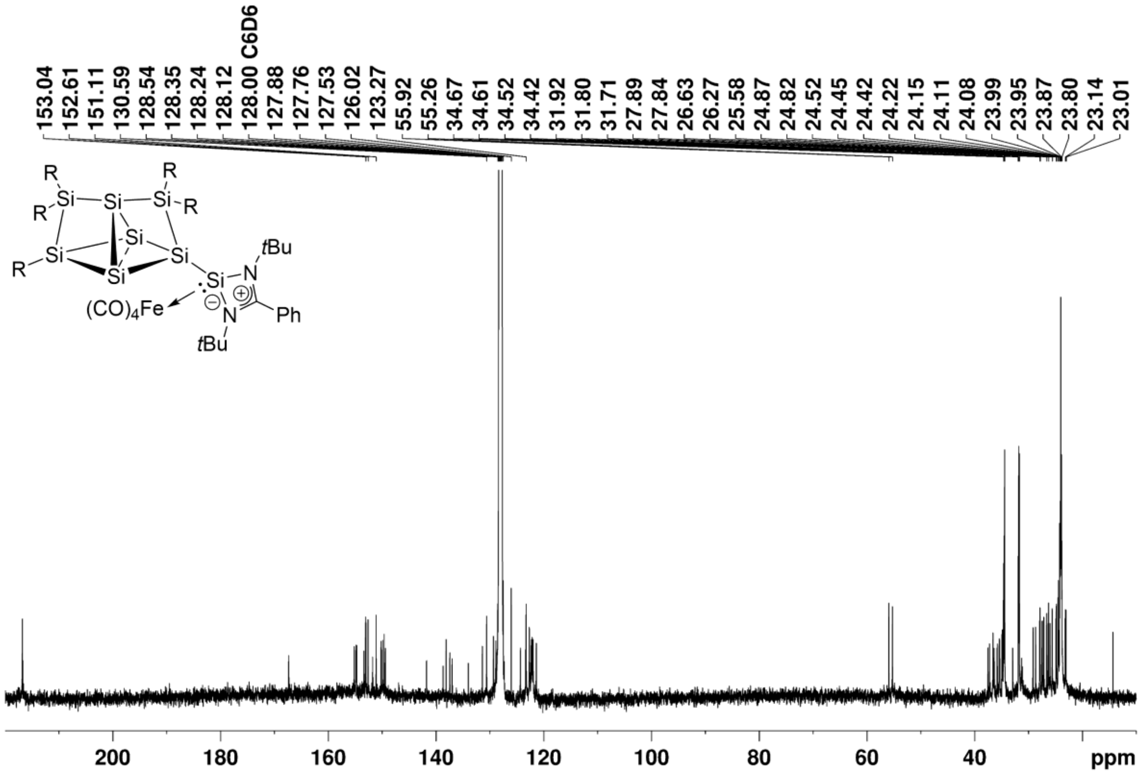
UV-Vis (hexane): λ (ε) = 525 (380 M^{-1} cm^{-1}), 342 nm (1200 M^{-1} cm^{-1}) nm.

Solid State FT-IR $\tilde{\nu}_{CO}$ = 1907 (w), 1923 (w), 1953 (w), 2026 (w) cm^{-1}.

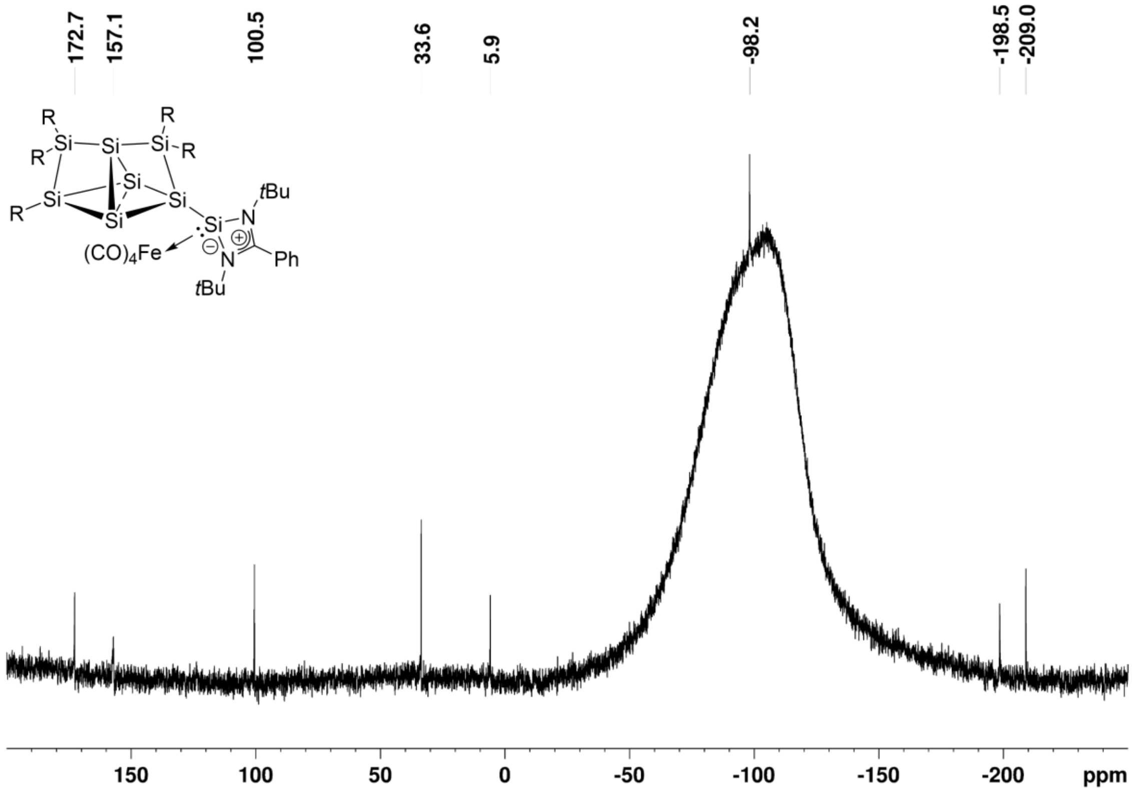
Melting Point: 251 – 267°C (decomposition).



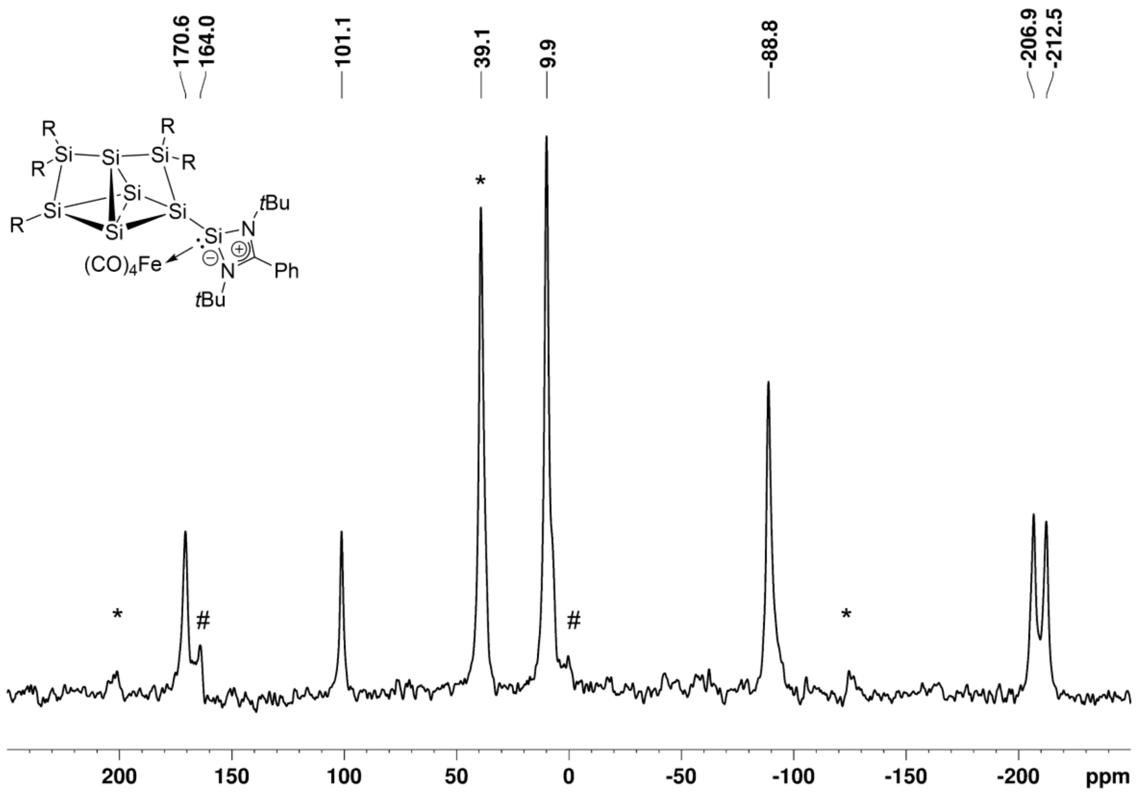
Supplementary Figure S1. ^{1}H NMR spectrum of Fe(CO)$_4$ siliconoid/silylene complex **2** in C_6D_6 (400.13 MHz, 300 K).



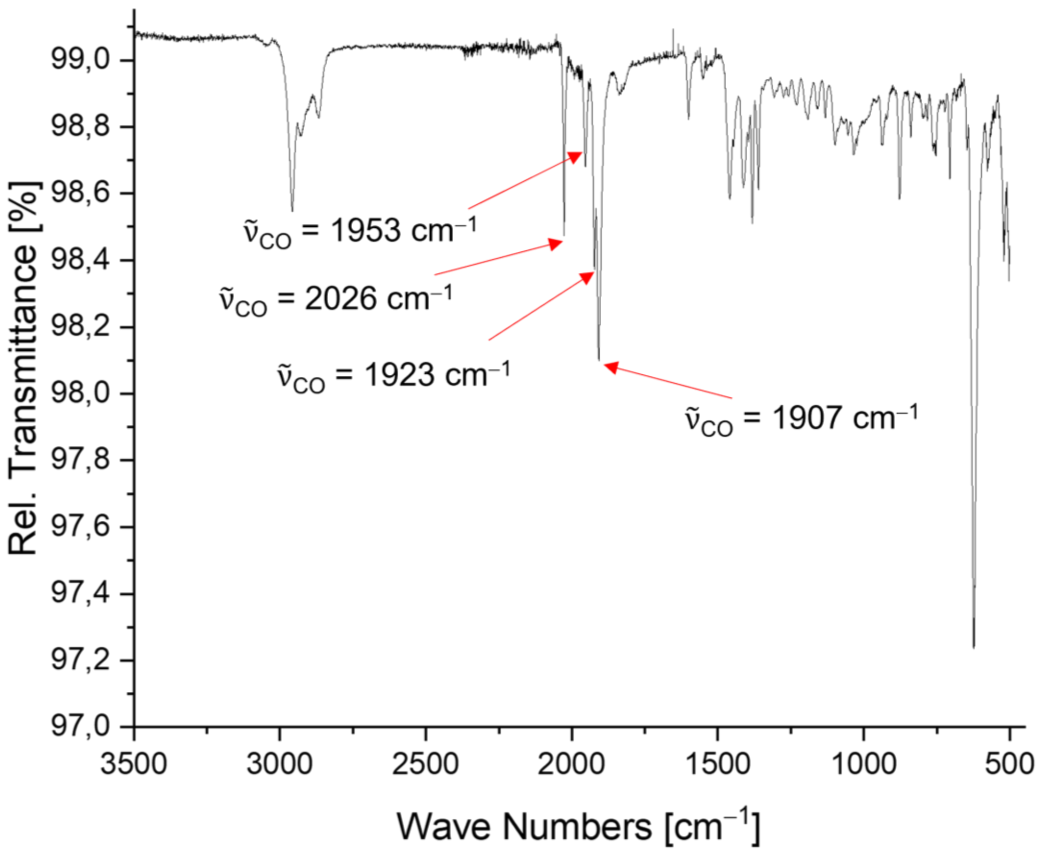
Supplementary Figure S2. $^{13}C\{^1H\}$ NMR spectrum of $Fe(CO)_4$ siliconoid/silylene complex **2** in C_6D_6 (100.61 MHz, 300 K).



Supplementary Figure S3. $^{29}Si\{^1H\}$ NMR spectrum of $Fe(CO)_4$ siliconoid/silylene complex **2** in C_6D_6 (79.49 MHz, 300 K).

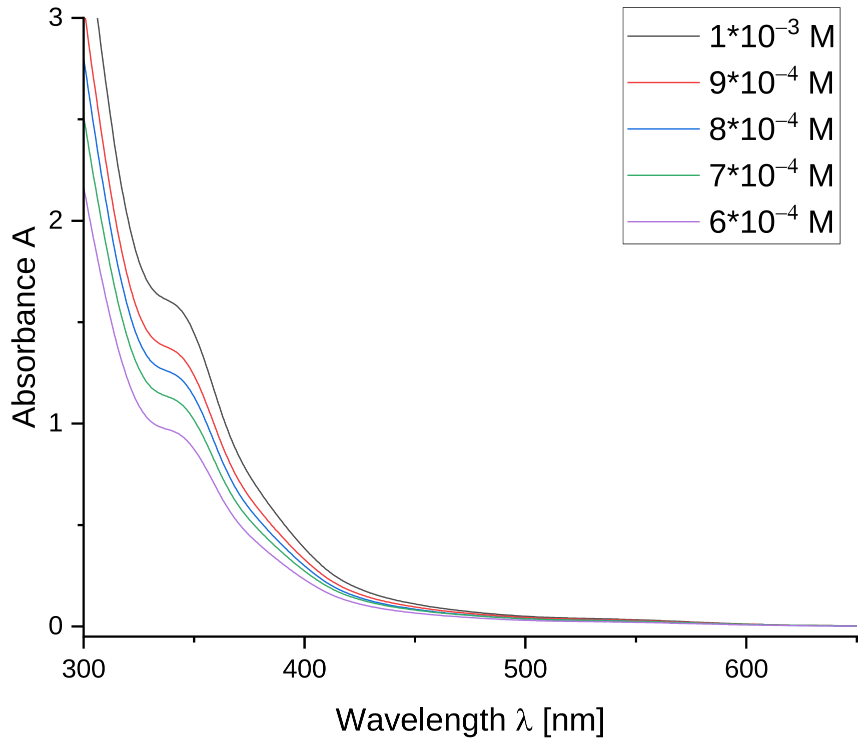


Supplementary Figure S 4. CP-MAS $^{29}Si\{^1H\}$ NMR spectrum of $Fe(CO)_4$ siliconoid/silylene complex **2** (79.53 MHz, 13 KHz, 300 K).

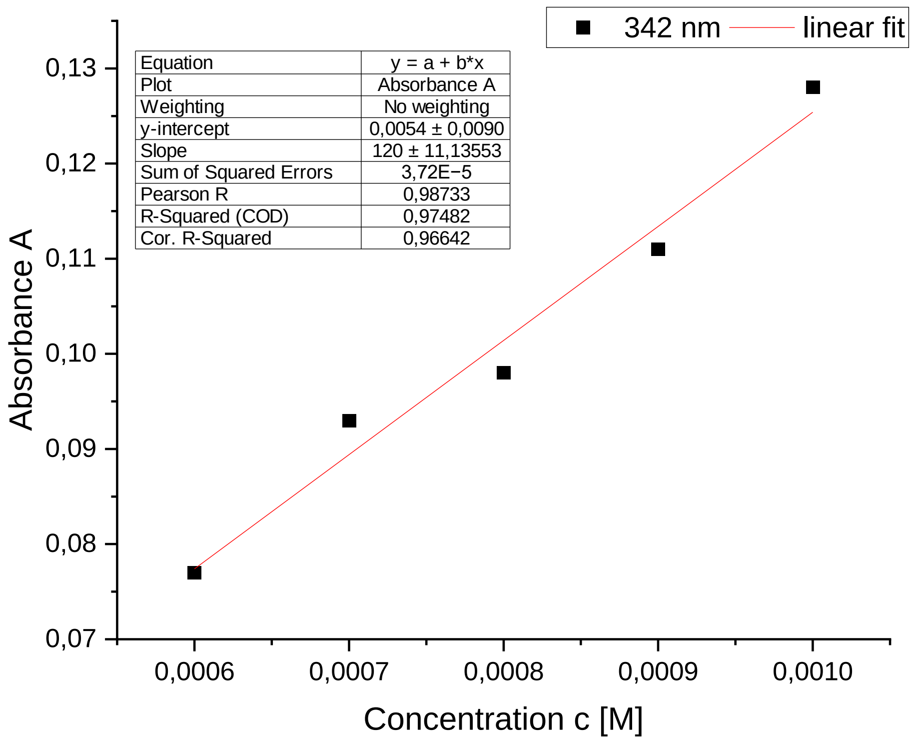


Supplementary Figure S5. FT-IR spectrum of $Fe(CO)_4$ siliconoid/silylene complex **2** in the solid state.

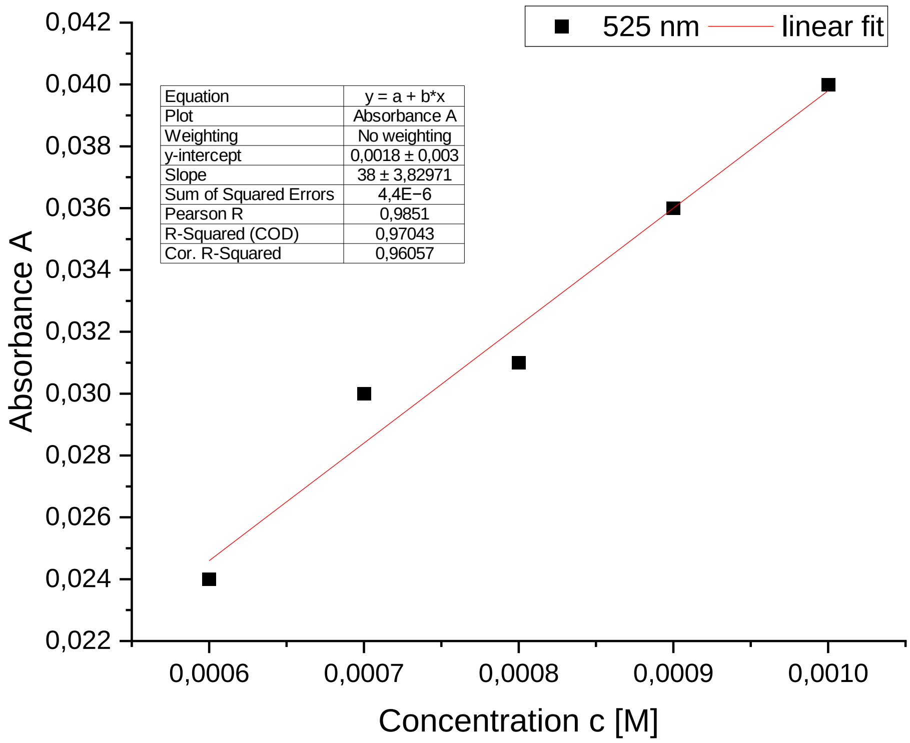
Supplementary Information



Supplementary Figure S6. UV-Vis spectra of $Fe(CO)_4$ siliconoid/silylene complex **2** in hexane at different concentrations.

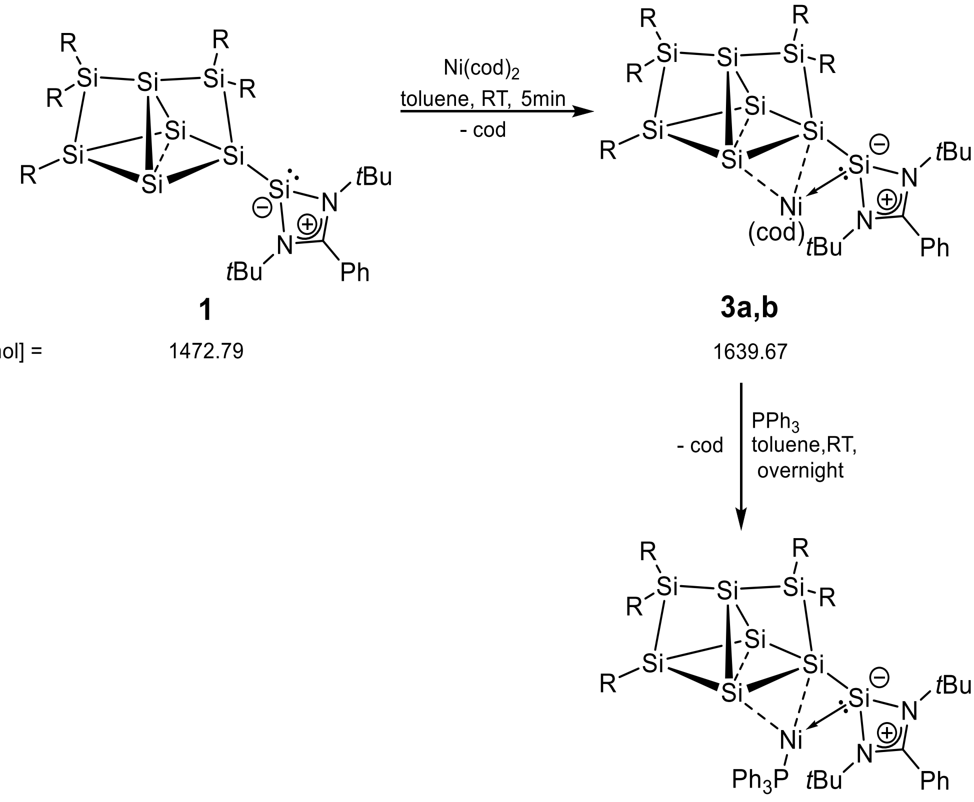


Supplementary Figure S7. Determination of the extinction ε = 1200 M^{-1} cm^{-1} of **2** by linear regression at λ = 342 nm.



Supplementary Figure S8. Determination of the extinction ε = 380 M^{-1} cm^{-1} of **2** by linear regression at λ_{max} = 525 nm.

2.2 Preparation of nickel siliconoid/silylene complexes 3a,b



1 M [g/mol] = 1472.79

3a,b 1639.67

3b M [g/mol] = 1793.77

Siliconoid/silylene hybrid **1**[4] is dissolved in toluene and the transition metal precursor is added either without (1) or with additional triphenylphosphine (2). All volatiles are removed under reduced pressure. The dark purple residue is taken up in pentane and separated from the precipitating LiCl salt by filtration. After washing 3x with 1 mL pentane, the desired product crystallizes from the concentrated mother liquor at −26°C.

2.2.1 Ni(cod) siliconoid/silylene complex 3a

Quantities: 1[4] 256.0 mg (0.174 mmol, 1.0 eq.), 2.5 mL toluene, bis(cycloocta-1,5-diene) nickel 55.0 mg (0.200 mmol, 1.1 eq.) let stir for 30min at ambient temperature, filtered from 5 mL pentane, washed residue with 3x 1mL pentane, removed solvent in vacuo, dissolved in 0.15 mL toluene and 0.4 mL pentane, stored at −30°C. Yield: 131.9 mg (0.174 mmol; 46 %) blackberry-red crystals of **3a** from pentane at −26°C.

^{1}H NMR (300.13 MHz, C_6D_6, 300 K) δ = 7.472 (d, $^4J_{HH}$ = 1.18 Hz, 1H, ArC-*H*), 7.420 (d, $^4J_{HH}$ = 1.27 Hz, 1H, ArC-*H*), 7.304 – 7.279 (m, 1H, ArC-*H*), 7.221 (d, $^4J_{HH}$ = 1.27 Hz, 1H, ArC-*H*), 7.135 (m, 2H, ArC-*H* overlapping with toluene), 7.115 (m, 1H, ArC-*H*), 7.069 – 7.00 (m, 2H, ArC-*H*, overlapping with toluene), 6.922 – 6.901 (m, 2H, ArC-*H*), 6. 857 (d, $^4J_{HH}$ = 1.27 Hz, 1H, ArC-*H*), 6.830 – 6.818 (m, 3H, ArC-*H*), 5.835 – 5.799 (bm, 1H, Tip-C*H*(CH_3)$_2$), 5.539 (dsept, $^2J_{HH}$ = 20.55 Hz, $^3J_{HH}$ = 6.58 Hz, 2H, Tip-C*H*(CH_3)$_2$), 5.229 (sept, $^3J_{HH}$ = 6.63 Hz, 1H, Tip-C*H*(CH_3)$_2$), 4.929 (sept, $^3J_{HH}$ = 6.46 Hz, 1H, Tip-C*H*(CH_3)$_2$), 4.683 – 4.643 (bm, 1H, Tip-C*H*(CH_3)$_2$), 4.460 (sept, $^3J_{HH}$ = 6.43 Hz, 1H, Tip-C*H*(CH_3)$_2$), 4.142 – 4.112 (bm, 1H, Tip-C*H*(CH_3)$_2$), 3.934 (sept, $^3J_{HH}$ = 6.43 Hz, 1H, Tip-C*H*(CH_3)$_2$), 3-615 – 3.515 (m, 3H, Tip-CH(C*H*$_3$)$_2$), 3.3987 (sept, $^3J_{HH}$ = 6.28 Hz, 1H, Tip-C*H*(CH_3)$_2$), 3.217 (sept, $^3J_{HH}$ = 6.28 Hz, 1H, Tip-C*H*(CH_3)$_2$), 2.947 (qd, $^3J_{HH}$ = 6.98 Hz, 3.07 Hz, 3H, cod(C*H*) overlapping with Tip-C*H*(CH_3)$_2$), 2.768 – 2.700 (m, 3H, Tip-CH(C*H*$_3$)$_2$), 2.660 (d, $^3J_{HH}$ = 6.41 Hz, 4H, Tip-CH(C*H*$_3$)$_2$), 2.619 – 2.551 (m, 3H, Tip-CH(C*H*$_3$)$_2$), 2.409 (d, $^3J_{HH}$ = 6.48 Hz, 3H, Tip-CH(C*H*$_3$)$_2$), 2.113 (s, 2H, Tip-CH(C*H*$_3$)$_2$ overlapping with toluene), 2.066 – 1.969 (m, 2H, cod(C*H*)), 1.783 (d, $^3J_{HH}$ = 6.42 Hz, 3H, Tip-CH(C*H*$_3$)$_2$), 1.623 (d, $^3J_{HH}$ = 6.61 Hz, 6H, Tip-CH(C*H*$_3$)$_2$), 1.574 (d, $^3J_{HH}$ = 6.61 Hz, 9H, Tip-CH(C*H*$_3$)$_2$), 1.477 (d, $^3J_{HH}$ = 6.62 Hz, 6H, Tip-CH(C*H*$_3$)$_2$), 1.435 – 1.395 (m, 12H, Tip-CH(C*H*$_3$)$_2$ overlapping with cod(C*H*$_2$)), 1.328 (d, $^4J_{HH}$ = 1.94Hz, 6H, Tip-CH(C*H*$_3$)$_2$), 1.269 (s, 9H, Si(N(C(C*H*$_3$)$_3$))$_2$CPh), 1.224 (d, $^4J_{HH}$ = 2.43 Hz, 3H, Tip-CH(C*H*$_3$)$_2$), 1.200 (d, $^4J_{HH}$ = 2.43 Hz, 3H, Tip-CH(C*H*$_3$)$_2$), 1.772 (d, $^4J_{HH}$ = 2.52 Hz, 3H, Tip-CH(C*H*$_3$)$_2$), 1.154 (d, $^4J_{HH}$ = 6.94 Hz, 3H, Tip-CH(C*H*$_3$)$_2$), 1.394 (dd, $^3J_{HH}$ = 6.90 Hz, 1.08 Hz, 6H, Tip-CH(C*H*$_3$)$_2$), 0.792 (d, $^4J_{HH}$ = 6.58 Hz, 3H, Tip-CH(C*H*$_3$)$_2$), 0.646 (t, $^3J_{HH}$ = 7.33 Hz, 9H, Tip-CH(C*H*$_3$)$_2$), 0.570 – 0.549 (m, 3H, Tip-CH(C*H*$_3$)$_2$), 0.538 (s, 9H, Si(N(C(C*H*$_3$)$_3$))$_2$CPh), 0.393 (d, $^3J_{HH}$ = 6.18 Hz, 3H, Tip-CH(C*H*$_3$)$_2$) ppm.

^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 300 K) δ = 162.22 (s, 1C, Ar-*C*), 156.09, 155.60, 155.20, 154.09, 153.29, 153.15, 153.07, 152.99, 152.83, 149.56, 149.28, 148.88, 148.74, 148.69, 140.93, 139.62, 138.77, 138.32, 137.69, 132.97 (s, each 1C, Ar-*C*), 129.99, 129.85, 129.31, 129.27, 128.50, 128.41, 126.00 (s, each 1C, Ar-*C*H), 125.63 (s, 1C, Ar-*C*), 123.67 (s, each 1C, Ar-*C*H), 123.32 (m, 1C, Ar-*C*H), 122.80, 122.34, 122.21, 121.68, 121.38, 120.53, (s, each 1C, Ar-*C*H), 89.64, 86.65 (s, each 2C, COD-*C*H), 54.70, 53.64 (s, each 1C, Si(N(*C*(CH_3)$_3$))$_2$CPh), 36.39, 36.15, 35.81, 35.47, 35.08, 35.01, 34.71, 34.67, 34.62, 34.58, 34.40, 34.01, 33.15 (s, each 1C, Tip-*i*Pr-*C*H), 32.85, 32.22 (s, each 3C, Si(N(*C*(CH_3)$_3$))$_2$CPh), 30.81 (s, 4C, COD-*C*H$_2$), 29.39, 28.65 (s, each 1C, Tip-*i*Pr-*C*H), 28.10, 28.03, 27.55, 27.51, 27.39, 27.06, 27.03, 26.86, 26.82, 26.75, 26.69, 26.58, 26.45, 26.40, 26.33, 26.02, 25.97, 25.26, 25.13, 25.00, 24.40, 24.38, 24.36, 24.17, 24.11, 24.08, 24.04, 24.01, 23.98, 23.78 (s, each 1C, Tip-*i*Pr-*C*H$_3$) ppm.

^{29}Si{^{1}H} NMR (59.63 MHz, C_6D_6, 300 K) δ = 89.1 (s, Ni*Si*(N(C(CH_3)$_3$))$_2$CPh), 50.0 (s, *Si*Tip), 39.0 (s, *Si*Tip$_2$), −10.2 (s, *Si*(Si(N*t*Bu)$_2$CPh)), −13.3 (s, *Si*Tip$_2$), −83.1 (s, *Si* unsubstituted), −154.0 (s, *Si*Ni), −340.7 (s, *Si* unsubstituted) ppm.

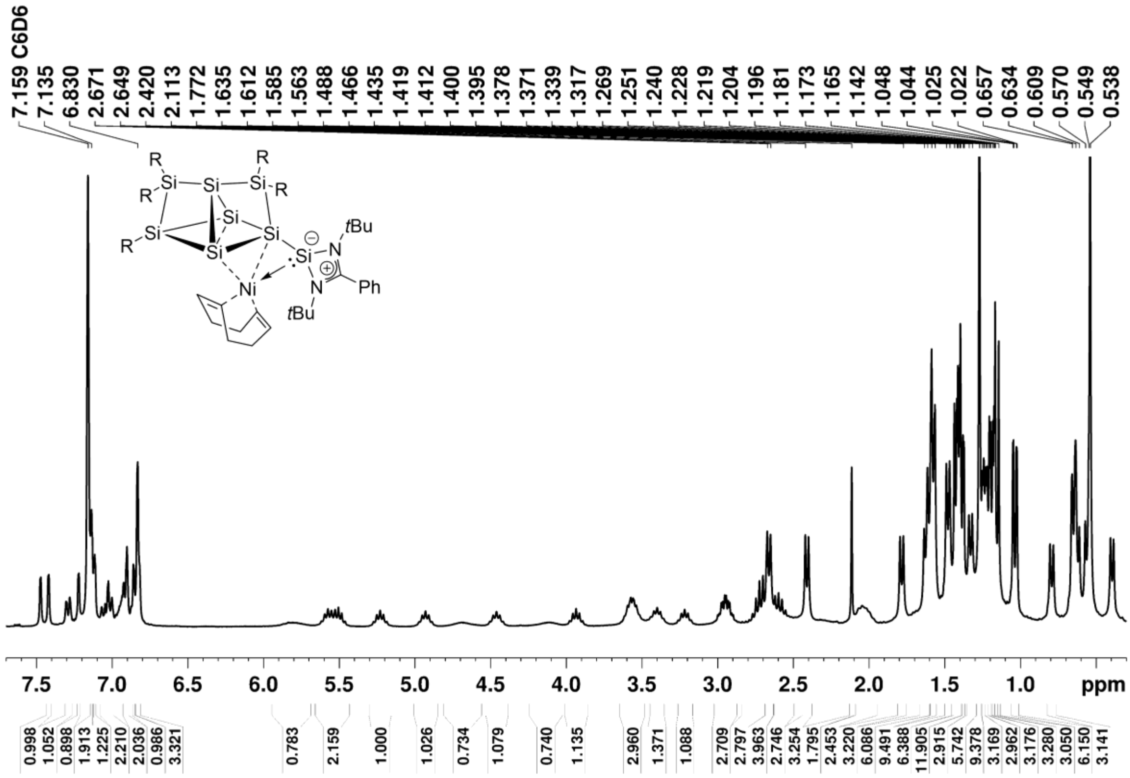
CP-MAS ^{29}Si{^{1}H} NMR (79.53 MHz, 10 KHz, 300 K) δ = 86.4 (s, Ni*Si*(N(C(CH_3)$_3$))$_2$CPh), 55.3 (s, *Si*Tip), 37.5 (s, *Si*Tip$_2$), 0.4 (s, *Si*(Si(N*t*Bu)$_2$CPh)), −16.2 (s, *Si*Tip$_2$), −85.1 (s, *Si* unsubstituted), −159.1 (s, *Si*Ni), −332.9 (s, *Si* unsubstituted) ppm.

Elemental analysis: calculated for $C_{98}H_{150}N_2NiSi_8$: C: 71.79%; H: 9.22%; N: 1.71%. Found: C: 71.67%; H: 8.75%; N: 1.64%. The lower values compared to those calculated are quite common for unsaturated silicon clusters due to incomplete combustion typically attributed to the formation of silicon carbides and/or nitrides. In addition, elemental analysis has come under scrutiny because of highly variable results of bona fide identical samples.[5]

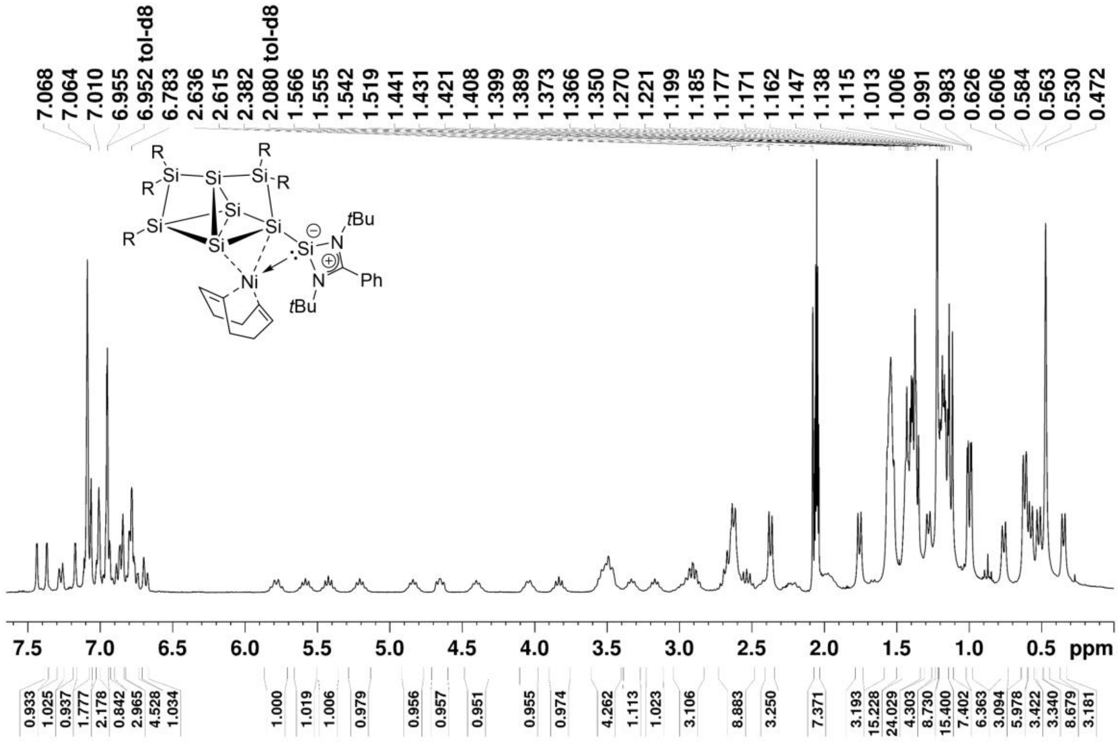
Supplementary Information

UV-Vis (hexane): λ_{max} (ε) = 538 (8190 M^{-1} cm^{-1}), 392 (9590 M^{-1} cm^{-1}) nm.

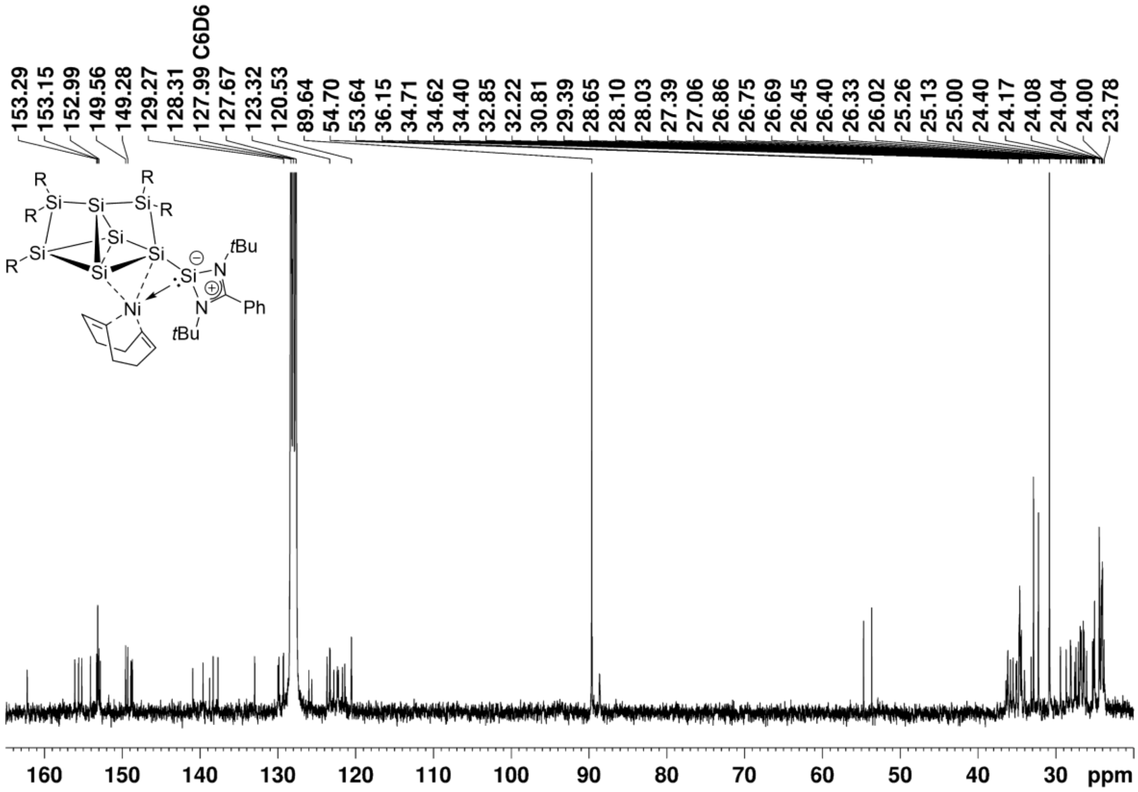
Melting Point: 185°C decomposition, 193 – 206°C melting.



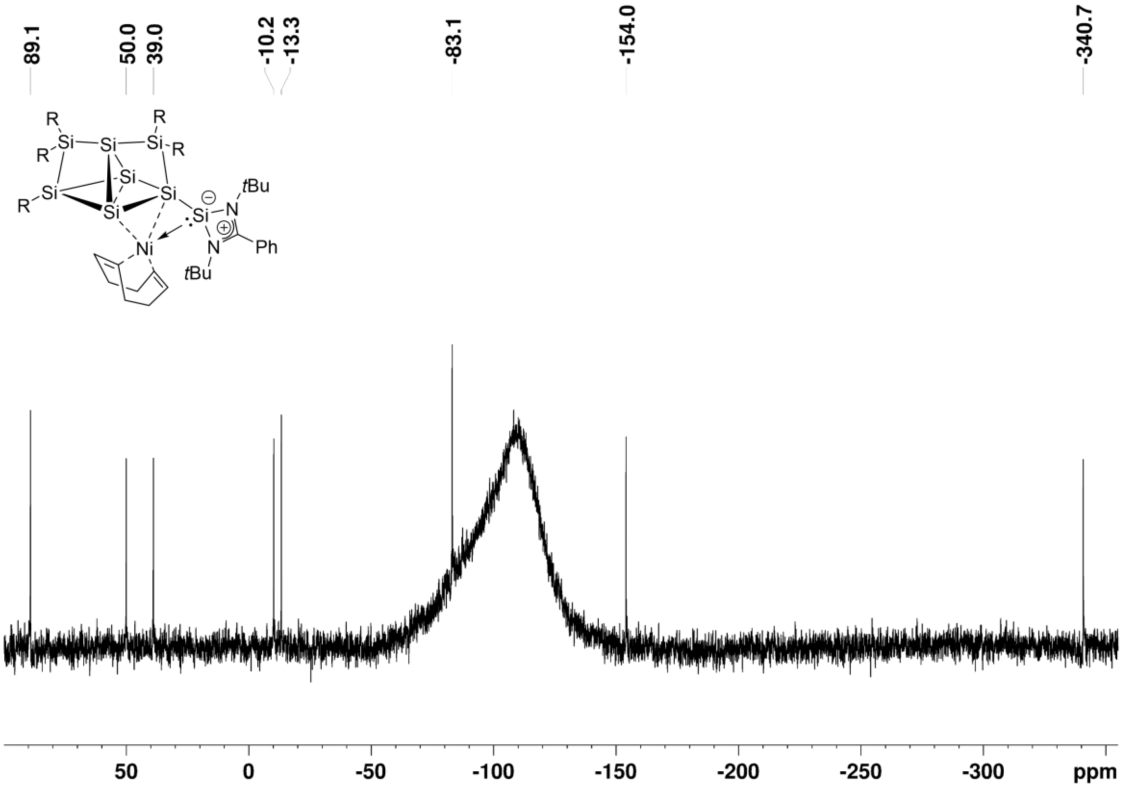
Supplementary Figure S9. ^{1}H NMR spectrum of Ni(cod) siliconoid/silylene complex **3a** in C_6D_6 (300.13 MHz, 300 K).



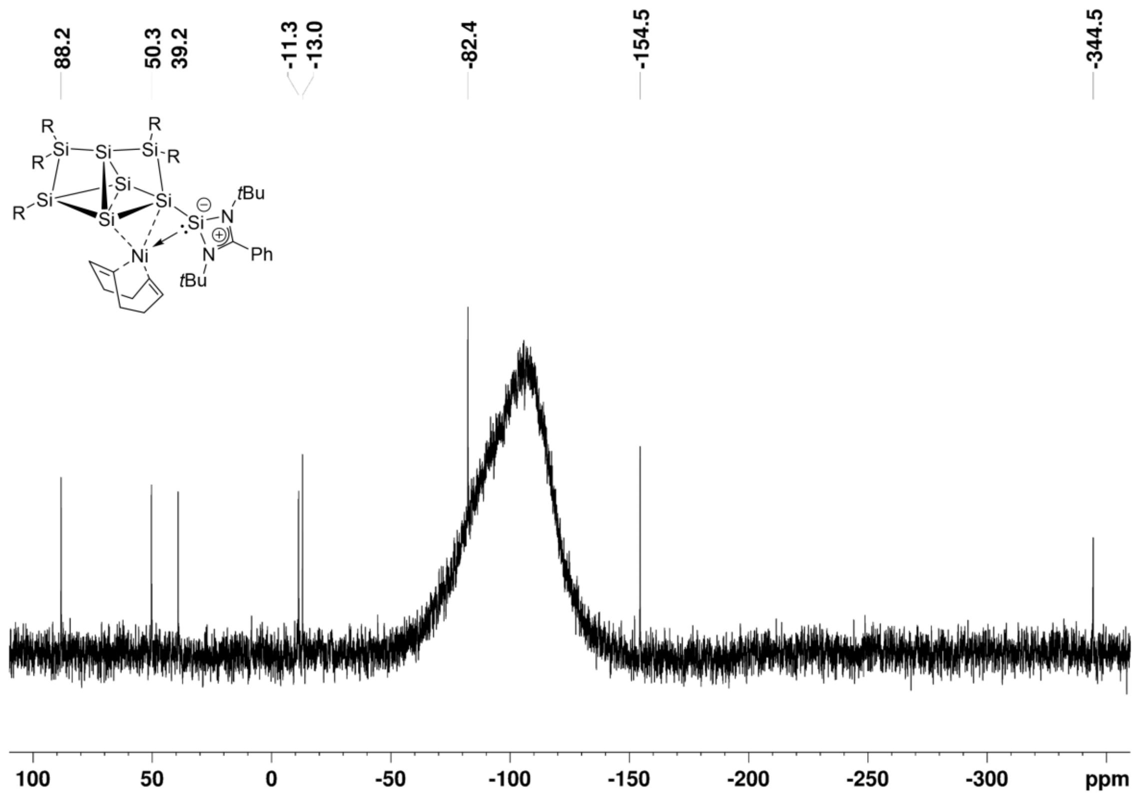
Supplementary Figure S10. ^{1}H NMR spectrum of Ni(cod) siliconoid/silylene complex **3a** in toluene-d_8 (300.13 MHz, 253 K).



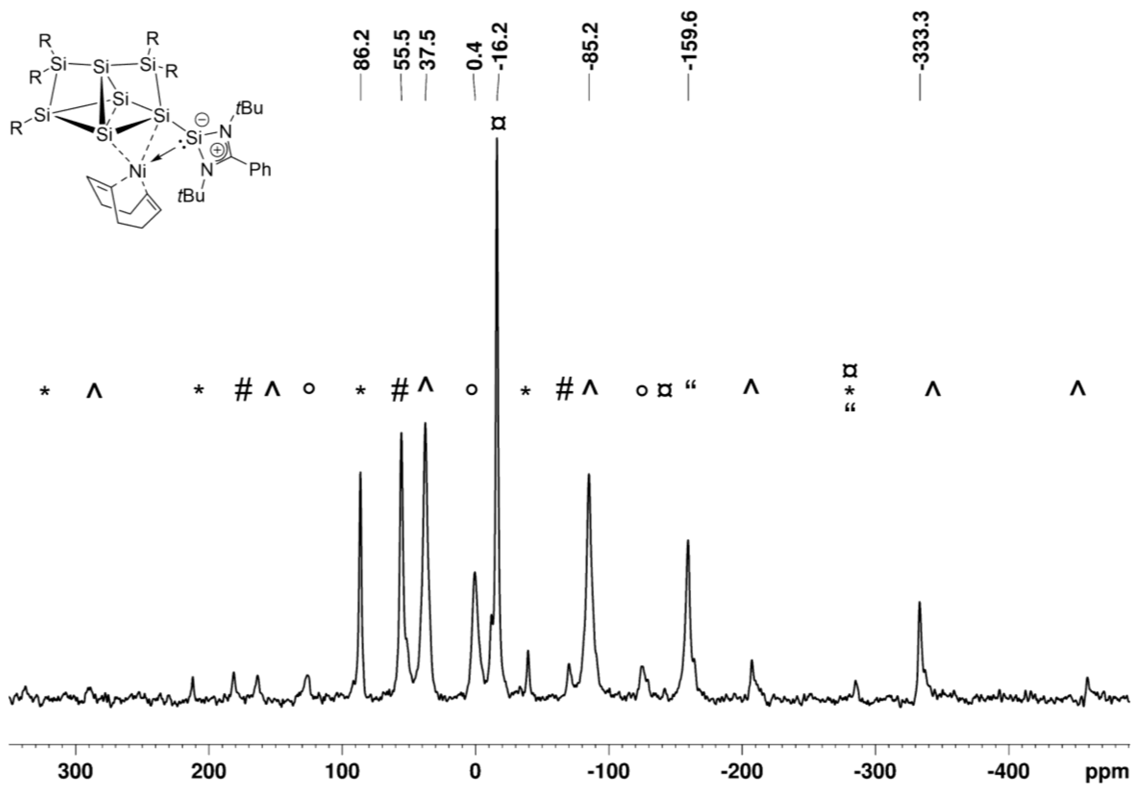
Supplementary Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of Ni(cod) siliconoid/silylene complex **3a** in C_6D_6 (75.47 MHz, 300 K).



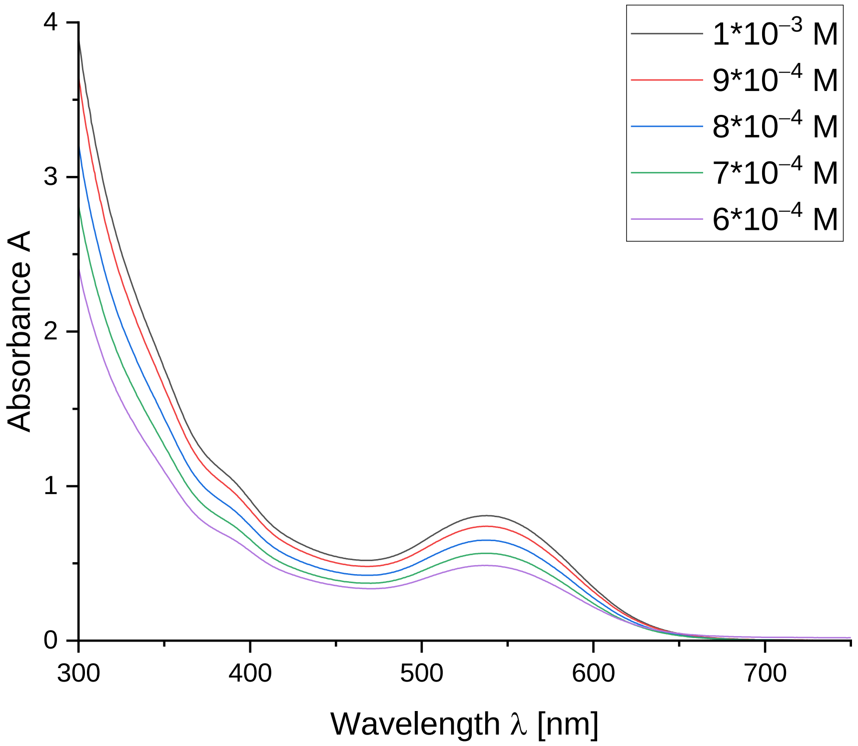
Supplementary Figure S12. $^{29}Si\{^{1}H\}$ NMR spectrum of Ni(cod) siliconoid/silylene complex **3a** in C_6D_6 (59.63 MHz, 300 K).



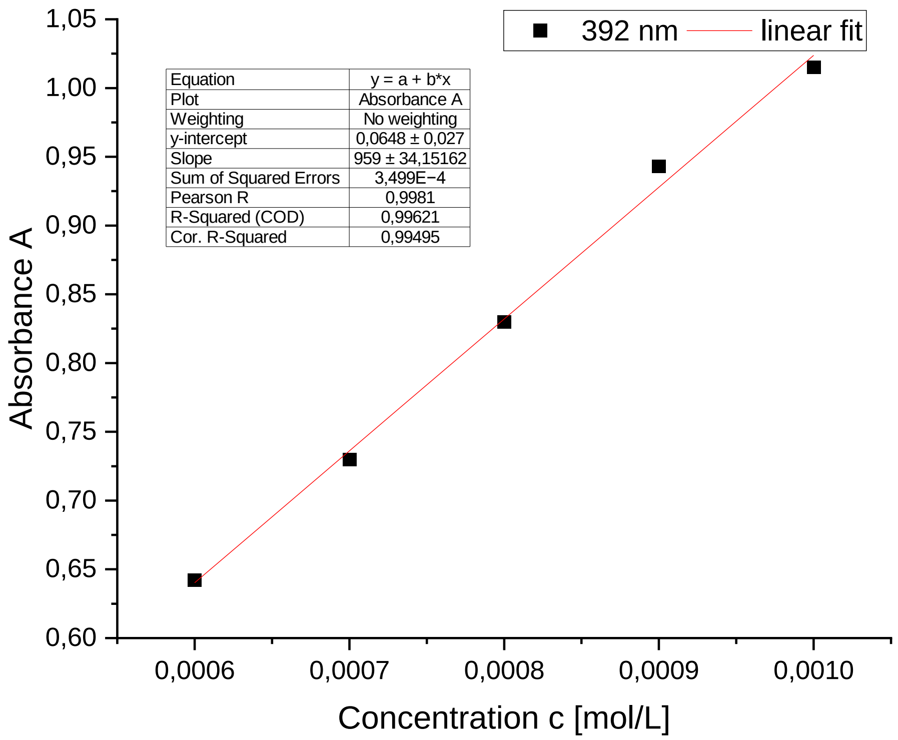
Supplementary Figure S13. $^{29}Si\{^{1}H\}$ NMR spectrum of Ni(cod) siliconoid/silylene complex **3a** in toluene-*d*8 (59.63 MHz, 223 K).



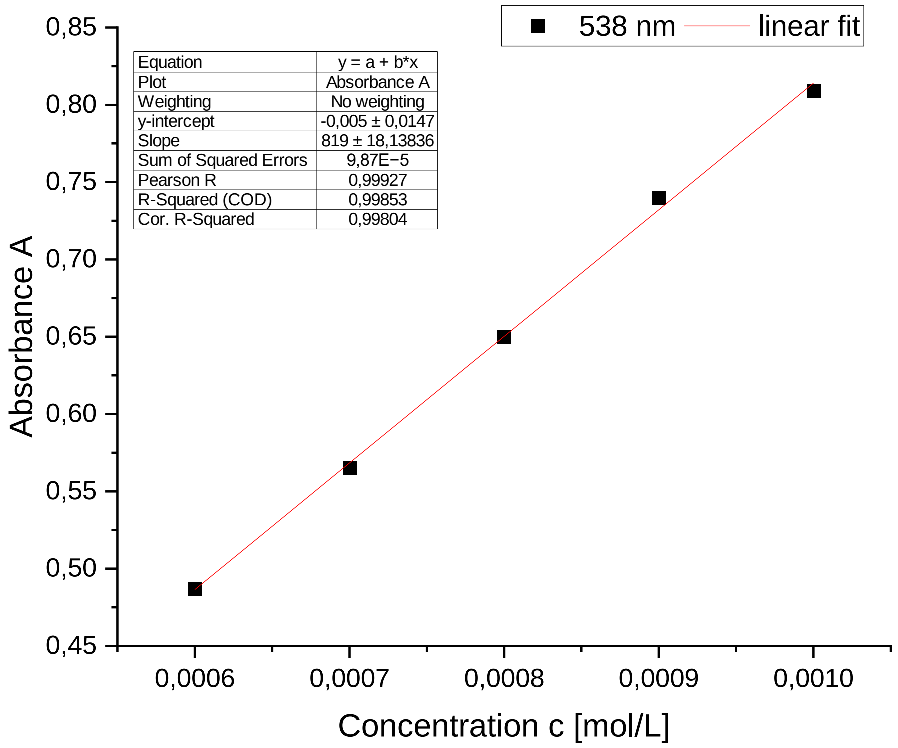
Supplementary Figure S14*.* CP-MAS $^{29}Si\{^{1}H\}$ NMR spectrum of Ni(cod) siliconoid/silylene complex (79.53 MHz, 10 KHz, 300 K), side spinning bands: *86.2, 55.5, ^ 37.5/ −85.2/ −333.3, ° 0.4, ¤ −16.2, " −159.6 ppm.



Supplementary Figure S15. UV-Vis spectra of Ni(cod) siliconoid/silylene complex **3a** in hexane at different concentrations.



Supplementary Figure S16. Determination of the extinction ε = 9590 M^{-1} cm^{-1} of **3a** by linear regression at λ = 392 nm.



Supplementary Figure S17. Determination of the extinction ε = 8190 M^{-1} cm^{-1} of **3a** by linear regression at λ_{max} = 538 nm.

2.2.2 Preparation of Ni(PPh_3) siliconoid/silylene complex 3b

Quantities: 1[4] 150.0 mg (0.0928 mmol, 1.0 eq.), 2.0 mL toluene, 29.3 mg bis(cycloocta-1,5-diene) nickel (0.107 mmol, 1.2 eq), triphenylphosphine 36.4 mg (0.103 mmol, 1.1 eq), let stir overnight at RT, filtered from 4 mL pentane, washed residue with 3x 0.5mL pentane. Yield: 82.1 mg (0.0458 mmol, 49 %) brown crystals of **3b** from pentane at −26°C.

^{1}H NMR (300.13 MHz, C_6D_6, 300 K) δ = 7.830 (t, $^3J_{HH}$ = 8.81 Hz, 6H, P(ArC-*H*)), 7.424 (dd, $^3J_{HH}$ = 4.41 Hz, 1.54 Hz, 2H, P(ArC-*H*)), 7.230 – 7.198 (m, 2H, ArC-*H*), 7.100 – 7.083 (m, 4H, ArC-*H*), 7.057 – 7.018 (m, 4H, ArC-*H*), 6.992 (d, $^4J_{HH}$ = 1.74 Hz, 2H, ArC-*H*), 6.966 – 6.927 (m, 6H, ArC-*H*), 6.903 – 6.868 (m, 3H, ArC-*H*), 6. 851 (d, $^4J_{HH}$ = 1.45 Hz, 1H, ArC-*H*), 6.652 (sept, 1H, Tip-C*H*(CH_3)$_2$), 5.576 – 5.500 (m, 2H, Tip-C*H*(CH_3)$_2$), 5.144 (sept, d, $^3J_{HH}$ = 6.51 Hz, 1H, Tip-C*H*(CH_3)$_2$), 4.350 (sept, d, $^3J_{HH}$ = 6.60 Hz, 1H, Tip-C*H*(CH_3)$_2$), 3.547 (sept, $^3J_{HH}$ = 6.41 Hz, 1H, Tip-C*H*(CH_3)$_2$), 3.481 – 3.366 (m, 3H, Tip-C*H*(CH_3)$_2$), 3.162 (sept, $^3J_{HH}$ = 6.41 Hz, 1H, Tip-C*H*(CH_3)$_2$), 2.924 (dsept, $^2J_{HH}$ = 21.54 Hz, $^3J_{HH}$ = 6.93 Hz, 2H, Tip-C*H*(CH_3)$_2$), 2.819 – 2.693 (m, 2H, Tip-C*H*(CH_3)$_2$), 2.623 (sept, $^3J_{HH}$ = 6.88 Hz, 1H, Tip-C*H*(CH_3)$_2$), 2.502 (d, $^3J_{HH}$ = 6.47 Hz, 3H, Tip-CH(CH_3)$_2$), 2.5240 (d, $^3J_{HH}$ = 6.47 Hz, 3H, Tip-CH(CH_3)$_2$), 1.718 (d, $^3J_{HH}$ = 6.31 Hz, 3H, Tip-CH(CH_3)$_2$), 1.680 (d, $^3J_{HH}$ = 6.58 Hz, 3H, Tip-CH(CH_3)$_2$), 1.620 – 1.576 (m, 9H, Tip-CH(CH_3)$_2$), 1.509 (d, $^3J_{HH}$ = 6.61 Hz, 3H, Tip-CH(CH_3)$_2$), 1.452 – 1.400 (m, 15H, Tip-CH(CH_3)$_2$), 1.315 (t, $^3J_{HH}$ = 6.59 Hz, 7H, Tip-CH(CH_3)$_2$), 1.257 (d, $^4J_{HH}$ = 2.66 Hz, 3H, Tip-CH(CH_3)$_2$), 1.234 (d, $^4J_{HH}$ = 2.53

Hz, 3H, Tip-CH(CH_3)$_2$), 1.218 (d, $^4J_{HH}$ = 2.15 Hz, 3H, Tip-CH(CH_3)$_2$), 1.195 (d, $^4J_{HH}$ = 2.10 Hz, 3H, Tip-CH(CH_3)$_2$), 1.123 – 1.057 (m, 12H, Tip-CH(CH_3)$_2$), 0.907 – 0.876 (m, 2H, Tip-CH(CH_3)$_2$), 0.849 (s, 9H, Si(N(C(CH_3)$_3$))$_2$CPh), 0.801 (d, $^4J_{HH}$ = 6.77 Hz, 3H, Tip-CH(CH_3)$_2$), 0.775 (s, 9H, Si(N(C(CH_3)$_3$))$_2$CPh), 0.715 (d, $^4J_{HH}$ = 6.51 Hz, 3H, Tip-CH(CH_3)$_2$), 0.551 (d, $^3J_{HH}$ = 6.26 Hz, 3H, Tip-CH(CH_3)$_2$), 0.518 (d, $^3J_{HH}$ = 6.50 Hz, 3H, Tip-CH(CH_3)$_2$), 0.476 (d, $^3J_{HH}$ = 6.36 Hz, 3H, Tip-CH(CH_3)$_2$), 0.403 (d, $^3J_{HH}$ = 6.22 Hz, 3H, Tip-CH(CH_3)$_2$) ppm.

^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 300 K) δ = 161.13 (s, Si(N(C(CH$_3$)$_3$))$_2$*C*Ph), 156.46, 155.47, 153.95, 153.90, 153.58, 153.48, 153.38, 153.24, 153.11, 152.92, 149.42, 149.23, 149.06, 148.66, 148.50, 141.11, 140.38, 139.38, 138.53, 138.04 (s, each 1C, Ar-*C*), 134.35 (d, $^2J_{C\text{-}P}$ = 13.9 Hz, 15C, P(Ar-*C*H)), 134.07 (d, $^2J_{C\text{-}P}$ = 14.6 Hz, 3C, P(Ar-*C*)), 133.01 (s, each 1C, Ar-*C*), 130 .06, 129.66, 129.25, 129.03, 128.38, 128.30 (s, each 1C, Ar-C*H*), 128.11, 127.87 (s, each 1C, Ar-*C*), 127.60, 126.01, 123.52 (s, each 1C, Ar-*C*H), 123.05 (s, 5C, P(Ar-*C*H)), 122.40 (d, ^4J = 5.09 Hz, Ar-*C*H), 121.86, 121.66, 121.52, 120.61 (s, each 1C, Ar-*C*H), 54.90, 53.43 (s, each 1C, Si(N(*C*(CH$_3$)$_3$))$_2$CPh), 35.95, 35.80 (s, each 1C, Tip-*C*H(CH$_3$)$_2$, 35.68 (s, 2C, Tip-*C*H(CH$_3$)$_2$), 35.53, 35.40, 35.29, 35.14, 34.77, 34.67 (s, each 1C, Tip-*C*H(CH$_3$)$_2$), 34.60 (s, 2C, Tip-*C*H(CH$_3$)$_2$, 34.54 (s, each 1C, Tip-*C*H(CH$_3$)$_2$), 34.39 (s, pentane), 34.31, 32.81 (s, each 1C, Tip-*C*H(CH$_3$)$_2$), 32.56, 32.20 (s, each 3C, Si(N(C(*C*H$_3$)$_3$))$_2$CPh), 32.11, 31.62, 31.41, 30.53, 29.12, 28.93, 28.45, 28.42, 27.88, 27.69, 27.55, 26.38, 25.92, 25.75 (s, each 1C, Tip-CH(*C*H$_3$)$_2$), 25.04 (s, 2C, Tip-CH(*C*H$_3$)$_2$), 24.87, 24.72, 24.54 (s, each 1C, Tip-CH(*C*H$_3$)$_2$), 24.48, 24.29, 24.24 (s, each 2C, Tip-CH(*C*H$_3$)$_2$), 24.14, 24.06, 24.03, 23.69, 23.33 (s, each 1C, Tip-CH(*C*H$_3$)$_2$), 22.68, 14.25 (s, pentane) ppm.
^{31}P{^{1}H} NMR (126.98 MHz, C_6D_6, 300 K) δ = 26.4 (s, 1P, Ni*P*(Ph)$_3$) ppm.

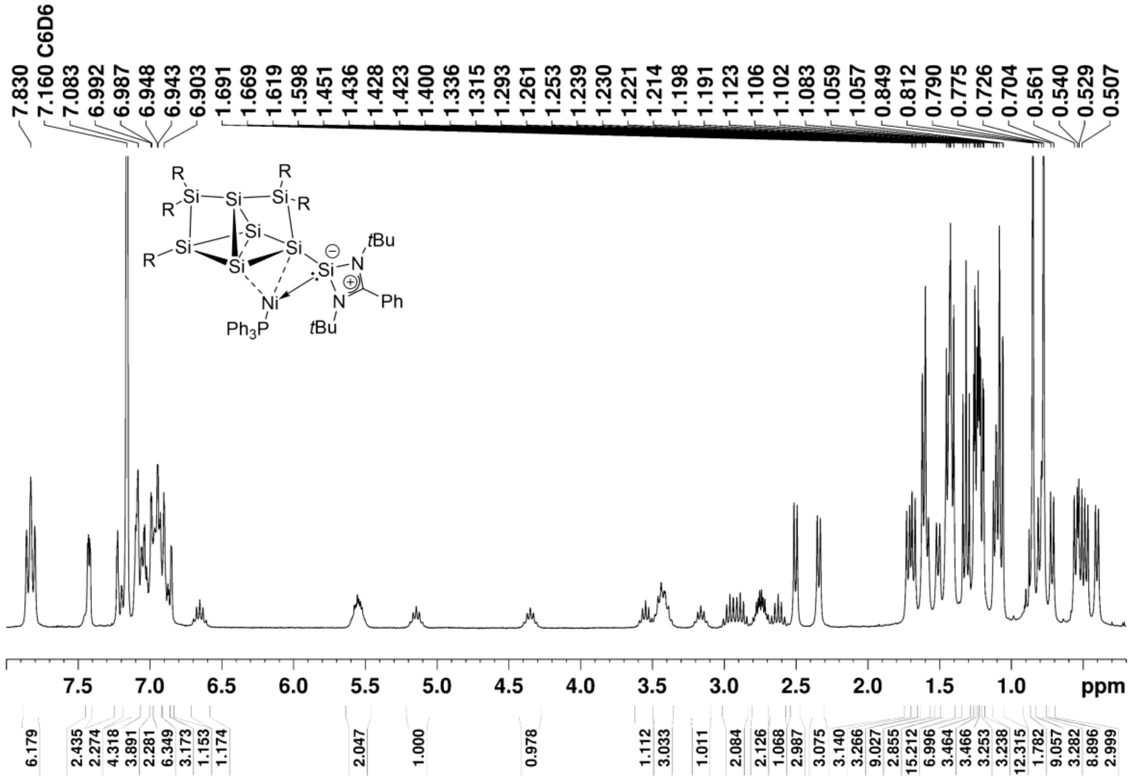
^{29}Si{^{1}H} NMR (79.49 MHz, C_6D_6, 300 K) δ = 73.6 (d, $^3J_{Si\text{-}P}$ = 4.67 Hz, *Si*(N*t*Bu)$_2$CPh), 63.9 (d, $^3J_{Si\text{-}P}$ = 9.06 Hz, *Si*Tip), 39.7 (s, *Si*Tip$_2$), 0.4 (d, $^3J_{Si\text{-}P}$ = 3.45 Hz, *Si*(Si(N*t*Bu)$_2$CPh), −41.4 (d, $^3J_{Si\text{-}P}$ = 11.84 Hz, *Si*Tip$_2$), −60.0 (d, $^3J_{Si\text{-}P}$ = 5.64 Hz, *Si*), −87.3 (d, $^3J_{Si\text{-}P}$ = 8.77 Hz, *Si*Ni), −287.6 (d, $^2J_{Si\text{-}P}$ = 27.84 Hz, *Si*) ppm.

CP-MAS ^{29}Si{^{1}H}-NMR (79.53 MHz, 13 KHz, 300 K) δ = 72.7 (s, Ni*Si*(N(C(CH$_3$)$_3$))$_2$CPh), 69.0 (s, *Si*Tip), 37.6 (s, *Si*Tip$_2$), −5.9 (s, $^3J_{Si\text{-}P}$ = 3.45 Hz, *Si*(Si(N(C(CH$_3$)$_3$))$_2$CPh)), −44.7 (s, *Si*Tip$_2$), −68.0 (s, *Si* unsubstituted), −82.8 (s, *Si*Ni), −279.6 (s, *Si* unsubstituted) ppm.

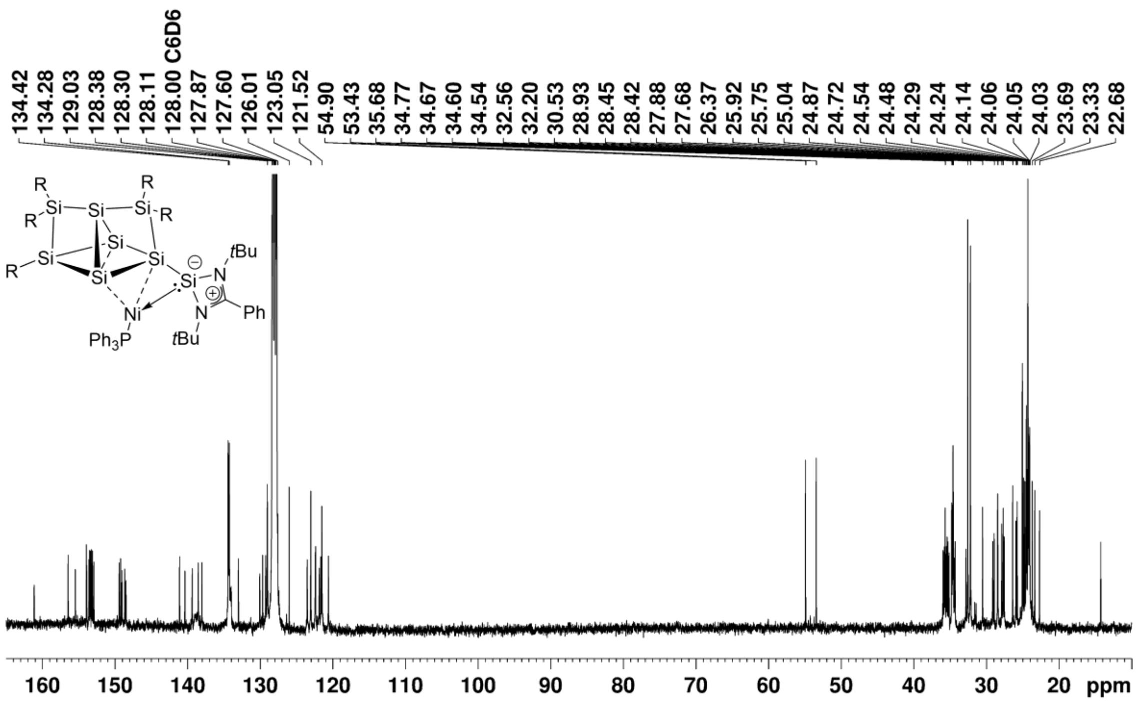
Elemental analysis: calculated for $C_{108}H_{153}N_2NiPSi_7$: C: 72.32%; H: 8.60%; N: 1.56%. Found: C: 67.11 %; H: 8.06%; N: 1.88%. The lower values compared to those calculated are quite common for unsaturated silicon clusters due to incomplete combustion typically attributed to the formation of silicon carbides and/or nitrides. In addition, elemental analysis has come under scrutiny because of highly variable results of bona fide identical samples.[5]

UV-Vis (hexane): λ_{max} (ε) = 365 (1879 M^{-1} cm^{-1}), 519 (1127 M^{-1} cm^{-1}), 596 (624 M^{-1} cm^{-1}) nm.

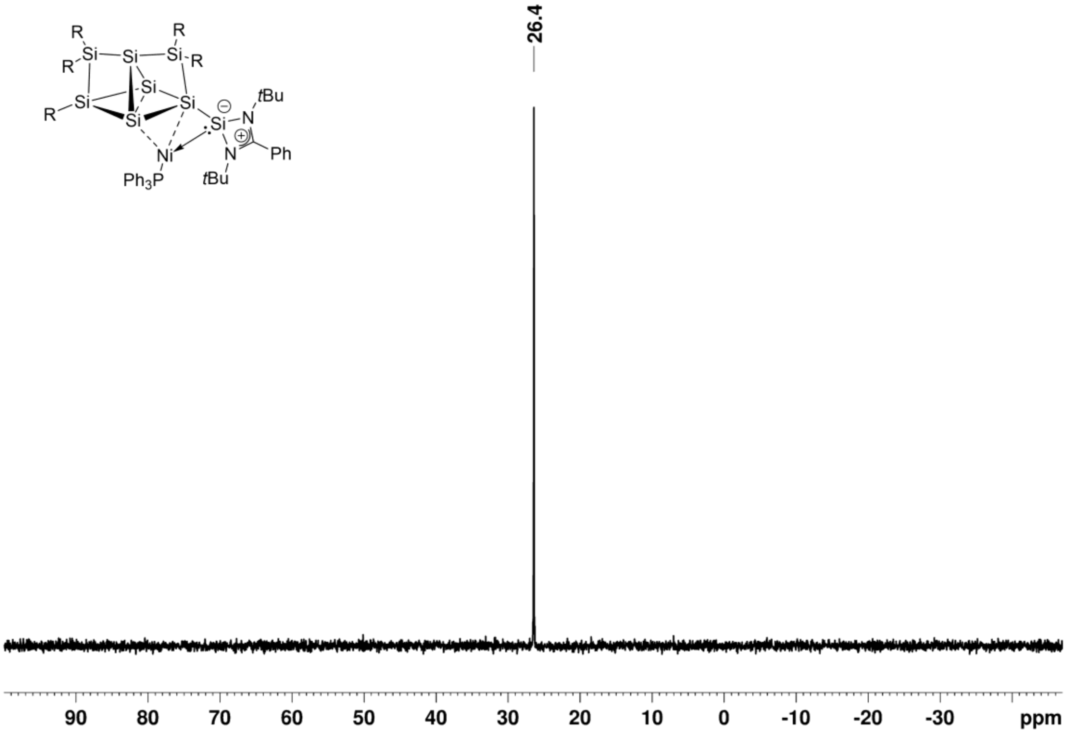
Melting Point: 187 – 191°C (melting, decomposition).



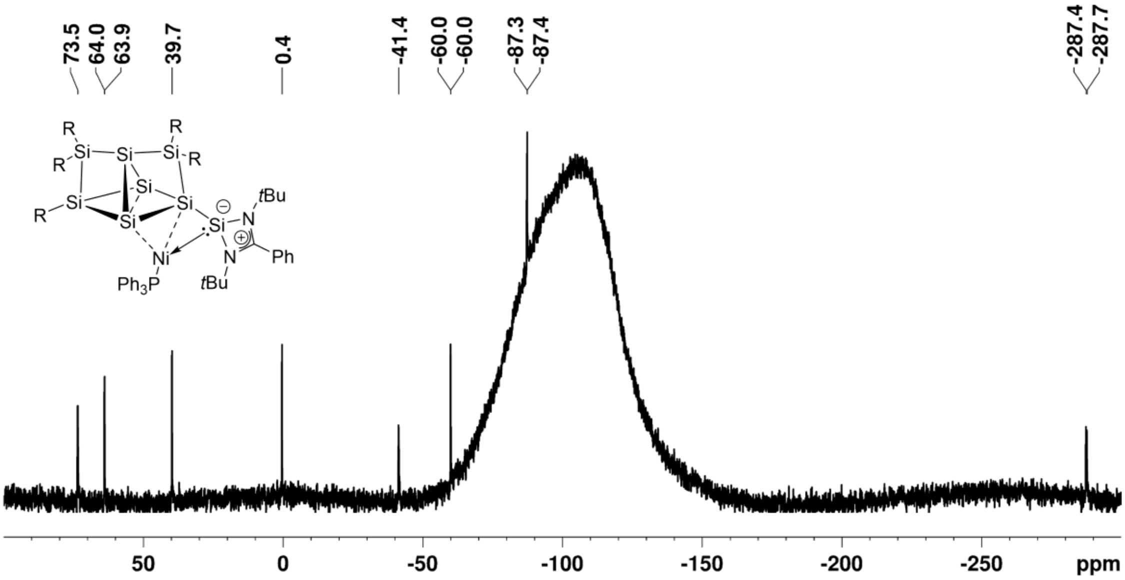
Supplementary Figure S18. ^{1}H NMR spectrum of $Ni(PPh_3)$ siliconoid/silylene complex **3b** in C_6D_6 (300.13 MHz, 300 K).



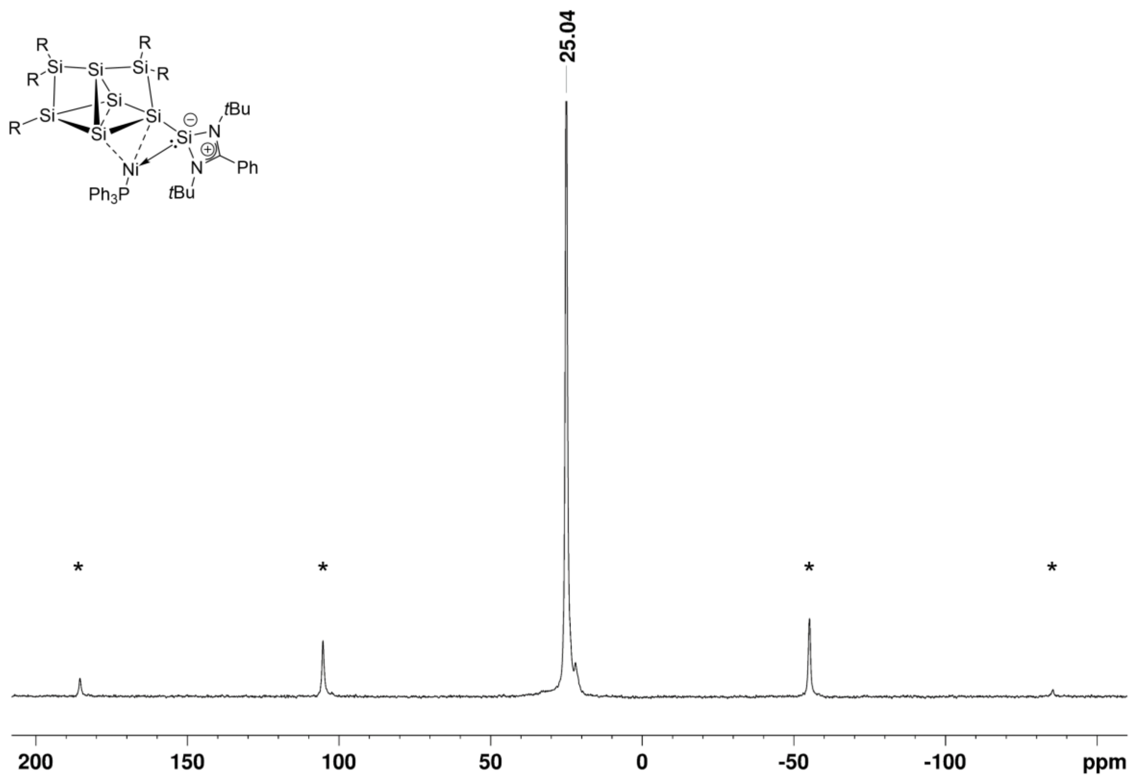
Supplementary Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of $Ni(PPh_3)$ siliconoid/silylene complex **3b** in C_6D_6 (100.61 MHz, 300 K).



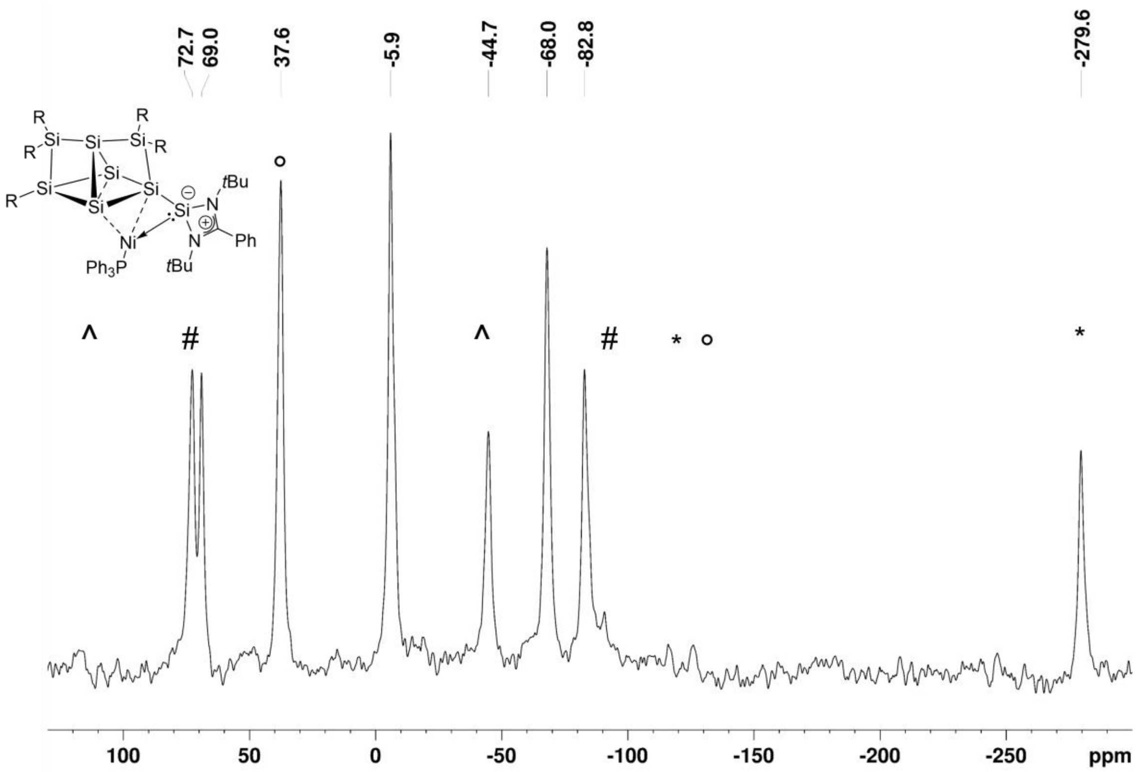
Supplementary Figure S20. $^{31}P\{^{1}H\}$ NMR spectrum of $Ni(PPh_3)$ siliconoid/silylene complex **3b** in C_6D_6 (161.98 MHz, 300 K).



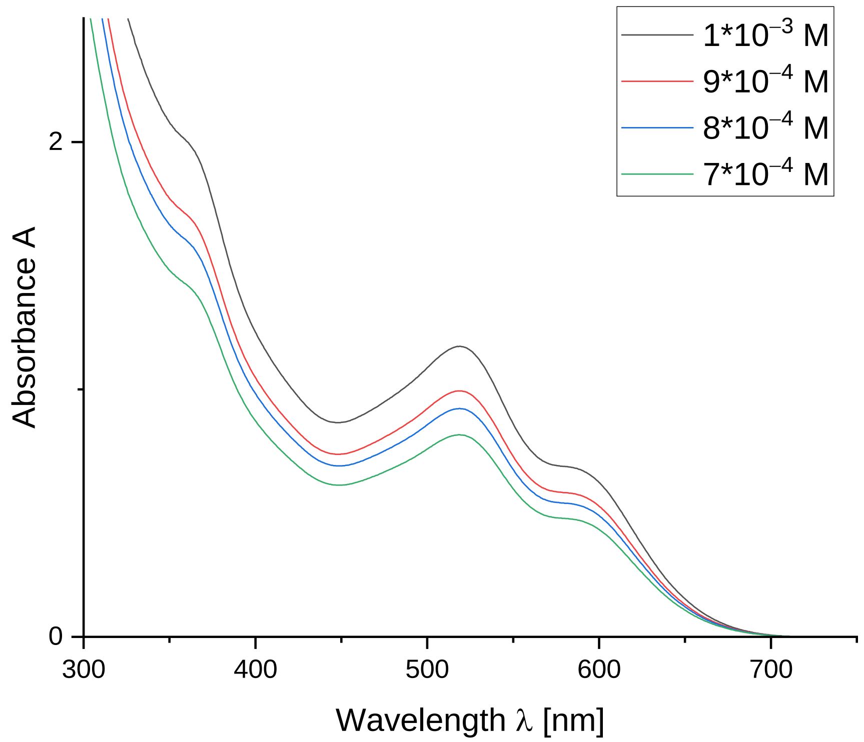
Supplementary Figure S21. $^{29}Si\{^{1}H\}$ NMR spectrum of $Ni(PPh_3)$ siliconoid/silylene complex **3b** in C_6D_6 (79.49 MHz, 300 K).



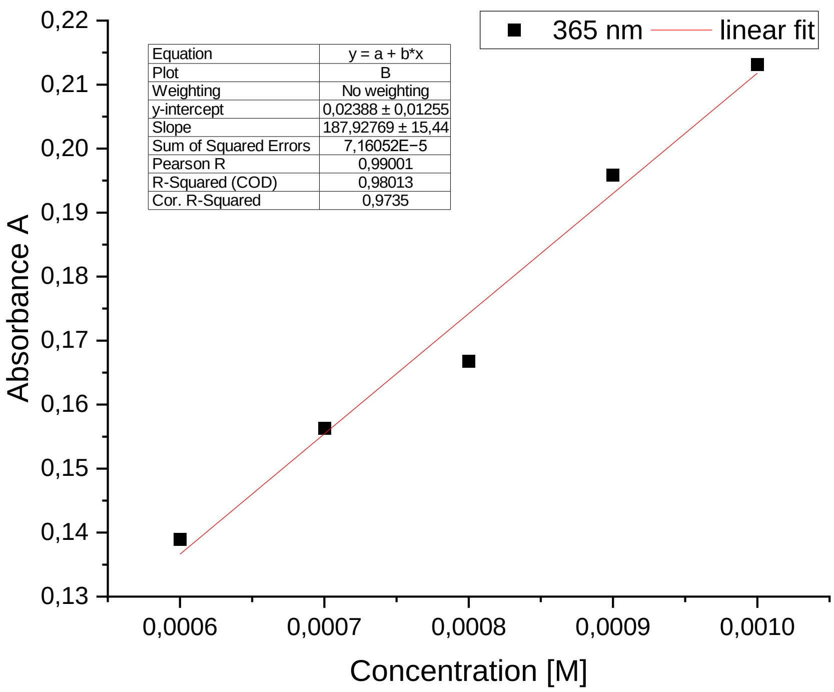
Supplementary Figure S22. CP-MAS $^{31}P\{^1H\}$ NMR spectrum of Ni(PPh$_3$) siliconoid/silylene complex **3b** (162.04 MHz, 13 KHz, 300 K), * side spinning bands.



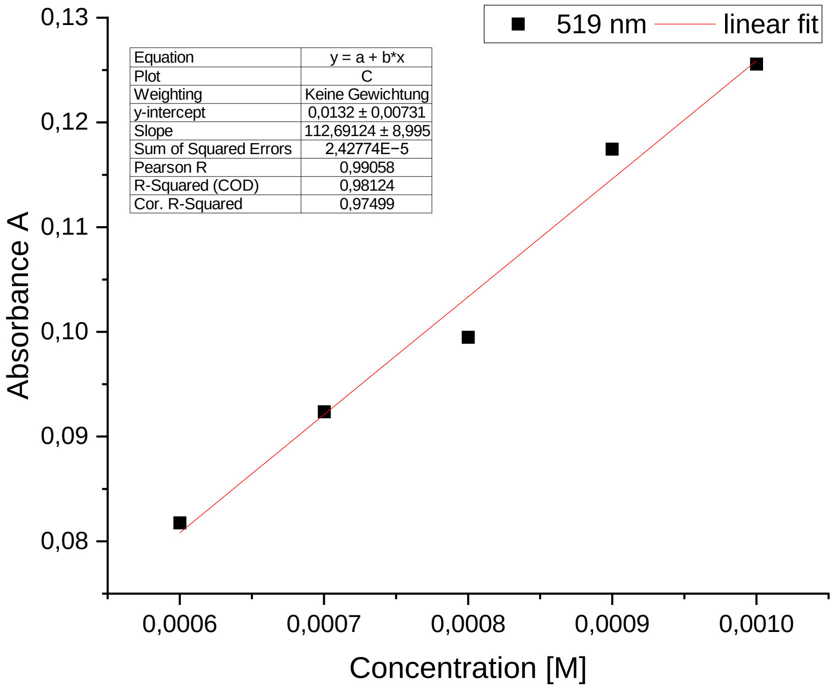
Supplementary Figure S23. CP-MAS $^{29}Si\{^1H\}$ NMR spectrum of Ni(PPh$_3$) siliconoid/silylene complex **3b** (79.53 MHz, 13 KHz, 300 K), side spinning bands # 72.7, ° 37.6, ^ −44.7, * −279.6 ppm.



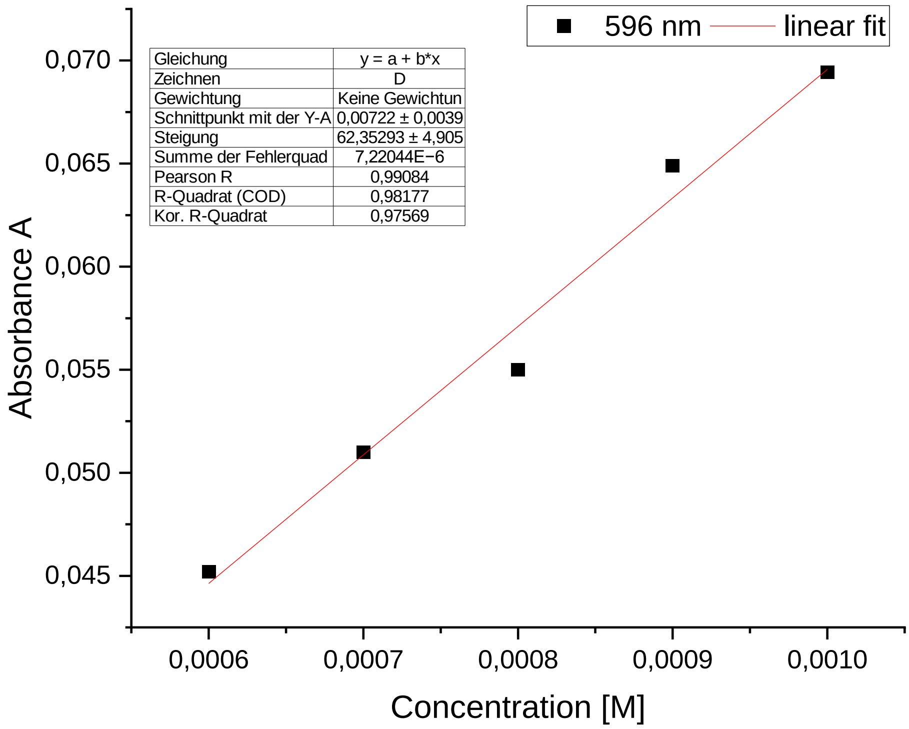
Supplementary Figure S24. UV-Vis spectra of Ni(PPh_3) siliconoid/silylene complex **3b** in hexane at different concentrations.



Supplementary Figure S25. Determination of the extinction ε = 1879 M^{-1} cm^{-1} of **3b** by linear regression at λ = 365 nm.



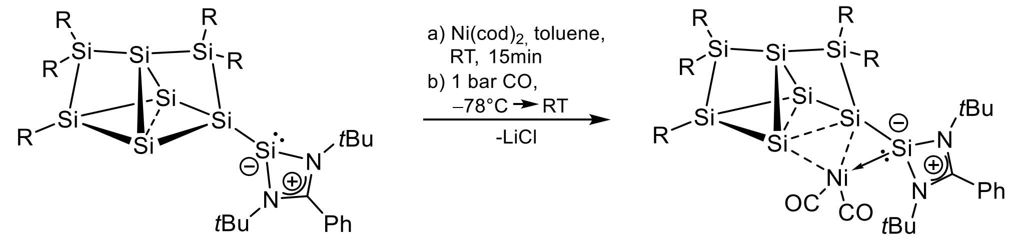
Supplementary Figure S26. Determination of the extinction ε = 1127 M^{-1} cm^{-1} of **3b** by linear regression at λ = 519 nm.



Supplementary Figure S27. Determination of the extinction ε = 624 M^{-1} cm^{-1} of **3b** by linear regression at λ_{max} = 596 nm.

Supplementary Information

2.3 Preparation of $Ni(CO)_2$ siliconoid/silylene complex 3c



1 **3c**

M [g/mol] = 1472.79 1587.50

1[4] (100 mg, 0.0638 mmol, 1.0 eq) was dissolved in 1.4 mL toluene and solid bis(cycloocta-1,5-diene) nickel (19.7 mg, 0.0701mmol, 1.1 eq) was added. The reaction mixture was stirred for 15 minutes at ambient temperature, then cooled to −80°C for 5 minutes and 1 bar CO gas was bubbled through under maintained Argon gas flow until the colour change to "blood red" was completed (no traces of blackberry red visible). The solvent and all volatiles were removed in vacuo and the product was extracted from 0.6 mL pentane. The residue was washed with 3 x 0.5 mL pentane. Red crystals of **3c** (121.5 mg, 0.1261 mmol, 44 %) were obtained from a concentrated solution in pentane at −70°C after five days.

^{1}H NMR (400.13 MHz, C_6D_6, 300 K) δ = 7.629 (q, C_8H_{10}), 7.7.450 (d, $^4J_{HH}$ = 1.58 Hz, 1H, Ar-*H*), 7.398 (d, $^4J_{HH}$ = 1.58 Hz, 1H, Ar-*H*), 7.251 (q, C_8H_{10}), 7.197 (d, $^4J_{HH}$ = 1.69 Hz, 1H, Ar-*H*), 7.190 – 7.171 (m, 2H, Ar-*H*), 7.137 (d, $^4J_{HH}$ = 1.67 Hz, 1H, Ar-*H*), 7.092 – 7.080 (m, 2H, Ar-*H*), 6.994 (d, $^4J_{HH}$ = 1.67 Hz, 1H, Ar-*H*), 6.898 (d, $^4J_{HH}$ = 1.74 Hz, 1H, Ar-*H*), 6.888 (d, $^4J_{HH}$ = 1.52 Hz, 1H, Ar-*H*), 6.872 (d, $^4J_{HH}$ = 1.52 Hz, 1H, Ar-*H*), 6.818 (d, $^4J_{HH}$ = 1.49 Hz, 1H, Ar-*H*), 6.772 – 6.695 (m, 2H, Ar-*H*), 5.672 (sept, $^3J_{HH}$ = 6.51 Hz, 1H, Tip-C*H*($CH_3)_2$), 5.597 (sept, $^3J_{HH}$ = 6.60 Hz, 1H, Tip-C*H*($CH_3)_2$), 5.407 (sept, $^3J_{HH}$ = 6.51 Hz, 1H, Tip-C*H*($CH_3)_2$), 4.928 (sept, $^3J_{HH}$ = 6.60 Hz, 1H, Tip-C*H*($CH_3)_2$), 4.346 (sept, $^3J_{HH}$ = 6.60 Hz, 1H, Tip-C*H*($CH_3)_2$), 4.002 (sept, $^3J_{HH}$ = 6.50 Hz, 1H, Tip-C*H*($CH_3)_2$), 3.439 (sept, $^3J_{HH}$ = 6.26 Hz, 2H, Tip-C*H*($CH_3)_2$), 3.336 (sept, $^3J_{HH}$ = 6.42 Hz, 1H, Tip-C*H*($CH_3)_2$), 3.217 (sept, $^3J_{HH}$ = 6.50 Hz, 1H, Tip-C*H*($CH_3)_2$), 2.906 (sept, $^3J_{HH}$ = 6.71 Hz, 2H, Tip-C*H*($CH_3)_2$), 2.738 – 2.655 (m, 3H, Tip-C*H*($CH_3)_2$), 2.760 – 2.635 (sept, 1H, Tip-C*H*($CH_3)_2$ overlapping with d, $^3J_{HH}$ = 6.58 Hz, 3H, Tip-CH(C$H_3)_2$), 2.381 (d, $^3J_{HH}$ = 6.49 Hz, 3H, Tip-CH(C$H_3)_2$), 1.743 (d, $^3J_{HH}$ = 6.63 Hz, 3H, Tip-CH(C$H_3)_2$), 1.676 (d, $^3J_{HH}$ = 6.63 Hz, 3H, Tip-CH(C$H_3)_2$), 1.632 – 1.599 (m, 14H, Tip-CH(C$H_3)_2$), 1.565 (d, $^3J_{HH}$ = 6.49 Hz, 3H, Tip-CH(C$H_3)_2$, 1.526 (d, $^3J_{HH}$ = 6.63 Hz, 3H, Tip-CH(C$H_3)_2$), 1.420 (d, $^3J_{HH}$ = 6.63 Hz, 3H, Tip-CH(C$H_3)_2$), 1.396 (d, $^3J_{HH}$ = 7.04 Hz, 6H, Tip-CH(C$H_3)_2$), 1.378 – 1.360 (m, 10H, Tip-CH(C$H_3)_2$), 1.339 (d, $^3J_{HH}$ = 3.04 Hz, 3H, Tip-CH(C$H_3)_2$), 1.318 – 1.3296 (m, 6H, Tip-CH(C$H_3)_2$), 1.182 (d, $^3J_{HH}$ = 2.21 Hz, 3H, Tip-CH(C$H_3)_2$), 1,165 (d, $^3J_{HH}$ = 2.21 Hz, 3H, Tip-CH(C$H_3)_2$), 1.150 (d, $^3J_{HH}$ = 2.21 Hz, 3H, Tip-CH(C$H_3)_2$), 1.133 (d, $^3J_{HH}$ = 2.21 Hz, 3H, Tip-CH(C$H_3)_2$), 1.124 (s, 9H, Si(N(C(C$H_3)_3))_2$CPh), 1.082 – 1.048 (m, 10H impurity), 0.724 (d, $^3J_{HH}$ = 6.63 Hz, 3H, Tip-CH(C$H_3)_2$), 0.651 (s, 9H, Si(N(C(C$H_3)_3))_2$CPh), 0.580 (d, $^3J_{HH}$ = 6.49 Hz, 6H, Tip-CH(C$H_3)_2$), 0.526 (dd, $^3J_{HH}$ = 9.53 Hz, 6.63 Hz, 6H, Tip-CH(C$H_3)_2$),) 0.391 (d, $^3J_{HH}$ = 6.21 Hz, 3H, Tip-CH(C$H_3)_2$) ppm.

^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 300 K) δ = 204.95 (s, Ni(*C*O)$_2$), 196.31 (s, Ni(*C*O)$_2$), 164.39 (s, Si(N(C(CH$_3$)$_3$))$_2$*C*Ph), 156.20, 156.09, 154.98, 153.95, 153.30, 153.13, 153.07, 152.97, 152.94, 150.03, 149.77, 149.26, 149.17, 139.88, 138.89, 138.71 (s, each 1C, Ar-*C*), 137.85 (s, toluene), 137.22, 137.10, 136.97, 134.88, 132.13 (s, each 1C, Ar-*C*), 130.40 (s, 1C, Ar-*C*H), 129.39 (s, toluene), 129.27, 128.88, 128.85, 128.75, 128.60 (s, each 1C, Ar-*C*H), 128.50, 125.63 (s, toluene), 123.35, 123.27, 123.18, 123.09, 122.27, 122.05 (s, each 1C, Ar-*C*H), 121.74 (d, ^4J-= 1.84 Hz, 1C, Ar-*C*), 121.33, 120.77 (s, each 1C, Ar-*C*H), 55.32, 54.70 (s, each 1C, Si(N(*C*(CH$_3$)$_3$))$_2$CPh), 37.42, 37.24, 26.46, 36.25, 35.67, 35.56, 35.48, 35.33, 34.69, 34.62, 34.59, 34.53 (s, each 1C, Tip-*C*H(CH$_3$)$_2$), 34.46 (s, pentane), 34.38, 34.28, 32.73 (s, each 1C, Tip-*C*H(CH$_3$)$_2$), 32.20, 31.74 (s, each 3C, Si(N(C(*C*H$_3$)$_3$))$_2$CPh), 31.38, 31.20, 29.30, 28.32, 28.23, 27.90, 27.43, 27.01, 26.78, 26.57, 26.32, 26.02, 25.69, 25.57, 25.34, 25.10, 24.78, 24.76, 24.75, 24.57, 24.39, 24.35, 24.21, 24.22, 24.18, 24.08, 24.01, 23.91, 23.82, 23.18 (s, each 1C, Tip-CH(*C*H$_3$)$_2$), 22.67 (s, pentane), 21.37 (s, toluene), 14.21 (s, pentane) ppm.

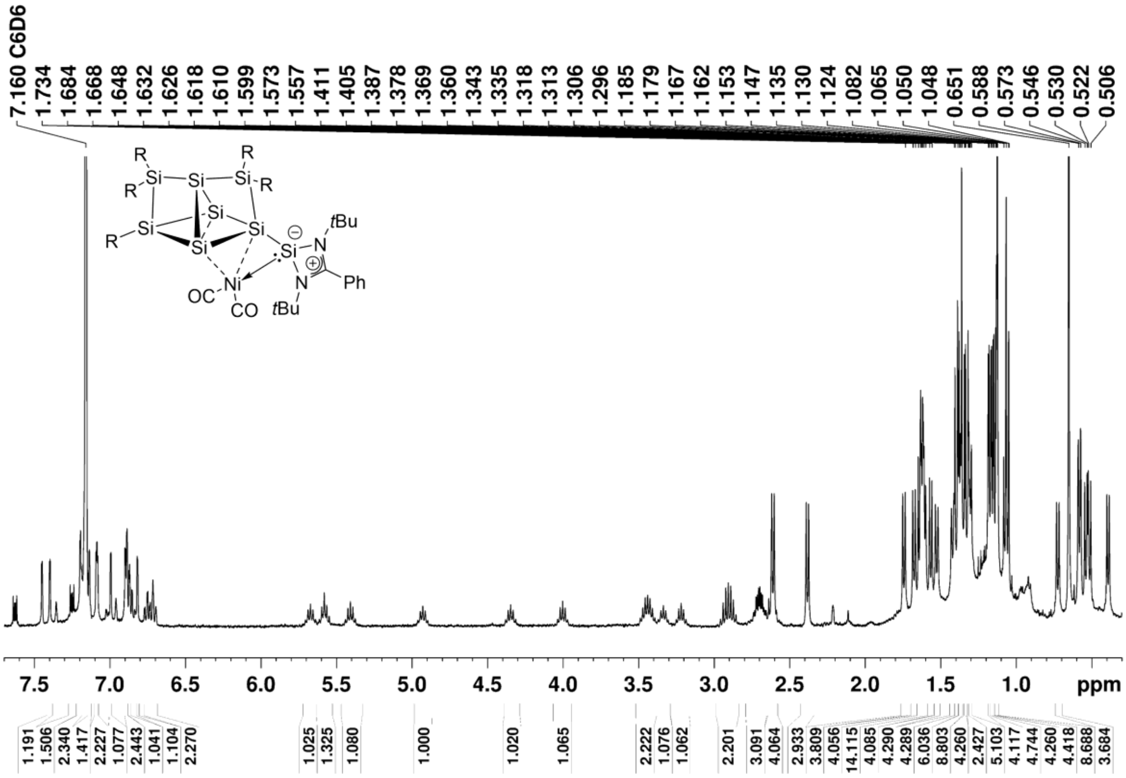
^{29}Si{^{1}H} NMR (59.63 MHz, C_6D_6, 300 K) δ = 96.6 (s, Ni*Si*(N(C(CH$_3$)$_3$))$_2$CPh), 70.9 (s, *Si*Tip), 44.6 (s, *Si*Tip$_2$), −3.9 (s, *Si*Tip$_2$), −10.0 (s, *Si*(Si(N(C(CH$_3$)$_3$))$_2$CPh)), −81.9 (s, *Si* unsubstituted), −160.4 (s, *Si*Ni), −342.0 (s, *Si* unsubstituted) ppm.

Elemental analysis: calculated for $C_{94}H_{138}N_2NiO_2Si_8$: C: 69.61; H: 8.76; N: 1.76%. Found: C: 68.56 %; H: 7.96%; N: 1.29%. The lower values compared to those calculated are quite common for unsaturated silicon clusters due to incomplete combustion typically attributed to the formation of silicon carbides and/or nitrides. In addition, elemental analysis has come under scrutiny because of highly variable results of bona fide identical samples.[5]

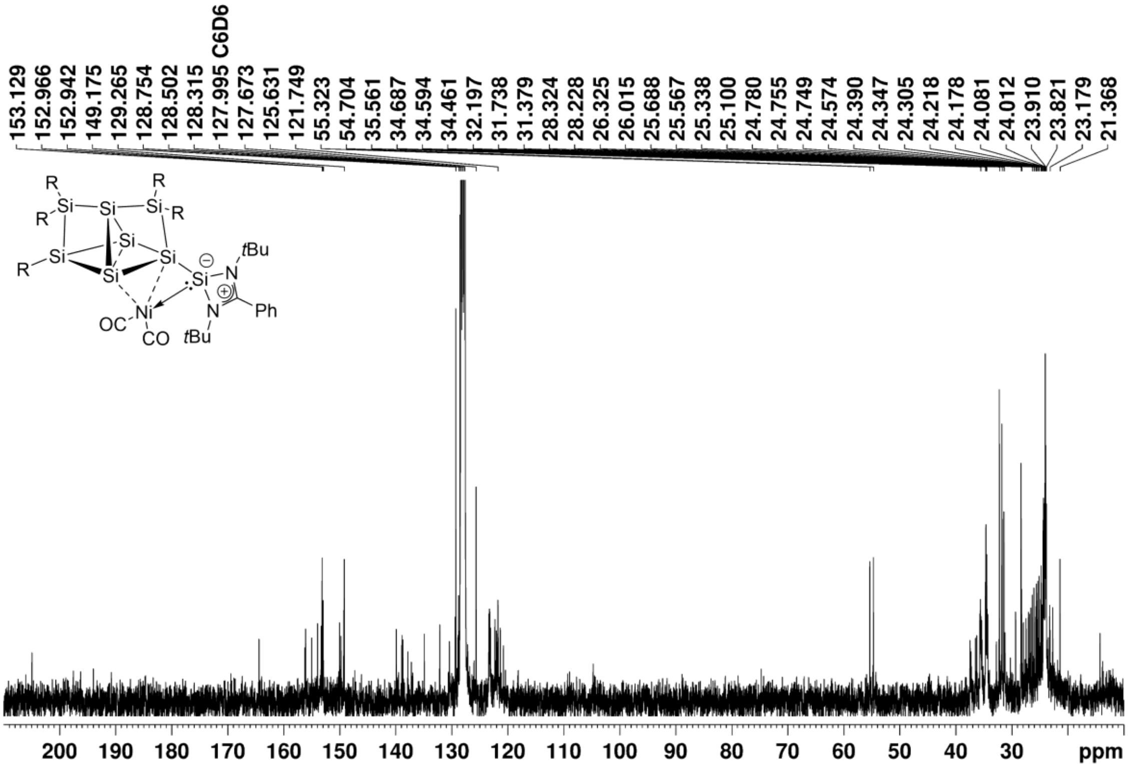
UV-Vis (hexane): λ_{max} (ε) = 363 (12350 M^{-1} cm^{-1}), 472 (7860 M^{-1} cm^{-1}), 523 (9630 M^{-1} cm^{-1}) nm.

Solid State FT-IR $\tilde{\nu}_{CO}$ = 2015 (s), 1976 (s) cm^{-1}.

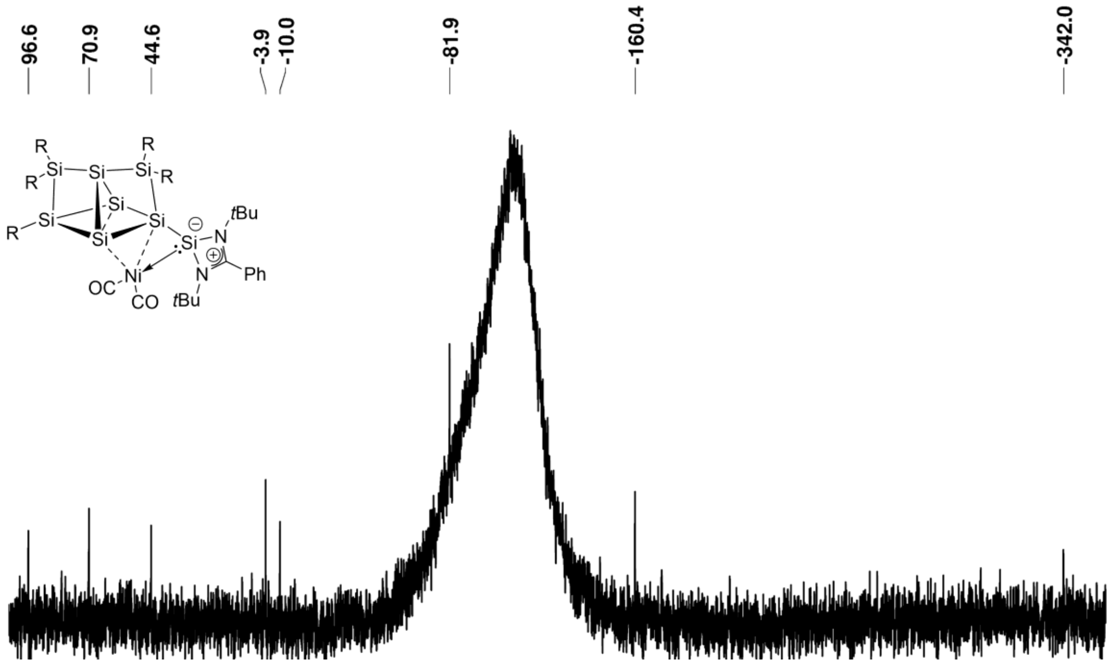
Melting Point: 107°C (decomposition), 205 – 245°C (melting).



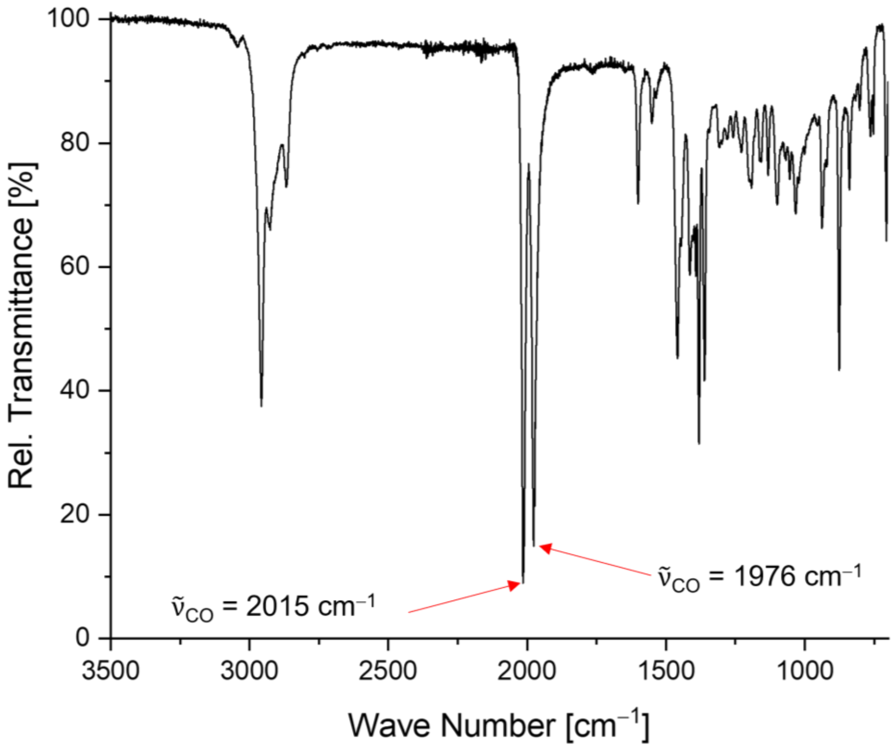
Supplementary Figure S28. ^{1}H NMR spectrum of NiCO)$_2$ siliconoid/silylene complex **3c** in C_6D_6 (400.13 MHz, 300 K).



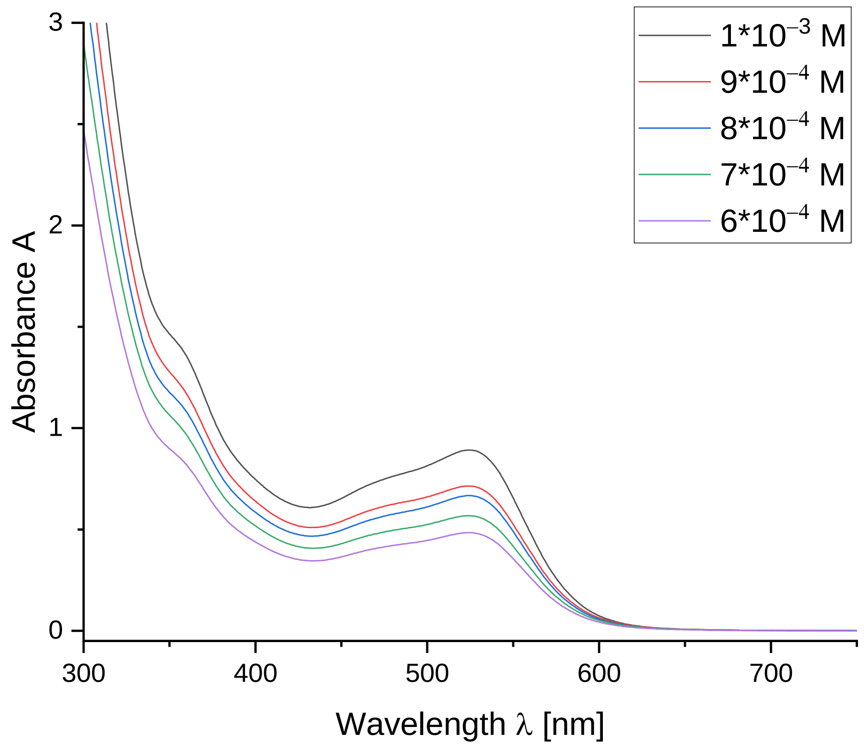
Supplementary Figure S29. ^{13}C NMR spectrum of NiCO)$_2$ siliconoid/silylene complex **3c** in C_6D_6 (75.47 MHz, 300 K).



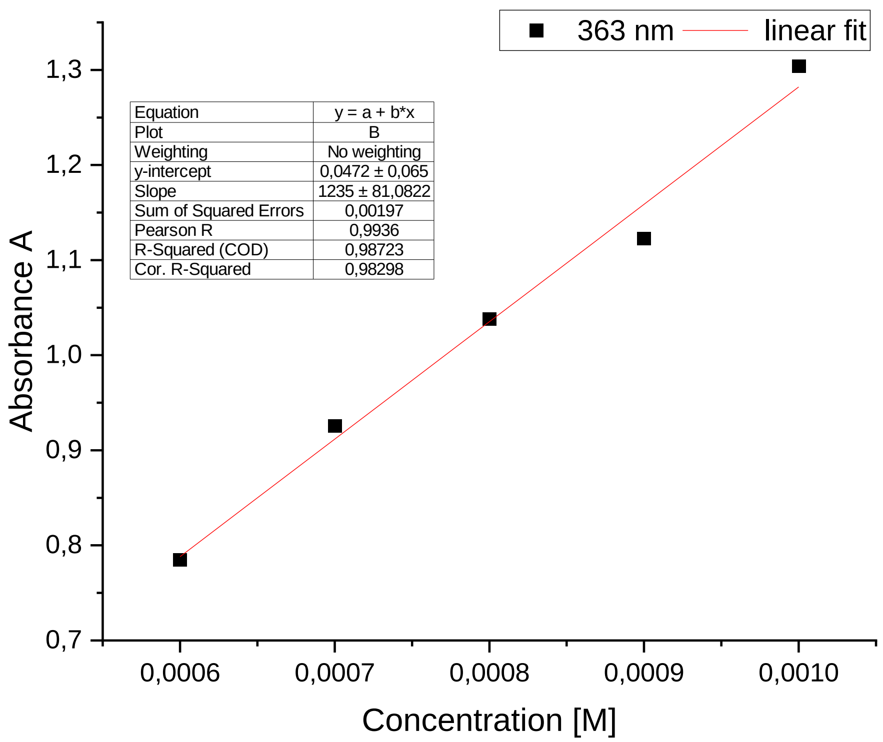
Supplementary Figure S30. ^{29}Si NMR spectrum of NiCO)$_2$ siliconoid/silylene complex **3c** in C_6D_6 (59.63 MHz, 300 K).



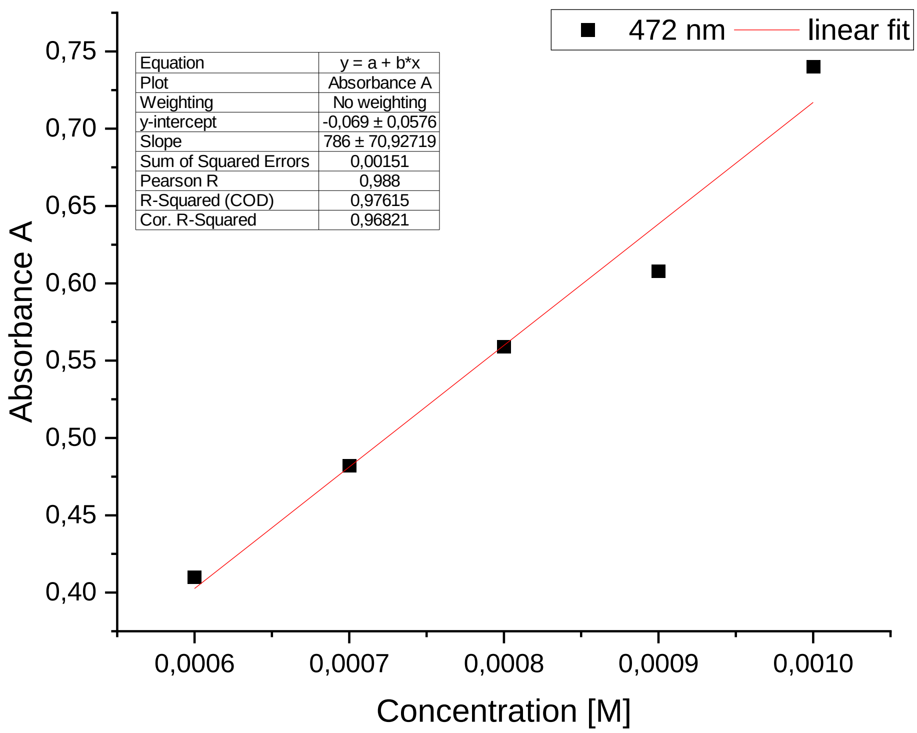
Supplementary Figure S31: FT-IR spectrum of NiCO)$_2$ siliconoid/silylene complex **3c** in the solid state.



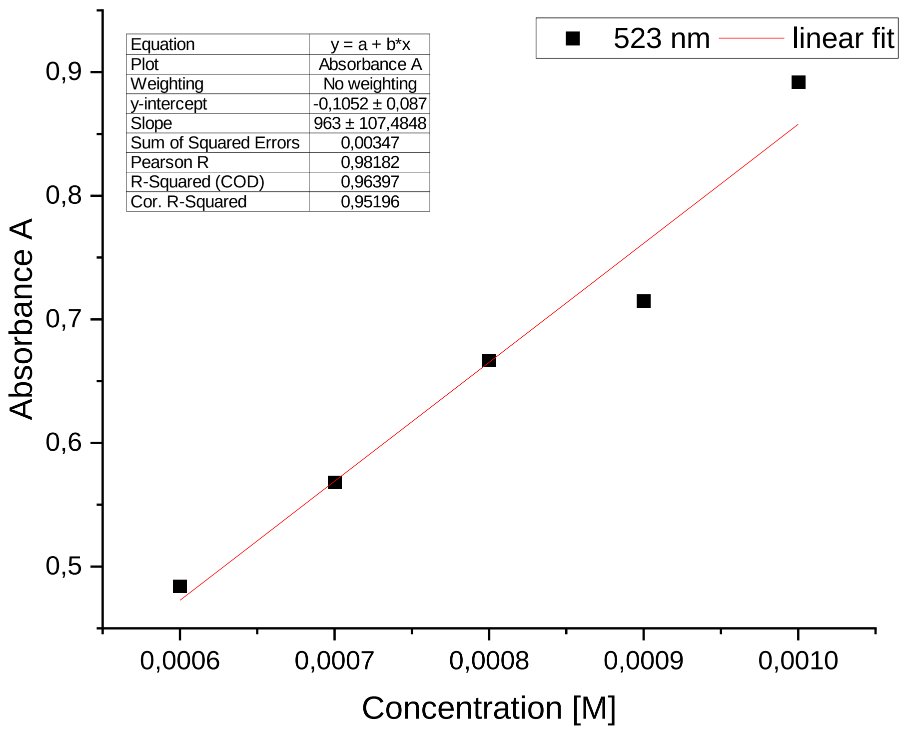
Supplementary Figure S32. UV-Vis spectra of NiCO)$_2$ siliconoid/silylene complex **3c** in hexane at different concentrations.



Supplementary Figure S33. Determination of the extinction ε = 12350 M^{-1} cm^{-1} of **3c** by linear regression at λ = 363 nm.



Supplementary Figure S34. Determination of the extinction ε = 7860 M^{-1} cm^{-1} of **3c** by linear regression at λ = 472 nm.



Supplementary Figure S35. Determination of the extinction ε = 9630 M^{-1} cm^{-1} of **3c** by linear regression at λ_{max} = 523 nm.

2.4 Hydrosilylation of terminal alkenes with diphenylsilane

General procedure

The substrate was dissolved in 0.1 mL C_6D_6. Diphenylsilane and mesitylene, as the internal standard, were added to the solution at ambient temperature. A reference ^{1}H NMR spectrum was recorded. A solution of the catalyst, **3a/b/c** or Ni(cod)$_2$ respectively, in 0.1 mL C_6D_6 was added to the reaction mixture. The reaction progress was monitored by ^{1}H NMR spectra until full conversion of the substrate. The conversion was determined by integration against the internal standard. The use of a slight excess of diphenylsilane (1.1 eq.) was chosen based on the complete consumption before the complete conversion of the substrate observed in preliminary, stoichiometric studies due to the dehydro-coupling side-reactions. To explore the substrate scope, stock solutions of **3a** and Ni(cod)$_2$ were prepared accordingly.

Quantities:

a) 0.5 mol%: substrate (0.6 mmol, 1.0 eq.), diphenylsilane (0.66 mmol, 1.1 eq.), mesitylene (0.30 mmol, 0.5 eq.), catalyst (0.008 mmol, 0.05 eq.)

b) 0.05 mol%: substrate (1.6 mmol, 1.0 eq.), diphenylsilane (1.76 mmol, 1.1 eq.), mesitylene (0.80 mmol, 0.5 eq.), catalyst (0.0008 mmol, 0.005 eq.)

Mercury drop test

In a glove box, a 50 mL Schlenk flask containing a stirring bar was charged with vinyltrimethylsilane (0.24 mL, 1.60 mmol, 1.0 eq.), C_6D_6 (0.1 mL), diphenylsilane (0.34 mL, 1.76 mmol, 1.1 eq.) and mesitylene (0.11 mL, 0.80 mmol, 0.5 eq.). Elemental mercury (1.68 g, 8.0 mmol, 5.0 eq) was added *via* disposable glass pipette. The addition of 0.1 mL of the corresponding stock solution of **3a** or Ni(cod)$_2$ in C_6D_6 was added with a syringe and the conversion was monitored with ^{1}H NMR spectroscopy. The mercury drop test revealed a slower reaction to **A** with an overall lower spectroscopic yield, however exhibiting a higher ratio of **A** compared to the twofold-substituted silylation product (23:6) than in the reaction without the presence of Hg (9:5), indicating that the catalyst is partially decomposed to nickel particles in the course of the reaction, which are known to be highly active but unselective in heterogenous catalysis.[6,7] In the case of Ni(cod)$_2$, the mercury drop test revealed a similar reactivity to the one without mercury (>99% conversion within 5.5 h).

Assignment

In addition to the ^{1}H NMR spectra reproduced in this present Supporting Information, the products obtained from the catalytic hydrosilylation were assigned according to the corresponding hetero nuclei and correlation NMR spectra as well as the results found in the literature.[8–13] A blank spectrum of diphenylsilane was recorded in C_6D_6 at ambient temperature.

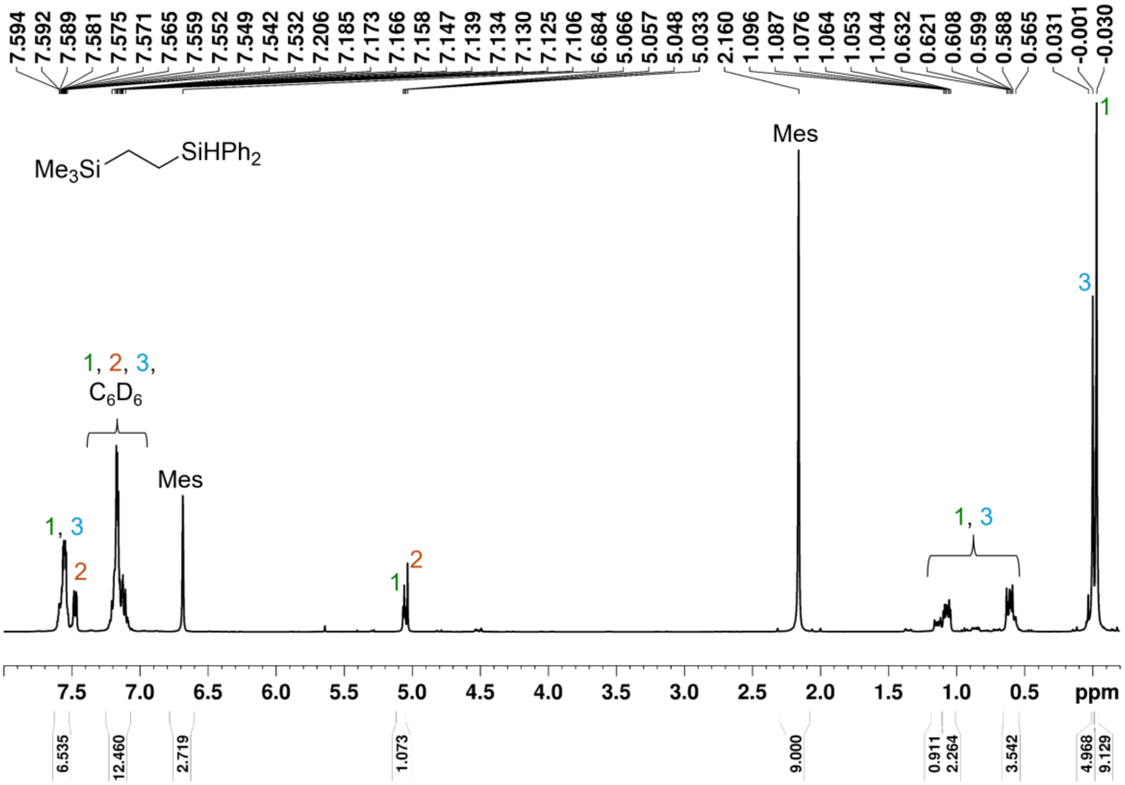
Ph_2SiH_2 reference spectrum:

^{1}H NMR (400.13, MHz, C_6D_6, 293 K) δ = 7.485 (m, 4H, H_{Ar}), 7.115 (m, 6H, H_{Ar} overlapping with C_6D_6), 5.068 (brs, 2H, Si-*H*) ppm.

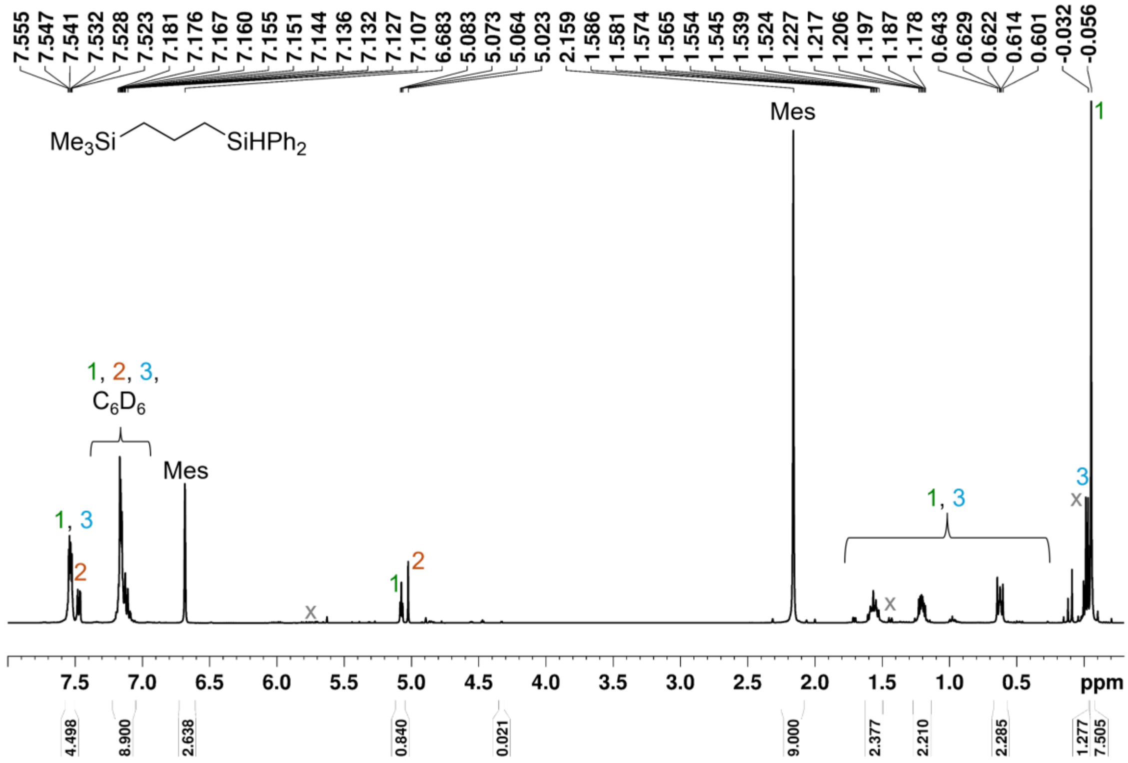
^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 293 K): δ = 136.00 (4C, C_{Ar}H), 131.62 (2C, C_{quart}), 130.11 (2C, C_{Ar}H), 128.44 (4C, C_{Ar}H) ppm.

^{29}Si{^{1}H} NMR (79.49 MHz, C_6D_6, 293 K): δ = −33.5 ppm.

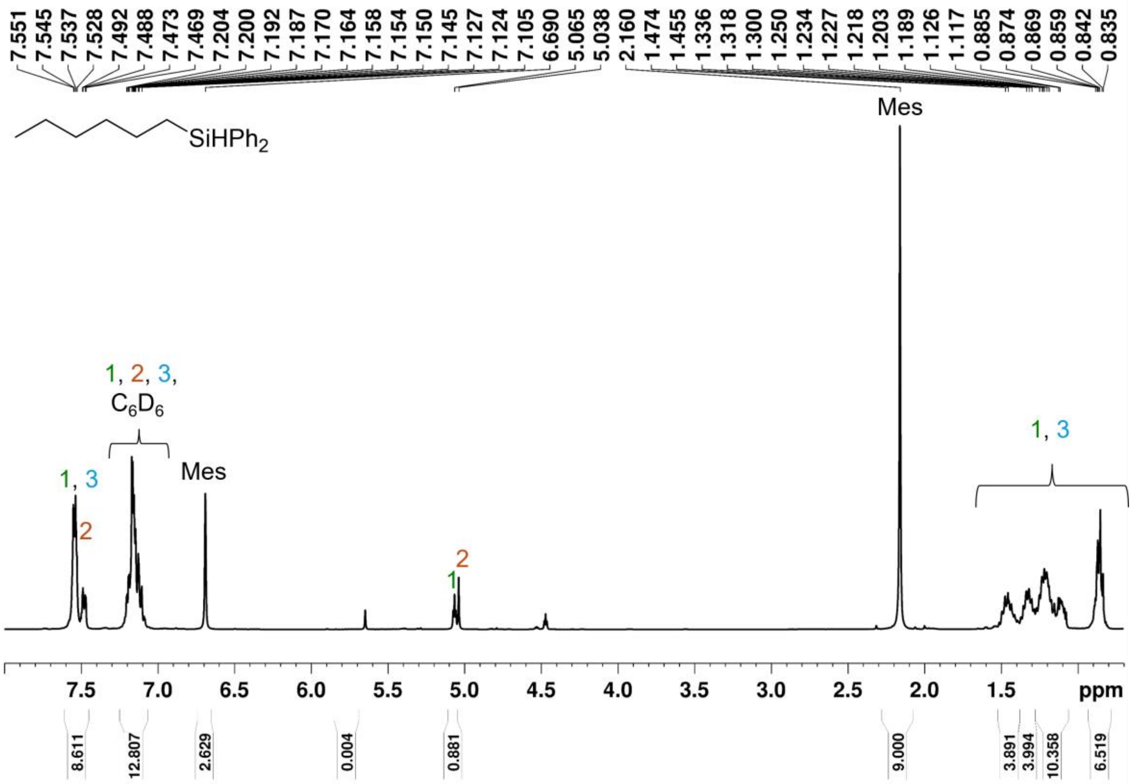
^{29}Si NMR (79.49 MHz, C_6D_6, 293 K): δ = −33.5 (t, $^2J_{Si\text{-}H}$ = 21.6 Hz) ppm.



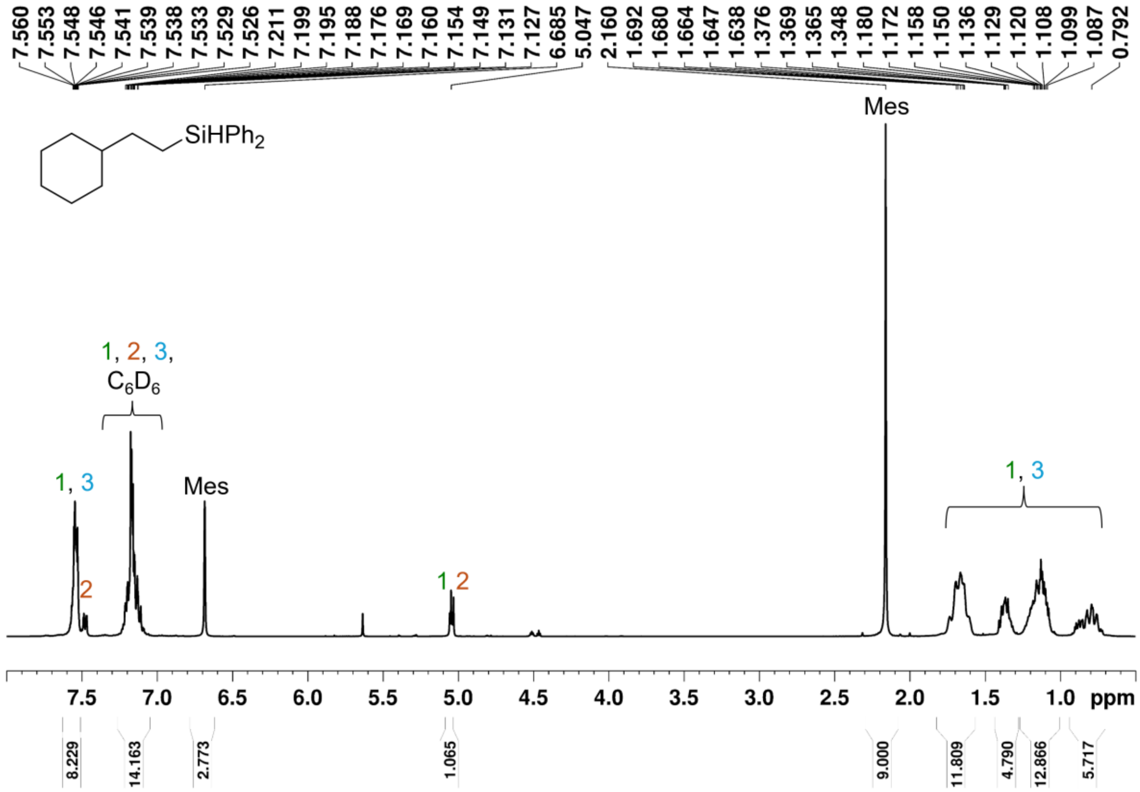
Supplementary Figure S36. ^{1}H NMR spectrum of the crude reaction mixture of the hydrosilylation of vinyltrimethylsilane and Ph_2SiH_2 catalyzed by 0.05 mol% **3a** in C_6D_6 after 8 h at 293 K. Internal standard mesitylene (Mes), 1 anti-Markovnikov product, 2 Ph_2SiH_2, 3 disubstituted product.



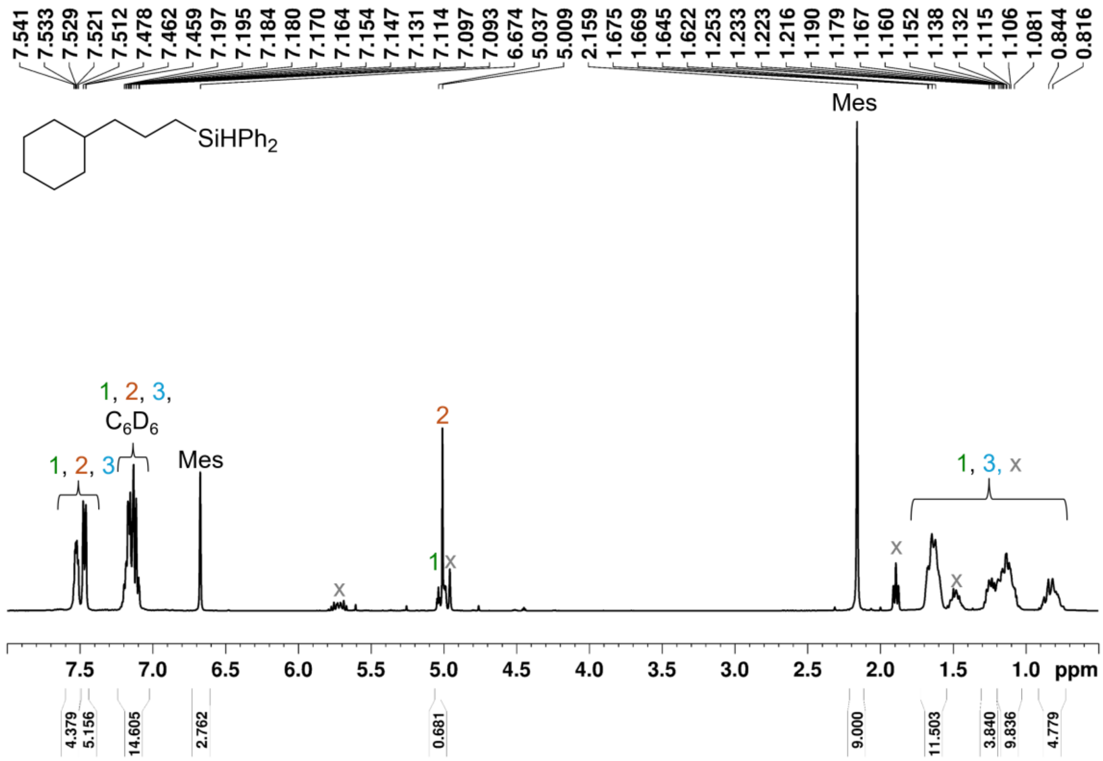
Supplementary Figure S37. ^{1}H NMR spectrum of the crude reaction mixture of the hydrosilylation of allyltrimethylsilane and Ph_2SiH_2 catalyzed by 0.05 mol% **3a** in C_6D_6 after 408 h at 293 K. Internal standard mesitylene (Mes), 1 anti-Markovnikov product, 2 Ph_2SiH_2, 3 disubstituted product, x allyltrimehtylsilane.



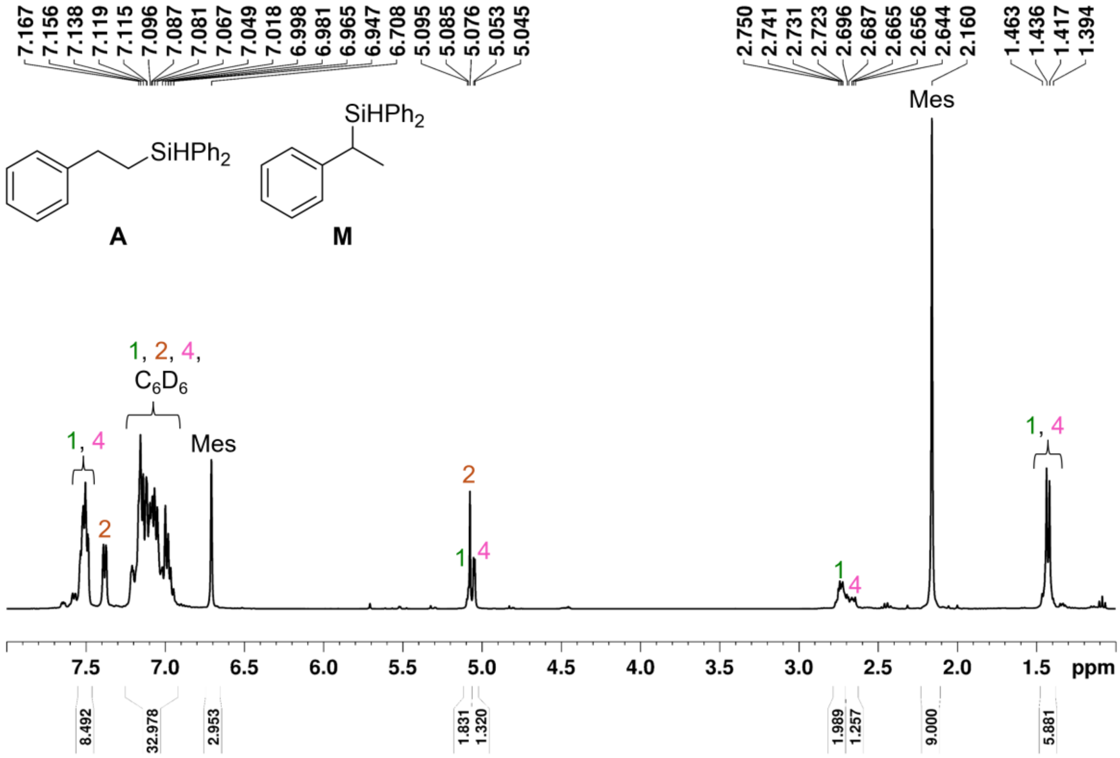
Supplementary Figure S 38. ^{1}H NMR spectrum of the crude reaction mixture of the hydrosilylation of 1-hexene and Ph_2SiH_2 catalyzed by 0.05 mol% **3a** in C_6D_6 after 15 min at 293 K. Internal standard mesitylene (Mes), 1 anti-Markovnikov product, 2 Ph_2SiH_2, 3 disubstituted product.



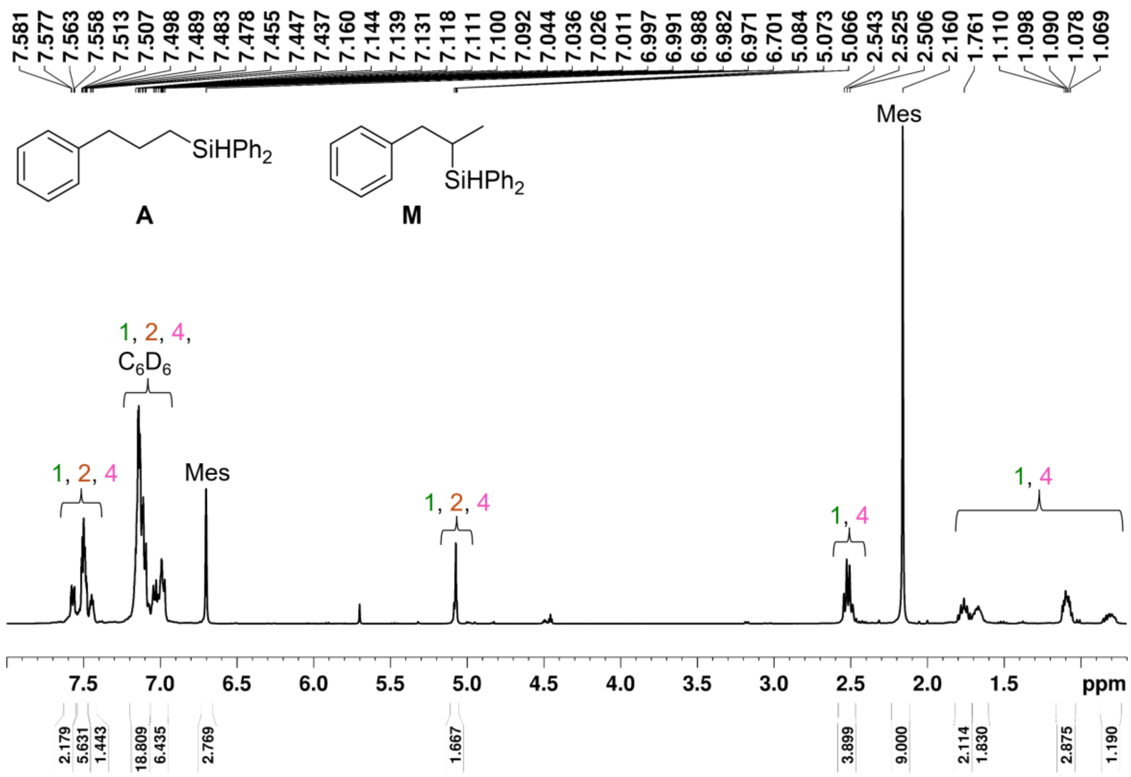
Supplementary Figure S39. ^{1}H NMR spectrum of the crude reaction mixture of the hydrosilylation of vinylcyclohexane and Ph_2SiH_2 catalyzed by 0.05 mol% **3a** in C_6D_6 after 168 h at 293 K. Internal standard mesitylene (Mes), 1 anti-Markovnikov product, 2 Ph_2SiH_2, 3 disubstituted product.



Supplementary Figure S40. ^{1}H NMR spectrum of the crude reaction mixture of the hydrosilylation of allylcyclohexane and Ph_2SiH_2 catalyzed by 0.05 mol% **3a** in C_6D_6 after 408 h at 293 K. Internal standard mesitylene (Mes), 1 anti-Markovnikov product, 2 Ph_2SiH_2, 3 disubstituted product, x allyltrimehtylsilane.



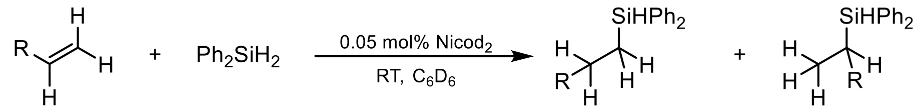
Supplementary Figure S41. ^{1}H NMR spectrum of the crude reaction mixture of the hydrosilylation of styrene and Ph_2SiH_2 catalyzed by 0.05 mol% **3a** in C_6D_6 after 54 h at 293 K. Internal standard mesitylene (Mes), 1 anti-Markovnikov product, 2 Ph_2SiH_2, 4 Markovnikov product.



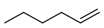
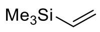
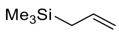
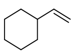
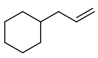
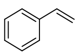
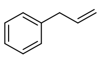
Supplementary Figure S42. ^{1}H NMR spectrum of the crude reaction mixture of the hydrosilylation of allylbenzene and Ph_2SiH_2 catalyzed by 0.05 mol% **3a** in C_6D_6 after 54 h at 293 K. Internal standard mesitylene (Mes), 1 anti-Markovnikov product, 2 Ph_2SiH_2, 4 Markovnikov product.

Supplementary Information

Supplementary Table S1. Catalytic hydrosilylation of terminal olefins with Ph_2SiH_2 using nickel complex $Ni(cod)_2$ as a catalyst.



anti-Markovnikov (**A**) Markovnikov (**M**)

Entry	Substrate	Time [h]	Conversion [%]	Product	Spectr. Yield [%]	TOF [h^{-1}]
1		0.083	>99	**A**	36	24000
2A		0.5	32	**A**	23	1272
2B		2	72	**A**	35	716
2C		5.5	>99	**A**	44	637
3A		0.083	24	**A**	18	5832
3B		0.5	69	**A**	35	2744
3C		3	93	**A**	41	620
4A		0.083	58	**A**	10	13848
4B		24	94	**A**	32	78
4C		216	>99	**A**	37	9
5A		4	12	**A**	7	62
5B		120	65	**A**	23	11
5C		336	78	**A**	29	5
6A		0.083	25	**A : M**	8 : 19	6096
6B		0.5	75	**A : M**	22 : 40	3008
6C		3	>99	**A : M**	30 : 43	500
7A		2	18	**A : M**	8 : 10	184
7B		120	72	**A : M**	31 : 31	12
7C		312	>99	**A : M**	41 : 35	6

3 Details on X-Ray Diffraction Studies

The data set was collected using a Rigaku XtaLAB Synergy-S diffractometer with a microfocus sealed tube and a HyPix-6000HE Hybrid Photon Counting (HPC) detector (**2**, **3c**), a Bruker D8 Venture diffractometer with a microfocus sealed tube and a Photon II detector (**3a**) and a Bruker X8 Apex diffractometer (**3b**). Graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) was used. Data were collected at 133(2) K (**2**, **3a**, **3c**)/ 154(2) K (**3b**) and corrected for absorption effects using the multi-scan method. The structure was solved by direct methods using SHELXT[14] and was refined by full matrix least squares calculations on F^2 (SHELXL2019 (**2**, **3c**), SHELXL2018 (**3a,b**))[15] in the graphical user interface Shelxle.[16]

Acknowledgments

Instrumentation and technical assistance for this work were provided by the Service Center X-ray Diffraction, with financial support from Saarland University and German Science Foundation (project number INST 256/506-1 (D8 Venture) and 256/582-1 (Synergy-S)).

3.1 Solid State Structure of $Fe(CO)_4$ siliconoid/silylene 2

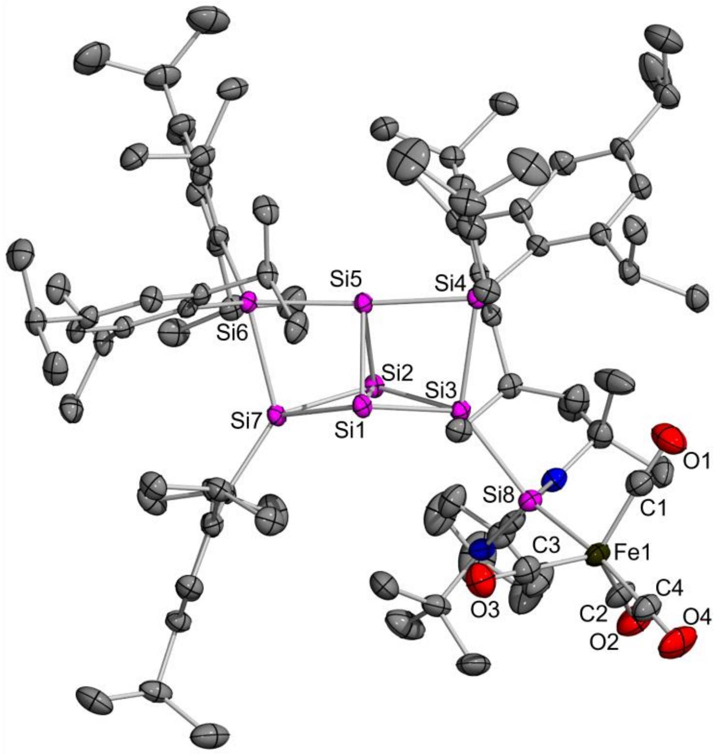
Refinement Details

All non-H-atoms were located in the electron density maps and refined anisotropically. C-bound H atoms were placed in positions of optimized geometry and treated as riding atoms. Their isotropic displacement parameters were coupled to the corresponding carrier atoms by a factor of 1.2 (CH, CH_2) or 1.5 (CH_3). *Disorder:* One tert-butyl group is split over two positions (fvar 2: 0.57/0.43).

Supplementary Table S2. Crystal data and structure refinement for $Fe(CO)_4$ siliconoid/silylene **2** (CCDC: 2504459).

Empirical formula	C_{99} H_{150} Fe N_2 O_4 Si_8	
Formula weight	1712.77	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 14.9881(3) Å	α = 104.518(2)°.
	b = 17.1703(3) Å	β = 100.700(2)°.
	c = 20.6186(4) Å	γ = 97.1940(10)°.
Volume	4964.47(17) $Å^3$	
Z	2	
Density (calculated)	1.146 Mg/m^3	
Absorption coefficient	0.297 mm^{-1}	
F(000)	1856	
Crystal size	0.220 x 0.200 x 0.100 mm^3	
Theta range for data collection	2.015 to 27.125°.	
Index ranges	-19<=h<=18, -21<=k<=22, -26<=l<=26	
Reflections collected	70038	
Independent reflections	21884 [R(int) = 0.0480]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	1.0000 and 0.8232
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	21884 / 36 / 1090
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R_1 = 0.0480, wR_2 = 0.1268
R indices (all data)	R_1 = 0.0665, wR_2 = 0.1357
Largest diff. peak and hole	0.673 and -0.486 e.Å^{-3}



Supplementary Figure S43. Molecular structure Fe(CO)$_4$ siliconoid/silylene **2** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids represent 50% probability.

3.2 Solid State Structure of Ni(cod) siliconoid/silylene 3a

Refinement Details

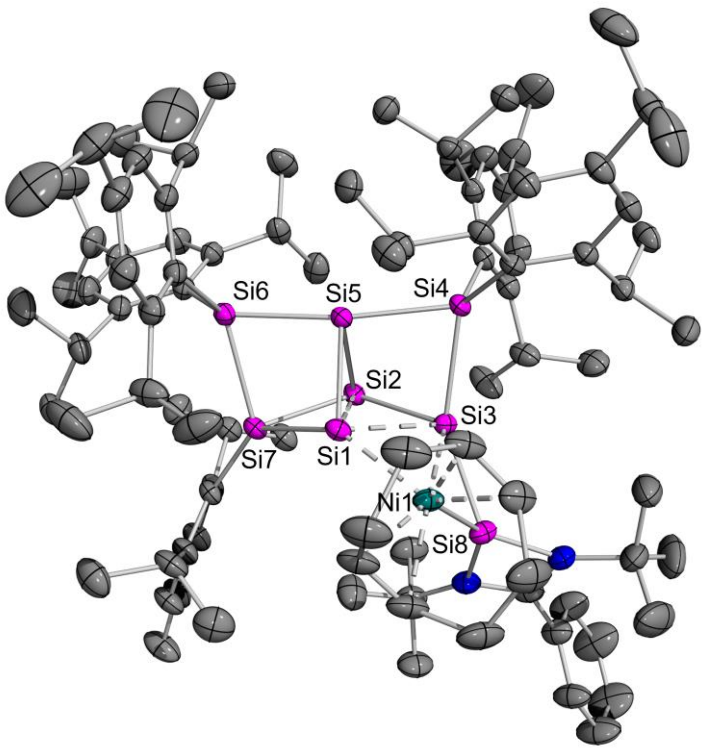
All non-H-atoms were located in the electron density maps and refined anisotropically. C-bound H atoms were placed in positions of optimized geometry and treated as riding atoms. Their isotropic displacement parameters were coupled to the corresponding carrier atoms by a factor of 1.2 (CH, CH_2) or 1.5 (CH_3). *Disorder:* Three isopropyl-groups and one tert-butyl group are split over two positions. One of the solvent n-pentane molecules is split over two positions. Its occupancy factors refined to 0.58 for the major component.

Supplementary Table S3. Crystal data and structure refinement for Ni(cod) siliconoid/silylene **3a** (CCDC: 2504461).

Empirical formula	C108 H174 N2 Ni Si8
Formula weight	1783.91
Temperature	133(2) K

Supplementary Information

Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 14.6865(6) Å	α = 87.707(2)°.
	b = 18.5075(7) Å	β = 73.3410(10)°.
	c = 22.7349(8) Å	γ = 67.462(2)°.
Volume	5451.0(4) Å^3	
Z	2	
Density (calculated)	1.087 Mg/m^3	
Absorption coefficient	0.310 mm^{-1}	
F(000)	1952	
Crystal size	0.360 x 0.240 x 0.080 mm^3	
Theta range for data collection	1.876 to 27.912°.	
Index ranges	-19<=h<=19, -24<=k<=24, -29<=l<=29	
Reflections collected	151157	
Independent reflections	26031 [R(int) = 0.0651]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7367 and 0.7072	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	26031 / 509 / 1281	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0409, wR2 = 0.1054	
R indices (all data)	R1 = 0.0545, wR2 = 0.1154	
Largest diff. peak and hole	0.513 and -0.448 e.Å^{-3}	



Supplementary Figure S44. Molecular structure Ni(cod) siliconoid/silylene **3a** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids represent 50% probability.

3.3 Solid State Structure of Ni(PPh_3) siliconoid/silylene 3b

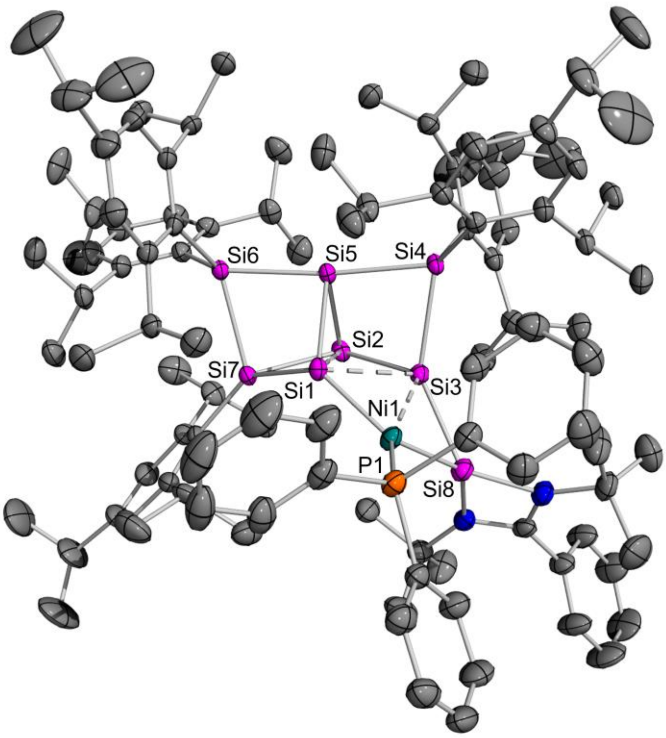
Refinement Details

All non-H-atoms were located in the electron density maps and refined anisotropically. C-bound H atoms were placed in positions of optimized geometry and treated as riding atoms. Their isotropic displacement parameters were coupled to the corresponding carrier atoms by a factor of 1.2 (CH) or 1.5 (CH_3). *Disorder:* Five isopropyl-groups and one tert-butyl-group were split over two positions. Their occupancy factors of the major components refined to 0.70, 0.67, 0.88, 0.76, 0.48 and 0.86, respectively. SQUEEZE: The scattering contribution of eight pentane solvent molecules in the unit cell has been treated with the SQUEEZE tool[17] in PLATON.[18] BerSQUEEZE found 250 electrons in the solvent accessible volume of 1839 Å^3.

Supplementary Table S4. Crystal data and structure refinement for Ni(PPh_3) siliconoid/silylene **3b** (CCDC: 2504467).

Empirical formula	C_{113} H_{165} N_2 Ni P Si_8	
Formula weight	1865.86	
Temperature	154(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	I2/a	
Unit cell dimensions	a = 38.3683(15) Å	α = 90°.

	b = 14.2013(5) Å	β = 92.947(2)°.
	c = 40.6910(14) Å	γ = 90°.
Volume	22142.4(14) $Å^3$	
Z	8	
Density (calculated)	1.119 Mg/m^3	
Absorption coefficient	0.322 mm^{-1}	
F(000)	8096	
Crystal size	0.200 x 0.200 x 0.080 mm^3	
Theta range for data collection	1.063 to 27.163°.	
Index ranges	-49<=h<=39, -18<=k<=18, -52<=l<=50	
Reflections collected	164785	
Independent reflections	24510 [R(int) = 0.1094]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7455 and 0.7117	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	24510 / 484 / 1281	
Goodness-of-fit on F^2	1.004	
Final R indices [I>2sigma(I)]	R_1 = 0.0494, wR_2 = 0.0955	
R indices (all data)	R_1 = 0.1078, wR_2 = 0.1171	
Largest diff. peak and hole	0.371 and -0.370 e.$Å^{-3}$	



Supplementary Figure S45. Molecular structure Ni(PPh_3) siliconoid/silylene **3b** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids represent 50% probability.

Supplementary Information

3.4 Solid State Structure of $Ni(CO)_2$ siliconoid/silylene 3c

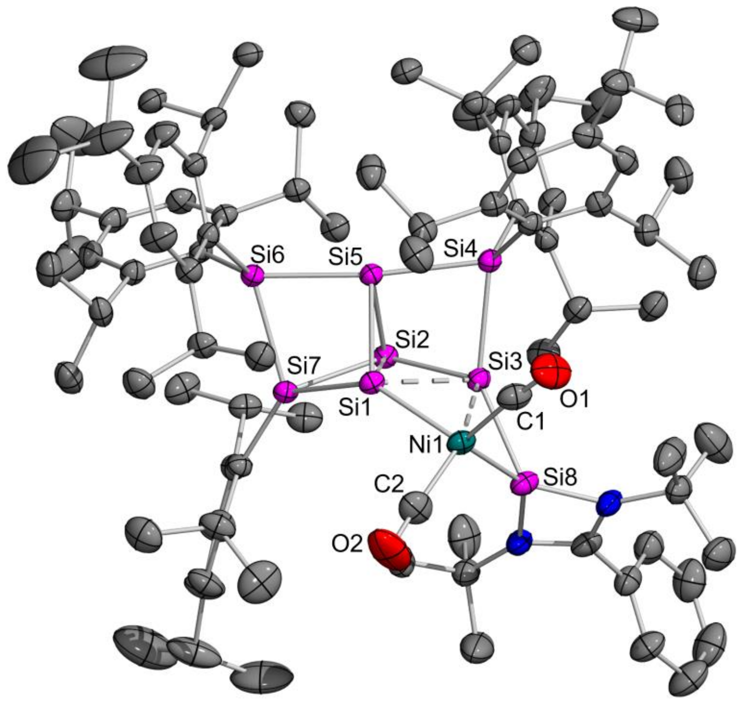
Refinement Details

All non H-atoms were located in the electron density maps and refined anisotropically. C-bound H atoms were placed in positions of optimized geometry and treated as riding atoms. Their isotropic displacement parameters were coupled to the corresponding carrier atoms by a factor of 1.2 (CH, CH_2) or 1.5 (CH_3). *Disorder:* three isopropyl-residues (fvar 2: 0.62/0.38; fvar 3: 0.68/0.32 and fvar 4: 0.80/0.20) and one n-pentane solvent (fvar 5: 0.59/0.41) are split over two positions. Three n-pentane solvent molecules are located over a crystallographic twofold axis and hence, they are handled using the PART-1 instruction of SHELX (sof: 0.5).

Supplementary Table S5. Crystal data and structure refinement for $Ni(CO)_2$ siliconoid/silylene **3c** (CCDC: 2504470).

Empirical formula	C_{209} H_{336} N_4 Ni_2 O_4 Si_{16}	
Formula weight	3535.66	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	I2/a	
Unit cell dimensions	a = 20.6821(5) Å	α = 90°.
	b = 34.0729(8) Å	β = 92.710(2)°.
	c = 31.1785(6) Å	γ = 90°.
Volume	21946.9(9) $Å^3$	
Z	4	
Density (calculated)	1.070 Mg/m^3	
Absorption coefficient	0.308 mm^{-1}	
F(000)	7720	
Crystal size	0.300 x 0.080 x 0.040 mm^3	
Theta range for data collection	1.972 to 26.372°.	
Index ranges	-25<=h<=25, -42<=k<=42, -35<=l<=38	
Reflections collected	151269	
Independent reflections	22428 [R(int) = 0.1233]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.69666	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	22428 / 640 / 1294	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R_1 = 0.0696, wR_2 = 0.1455	
R indices (all data)	R_1 = 0.1066, wR_2 = 0.1609	

Largest diff. peak and hole	0.855 and -0.337 e.Å^{-3}



Supplementary Figure S46. Molecular structure Ni(CO)$_2$ siliconoid/silylene **3c** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids represent 50% probability.

3.5 Calculation of Percent Buried Volume

The percent buried volume %V$_{bur}$ of **X**-Fe(CO)$_4$, **2** and **3b** was determined with the Sambvca open-source application on the corresponding crystallographic data, applying the common parameters of 3.50 Å sphere radius, 0.00 Å or 2.28 Å distance metal-ligand bond, with the hydrogen atoms included and the scaled bond radii used as recommended by Cavallo).[19]

%V$_{bur}$ of **X**-Fe(CO)$_4$[20]

Parameters: **center of sphere:** Fe1

z-axis: C4 (CO linear to Fe-Si7)

xz plane: C1, C2, C3 (remaining CO ligands)

deleted atoms: C1, C2, C3, C4, O1, O2, O3, O4

atomic radii: Bondi radii scaled by 1.17

Sphere radius: 3.5

Distance coordination point to center of sphere: 0.0

Mesh spacing for numerical integration: 0.10

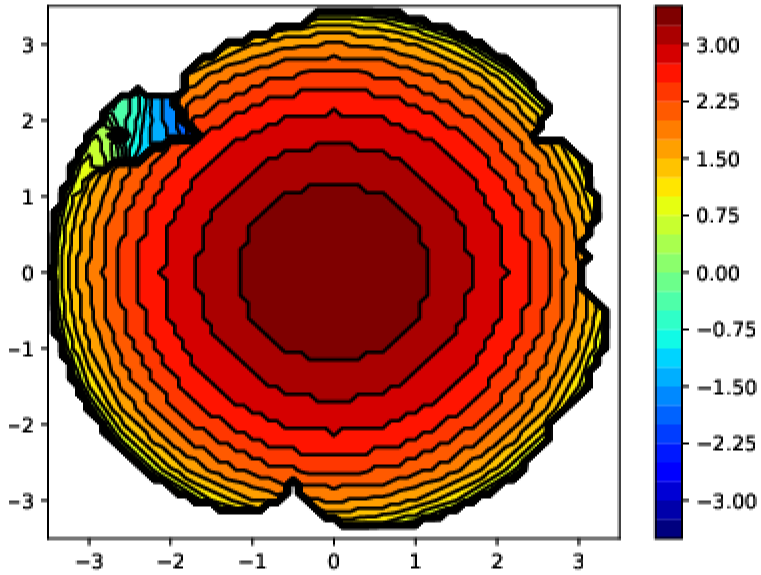
H atoms: included

Supplementary Information

Supplementary Table S6. Distribution of ligand volume in **X**.[19]

%V Free	%V Buried	% V Tot/V Ex
35.3	64.7	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	10.1	34.7	44.9	22.6	77.4
NW	15.7	29.2	44.9	35.0	65.0
NE	18.4	26.4	44.9	41.1	58.9
SE	19.1	25.8	44.9	42.5	57.5



Supplementary Figure S47. Steric map of **X** produced by SambVca.[19]

%V_{bur} of **2**

Parameters: **center of sphere:** Fe1

z-axis: C4 (CO linear to Fe-Si8)

xz plane: C1, C2, C3 (remaining CO ligands)

deleted atoms: C1, C2, C3, C4, O1, O2, O3, O4

atomic radii: Bondi radii scaled by 1.17

Sphere radius: 3.5

Distance coordination point to center of sphere: 0.0

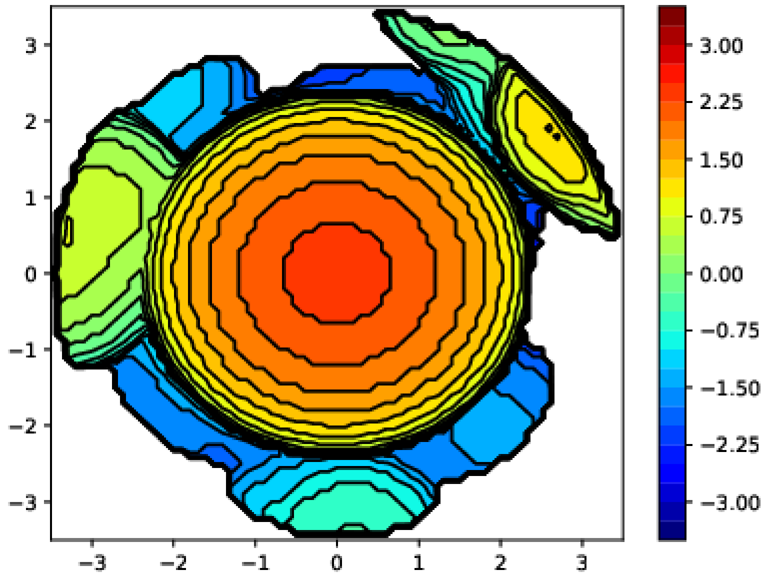
Mesh spacing for numerical integration: 0.10

H atoms: included

Supplementary Table S7. Distribution of ligand volume in **2**.[19]

%V Free	%V Buried	% V Tot/V Ex
44.7	55.3	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	20.0	24.9	44.9	44.5	55.5
NW	18.3	26.6	44.9	40.7	59.3
NE	19.0	25.9	44.9	42.3	57.7
SE	22.9	21.9	44.9	51.1	48.9



Supplementary Figure S48. Steric map of **2** produced by SambVca.[19]

3b

Parameters: **center of sphere:** Ni1

z-axis: P1

xz plane: C91, C97, C103 (*ipso*-Cs of phenyl ligands)

deleted atoms: P1, C91-C108, H92-108

atomic radii: Bondi radii scaled by 1.17

Sphere radius: 3.5

Distance coordination point to center of sphere: 0.0

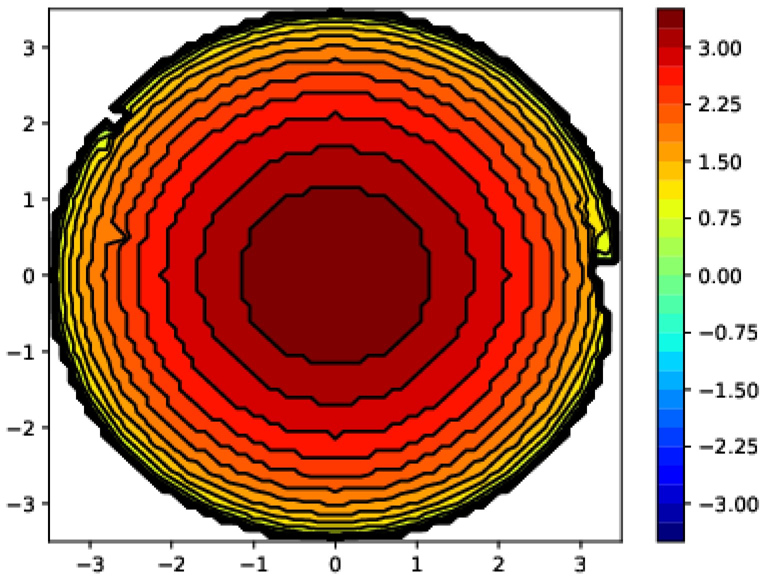
Mesh spacing for numerical integration: 0.10

H atoms: included

Supplementary Table S8. Distribution of ligand volume in **3b**.[19]

%V Free	%V Buried	% V Tot/V Ex
30.1	69.9	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	10.8	34.1	44.9	24.1	75.9
NW	14.3	30.5	44.9	31.9	68.1
NE	10.6	34.3	44.9	23.6	76.4
SE	18.4	26.5	44.9	41.0	59.0



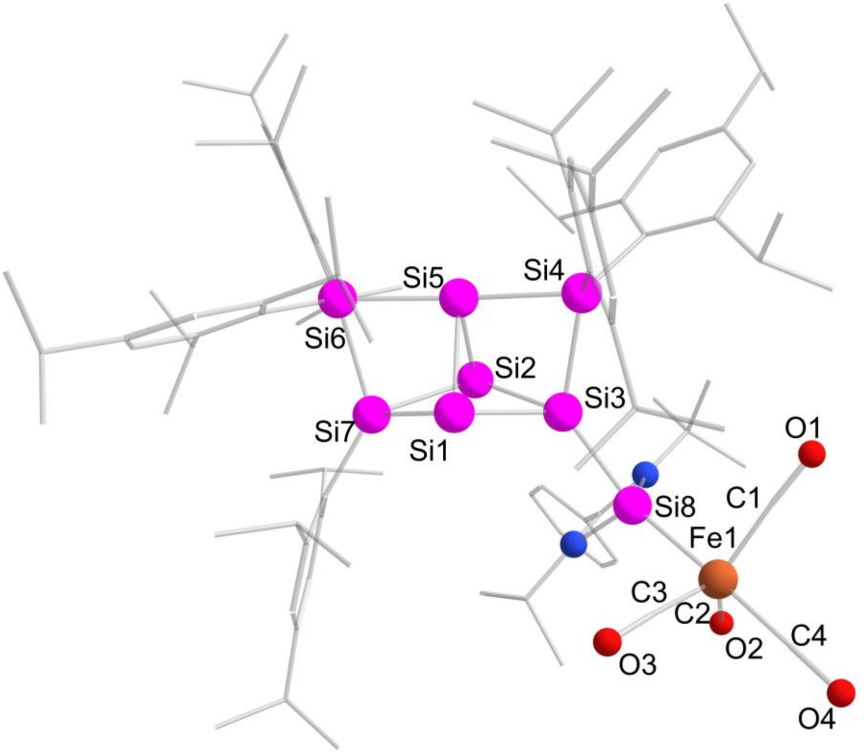
Supplementary Figure S49. Steric map of **3b** produced by SambVca.[19]

4 Computational Details

Computations were carried out with orca 5.0.4/6.0.1.[21,22] Structural optimizations in the gas-phase, frequency analyses and single point calculations for **2** and **3a-c** were performed at the B3LYP/def2-TZVP level of theory[23–29] including the dispersion correction by Grimme (D3BJ).[30] Tighter than default convergence had to be chosen for the optimization (tightopt) and scf (thightscf). Implicit correction for solvation effects (solvents: hexane or benzene) were investigated with the CPCM model[31] for spectroscopic calculations. NMR chemical shifts (GIAO)[32] for **2-3a-c** were calculated using TPSSh/def2-TZVP.[26–29,33] UV-Vis data was received using time-dependent calculations (TD-DFT).[34] FT-IR spectra were corrected according to literature procedures by multiplying the harmonic frequencies with 1.0044.[35] Moreover, a constant offset value of $\Delta\tilde{\nu}_{CO}$ = 100 cm^{-1} was subtracted, determined by comparison of the calculated CO stretching frequency (2243 cm^{-1} at the B3LYP/def2-TZVP level of theory) with the experimental value reported in the literature (2143 cm^{-1}).[36] Pictures of Kohn-Sham orbitals were displayed with ChemCraft 1.8.[37]

4.1 $Fe(CO)_4$ siliconoid/silylene 2

4.1.1 Optimization and molecular orbitals



Supplementary Figure S 50. Optimized molecular structure of $Fe(CO)_4$ siliconoid/silylene **2** at B3LYP/def2-TZVP.[23–29] Hydrogen atoms are omitted for clarity.

Supplementary Table S9. Coordinates of $Fe(CO)_4$ siliconoid/silylene **2** at B3LYP/def2-TZVP.[23–29]

Fe	-5.066573	5.160465	17.213219
Si	-3.08786	6.274186	17.162991
C	-5.921721	6.70898	17.325657
C	-4.400704	4.463731	18.701501
C	-4.680145	4.484404	15.615365
C	-6.579618	4.207269	17.333629
Si	-2.20004	7.933712	15.721009
N	-1.578527	5.276905	17.52376
N	-2.35152	6.856205	18.746616
C	-1.404553	5.919456	18.680009
O	-6.523026	7.683711	17.435108
O	-3.964407	4.0198	19.673265
O	-4.463839	4.004459	14.590218
O	-7.541785	3.594582	17.416102
Si	-1.198581	7.677349	13.660494
Si	0.120575	8.404824	15.811979
Si	-2.78731	10.174186	15.054281
C	-0.958228	4.063619	16.947838
C	-2.665524	7.883257	19.755149
C	-0.379185	5.633856	19.703783

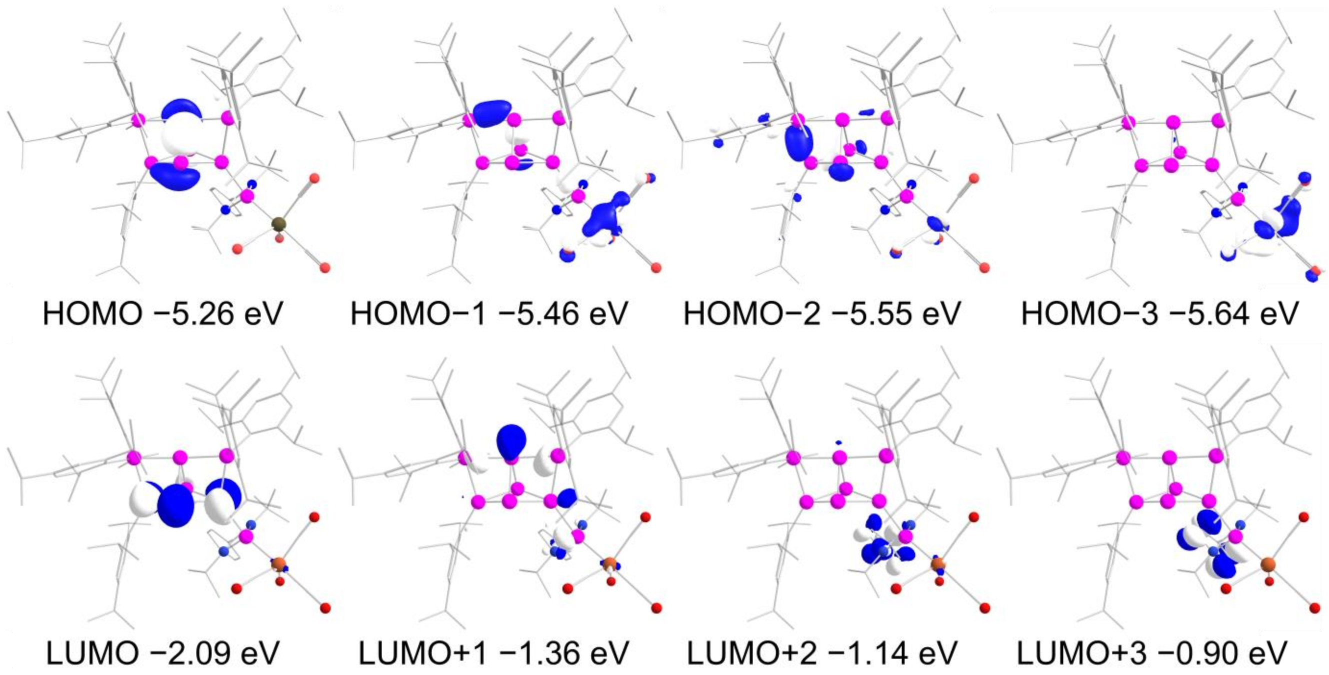
Si	-0.603881	9.881335	14.125511
Si	1.095821	7.454585	13.889628
C	-3.208425	11.515113	16.356629
C	-3.932925	10.409296	13.551816
C	-1.03906	4.225861	15.429661
C	-1.741454	2.822993	17.392956
C	0.510623	3.909789	17.337751
C	-3.450061	8.977987	19.027591
C	-1.404758	8.510875	20.357389
C	-3.533082	7.260697	20.855236
C	-0.66815	4.743489	20.73342
C	0.869124	6.243961	19.631451
Si	1.356412	9.618702	12.814598
C	1.856751	5.741767	13.626753
C	-2.207692	12.320103	16.952745
C	-4.556874	11.876959	16.580353
C	-3.828142	11.652641	12.881088
C	-4.828491	9.451505	13.036466
H	-0.630387	3.346611	14.934469
H	-0.462901	5.090662	15.108643
H	-2.066054	4.349639	15.093549
H	-1.295922	1.931559	16.948127
H	-2.781627	2.882007	17.079592
H	-1.715588	2.715986	18.47755
H	0.940621	3.103845	16.743509
H	0.642449	3.663542	18.388762
H	1.068107	4.813346	17.113315
H	-3.779576	9.735973	19.738132
H	-2.834265	9.472128	18.277292
H	-4.33674	8.576872	18.53808
H	-1.693458	9.383379	20.945095
H	-0.875735	7.825955	21.015196
H	-0.724291	8.838898	19.571052
H	-3.79778	8.018491	21.594723
H	-4.451046	6.849504	20.436376
H	-2.99856	6.457579	21.362608
H	-1.64185	4.274638	20.778924
C	0.301822	4.459956	21.687111
C	1.833563	5.956649	20.584058
H	1.076132	6.940369	18.830904
C	2.647072	11.006978	13.111512
C	1.427425	9.102548	10.984975
C	2.802575	5.224008	14.531783
C	1.272559	4.867907	12.681466
C	-2.555019	13.494276	17.609386
C	-0.731742	11.97064	16.920983
C	-4.853361	13.062063	17.251073

C	-5.745987	11.019639	16.175857
C	-4.569577	11.891789	11.731911
C	-2.950961	12.789988	13.378536
C	-5.556374	9.743502	11.882932
C	-5.083817	8.087334	13.655459
H	0.079751	3.765813	22.487008
C	1.551693	5.062929	21.612515
H	2.805323	6.428905	20.523925
C	3.567341	10.999877	14.179449
C	2.689807	12.112249	12.221543
C	0.366281	9.188421	10.058898
C	2.660615	8.566988	10.546152
C	3.003588	3.848984	14.600652
C	3.683048	6.132386	15.371745
C	1.527142	3.504764	12.769474
C	0.416091	5.355596	11.525161
H	-1.767001	14.107232	18.027292
C	-3.873227	13.90625	17.742119
H	-0.63409	10.959717	16.534482
C	0.054535	12.896163	15.985502
C	-0.120403	11.950443	18.327542
H	-5.890306	13.341187	17.390238
H	-5.369968	10.072124	15.787722
C	-6.613831	11.672927	15.092986
C	-6.614867	10.69644	17.39983
H	-4.471525	12.850498	11.238121
C	-5.441264	10.946388	11.208657
H	-2.429009	12.459237	14.271171
C	-1.874912	13.178667	12.370512
C	-3.778367	14.012001	13.794021
H	-6.241559	9.000611	11.493696
H	-4.481683	8.003469	14.56197
C	-6.547092	7.90063	14.075656
C	-4.659741	6.960189	12.70874
H	2.305818	4.838082	22.355599
C	4.481996	12.040937	14.327455
C	3.640289	9.897155	15.21647
C	3.649865	13.103613	12.388307
C	1.723961	12.312414	11.063105
C	0.563017	8.771861	8.746461
C	-1.01019	9.726232	10.410783
C	2.81093	8.179758	9.217805
C	3.876572	8.415609	11.452285
H	3.699354	3.448052	15.3278
C	2.349605	2.967257	13.752446
H	3.534214	7.145866	14.997717
C	5.16386	5.782584	15.170251

C	3.331204	6.144853	16.859149
H	1.063295	2.842294	12.049651
H	0.352846	6.441966	11.585208
C	-1.008623	4.797781	11.577816
C	1.074289	5.037494	10.176474
C	-4.23117	15.219302	18.401984
H	1.109222	12.618946	15.95133
H	-0.012292	13.934435	16.317861
H	-0.330127	12.84737	14.966447
H	0.894821	11.551965	18.291386
H	-0.708423	11.323141	18.998767
H	-0.066431	12.94865	18.765686
H	-7.435398	11.009855	14.816408
H	-6.046959	11.896885	14.194037
H	-7.049655	12.603397	15.463632
H	-7.408361	10.003035	17.127278
H	-7.079165	11.600003	17.797274
H	-6.02983	10.239766	18.196145
C	-6.24639	11.219438	9.957202
H	-1.263457	13.98541	12.774847
H	-2.303789	13.525934	11.429388
H	-1.220806	12.33684	12.14711
H	-3.129266	14.773729	14.230755
H	-4.525991	13.744221	14.536835
H	-4.28929	14.453508	12.935856
H	-6.671235	6.930084	14.556875
H	-7.213656	7.936155	13.212252
H	-6.86575	8.666931	14.78
H	-4.789038	5.988653	13.181964
H	-3.61442	7.059335	12.419882
H	-5.258128	6.973691	11.795665
H	5.169955	12.02373	15.163671
C	4.557787	13.095216	13.436492
H	2.960719	9.105101	14.906746
C	3.1607	10.374312	16.589341
C	5.046903	9.298637	15.309236
H	3.677914	13.921981	11.681524
H	0.890039	11.625264	11.194377
C	1.141572	13.732464	11.047194
C	2.379272	12.015626	9.708211
H	-0.26125	8.849533	8.048822
C	1.779776	8.27855	8.297429
H	-0.985744	10.063541	11.446751
C	-1.418406	10.922852	9.543754
C	-2.077026	8.630549	10.319613
H	3.765232	7.790428	8.884452
H	3.571713	8.615449	12.480452

C	4.972553	9.43151	11.106037
C	4.442292	6.991171	11.436463
C	2.555408	1.473174	13.87647
H	5.802657	6.506988	15.675427
H	5.425506	5.772377	14.11245
H	5.394294	4.79879	15.581272
H	4.01619	6.795557	17.407874
H	3.396313	5.146521	17.295057
H	2.32069	6.52056	17.010288
H	-1.610934	5.214535	10.768213
H	-1.496696	5.041097	12.521574
H	-1.011436	3.711286	11.47087
H	0.49413	5.485104	9.368528
H	1.127969	3.96096	10.001306
H	2.083776	5.442521	10.125029
H	-5.323534	15.281376	18.419796
C	-3.710664	16.40611	17.58085
C	-3.737977	15.289915	19.851649
H	-6.841876	10.323255	9.758114
C	-5.340913	11.455375	8.742551
C	-7.218742	12.38812	10.158929
C	5.583603	14.193787	13.605865
H	3.17248	9.549839	17.305711
H	2.141648	10.750538	16.530867
H	3.798449	11.172034	16.976405
H	5.081013	8.527512	16.07725
H	5.786397	10.054129	15.574981
H	5.352186	8.853357	14.361347
H	0.293559	13.786434	10.362684
H	1.87968	14.459577	10.705739
H	0.804147	14.036898	12.035686
H	1.665323	12.1692	8.896624
H	2.743529	10.994392	9.646479
H	3.222581	12.690674	9.545973
C	1.982428	7.871483	6.853913
H	-2.374709	11.318082	9.886331
H	-1.532426	10.634467	8.497077
H	-0.682529	11.724329	9.588341
H	-3.035421	8.998561	10.686247
H	-1.798885	7.759821	10.913243
H	-2.208495	8.298888	9.286856
H	5.823822	9.314096	11.780128
H	4.613838	10.454714	11.194388
H	5.32836	9.279824	10.084777
H	5.269394	6.910957	12.144496
H	4.83108	6.725984	10.452016
H	3.687793	6.25793	11.714981

H	3.252605	1.31326	14.704659
C	1.245043	0.756595	14.225311
C	3.189035	0.878571	12.613119
H	-4.020309	17.35288	18.029149
H	-4.089644	16.36968	16.558301
H	-2.619487	16.398116	17.53281
H	-4.063316	16.219656	20.323604
H	-2.647408	15.256634	19.900332
H	-4.124107	14.454404	20.43787
H	-5.937888	11.595965	7.838726
H	-4.669309	10.610643	8.582599
H	-4.726475	12.347981	8.878396
H	-7.837409	12.533083	9.270481
H	-6.679552	13.319262	10.346365
H	-7.876435	12.206397	11.010305
H	6.165979	13.952865	14.500591
C	6.552901	14.242909	12.418563
C	4.919038	15.55669	13.834645
H	3.013969	7.51759	6.763144
C	1.815652	9.068387	5.909476
C	1.058209	6.716852	6.450096
H	1.41375	-0.314362	14.356713
H	0.505002	0.884083	13.43258
H	0.814198	1.147597	15.148636
H	3.387016	-0.18713	12.746789
H	4.130772	1.376048	12.37595
H	2.526776	0.989197	11.75203
H	7.325365	14.998017	12.580732
H	6.028345	14.49553	11.494485
H	7.0408	13.278052	12.271005
H	5.670776	16.326973	14.021019
H	4.241685	15.523376	14.689552
H	4.338324	15.860894	12.961217
H	2.026115	8.778588	4.87756
H	2.491095	9.880461	6.183351
H	0.795477	9.456695	5.946449
H	1.245896	6.416721	5.416766
H	0.008464	7.008216	6.527257
H	1.212031	5.848115	7.091257



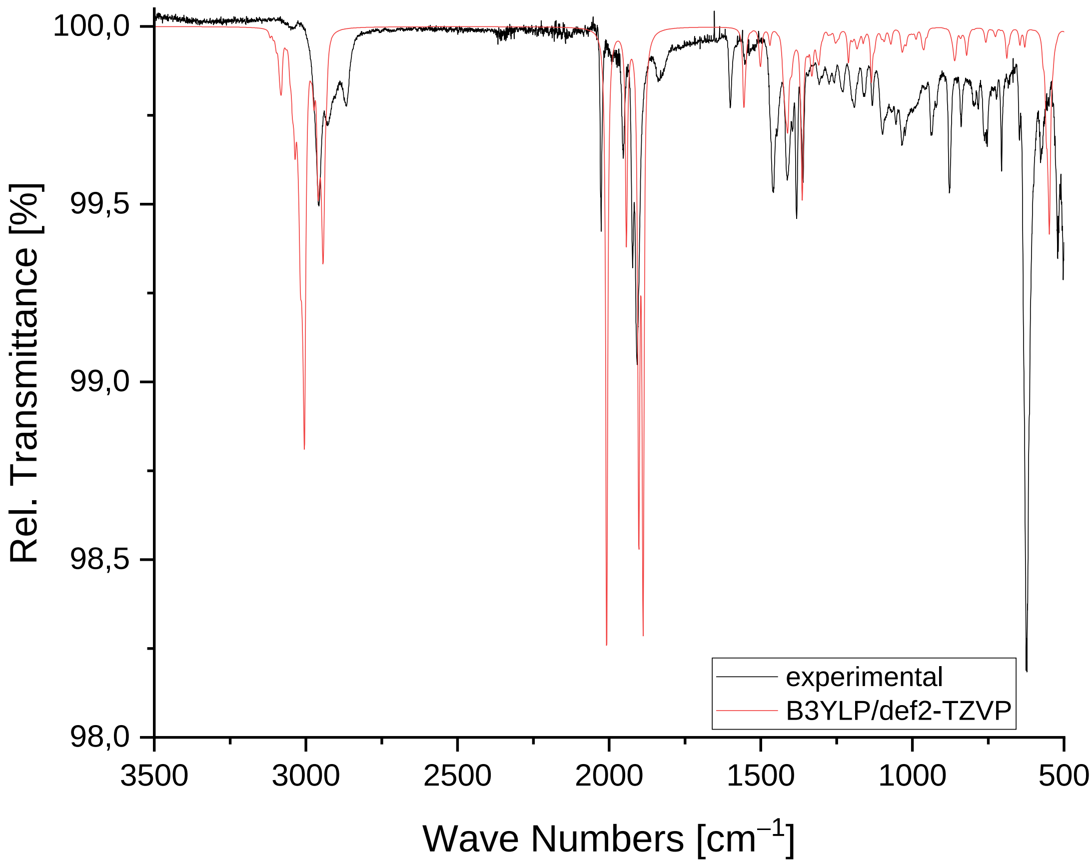
Supplementary Figure S51. Selected frontier orbitals of $Fe(CO)_4$ siliconoid/silylene **2** at B3LYP/def2-TZVP level of theory (contour value 0.05).[23–29] Hydrogen atoms are omitted for clarity.

4.1.2 Experimental vs. calculated NMR shifts

Supplementary Table S10. Comparison of experimental vs. calculated NMR chemical shifts for compound **2** at the TPSSh/def2-TZVP level of theory.[26–29,33]

	Exp. **2** $\delta(^{29}Si)$ [ppm]	Calc. **2** $\delta(^{29}Si)$ [ppm]
Si3 (*Si*NHSi)	172.7	175.4
Si8 (NH*Si*)	157.1	171.3
Si7 (*Si*Tip)	100.5	106.3
Si6 (*Si*Tip_2)	33.6	23.4
Si4 (*Si*Tip_2)	5.9	−7.3
Si5 (unsubstituted)	−98.2	−96.6
Si1 (unsubstituted)	−198.5	−200.6
Si2 (unsubstituted)	−209.0	−214.2

4.1.3 Experimental vs. calculated FT-IR spectra



Supplementary Figure S52. Experimental vs. theoretical FT-IR spectrum of $Fe(CO)_4$ siliconoid/silylene **2** at the B3LYP/def2-TZVP level of theory.[23–29]

4.1.4 TD-DFT calculations

Supplementary Table S11. Transition Energy, wavelength, and oscillator strengths of the electronic transition of **2** calculated at the TD-TPSSh/def2-TZVPP.[26–29,33,34] level of theory (the 442nd orbital is the highest occupied orbital (HOMO) and 443rd orbital is the lowest unoccupied molecular orbital (LUMO) shown in Supplementary Figure S51).

```
STATE  1:  E=   0.086311 au      2.349 eV    18943.0 cm**-1 <S**2> =   0.000000 Mult 1
   442a -> 443a  :     0.985982 (c= -0.99296646)

STATE  2:  E=   0.092487 au      2.517 eV    20298.5 cm**-1 <S**2> =   0.000000 Mult 1
   438a -> 443a  :     0.026654 (c= -0.16326156)
   439a -> 443a  :     0.018809 (c= -0.13714414)
   441a -> 443a  :     0.943242 (c=  0.97120660)

STATE  3:  E=   0.096374 au      2.622 eV    21151.6 cm**-1 <S**2> =   0.000000 Mult 1
   437a -> 443a  :     0.048696 (c=  0.22067112)
   440a -> 443a  :     0.924143 (c=  0.96132341)

STATE  4:  E=   0.100662 au      2.739 eV    22092.8 cm**-1 <S**2> =   0.000000 Mult 1
   438a -> 443a  :     0.091020 (c=  0.30169581)
   439a -> 443a  :     0.848619 (c=  0.92120535)
```

```
  440a -> 443a  :     0.018409 (c= -0.13568144)
  441a -> 443a  :     0.031345 (c=  0.17704561)

STATE  5:  E=   0.103636 au      2.820 eV    22745.5 cm**-1 <S**2> =   0.000000 Mult 1
  438a -> 443a  :     0.862558 (c= -0.92874027)
  439a -> 443a  :     0.107539 (c=  0.32793153)
  441a -> 443a  :     0.012856 (c= -0.11338407)

STATE  6:  E=   0.113231 au      3.081 eV    24851.3 cm**-1 <S**2> =   0.000000 Mult 1
  437a -> 443a  :     0.041700 (c=  0.20420462)
  441a -> 444a  :     0.023548 (c= -0.15345247)
  442a -> 444a  :     0.898991 (c= -0.94815137)

STATE  7:  E=   0.114828 au      3.125 eV    25201.8 cm**-1 <S**2> =   0.000000 Mult 1
  434a -> 443a  :     0.016916 (c= -0.13006298)
  435a -> 443a  :     0.062523 (c=  0.25004571)
  436a -> 443a  :     0.749213 (c= -0.86557067)
  437a -> 443a  :     0.128598 (c= -0.35860563)

STATE  8:  E=   0.116576 au      3.172 eV    25585.4 cm**-1 <S**2> =   0.000000 Mult 1
  427a -> 443a  :     0.015335 (c=  0.12383485)
  434a -> 443a  :     0.014288 (c=  0.11953045)
  435a -> 443a  :     0.027960 (c= -0.16721171)
  436a -> 443a  :     0.196865 (c= -0.44369447)
  437a -> 443a  :     0.553990 (c=  0.74430479)
  440a -> 443a  :     0.021423 (c= -0.14636723)
  440a -> 444a  :     0.030601 (c= -0.17493054)
  442a -> 444a  :     0.049721 (c=  0.22298250)

STATE  9:  E=   0.121142 au      3.296 eV    26587.6 cm**-1 <S**2> =   0.000000 Mult 1
  435a -> 443a  :     0.010094 (c= -0.10046657)
  441a -> 444a  :     0.903690 (c= -0.95062586)
  441a -> 445a  :     0.013464 (c= -0.11603370)
  442a -> 444a  :     0.016306 (c=  0.12769514)

STATE 10:  E=   0.122638 au      3.337 eV    26916.0 cm**-1 <S**2> =   0.000000 Mult 1
  433a -> 443a  :     0.028461 (c= -0.16870528)
  434a -> 443a  :     0.349310 (c=  0.59102462)
  435a -> 443a  :     0.459924 (c=  0.67817733)
  437a -> 443a  :     0.010435 (c=  0.10215245)
  440a -> 444a  :     0.114328 (c=  0.33812387)

STATE 11:  E=   0.123817 au      3.369 eV    27174.8 cm**-1 <S**2> =   0.000000 Mult 1
  430a -> 443a  :     0.022494 (c=  0.14998024)
  431a -> 443a  :     0.037893 (c=  0.19466030)
  434a -> 443a  :     0.416581 (c=  0.64543083)
  435a -> 443a  :     0.034600 (c= -0.18601091)
  437a -> 443a  :     0.041571 (c= -0.20388933)
  440a -> 444a  :     0.365009 (c= -0.60415941)

STATE 12:  E=   0.124587 au      3.390 eV    27343.7 cm**-1 <S**2> =   0.000000 Mult 1
  431a -> 443a  :     0.052329 (c=  0.22875540)
  432a -> 443a  :     0.028475 (c=  0.16874499)
  433a -> 443a  :     0.484934 (c= -0.69637186)
  434a -> 443a  :     0.163273 (c= -0.40407087)
  435a -> 443a  :     0.113234 (c=  0.33650316)
  440a -> 444a  :     0.134003 (c= -0.36606448)

STATE 13:  E=   0.125353 au      3.411 eV    27511.9 cm**-1 <S**2> =   0.000000 Mult 1
  430a -> 443a  :     0.022075 (c=  0.14857775)
  431a -> 443a  :     0.094465 (c= -0.30735159)
```

```
   432a -> 443a  :     0.117333 (c= -0.34253954)
   433a -> 443a  :     0.443083 (c= -0.66564485)
   434a -> 443a  :     0.019326 (c=  0.13901727)
   435a -> 443a  :     0.137939 (c= -0.37140193)
   437a -> 443a  :     0.010104 (c= -0.10051752)
   440a -> 444a  :     0.104668 (c=  0.32352502)

STATE 14:  E=   0.126901 au      3.453 eV    27851.5 cm**-1 <S**2> =   0.000000 Mult 1
   430a -> 443a  :     0.026695 (c=  0.16338700)
   431a -> 443a  :     0.163721 (c=  0.40462415)
   432a -> 443a  :     0.735415 (c= -0.85756367)
   435a -> 443a  :     0.020802 (c=  0.14422820)
   440a -> 444a  :     0.010847 (c= -0.10414877)

STATE 15:  E=   0.127299 au      3.464 eV    27938.8 cm**-1 <S**2> =   0.000000 Mult 1
   430a -> 443a  :     0.011124 (c= -0.10547124)
   431a -> 443a  :     0.020476 (c= -0.14309432)
   439a -> 444a  :     0.797963 (c=  0.89328761)
   439a -> 445a  :     0.027952 (c=  0.16718912)
   440a -> 444a  :     0.014305 (c= -0.11960342)
   440a -> 445a  :     0.010192 (c= -0.10095499)
   441a -> 445a  :     0.023446 (c=  0.15312096)
   442a -> 445a  :     0.034360 (c= -0.18536585)

STATE 16:  E=   0.127681 au      3.474 eV    28022.7 cm**-1 <S**2> =   0.000000 Mult 1
   430a -> 443a  :     0.014464 (c= -0.12026623)
   431a -> 443a  :     0.102948 (c= -0.32085443)
   439a -> 444a  :     0.010095 (c=  0.10047461)
   440a -> 444a  :     0.010309 (c= -0.10153557)
   442a -> 445a  :     0.796798 (c=  0.89263567)

STATE 17:  E=   0.127902 au      3.480 eV    28071.2 cm**-1 <S**2> =   0.000000 Mult 1
   428a -> 443a  :     0.014035 (c= -0.11846730)
   429a -> 443a  :     0.011015 (c=  0.10495393)
   430a -> 443a  :     0.814618 (c=  0.90256197)
   431a -> 443a  :     0.067410 (c= -0.25963431)
   432a -> 443a  :     0.017896 (c=  0.13377645)
   435a -> 443a  :     0.013872 (c=  0.11778087)
   442a -> 446a  :     0.011878 (c=  0.10898566)

STATE 18:  E=   0.128353 au      3.493 eV    28170.2 cm**-1 <S**2> =   0.000000 Mult 1
   427a -> 443a  :     0.058954 (c= -0.24280479)
   428a -> 443a  :     0.016131 (c= -0.12700658)
   429a -> 443a  :     0.276604 (c=  0.52593126)
   430a -> 443a  :     0.049850 (c= -0.22327037)
   431a -> 443a  :     0.258018 (c= -0.50795471)
   432a -> 443a  :     0.037089 (c= -0.19258383)
   435a -> 443a  :     0.012652 (c=  0.11248137)
   437a -> 444a  :     0.012087 (c=  0.10994290)
   439a -> 444a  :     0.050787 (c= -0.22536017)
   440a -> 444a  :     0.075138 (c= -0.27411273)
   442a -> 445a  :     0.105861 (c= -0.32536261)

STATE 19:  E=   0.129214 au      3.516 eV    28359.2 cm**-1 <S**2> =   0.000000 Mult 1
   427a -> 443a  :     0.060839 (c=  0.24665619)
   429a -> 443a  :     0.689109 (c=  0.83012566)
   431a -> 443a  :     0.105746 (c=  0.32518675)
   432a -> 443a  :     0.017841 (c=  0.13356924)
   437a -> 444a  :     0.011291 (c= -0.10625947)
   439a -> 444a  :     0.011181 (c=  0.10574092)
   440a -> 444a  :     0.042212 (c=  0.20545666)
```

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   442a -> 445a  :     0.012537 (c=  0.11196882)

STATE 20:  E=   0.130083 au      3.540 eV    28549.8 cm**-1 <S**2> =   0.000000 Mult 1
   438a -> 444a  :     0.545367 (c=  0.73848953)
   438a -> 445a  :     0.024772 (c=  0.15739141)
   438a -> 450a  :     0.014920 (c=  0.12214769)
   439a -> 444a  :     0.028580 (c= -0.16905487)
   441a -> 444a  :     0.016780 (c= -0.12953777)
   441a -> 445a  :     0.267793 (c=  0.51748701)
   441a -> 450a  :     0.013204 (c=  0.11490956)

STATE 21:  E=   0.131043 au      3.566 eV    28760.6 cm**-1 <S**2> =   0.000000 Mult 1
   427a -> 443a  :     0.011025 (c= -0.10500213)
   428a -> 443a  :     0.862728 (c=  0.92883162)
   437a -> 444a  :     0.016732 (c=  0.12935413)
   442a -> 446a  :     0.057113 (c=  0.23898260)

STATE 22:  E=   0.133049 au      3.620 eV    29200.9 cm**-1 <S**2> =   0.000000 Mult 1
   437a -> 444a  :     0.048931 (c=  0.22120291)
   438a -> 444a  :     0.304674 (c= -0.55197278)
   439a -> 444a  :     0.010730 (c= -0.10358509)
   441a -> 445a  :     0.485937 (c=  0.69709173)
   442a -> 446a  :     0.055723 (c= -0.23605643)

STATE 23:  E=   0.133251 au      3.626 eV    29245.2 cm**-1 <S**2> =   0.000000 Mult 1
   427a -> 443a  :     0.031030 (c= -0.17615209)
   428a -> 443a  :     0.013995 (c= -0.11830000)
   437a -> 444a  :     0.226281 (c= -0.47568999)
   438a -> 444a  :     0.030634 (c= -0.17502598)
   441a -> 445a  :     0.072670 (c=  0.26957290)
   442a -> 446a  :     0.524427 (c=  0.72417331)
   442a -> 447a  :     0.024974 (c= -0.15803014)

STATE 24:  E=   0.134205 au      3.652 eV    29454.6 cm**-1 <S**2> =   0.000000 Mult 1
   426a -> 443a  :     0.076039 (c= -0.27575101)
   427a -> 443a  :     0.416790 (c=  0.64559268)
   437a -> 443a  :     0.012662 (c= -0.11252524)
   437a -> 444a  :     0.220833 (c=  0.46992874)
   442a -> 446a  :     0.126915 (c=  0.35625174)
   442a -> 447a  :     0.051322 (c= -0.22654291)
   442a -> 449a  :     0.020005 (c= -0.14143922)

STATE 25:  E=   0.135469 au      3.686 eV    29732.1 cm**-1 <S**2> =   0.000000 Mult 1
   425a -> 443a  :     0.113565 (c=  0.33699455)
   426a -> 443a  :     0.262143 (c=  0.51199877)
   427a -> 443a  :     0.263370 (c=  0.51319541)
   431a -> 443a  :     0.017651 (c= -0.13285790)
   437a -> 444a  :     0.221825 (c= -0.47098251)
   440a -> 444a  :     0.015002 (c= -0.12248154)
   442a -> 449a  :     0.011073 (c= -0.10523067)

STATE 26:  E=   0.136468 au      3.713 eV    29951.3 cm**-1 <S**2> =   0.000000 Mult 1
   425a -> 443a  :     0.015475 (c=  0.12439897)
   426a -> 443a  :     0.036219 (c=  0.19031310)
   437a -> 444a  :     0.020369 (c=  0.14272083)
   439a -> 444a  :     0.029847 (c=  0.17276404)
   439a -> 445a  :     0.204555 (c= -0.45227726)
   439a -> 449a  :     0.045188 (c= -0.21257470)
   439a -> 450a  :     0.012790 (c= -0.11309207)
   440a -> 445a  :     0.254677 (c=  0.50465515)
   440a -> 447a  :     0.012164 (c= -0.11029255)
```

441a -> 445a : 0.018288 (c= 0.13523387)
441a -> 449a : 0.056572 (c= -0.23784922)
442a -> 447a : 0.190590 (c= -0.43656580)

STATE 27: E= 0.136960 au 3.727 eV 30059.2 cm**-1 <S**2> = 0.000000 Mult 1
426a -> 443a : 0.055783 (c= 0.23618387)
438a -> 444a : 0.012299 (c= 0.11090052)
439a -> 445a : 0.196164 (c= 0.44290432)
439a -> 449a : 0.020610 (c= 0.14356035)
440a -> 445a : 0.036198 (c= -0.19025799)
441a -> 446a : 0.018186 (c= 0.13485690)
442a -> 446a : 0.021457 (c= -0.14648196)
442a -> 447a : 0.538472 (c= -0.73380627)
442a -> 448a : 0.014606 (c= 0.12085502)

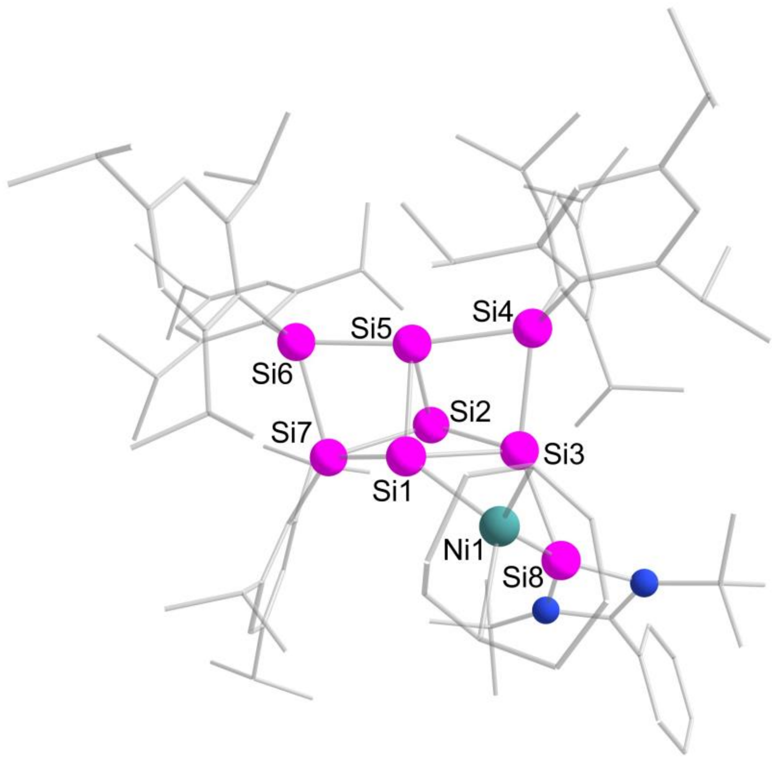
STATE 28: E= 0.137671 au 3.746 eV 30215.2 cm**-1 <S**2> = 0.000000 Mult 1
426a -> 443a : 0.260602 (c= 0.51049182)
427a -> 443a : 0.010432 (c= -0.10213913)
428a -> 443a : 0.013968 (c= -0.11818591)
431a -> 443a : 0.010231 (c= 0.10114605)
435a -> 443a : 0.015899 (c= -0.12609179)
437a -> 444a : 0.062231 (c= 0.24946215)
439a -> 445a : 0.028346 (c= 0.16836174)
439a -> 447a : 0.010336 (c= -0.10166494)
439a -> 449a : 0.011427 (c= 0.10689835)
440a -> 445a : 0.120214 (c= 0.34671923)
440a -> 449a : 0.016953 (c= -0.13020444)
441a -> 446a : 0.059609 (c= -0.24414948)
441a -> 447a : 0.043729 (c= -0.20911434)
441a -> 449a : 0.089369 (c= 0.29894640)
442a -> 446a : 0.069216 (c= 0.26308881)
442a -> 447a : 0.027996 (c= 0.16731861)
442a -> 449a : 0.038981 (c= -0.19743676)

STATE 29: E= 0.137828 au 3.750 eV 30249.7 cm**-1 <S**2> = 0.000000 Mult 1
425a -> 443a : 0.553826 (c= 0.74419508)
427a -> 443a : 0.026877 (c= -0.16394163)
435a -> 443a : 0.011033 (c= -0.10503627)
437a -> 444a : 0.043812 (c= 0.20931404)
440a -> 445a : 0.080444 (c= -0.28362651)
441a -> 446a : 0.051803 (c= 0.22760214)
441a -> 447a : 0.021282 (c= 0.14588181)
442a -> 446a : 0.015305 (c= 0.12371223)
442a -> 447a : 0.019503 (c= 0.13965260)
442a -> 449a : 0.071946 (c= 0.26822661)

STATE 30: E= 0.138289 au 3.763 eV 30350.8 cm**-1 <S**2> = 0.000000 Mult 1
425a -> 443a : 0.017588 (c= -0.13262099)
426a -> 443a : 0.064482 (c= 0.25393343)
437a -> 444a : 0.017763 (c= 0.13327859)
439a -> 445a : 0.194793 (c= -0.44135380)
440a -> 445a : 0.380085 (c= -0.61651058)
441a -> 446a : 0.187861 (c= -0.43342928)
441a -> 447a : 0.017321 (c= -0.13161102)
442a -> 447a : 0.020820 (c= -0.14429020)
442a -> 449a : 0.019601 (c= 0.14000441)

4.2 Ni(cod) siliconoid/silylene 3a

4.2.1 Optimization and molecular orbitals



Supplementary Figure S1. Optimized molecular structure of Ni(cod) siliconoid/silylene **3a** at the B3LYP/def2-TZVP level of theory.[23–29] Hydrogen atoms are omitted for clarity. Contour value at 0.05.

Supplementary Table S12. Coordinates of Ni(cod) siliconoid/silylene **3a** at the B3LYP/def2-TZVP level of theory.[23–29]

Ni	18.45466	8.9424	18.70953
Si	17.892297	11.061103	17.954707
Si	17.447081	9.140304	16.54695
Si	16.891888	7.501234	18.036751
C	20.597281	8.955439	18.441452
C	20.211351	7.657259	18.673526
C	18.401899	8.443955	20.833313
C	19.012818	9.66467	20.770055
Si	15.977399	10.957959	16.07106
Si	18.069348	11.930833	15.756746
Si	16.102104	12.524356	17.818329
Si	18.879789	9.942347	14.783437
N	15.084273	7.219591	18.29722
N	16.437562	5.804329	17.441658
C	15.170959	5.96751	17.846058
C	21.183299	9.90199	19.45659
C	20.3207	6.933799	20.001074
C	19.112215	7.117147	20.950513
C	20.506774	9.869458	20.835193
Si	17.339288	14.064386	16.417274

C	14.519107	12.765402	18.850757
C	18.103737	9.777943	13.034334
C	20.762013	9.571394	14.680944
C	13.913021	8.023519	18.688121
C	17.194583	4.587487	17.122169
C	14.095782	4.953465	17.818952
C	18.801242	15.225229	16.869045
C	15.997725	15.109762	15.557673
C	13.264314	12.791888	18.193257
C	14.530245	12.673567	20.254911
C	16.993833	8.962842	12.709449
C	18.609203	10.625843	12.017744
C	21.181003	8.439292	13.950082
C	21.766989	10.479817	15.115353
C	13.137932	8.44273	17.435559
C	12.995875	7.272932	19.660051
C	14.460594	9.262541	19.389851
C	16.390268	3.588939	16.281951
C	17.670144	3.924864	18.422339
C	18.396783	5.052223	16.30549
C	13.262908	4.851845	16.708037
C	13.917363	4.089257	18.896589
C	19.383792	15.284949	18.153796
C	19.389818	16.014755	15.85047
C	15.508614	14.925988	14.248692
C	15.457171	16.16508	16.331777
C	12.099588	12.607731	18.92857
C	13.102488	13.064118	16.70657
C	13.334853	12.497512	20.949786
C	15.799053	12.777429	21.079994
C	16.387854	9.084874	11.459155
C	16.410961	7.887623	13.614659
C	17.975276	10.702915	10.784044
C	19.87603	11.448165	12.180264
C	22.518604	8.287912	13.588287
C	20.244509	7.316699	13.533037
C	23.083902	10.289303	14.714609
C	21.502685	11.688764	16.005802
C	12.260204	3.892399	16.675137
C	12.915432	3.129863	18.86201
C	20.514423	16.063109	18.381068
C	18.829902	14.548908	19.358152
C	20.495634	16.81099	16.138626
C	18.882873	16.062005	14.416164
C	14.530998	15.788733	13.75436
C	15.993796	13.830061	13.312925
C	14.506913	17.015966	15.782439

C	15.894214	16.452911	17.762893
C	12.110662	12.429525	20.306336
C	12.465084	11.888267	15.962012
C	12.28776	14.340017	16.461354
C	15.712644	13.958647	22.054786
C	16.105415	11.480087	21.831728
C	16.841757	9.960146	10.488025
C	16.595254	6.48234	13.026246
C	14.93206	8.119595	13.939533
C	19.661446	12.934376	11.912493
C	21.012475	10.900834	11.307493
C	23.483354	9.216012	13.929613
C	20.719852	5.978733	14.114491
C	20.100993	7.210253	12.009845
C	21.319624	12.979554	15.200679
C	22.609963	11.921772	17.043536
C	12.085592	3.029613	17.750797
C	21.088815	16.841288	17.389659
C	19.776915	13.44775	19.837519
C	18.491463	15.50913	20.503092
C	20.015985	15.989057	13.384427
C	18.045549	17.32069	14.154055
C	14.027874	16.848005	14.491086
C	14.931276	12.744244	13.108222
C	16.438292	14.373659	11.949764
C	14.718562	16.458593	18.747081
C	16.685799	17.763209	17.849846
C	10.836593	12.165911	21.079015
C	16.130467	10.096316	9.160027
C	24.916329	9.062269	13.470809
C	22.3181	17.68255	17.653775
C	12.998897	17.788795	13.902365
C	17.04123	9.728984	7.982902
C	15.542867	11.502878	8.987982
C	25.320412	10.203632	12.528975
C	25.888048	8.949052	14.651054
C	23.528351	16.80596	17.999441
C	22.067148	18.731715	18.743267
C	11.698684	17.800339	14.7149
C	13.56546	19.206276	13.751756
H	13.408713	5.518114	15.86848
H	11.616671	3.817439	15.808339
H	11.304111	2.281433	17.724208
H	12.780607	2.462319	19.703088
H	14.55805	4.178304	19.763706
H	13.804515	8.941282	16.733321
H	12.341191	9.137289	17.704057

H	12.689324	7.580089	16.942545
H	12.245257	7.966896	20.04134
H	13.565715	6.889235	20.508053
H	12.473525	6.444622	19.186725
H	15.161035	9.794695	18.748958
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H	15.952905	4.077555	15.411234
H	15.59361	3.113085	16.847913
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H	18.24626	4.633255	19.018534
H	18.070778	5.508841	15.372915
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H	18.381411	11.366304	10.031102
H	20.211988	11.363459	13.207658
H	19.30346	13.121313	10.899159
H	20.600079	13.474112	12.034388
H	18.936712	13.356321	12.605907
H	20.764853	10.979329	10.246386
H	21.216112	9.856761	11.533157
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H	20.001756	5.188651	13.890486
H	20.843439	6.040475	15.195698
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H	19.486527	6.349796	11.73896
H	21.077061	7.077602	11.539601
H	20.580024	11.505622	16.555861
H	22.202555	13.170432	14.585409
H	21.173237	13.829852	15.867243
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H	22.898428	11.002494	17.550316
H	22.263392	12.637886	17.790574
H	20.950484	16.068471	19.371869
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H	18.248706	15.191766	14.252341
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H	20.7068	15.178024	13.603119
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H	18.660416	18.212954	14.2948
H	17.188011	17.389811	14.817106
H	17.675715	17.324951	13.126593
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H	19.995523	12.750263	19.030136
H	19.324497	12.88413	20.656178
H	20.721868	13.863543	20.19442
H	17.745067	16.242151	20.197727
H	19.373383	16.05494	20.841522
H	18.098033	14.957806	21.354973
H	22.547197	18.215175	16.725599
H	23.722962	16.078104	17.210007
H	24.424147	17.416763	18.133671
H	22.944584	19.368915	18.875329
H	21.852095	18.257192	19.703153
H	21.216819	19.365976	18.487533
H	23.357685	16.253432	18.926126
H	14.156558	15.6383	12.749131
H	14.125778	17.83125	16.384241
H	16.557371	15.652309	18.088193
H	14.007637	17.254218	18.517302
H	15.082815	16.626748	19.763072
H	14.185938	15.509386	18.735839
H	17.578852	17.729161	17.228167
H	16.998342	17.956422	18.877968
H	16.07343	18.606282	17.523275

H	12.76208	17.417393	12.900488
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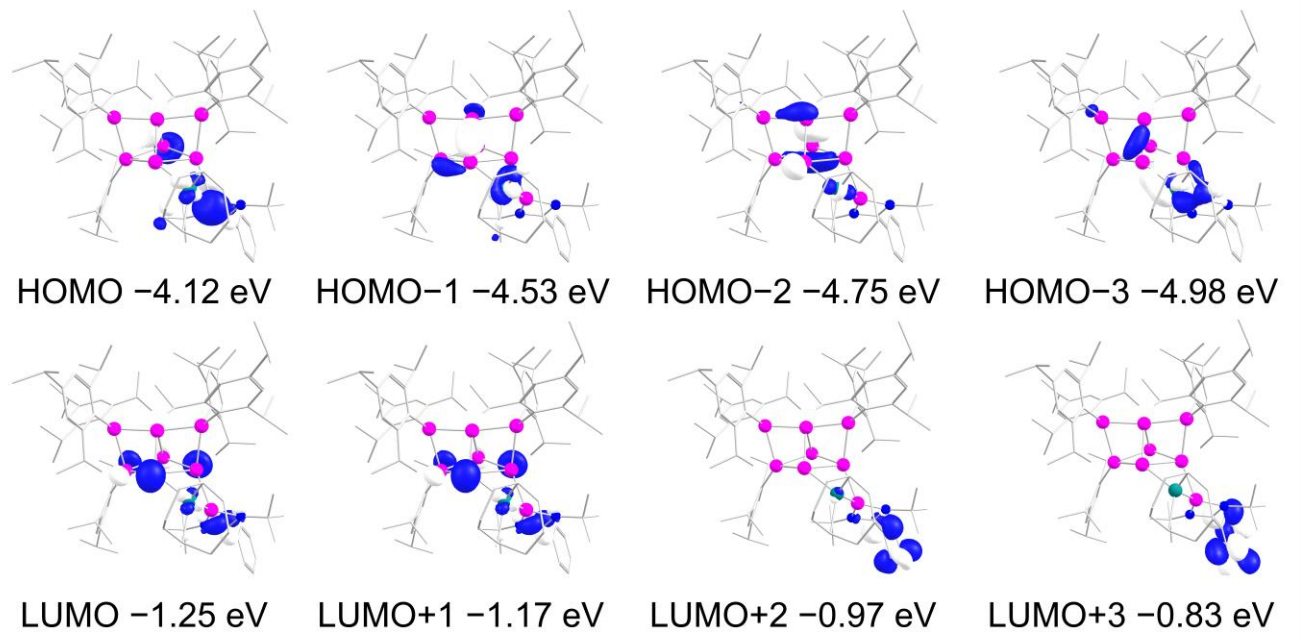
H	11.870758	18.177219	15.725343
H	11.279016	16.797569	14.802248
H	14.478173	19.201762	13.153809
H	13.808871	19.63369	14.727024
H	12.839472	19.86478	13.269124
H	16.854447	13.34565	13.776097
H	14.056513	13.149097	12.592431
H	14.604991	12.325917	14.058147
H	15.33747	11.926418	12.509794
H	16.845899	13.56358	11.345418
H	17.201062	15.146384	12.046908
H	15.59858	14.801825	11.399789
H	11.151111	12.608539	18.406607
H	13.357574	12.400294	22.028654
H	16.629586	12.964997	20.396529
H	15.54596	14.895821	21.523561
H	16.63314	14.049224	22.63398
H	14.892818	13.825015	22.762467
H	16.224284	10.649067	21.139557
H	15.30115	11.228285	22.525949
H	17.024981	11.578952	22.412142
H	14.091725	13.233538	16.28263
H	12.353546	12.12667	14.90269
H	11.473388	11.663106	16.360192
H	13.079219	10.994022	16.04491
H	12.287197	14.577117	15.397317
H	12.706627	15.192612	16.990366
H	11.250908	14.2168	16.782129
H	11.104586	12.137528	22.139716
C	10.247711	10.797798	20.710434
C	9.802128	13.280852	20.889743
H	9.356922	10.583674	21.305509
H	10.974005	10.001484	20.8827
H	9.963465	10.768564	19.656273
H	10.218398	14.251556	21.163524
H	8.920908	13.097842	21.508752
H	9.47162	13.340477	19.850785
H	20.753577	9.237948	17.408843
H	20.103777	7.029229	17.80083
H	21.235751	7.250328	20.504422
H	20.444206	5.865898	19.807743
H	18.381196	6.336563	20.738103
H	19.440578	6.9612	21.986955
H	17.343075	8.42477	21.056254
H	18.401606	10.541578	20.908551

H	20.950645	9.090799	21.456394
H	20.710838	10.813512	21.344242
H	21.098158	10.909044	19.056681
H	22.259683	9.711643	19.568597



Supplementary Figure S53. Selected frontier orbitals of Ni(cod) siliconoid/silylene **3a** at B3LYP/def2-TZVP level of theory (contour value at 0.05).[23–29] Hydrogen atoms are omitted for clarity.

4.2.2 Experimental vs. calculated NMR shifts

Supplementary Table S13. Comparison of experimental vs. calculated NMR chemical shifts for Ni(cod) siliconoid/silylene **3a** at the TPSSh/def2-TZVP level of theory.[26–29,33]

	Exp. **3a** $\delta(^{29}Si)$ [ppm]	Calc. **3a** $\delta(^{29}Si)$ [ppm]
Si3 (*Si*NHSi)	−10.2	0.7
Si8 (NHS*i*)	89.1	90.5
Si7 (*Si*Tip)	50.0	60.0
Si6 (*Si*Tip$_2$)	39.0	32.9
Si4 (*Si*Tip$_2$)	−13.3	−19.0
Si5 (unsubstituted)	−83.1	−80.8
Si1 (unsubstituted)	−154.0	−151.9
Si2 (unsubstituted)	−340.7	−346.2

4.2.3 TD-DFT calculations

Supplementary Table S14. Transition Energy. wavelength. and oscillator strengths of the electronic transition of Ni(cod) siliconoid/silylene **3a** calculated at the TD-TPSSh/def2-TZVP.[26–29,33,34] level of theory (the 445^{th} orbital is the highest occupied orbital (HOMO) and 446^{th} orbital is the lowest unoccupied molecular orbital (LUMO) shown in Supplementary Figure S53).

```
STATE  1:  E=  0.083385 au      2.269 eV    18300.9 cm**-1 <S**2> =   0.000000 Mult 1
   443a -> 446a  :     0.011432 (c= -0.10691906)
   444a -> 446a  :     0.189275 (c=  0.43505786)
   445a -> 446a  :     0.516370 (c= -0.71858895)
   445a -> 447a  :     0.190026 (c=  0.43591937)
   445a -> 448a  :     0.048401 (c= -0.22000263)

STATE  2:  E=  0.087666 au      2.386 eV    19240.5 cm**-1 <S**2> =   0.000000 Mult 1
   443a -> 446a  :     0.034645 (c=  0.18613295)
   444a -> 446a  :     0.726046 (c=  0.85208323)
   445a -> 446a  :     0.052594 (c=  0.22933452)
   445a -> 447a  :     0.135751 (c= -0.36844452)

STATE  3:  E=  0.088283 au      2.402 eV    19375.8 cm**-1 <S**2> =   0.000000 Mult 1
   443a -> 446a  :     0.021628 (c= -0.14706523)
   444a -> 446a  :     0.022816 (c= -0.15104870)
   445a -> 446a  :     0.236832 (c= -0.48665352)
   445a -> 447a  :     0.654462 (c= -0.80898846)
   445a -> 448a  :     0.029734 (c= -0.17243672)

STATE  4:  E=  0.096911 au      2.637 eV    21269.5 cm**-1 <S**2> =   0.000000 Mult 1
   443a -> 446a  :     0.101779 (c=  0.31902874)
   444a -> 447a  :     0.046828 (c= -0.21639831)
   445a -> 446a  :     0.035528 (c=  0.18848842)
   445a -> 448a  :     0.748071 (c= -0.86491075)
   445a -> 451a  :     0.012017 (c= -0.10962389)

STATE  5:  E=  0.098576 au      2.682 eV    21634.9 cm**-1 <S**2> =   0.000000 Mult 1
   442a -> 446a  :     0.611813 (c=  0.78218496)
   443a -> 446a  :     0.061309 (c= -0.24760556)
   444a -> 447a  :     0.227232 (c= -0.47668854)
   444a -> 448a  :     0.020730 (c=  0.14398064)
   445a -> 448a  :     0.010527 (c=  0.10259909)

STATE  6:  E=  0.098839 au      2.690 eV    21692.6 cm**-1 <S**2> =   0.000000 Mult 1
   445a -> 449a  :     0.995456 (c= -0.99772528)

STATE  7:  E=  0.099683 au      2.713 eV    21877.9 cm**-1 <S**2> =   0.000000 Mult 1
   442a -> 446a  :     0.059601 (c=  0.24413405)
   443a -> 446a  :     0.359974 (c= -0.59997839)
   444a -> 447a  :     0.387787 (c=  0.62272532)
   444a -> 448a  :     0.019063 (c= -0.13806779)
   445a -> 446a  :     0.017034 (c=  0.13051551)
   445a -> 448a  :     0.103391 (c= -0.32154539)
   445a -> 450a  :     0.016132 (c=  0.12701138)

STATE  8:  E=  0.101674 au      2.767 eV    22314.8 cm**-1 <S**2> =   0.000000 Mult 1
   442a -> 446a  :     0.157245 (c= -0.39654150)
   443a -> 446a  :     0.288001 (c= -0.53665721)
   444a -> 447a  :     0.148598 (c= -0.38548423)
   445a -> 446a  :     0.059421 (c=  0.24376525)
   445a -> 448a  :     0.015773 (c= -0.12558895)
   445a -> 450a  :     0.253762 (c= -0.50374768)

STATE  9:  E=  0.104272 au      2.837 eV    22885.1 cm**-1 <S**2> =   0.000000 Mult 1
   441a -> 446a  :     0.037269 (c=  0.19305180)
```

```
  442a -> 446a  :     0.053510 (c= -0.23132189)
  443a -> 446a  :     0.045147 (c= -0.21247761)
  444a -> 446a  :     0.015297 (c=  0.12368296)
  444a -> 447a  :     0.115523 (c= -0.33988606)
  444a -> 448a  :     0.016450 (c= -0.12825648)
  445a -> 450a  :     0.627163 (c=  0.79193652)
  445a -> 451a  :     0.028855 (c=  0.16986808)

STATE 10:  E=   0.106830 au      2.907 eV    23446.5 cm**-1 <S**2> =   0.000000 Mult 1
  443a -> 447a  :     0.014203 (c=  0.11917719)
  444a -> 447a  :     0.033465 (c=  0.18293556)
  444a -> 448a  :     0.896608 (c=  0.94689413)
  445a -> 450a  :     0.019291 (c=  0.13889108)

STATE 11:  E=   0.110187 au      2.998 eV    24183.4 cm**-1 <S**2> =   0.000000 Mult 1
  440a -> 446a  :     0.054144 (c= -0.23268882)
  441a -> 446a  :     0.069531 (c=  0.26368663)
  442a -> 447a  :     0.029740 (c=  0.17245290)
  443a -> 447a  :     0.592754 (c= -0.76990544)
  443a -> 448a  :     0.067045 (c=  0.25893073)
  445a -> 451a  :     0.112023 (c=  0.33469904)

STATE 12:  E=   0.110424 au      3.005 eV    24235.2 cm**-1 <S**2> =   0.000000 Mult 1
  440a -> 446a  :     0.040442 (c= -0.20110085)
  441a -> 446a  :     0.346095 (c=  0.58829801)
  445a -> 451a  :     0.546615 (c= -0.73933385)

STATE 13:  E=   0.110698 au      3.012 eV    24295.4 cm**-1 <S**2> =   0.000000 Mult 1
  440a -> 446a  :     0.197356 (c=  0.44424763)
  441a -> 446a  :     0.158476 (c= -0.39809095)
  442a -> 446a  :     0.012104 (c= -0.11001794)
  442a -> 447a  :     0.028935 (c= -0.17010158)
  443a -> 447a  :     0.257880 (c= -0.50781896)
  443a -> 448a  :     0.027391 (c=  0.16550193)
  445a -> 450a  :     0.017013 (c=  0.13043204)
  445a -> 451a  :     0.211001 (c= -0.45934896)

STATE 14:  E=   0.111719 au      3.040 eV    24519.4 cm**-1 <S**2> =   0.000000 Mult 1
  444a -> 449a  :     0.995849 (c=  0.99792252)

STATE 15:  E=   0.113376 au      3.085 eV    24883.2 cm**-1 <S**2> =   0.000000 Mult 1
  440a -> 446a  :     0.020744 (c=  0.14402607)
  441a -> 446a  :     0.055346 (c= -0.23525685)
  442a -> 446a  :     0.012901 (c=  0.11358255)
  442a -> 447a  :     0.745817 (c=  0.86360689)
  442a -> 448a  :     0.066960 (c= -0.25876557)
  442a -> 450a  :     0.014727 (c= -0.12135572)
  444a -> 450a  :     0.028627 (c= -0.16919656)

STATE 16:  E=   0.114091 au      3.105 eV    25040.1 cm**-1 <S**2> =   0.000000 Mult 1
  440a -> 446a  :     0.023437 (c= -0.15309071)
  441a -> 446a  :     0.020166 (c= -0.14200590)
  444a -> 450a  :     0.071302 (c=  0.26702350)
  445a -> 452a  :     0.832679 (c= -0.91251245)
  445a -> 453a  :     0.010213 (c= -0.10105994)

STATE 17:  E=   0.115254 au      3.136 eV    25295.4 cm**-1 <S**2> =   0.000000 Mult 1
  440a -> 446a  :     0.089954 (c=  0.29992256)
  441a -> 446a  :     0.022278 (c=  0.14925664)
  442a -> 447a  :     0.016400 (c=  0.12806330)
  443a -> 448a  :     0.011549 (c=  0.10746703)
```

444a -> 450a : 0.721015 (c= 0.84912615)
444a -> 451a : 0.011720 (c= -0.10825705)
445a -> 452a : 0.041912 (c= 0.20472541)

STATE 18: E= 0.116696 au 3.175 eV 25611.7 cm**-1 <S**2> = 0.000000 Mult 1
440a -> 446a : 0.049909 (c= 0.22340305)
441a -> 446a : 0.037458 (c= 0.19354155)
443a -> 448a : 0.016204 (c= -0.12729434)
445a -> 452a : 0.046768 (c= -0.21625983)
445a -> 453a : 0.760765 (c= 0.87221870)
445a -> 455a : 0.035034 (c= 0.18717384)

STATE 19: E= 0.117873 au 3.207 eV 25870.0 cm**-1 <S**2> = 0.000000 Mult 1
440a -> 446a : 0.047149 (c= 0.21713921)
441a -> 446a : 0.014848 (c= 0.12185056)
443a -> 447a : 0.077355 (c= -0.27812731)
443a -> 448a : 0.652797 (c= -0.80795825)
444a -> 451a : 0.042291 (c= 0.20564669)
445a -> 453a : 0.072490 (c= -0.26923997)
445a -> 454a : 0.012673 (c= 0.11257473)

STATE 20: E= 0.118289 au 3.219 eV 25961.5 cm**-1 <S**2> = 0.000000 Mult 1
438a -> 446a : 0.014644 (c= 0.12101376)
439a -> 446a : 0.013983 (c= 0.11825020)
440a -> 446a : 0.172327 (c= 0.41512300)
440a -> 447a : 0.023075 (c= -0.15190425)
441a -> 446a : 0.120048 (c= 0.34647911)
443a -> 448a : 0.112931 (c= 0.33605167)
443a -> 450a : 0.015749 (c= -0.12549533)
444a -> 450a : 0.032590 (c= -0.18052695)
444a -> 451a : 0.014182 (c= -0.11909007)
445a -> 450a : 0.012019 (c= -0.10963270)
445a -> 451a : 0.023114 (c= 0.15203363)
445a -> 452a : 0.035491 (c= -0.18839031)
445a -> 453a : 0.069434 (c= -0.26350280)
445a -> 454a : 0.209576 (c= 0.45779489)
445a -> 457a : 0.012786 (c= 0.11307668)

STATE 21: E= 0.119303 au 3.246 eV 26183.9 cm**-1 <S**2> = 0.000000 Mult 1
442a -> 447a : 0.015057 (c= -0.12270730)
443a -> 448a : 0.068239 (c= -0.26122572)
444a -> 451a : 0.776575 (c= -0.88123518)
444a -> 452a : 0.037932 (c= 0.19476178)
444a -> 453a : 0.013357 (c= 0.11557234)
445a -> 454a : 0.016957 (c= 0.13022059)

STATE 22: E= 0.120301 au 3.274 eV 26403.0 cm**-1 <S**2> = 0.000000 Mult 1
438a -> 446a : 0.036876 (c= 0.19203215)
439a -> 446a : 0.218163 (c= 0.46707894)
439a -> 447a : 0.010152 (c= -0.10075949)
440a -> 447a : 0.028087 (c= -0.16759120)
441a -> 446a : 0.026184 (c= 0.16181347)
441a -> 447a : 0.019977 (c= 0.14133858)
442a -> 448a : 0.018853 (c= 0.13730728)
444a -> 451a : 0.032581 (c= -0.18050255)
445a -> 453a : 0.010814 (c= -0.10398940)
445a -> 454a : 0.434603 (c= -0.65924411)
445a -> 455a : 0.047286 (c= 0.21745342)

STATE 23: E= 0.120685 au 3.284 eV 26487.2 cm**-1 <S**2> = 0.000000 Mult 1
437a -> 446a : 0.033779 (c= 0.18379159)

439a -> 446a : 0.443319 (c= 0.66582186)
440a -> 446a : 0.077201 (c= -0.27785138)
444a -> 450a : 0.013866 (c= 0.11775418)
445a -> 453a : 0.016682 (c= 0.12915737)
445a -> 454a : 0.113323 (c= 0.33663492)
445a -> 455a : 0.176764 (c= -0.42043294)
445a -> 456a : 0.014109 (c= 0.11878040)

STATE 24: E= 0.122088 au 3.322 eV 26795.2 cm**-1 <S**2> = 0.000000 Mult 1
439a -> 446a : 0.051154 (c= -0.22617341)
440a -> 446a : 0.018114 (c= 0.13458938)
441a -> 447a : 0.026078 (c= 0.16148785)
442a -> 447a : 0.023590 (c= 0.15359186)
442a -> 448a : 0.221448 (c= 0.47058251)
445a -> 453a : 0.012558 (c= 0.11206142)
445a -> 454a : 0.051346 (c= -0.22659662)
445a -> 455a : 0.508078 (c= -0.71279564)
445a -> 456a : 0.014414 (c= 0.12005735)

STATE 25: E= 0.122484 au 3.333 eV 26882.2 cm**-1 <S**2> = 0.000000 Mult 1
440a -> 446a : 0.028709 (c= -0.16943706)
440a -> 447a : 0.026980 (c= 0.16425725)
441a -> 447a : 0.087093 (c= 0.29511576)
442a -> 447a : 0.042513 (c= 0.20618563)
442a -> 448a : 0.480229 (c= 0.69298571)
445a -> 454a : 0.085953 (c= 0.29317692)
445a -> 455a : 0.132346 (c= 0.36379332)

STATE 26: E= 0.123100 au 3.350 eV 27017.4 cm**-1 <S**2> = 0.000000 Mult 1
440a -> 447a : 0.014324 (c= -0.11968461)
441a -> 447a : 0.517138 (c= -0.71912303)
441a -> 448a : 0.049129 (c= 0.22164982)
442a -> 447a : 0.011208 (c= 0.10586644)
442a -> 448a : 0.129138 (c= 0.35935741)
444a -> 452a : 0.022131 (c= 0.14876405)
445a -> 456a : 0.097353 (c= -0.31201431)
445a -> 457a : 0.041252 (c= 0.20310669)
445a -> 460a : 0.014649 (c= -0.12103396)

STATE 27: E= 0.123466 au 3.360 eV 27097.6 cm**-1 <S**2> = 0.000000 Mult 1
443a -> 449a : 0.978057 (c= -0.98896766)

STATE 28: E= 0.123817 au 3.369 eV 27174.7 cm**-1 <S**2> = 0.000000 Mult 1
438a -> 446a : 0.015701 (c= 0.12530530)
441a -> 447a : 0.168338 (c= -0.41028996)
442a -> 448a : 0.018389 (c= 0.13560468)
443a -> 449a : 0.015379 (c= -0.12401042)
443a -> 450a : 0.082141 (c= -0.28660221)
445a -> 455a : 0.016554 (c= 0.12866265)
445a -> 456a : 0.213787 (c= 0.46237113)
445a -> 457a : 0.254089 (c= -0.50407223)
445a -> 458a : 0.022300 (c= 0.14933092)
445a -> 460a : 0.080564 (c= 0.28383878)
445a -> 461a : 0.051960 (c= -0.22794664)

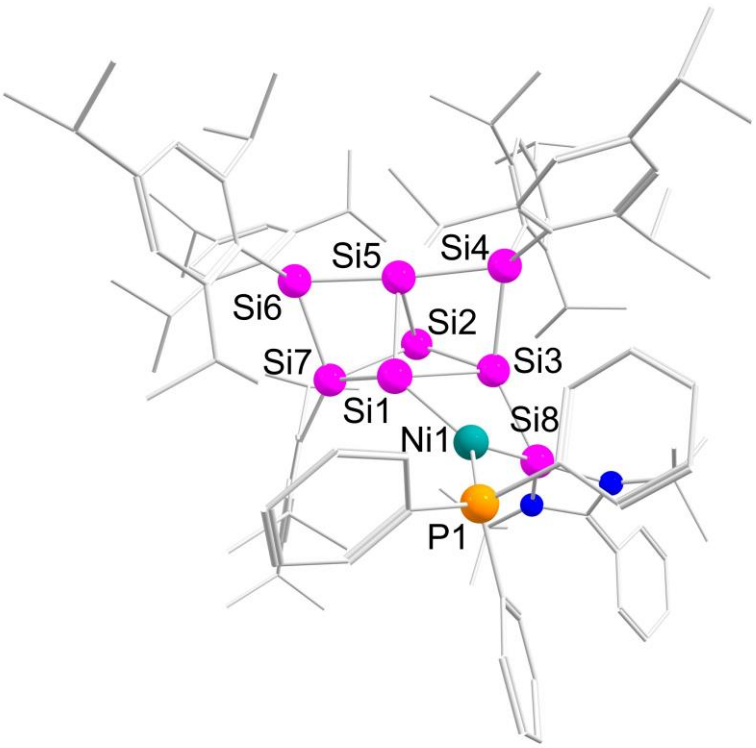
STATE 29: E= 0.124215 au 3.380 eV 27261.9 cm**-1 <S**2> = 0.000000 Mult 1
440a -> 447a : 0.017508 (c= -0.13231759)
441a -> 447a : 0.016472 (c= 0.12834327)
444a -> 451a : 0.070670 (c= 0.26583882)
444a -> 452a : 0.701188 (c= 0.83736991)
444a -> 453a : 0.080264 (c= 0.28330960)

```
   444a -> 454a  :     0.015041 (c=  0.12264069)
   445a -> 456a  :     0.012464 (c=  0.11164087)

 STATE 30:  E=   0.125447 au      3.414 eV    27532.5 cm**-1 <S**2> =   0.000000 Mult 1
   438a -> 446a  :     0.030534 (c=  0.17474092)
   439a -> 446a  :     0.019015 (c= -0.13789490)
   440a -> 447a  :     0.304872 (c= -0.55215223)
   440a -> 448a  :     0.023920 (c=  0.15466103)
   442a -> 450a  :     0.017156 (c=  0.13097958)
   443a -> 450a  :     0.050936 (c=  0.22568996)
   444a -> 452a  :     0.082585 (c= -0.28737578)
   444a -> 453a  :     0.047041 (c=  0.21688900)
   444a -> 455a  :     0.010708 (c=  0.10348105)
   445a -> 454a  :     0.012094 (c=  0.10997456)
   445a -> 455a  :     0.015145 (c= -0.12306418)
   445a -> 456a  :     0.145021 (c= -0.38081607)
   445a -> 457a  :     0.068600 (c= -0.26191543)
   445a -> 458a  :     0.047196 (c=  0.21724677)
   445a -> 460a  :     0.021540 (c=  0.14676366)
   445a -> 461a  :     0.017694 (c= -0.13301787)
```

4.3 Ni(PPh_3) siliconoid/silylene 3b

4.3.1 Optimization and molecular orbitals



Supplementary Figure S54. Calculated structure of Ni(PPh_3) siliconoid/silylene **3b** at the B3LYP/def2-TZVP level of theory.[23–29] Hydrogen atoms are omitted for clarity.

Supplementary Table S15. Coordinates of Ni(PPh_3) siliconoid/silylene **3b** at the B3LYP/def2-TZVP level of theory.[23–29]

Ni	20.167835	10.285606	23.707713
Si	18.620602	9.077116	24.660077
P	19.510486	11.655672	22.122047
Si	22.277925	9.976204	24.259896
Si	20.503717	9.39304	25.900699
N	18.048507	7.348857	24.388392
C	16.811029	7.671676	24.779645
C	18.596592	6.11476	23.79516
N	16.880585	8.947848	25.190527
C	15.853229	9.898658	25.636065
C	18.685256	12.975751	23.089936
C	20.634271	12.588611	21.013947
C	18.224583	11.085347	20.941211
Si	23.622821	8.131859	24.180682
Si	23.375485	10.091814	26.33133
Si	22.391858	7.980396	26.195998
Si	21.476965	10.910637	27.487906
C	21.585508	10.195735	29.263618
C	21.026973	12.772874	27.573194
Si	25.370709	9.339331	25.310132
C	26.551274	8.018355	26.011401
C	26.421009	10.785641	24.611513
C	23.578418	6.625168	23.029363
C	15.602201	6.824742	24.729029
C	14.915795	6.646643	23.529888
C	15.141282	6.200052	25.885428
C	14.008118	5.399401	25.841031
C	13.326843	5.222302	24.642538
C	13.781371	5.848903	23.487535
C	18.045343	4.863062	24.485726
C	20.109405	6.165046	24.00175
C	18.285919	6.081257	22.292827
C	16.497566	11.280867	25.528263
C	15.483457	9.609061	27.095243
C	14.606444	9.860061	24.745018
C	23.829826	5.343251	23.56748
C	23.049014	6.716085	21.724364
C	23.518083	4.211761	22.81859
C	24.390042	5.122063	24.963573
C	22.957449	4.291973	21.552913
C	22.740755	5.556145	21.021853
C	22.573406	3.04079	20.792608
C	22.759767	8.042052	21.041681
C	23.387064	8.119988	19.644843
C	21.255087	8.316484	20.968556
C	23.338153	4.49401	25.88638

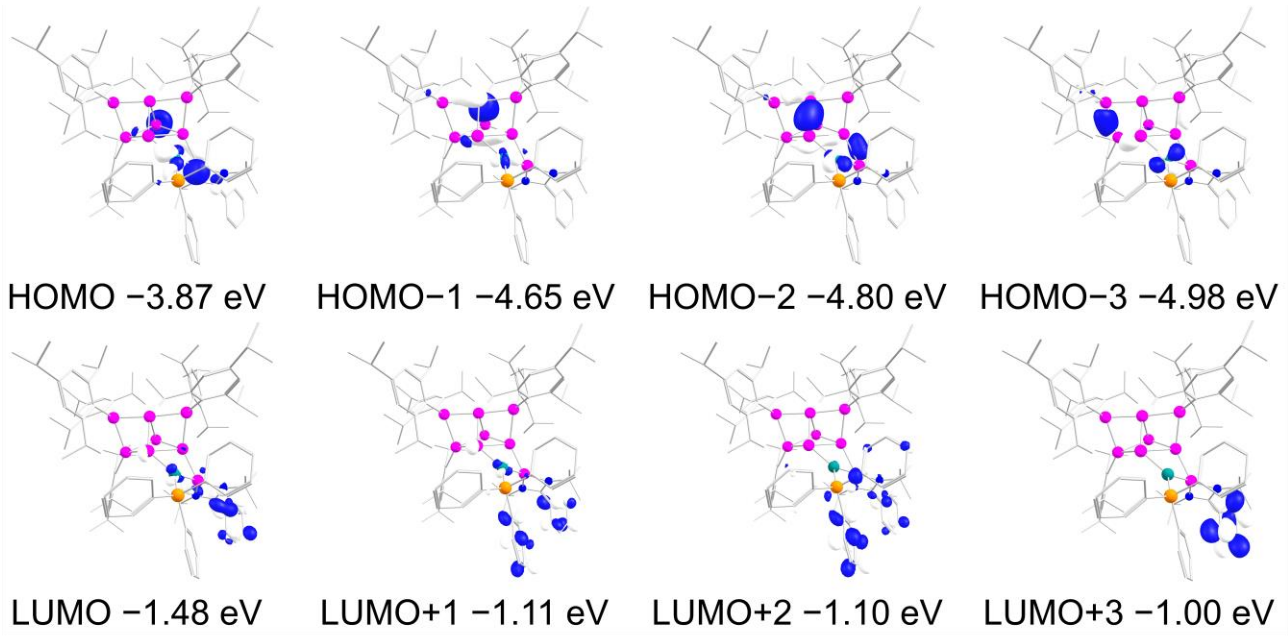
C	25.657483	4.260544	24.965522
C	21.049173	2.929941	20.652288
C	23.260388	2.959593	19.425111
C	22.560038	10.759055	30.118328
C	20.867052	9.073136	29.74032
C	21.194818	8.514226	30.972747
C	19.690594	8.432748	29.017737
C	22.187831	9.033744	31.789739
C	22.838773	10.174673	31.35001
C	22.570479	8.37573	33.097531
C	23.323238	12.02526	29.772223
C	24.835063	11.819391	29.770719
C	22.930233	13.194525	30.683279
C	19.918955	6.950483	28.703035
C	18.381616	8.600756	29.801076
C	21.367121	8.156999	34.020209
C	23.320101	7.060804	32.843147
C	20.014147	13.186692	28.468458
C	21.772164	13.779675	26.91162
C	21.566295	15.116767	27.240733
C	22.800239	13.485245	25.830178
C	20.622548	15.521141	28.171887
C	19.838632	14.537125	28.753933
C	20.416727	16.986485	28.486324
C	19.036149	12.222698	29.121937
C	17.588589	12.589578	28.765173
C	19.200988	12.159289	30.644921
C	24.234743	13.476382	26.369632
C	22.705669	14.447621	24.640418
C	20.551347	17.277032	29.984756
C	19.068773	17.48	27.943622
C	26.561168	7.536124	27.335108
C	27.465079	7.456846	25.086513
C	28.367247	6.486838	25.502528
C	27.540851	7.897802	23.630218
C	28.388426	6.011861	26.807148
C	27.468518	6.541184	27.697402
C	29.390614	4.968066	27.251305
C	25.631117	8.050572	28.422221
C	26.393634	8.57969	29.642822
C	24.618848	6.985418	28.856957
C	27.371078	6.741398	22.639855
C	28.834795	8.672815	23.35417
C	29.301567	3.685114	26.417439
C	30.816568	5.534222	27.237984
C	26.306026	11.286015	23.297742
C	27.352168	11.419126	25.472427

C	27.073317	12.377246	22.893213
C	25.373742	10.704873	22.252477
C	27.989344	12.991443	23.727369
C	28.117648	12.484333	25.012183
C	28.805282	14.175712	23.257963
C	27.591829	10.988577	26.912132
C	28.878687	10.162674	27.042073
C	27.651567	12.180006	27.875776
C	24.219143	11.663624	21.953076
C	26.1081	10.316443	20.96493
C	28.44695	15.444964	24.04122
C	30.310651	13.893257	23.323488
C	17.59611	9.863023	21.172058
C	17.849597	11.829254	19.819778
C	16.857796	11.368884	18.964273
C	16.232685	10.150905	19.209918
C	16.607901	9.397277	20.314804
C	19.20881	13.24759	24.356054
C	17.556427	13.673429	22.664035
C	18.629872	14.205827	25.175204
C	17.504444	14.895936	24.741035
C	16.967706	14.626046	23.48736
C	21.095365	12.008098	19.829123
C	21.146177	13.829964	21.388382
C	22.042293	12.649231	19.044694
C	22.553522	13.882573	19.433963
C	22.100086	14.469917	20.607752
H	15.682985	6.329252	26.812694
H	13.659534	4.911237	26.74173
H	12.44337	4.598219	24.608531
H	13.249951	5.71869	22.553794
H	15.262255	7.149284	22.6374
H	20.595022	5.325261	23.505596
H	20.356561	6.135875	25.061689
H	20.53275	7.078202	23.589741
H	18.673638	6.97454	21.804678
H	17.212669	6.019805	22.113439
H	18.756904	5.211221	21.832829
H	16.990845	4.700285	24.274078
H	18.17926	4.933399	25.566072
H	18.598479	3.99218	24.131411
H	14.885092	9.973321	23.696135
H	13.9477	10.687498	25.013641
H	14.046908	8.934275	24.861164
H	16.69888	11.540498	24.490733
H	17.4421	11.306782	26.071227
H	15.841962	12.039757	25.95366

H	14.786565	10.362909	27.465485
H	16.374372	9.625572	27.721939
H	15.008255	8.633104	27.192102
H	23.703092	3.231397	23.241318
H	22.312074	5.643095	20.031518
H	23.203509	8.834618	21.644178
H	22.894527	7.443311	18.94382
H	24.445518	7.859009	19.672223
H	23.290874	9.132169	19.24611
H	21.060241	9.217591	20.388994
H	20.831728	8.472255	21.962502
H	20.727135	7.48738	20.493635
H	24.662992	6.092113	25.38127
H	25.442405	3.23712	24.650703
H	26.071021	4.222746	25.973669
H	26.424166	4.66436	24.309281
H	22.44238	5.110877	25.941598
H	23.736926	4.386646	26.897167
H	23.053748	3.502003	25.527912
H	20.770283	1.99882	20.153418
H	20.651433	3.759471	20.063179
H	20.565139	2.952301	21.630492
H	23.012787	2.021203	18.923643
H	24.345004	3.017825	19.528676
H	22.943416	3.77785	18.775048
H	20.648202	7.640799	31.304076
H	23.593894	10.61989	31.987159
H	23.050825	12.3232	28.764796
H	25.12413	11.063585	29.041737
H	25.207596	11.504498	30.746592
H	25.337261	12.750555	29.510418
H	23.446807	14.103668	30.368129
H	23.199424	12.99387	31.722703
H	21.860077	13.386336	30.639576
H	19.550961	8.944839	28.066597
H	18.154335	9.64837	29.988292
H	18.429521	8.09493	30.767503
H	17.551521	8.166196	29.239195
H	19.110658	6.573641	28.071086
H	19.940011	6.349474	29.614741
H	20.858006	6.801738	28.171895
H	23.259282	9.056528	33.607521
H	23.63968	6.607088	33.784347
H	22.680434	6.345006	32.321861
H	24.202618	7.226925	32.223866
H	21.689115	7.749874	34.981287
H	20.838095	9.093649	34.203992

H	20.656198	7.451694	33.584763
H	22.154603	15.876583	26.742371
H	19.061226	14.825448	29.449764
H	19.222467	11.227029	28.718484
H	20.172525	11.760806	30.926527
H	18.434444	11.52097	31.088127
H	19.095859	13.153388	31.084211
H	17.469973	12.742257	27.694774
H	17.280595	13.507492	29.269123
H	16.905682	11.797717	29.079521
H	22.588915	12.490516	25.44287
H	23.291612	14.059887	23.806494
H	23.099485	15.436793	24.882388
H	21.676245	14.568325	24.307766
H	24.942335	13.235902	25.574627
H	24.363754	12.736774	27.157007
H	24.496109	14.45476	26.780985
H	21.205609	17.539383	27.967304
H	18.991729	17.301082	26.869674
H	18.241019	16.958746	28.43
H	18.944681	18.550301	28.123601
H	20.468637	18.34883	30.178357
H	19.767623	16.775355	30.556399
H	21.513899	16.932273	30.365809
H	29.070935	6.085704	24.78372
H	27.466944	6.172502	28.716366
H	25.059396	8.879709	28.0063
H	24.075071	6.588759	28.000916
H	23.885778	7.416232	29.54148
H	25.117236	6.154746	29.363491
H	26.955839	7.784534	30.136039
H	25.693088	8.993246	30.369457
H	27.099636	9.362934	29.367184
H	26.71363	8.576655	23.433789
H	28.860403	9.022192	22.320159
H	29.708256	8.037165	23.515486
H	28.921019	9.542013	24.003923
H	27.41039	7.120812	21.616241
H	26.411661	6.244259	22.770987
H	28.161802	5.995792	22.744462
H	29.145896	4.709733	28.286281
H	29.551535	3.876861	25.371908
H	28.295766	3.264242	26.445519
H	29.999384	2.933384	26.793314
H	31.117431	5.805559	26.223551
H	31.53032	4.7976	27.614515
H	30.887384	6.430504	27.85636

H	26.957396	12.757298	21.885483
H	28.830852	12.941353	25.68461
H	26.753442	10.365808	27.225923
H	28.845429	9.260822	26.437165
H	29.041306	9.865427	28.080199
H	29.737389	10.75837	26.723741
H	28.570766	12.752301	27.742448
H	27.637603	11.828582	28.90822
H	26.810309	12.85557	27.730479
H	24.940772	9.79392	22.661693
H	24.582001	12.584715	21.49377
H	23.688513	11.932384	22.866199
H	23.498213	11.214146	21.270078
H	25.420949	9.836092	20.269635
H	26.925998	9.625279	21.16812
H	26.527177	11.189537	20.462189
H	28.545122	14.348142	22.208858
H	28.996367	16.307101	23.655659
H	28.696214	15.33385	25.098787
H	27.378934	15.658288	23.972262
H	30.566823	13.000304	22.751021
H	30.635605	13.733244	24.353768
H	30.879662	14.734958	22.921896
H	18.342117	12.768651	19.60777
H	16.575934	11.95927	18.101522
H	15.464573	9.789558	18.537826
H	16.1418	8.437805	20.502284
H	17.896494	9.283002	22.034189
H	20.068607	12.691255	24.706449
H	19.053246	14.402998	26.149103
H	17.044273	15.637569	25.381963
H	16.087092	15.156658	23.147284
H	17.123252	13.465383	21.695977
H	20.702074	11.053506	19.508202
H	22.384349	12.182626	18.129425
H	23.297787	14.380425	18.825896
H	22.488077	15.430935	20.92098
H	20.79781	14.301585	22.295018
H	22.914024	2.18748	21.38697



Supplementary Figure S55. Selected frontier orbitals of Ni(PPh_3) siliconoid/silylene **3b** at B3LYP/def2-TZVP level of theory (contour value 0.05).[23–29] Hydrogen atoms are omitted for clarity.

4.3.2 Experimental vs. calculated NMR shifts

Supplementary Table S16. Comparison of experimental vs. calculated NMR chemical shifts for compound Ni(PPh_3) siliconoid/silylene **3b** at the TPSSh/def2-TVZP level of theory.[26–29,33]

	Exp. **3b** δ(^{29}Si) [ppm]	Calc. **3b** δ(^{29}Si) [ppm]
Si3 (*Si*NHSi)	0.4	−6.5
Si8 (NHS*i*)	73.5	84.6
Si7 (*Si*Tip)	63.9	65.4
Si6 (*Si*Tip_2)	39.7	30.6
Si4 (*Si*Tip_2)	−41.4	−45.2
Si5 (unsubstituted)	−60.0	−68.2
Si1 (unsubstituted)	−87.3	−68.5
Si2 (unsubstituted)	−287.6	−291.0

4.3.3 TD-DFT calculations

Supplementary Table S17. Transition Energy. wavelength. and oscillator strengths of the electronic transition of **3b** calculated at the TD-TPSSh/def2-TZVP level of theory.[26–29,33,34] (the 485th orbital is the highest occupied orbital (HOMO) and 486th orbital is the lowest unoccupied molecular orbital (LUMO) shown in Supplementary Figure S55).

```
STATE  1:  E=   0.061541 au      1.675 eV    13506.8 cm**-1 <S**2> =   0.000000 Mult 1
   484a -> 485a  :     0.896349 (c= -0.94675721)
   484a -> 486a  :     0.042288 (c= -0.20563982)
   484a -> 488a  :     0.022256 (c= -0.14918536)

STATE  2:  E=   0.079702 au      2.169 eV    17492.6 cm**-1 <S**2> =   0.000000 Mult 1
   482a -> 485a  :     0.026768 (c= -0.16360917)
   483a -> 485a  :     0.024734 (c=  0.15727088)
```

```
  484a -> 486a  :     0.767862 (c=  0.87627710)
  484a -> 487a  :     0.035725 (c=  0.18901015)
  484a -> 488a  :     0.114284 (c= -0.33805947)

STATE  3:  E=   0.082033 au      2.232 eV    18004.1 cm**-1 <S**2> =   0.000000 Mult 1
  484a -> 485a  :     0.017014 (c=  0.13043664)
  484a -> 486a  :     0.030942 (c= -0.17590265)
  484a -> 487a  :     0.922539 (c=  0.96048886)

STATE  4:  E=   0.083644 au      2.276 eV    18357.7 cm**-1 <S**2> =   0.000000 Mult 1
  481a -> 485a  :     0.035895 (c= -0.18946097)
  482a -> 485a  :     0.023219 (c=  0.15237695)
  483a -> 485a  :     0.756897 (c= -0.86999843)
  483a -> 487a  :     0.011471 (c=  0.10710315)
  484a -> 488a  :     0.140011 (c= -0.37418072)

STATE  5:  E=   0.085929 au      2.338 eV    18859.3 cm**-1 <S**2> =   0.000000 Mult 1
  478a -> 485a  :     0.020508 (c=  0.14320531)
  480a -> 485a  :     0.034744 (c= -0.18639676)
  482a -> 485a  :     0.296719 (c=  0.54471964)
  483a -> 485a  :     0.112468 (c=  0.33536190)
  484a -> 486a  :     0.027096 (c= -0.16460868)
  484a -> 488a  :     0.441311 (c= -0.66431249)

STATE  6:  E=   0.087996 au      2.395 eV    19313.0 cm**-1 <S**2> =   0.000000 Mult 1
  479a -> 485a  :     0.065321 (c= -0.25557990)
  480a -> 485a  :     0.029641 (c= -0.17216701)
  481a -> 485a  :     0.819704 (c= -0.90537520)
  481a -> 487a  :     0.013734 (c=  0.11719024)
  482a -> 485a  :     0.010166 (c= -0.10082526)
  483a -> 485a  :     0.026851 (c=  0.16386248)

STATE  7:  E=   0.088564 au      2.410 eV    19437.5 cm**-1 <S**2> =   0.000000 Mult 1
  482a -> 485a  :     0.082596 (c=  0.28739447)
  484a -> 489a  :     0.010216 (c= -0.10107525)
  484a -> 490a  :     0.864804 (c= -0.92994816)

STATE  8:  E=   0.090650 au      2.467 eV    19895.3 cm**-1 <S**2> =   0.000000 Mult 1
  478a -> 485a  :     0.014729 (c=  0.12136355)
  480a -> 485a  :     0.247037 (c= -0.49702867)
  481a -> 485a  :     0.020547 (c=  0.14334352)
  482a -> 485a  :     0.397028 (c= -0.63010125)
  484a -> 486a  :     0.029353 (c= -0.17132719)
  484a -> 488a  :     0.115220 (c= -0.33944006)
  484a -> 489a  :     0.034622 (c= -0.18607082)
  484a -> 490a  :     0.079781 (c= -0.28245543)

STATE  9:  E=   0.091043 au      2.477 eV    19981.5 cm**-1 <S**2> =   0.000000 Mult 1
  484a -> 489a  :     0.953121 (c= -0.97627903)
  484a -> 490a  :     0.023046 (c=  0.15180963)

STATE 10:  E=   0.094246 au      2.565 eV    20684.7 cm**-1 <S**2> =   0.000000 Mult 1
  479a -> 485a  :     0.012736 (c= -0.11285295)
  480a -> 485a  :     0.046337 (c= -0.21525998)
  481a -> 485a  :     0.017704 (c=  0.13305512)
  484a -> 491a  :     0.712125 (c=  0.84387490)
  484a -> 492a  :     0.128624 (c=  0.35864253)
  484a -> 493a  :     0.037360 (c= -0.19328864)

STATE 11:  E=   0.095291 au      2.593 eV    20913.9 cm**-1 <S**2> =   0.000000 Mult 1
  480a -> 485a  :     0.011281 (c= -0.10621051)
```

```
  484a -> 491a  :     0.170377 (c= -0.41276745)
  484a -> 492a  :     0.788219 (c=  0.88781691)

STATE 12:  E=   0.096605 au      2.629 eV    21202.4 cm**-1 <S**2> =   0.000000 Mult 1
  478a -> 485a  :     0.063240 (c=  0.25147517)
  479a -> 485a  :     0.154794 (c= -0.39343855)
  480a -> 485a  :     0.309627 (c= -0.55644161)
  481a -> 485a  :     0.027224 (c=  0.16499697)
  482a -> 485a  :     0.053299 (c=  0.23086666)
  483a -> 485a  :     0.023313 (c= -0.15268491)
  484a -> 485a  :     0.021662 (c= -0.14717936)
  484a -> 486a  :     0.045656 (c=  0.21367187)
  484a -> 488a  :     0.092683 (c=  0.30443820)
  484a -> 491a  :     0.040507 (c= -0.20126353)
  484a -> 492a  :     0.072132 (c= -0.26857319)

STATE 13:  E=   0.100256 au      2.728 eV    22003.7 cm**-1 <S**2> =   0.000000 Mult 1
  483a -> 486a  :     0.022004 (c= -0.14833663)
  484a -> 491a  :     0.032236 (c= -0.17954512)
  484a -> 493a  :     0.895534 (c= -0.94632682)
  484a -> 494a  :     0.016980 (c= -0.13030674)

STATE 14:  E=   0.102011 au      2.776 eV    22388.9 cm**-1 <S**2> =   0.000000 Mult 1
  478a -> 485a  :     0.054471 (c=  0.23339017)
  479a -> 485a  :     0.441583 (c= -0.66451720)
  480a -> 485a  :     0.155701 (c=  0.39458939)
  481a -> 485a  :     0.021192 (c=  0.14557574)
  482a -> 485a  :     0.020186 (c= -0.14207724)
  483a -> 486a  :     0.135157 (c= -0.36763703)
  483a -> 488a  :     0.028736 (c= -0.16951681)
  484a -> 488a  :     0.012814 (c= -0.11320037)
  484a -> 494a  :     0.017451 (c=  0.13210167)

STATE 15:  E=   0.102557 au      2.791 eV    22508.8 cm**-1 <S**2> =   0.000000 Mult 1
  478a -> 485a  :     0.064751 (c=  0.25446269)
  479a -> 485a  :     0.062273 (c= -0.24954605)
  480a -> 485a  :     0.037514 (c=  0.19368416)
  481a -> 486a  :     0.051341 (c=  0.22658620)
  482a -> 485a  :     0.013993 (c= -0.11828998)
  482a -> 486a  :     0.017447 (c= -0.13208626)
  483a -> 486a  :     0.635325 (c=  0.79707305)
  483a -> 488a  :     0.034882 (c=  0.18676817)
  484a -> 493a  :     0.014625 (c= -0.12093437)

STATE 16:  E=   0.104971 au      2.856 eV    23038.5 cm**-1 <S**2> =   0.000000 Mult 1
  478a -> 485a  :     0.038170 (c= -0.19537224)
  484a -> 493a  :     0.015810 (c= -0.12573613)
  484a -> 494a  :     0.881353 (c=  0.93880384)
  484a -> 495a  :     0.011613 (c= -0.10776263)

STATE 17:  E=   0.106147 au      2.888 eV    23296.6 cm**-1 <S**2> =   0.000000 Mult 1
  478a -> 485a  :     0.312606 (c=  0.55911136)
  479a -> 485a  :     0.075988 (c=  0.27565966)
  480a -> 485a  :     0.019857 (c=  0.14091648)
  482a -> 486a  :     0.107478 (c= -0.32783887)
  482a -> 488a  :     0.024156 (c= -0.15542294)
  483a -> 486a  :     0.017746 (c= -0.13321413)
  483a -> 487a  :     0.052044 (c=  0.22813132)
  484a -> 494a  :     0.013418 (c=  0.11583408)
  484a -> 495a  :     0.310525 (c= -0.55724728)
```

STATE 18: E= 0.106212 au 2.890 eV 23310.8 cm**-1 <S**2> = 0.000000 Mult 1
478a -> 485a : 0.022154 (c= 0.14884112)
481a -> 486a : 0.120782 (c= 0.34753773)
482a -> 486a : 0.556643 (c= 0.74608492)
482a -> 488a : 0.070715 (c= 0.26592225)
483a -> 487a : 0.018992 (c= -0.13781036)
484a -> 495a : 0.137826 (c= -0.37124941)

STATE 19: E= 0.106570 au 2.900 eV 23389.4 cm**-1 <S**2> = 0.000000 Mult 1
478a -> 485a : 0.299510 (c= -0.54727532)
479a -> 485a : 0.065466 (c= -0.25586305)
481a -> 486a : 0.149368 (c= 0.38648114)
482a -> 486a : 0.088228 (c= -0.29703227)
483a -> 488a : 0.017704 (c= -0.13305716)
484a -> 494a : 0.032504 (c= -0.18028994)
484a -> 495a : 0.268370 (c= -0.51804444)

STATE 20: E= 0.107243 au 2.918 eV 23537.2 cm**-1 <S**2> = 0.000000 Mult 1
479a -> 486a : 0.010086 (c= -0.10042821)
480a -> 486a : 0.011357 (c= -0.10656860)
481a -> 486a : 0.395923 (c= -0.62922397)
481a -> 488a : 0.024549 (c= -0.15668271)
483a -> 486a : 0.028005 (c= 0.16734597)
483a -> 487a : 0.194709 (c= -0.44125831)
483a -> 488a : 0.022203 (c= 0.14900693)
484a -> 495a : 0.228699 (c= -0.47822450)
484a -> 496a : 0.019854 (c= 0.14090342)

STATE 21: E= 0.108086 au 2.941 eV 23722.2 cm**-1 <S**2> = 0.000000 Mult 1
481a -> 486a : 0.077172 (c= -0.27779811)
481a -> 487a : 0.018955 (c= 0.13767650)
481a -> 488a : 0.026239 (c= -0.16198423)
482a -> 486a : 0.055460 (c= 0.23549933)
483a -> 486a : 0.031088 (c= 0.17631852)
483a -> 487a : 0.462073 (c= 0.67975943)
483a -> 488a : 0.066998 (c= -0.25883956)
484a -> 496a : 0.186298 (c= 0.43162281)

STATE 22: E= 0.108649 au 2.956 eV 23845.7 cm**-1 <S**2> = 0.000000 Mult 1
481a -> 486a : 0.049157 (c= 0.22171333)
481a -> 488a : 0.013290 (c= 0.11528433)
482a -> 486a : 0.012180 (c= -0.11036386)
483a -> 486a : 0.020140 (c= -0.14191567)
483a -> 487a : 0.037711 (c= -0.19419216)
483a -> 488a : 0.049673 (c= 0.22287408)
484a -> 496a : 0.759085 (c= 0.87125474)

STATE 23: E= 0.110141 au 2.997 eV 24173.1 cm**-1 <S**2> = 0.000000 Mult 1
479a -> 485a : 0.013893 (c= 0.11786654)
480a -> 486a : 0.017625 (c= 0.13275733)
481a -> 486a : 0.010046 (c= 0.10022974)
481a -> 488a : 0.024396 (c= -0.15619264)
482a -> 485a : 0.010656 (c= 0.10322907)
482a -> 487a : 0.128707 (c= 0.35875730)
483a -> 486a : 0.056803 (c= 0.23833297)
483a -> 487a : 0.107762 (c= -0.32827055)
483a -> 488a : 0.555472 (c= -0.74529973)
484a -> 496a : 0.010614 (c= 0.10302547)

STATE 24: E= 0.110938 au 3.019 eV 24348.2 cm**-1 <S**2> = 0.000000 Mult 1
482a -> 487a : 0.207041 (c= -0.45501762)

```
   482a -> 488a  :     0.030943 (c=  0.17590490)
   483a -> 487a  :     0.012711 (c= -0.11274365)
   483a -> 488a  :     0.028724 (c= -0.16948244)
   484a -> 497a  :     0.666219 (c= -0.81622263)

STATE 25:  E=   0.111874 au      3.044 eV    24553.5 cm**-1 <S**2> =   0.000000 Mult 1
   480a -> 486a  :     0.025211 (c=  0.15878103)
   482a -> 486a  :     0.044339 (c= -0.21056716)
   482a -> 487a  :     0.383836 (c= -0.61954526)
   482a -> 488a  :     0.143644 (c=  0.37900400)
   483a -> 488a  :     0.048939 (c= -0.22122139)
   484a -> 497a  :     0.268648 (c=  0.51831245)
   484a -> 500a  :     0.018620 (c=  0.13645506)

STATE 26:  E=   0.112775 au      3.069 eV    24751.3 cm**-1 <S**2> =   0.000000 Mult 1
   480a -> 486a  :     0.029997 (c= -0.17319636)
   481a -> 486a  :     0.019467 (c=  0.13952447)
   481a -> 487a  :     0.607177 (c=  0.77921554)
   481a -> 488a  :     0.139599 (c= -0.37362981)
   482a -> 487a  :     0.032997 (c=  0.18165122)
   482a -> 488a  :     0.034254 (c=  0.18507793)
   483a -> 488a  :     0.029174 (c=  0.17080537)
   483a -> 490a  :     0.011364 (c= -0.10660336)

STATE 27:  E=   0.113253 au      3.082 eV    24856.1 cm**-1 <S**2> =   0.000000 Mult 1
   476a -> 485a  :     0.017831 (c=  0.13353163)
   478a -> 486a  :     0.035228 (c=  0.18769188)
   480a -> 486a  :     0.626016 (c= -0.79121191)
   481a -> 487a  :     0.062664 (c= -0.25032736)
   482a -> 488a  :     0.047024 (c=  0.21684936)
   483a -> 490a  :     0.053552 (c=  0.23141219)
   484a -> 498a  :     0.014312 (c=  0.11963187)
   484a -> 499a  :     0.035970 (c= -0.18965629)

STATE 28:  E=   0.113867 au      3.098 eV    24990.9 cm**-1 <S**2> =   0.000000 Mult 1
   476a -> 485a  :     0.010311 (c= -0.10154497)
   481a -> 487a  :     0.024340 (c= -0.15601169)
   481a -> 488a  :     0.032043 (c=  0.17900449)
   482a -> 486a  :     0.050979 (c= -0.22578589)
   482a -> 487a  :     0.143173 (c=  0.37838205)
   482a -> 488a  :     0.549474 (c=  0.74126544)
   483a -> 487a  :     0.013435 (c=  0.11591105)
   483a -> 488a  :     0.010811 (c=  0.10397652)
   483a -> 490a  :     0.020595 (c= -0.14350884)
   484a -> 498a  :     0.068643 (c= -0.26199777)
   484a -> 499a  :     0.011043 (c=  0.10508398)

STATE 29:  E=   0.113988 au      3.102 eV    25017.4 cm**-1 <S**2> =   0.000000 Mult 1
   480a -> 486a  :     0.012348 (c= -0.11112229)
   482a -> 487a  :     0.011483 (c= -0.10715993)
   482a -> 488a  :     0.018875 (c= -0.13738799)
   483a -> 490a  :     0.014875 (c=  0.12196241)
   484a -> 498a  :     0.885651 (c= -0.94109021)

STATE 30:  E=   0.114486 au      3.115 eV    25126.7 cm**-1 <S**2> =   0.000000 Mult 1
   477a -> 485a  :     0.019038 (c=  0.13797865)
   479a -> 488a  :     0.010742 (c= -0.10364192)
   481a -> 486a  :     0.047410 (c=  0.21773753)
   481a -> 487a  :     0.175534 (c= -0.41896768)
   481a -> 488a  :     0.406791 (c= -0.63780194)
   481a -> 490a  :     0.014903 (c= -0.12207693)
```

483a -> 488a : 0.024067 (c= 0.15513618)
483a -> 490a : 0.125329 (c= -0.35401785)
484a -> 499a : 0.100853 (c= 0.31757387)
484a -> 500a : 0.011222 (c= 0.10593584)

STATE 31: E= 0.115209 au 3.135 eV 25285.5 cm**-1 <S**2> = 0.000000 Mult 1
482a -> 488a : 0.012558 (c= -0.11206414)
483a -> 490a : 0.416936 (c= -0.64570581)
484a -> 499a : 0.491911 (c= -0.70136393)

STATE 32: E= 0.115611 au 3.146 eV 25373.7 cm**-1 <S**2> = 0.000000 Mult 1
477a -> 485a : 0.018693 (c= -0.13672171)
478a -> 486a : 0.015365 (c= -0.12395390)
480a -> 486a : 0.079992 (c= 0.28282807)
481a -> 487a : 0.025505 (c= -0.15970252)
481a -> 488a : 0.193381 (c= -0.43975062)
482a -> 488a : 0.019884 (c= 0.14100997)
483a -> 488a : 0.020183 (c= 0.14206658)
483a -> 490a : 0.220418 (c= 0.46948735)
484a -> 499a : 0.281493 (c= -0.53055939)
484a -> 500a : 0.034452 (c= -0.18561366)

STATE 33: E= 0.117439 au 3.196 eV 25774.9 cm**-1 <S**2> = 0.000000 Mult 1
477a -> 485a : 0.369714 (c= 0.60804104)
478a -> 486a : 0.024279 (c= -0.15581818)
480a -> 487a : 0.183186 (c= 0.42800280)
480a -> 488a : 0.054160 (c= -0.23272298)
482a -> 486a : 0.010341 (c= 0.10169096)
482a -> 490a : 0.212275 (c= -0.46073300)
483a -> 490a : 0.038222 (c= 0.19550498)

STATE 34: E= 0.117917 au 3.209 eV 25879.9 cm**-1 <S**2> = 0.000000 Mult 1
477a -> 485a : 0.041106 (c= -0.20274635)
480a -> 487a : 0.082419 (c= 0.28708627)
483a -> 491a : 0.011920 (c= 0.10917860)
484a -> 500a : 0.704107 (c= 0.83911096)
484a -> 501a : 0.014406 (c= 0.12002599)
484a -> 502a : 0.029724 (c= -0.17240747)

STATE 35: E= 0.118524 au 3.225 eV 26013.0 cm**-1 <S**2> = 0.000000 Mult 1
477a -> 485a : 0.017004 (c= 0.13040041)
479a -> 486a : 0.011984 (c= -0.10946923)
480a -> 487a : 0.124580 (c= -0.35295941)
480a -> 488a : 0.014542 (c= 0.12058929)
483a -> 489a : 0.704153 (c= 0.83913827)
483a -> 491a : 0.011553 (c= 0.10748429)
484a -> 501a : 0.046993 (c= 0.21677874)
484a -> 502a : 0.013419 (c= -0.11583984)

STATE 36: E= 0.118572 au 3.226 eV 26023.5 cm**-1 <S**2> = 0.000000 Mult 1
476a -> 485a : 0.011479 (c= -0.10713847)
477a -> 485a : 0.036471 (c= 0.19097290)
479a -> 486a : 0.043200 (c= -0.20784570)
480a -> 487a : 0.240251 (c= -0.49015387)
480a -> 488a : 0.026106 (c= 0.16157346)
482a -> 490a : 0.033951 (c= -0.18425787)
483a -> 489a : 0.257326 (c= -0.50727316)
484a -> 499a : 0.016384 (c= -0.12799915)
484a -> 500a : 0.023161 (c= 0.15218878)
484a -> 501a : 0.180962 (c= 0.42539640)
484a -> 502a : 0.054691 (c= -0.23386066)

```
STATE 37:  E=   0.119102 au      3.241 eV    26139.8 cm**-1 <S**2> =   0.000000 Mult 1
   478a -> 486a  :     0.032191 (c= -0.17941896)
   479a -> 486a  :     0.574423 (c=  0.75790707)
   479a -> 488a  :     0.062411 (c=  0.24982278)
   480a -> 486a  :     0.022538 (c= -0.15012731)
   480a -> 487a  :     0.080563 (c= -0.28383552)
   480a -> 488a  :     0.058791 (c=  0.24246868)
   481a -> 486a  :     0.013014 (c= -0.11407868)
   483a -> 491a  :     0.021139 (c=  0.14539269)
   484a -> 501a  :     0.041034 (c= -0.20256812)

STATE 38:  E=   0.119553 au      3.253 eV    26238.9 cm**-1 <S**2> =   0.000000 Mult 1
   477a -> 485a  :     0.155397 (c= -0.39420472)
   479a -> 486a  :     0.030434 (c=  0.17445382)
   480a -> 486a  :     0.013325 (c= -0.11543578)
   480a -> 487a  :     0.016506 (c=  0.12847449)
   480a -> 488a  :     0.023272 (c=  0.15255081)
   481a -> 491a  :     0.013301 (c= -0.11533051)
   482a -> 490a  :     0.284429 (c= -0.53331926)
   482a -> 491a  :     0.023940 (c=  0.15472413)
   483a -> 491a  :     0.306767 (c= -0.55386564)
   484a -> 501a  :     0.063293 (c=  0.25158181)

STATE 39:  E=   0.119719 au      3.258 eV    26275.2 cm**-1 <S**2> =   0.000000 Mult 1
   476a -> 485a  :     0.018169 (c=  0.13479115)
   479a -> 486a  :     0.053771 (c=  0.23188614)
   480a -> 487a  :     0.044750 (c=  0.21154282)
   482a -> 490a  :     0.123628 (c=  0.35160818)
   483a -> 491a  :     0.019318 (c=  0.13898909)
   484a -> 500a  :     0.028793 (c= -0.16968563)
   484a -> 501a  :     0.577201 (c=  0.75973731)
   484a -> 502a  :     0.048012 (c=  0.21911527)
   484a -> 503a  :     0.026335 (c= -0.16227938)

STATE 40:  E=   0.119967 au      3.264 eV    26329.7 cm**-1 <S**2> =   0.000000 Mult 1
   476a -> 485a  :     0.079655 (c=  0.28223203)
   477a -> 485a  :     0.153660 (c= -0.39199503)
   478a -> 486a  :     0.019544 (c=  0.13980028)
   480a -> 488a  :     0.032746 (c= -0.18095938)
   481a -> 491a  :     0.029467 (c=  0.17165928)
   482a -> 490a  :     0.178502 (c= -0.42249497)
   483a -> 491a  :     0.415977 (c=  0.64496315)
   484a -> 500a  :     0.013819 (c= -0.11755508)

STATE 41:  E=   0.120215 au      3.271 eV    26384.1 cm**-1 <S**2> =   0.000000 Mult 1
   476a -> 485a  :     0.195989 (c= -0.44270610)
   479a -> 486a  :     0.036036 (c= -0.18983237)
   480a -> 486a  :     0.028806 (c= -0.16972396)
   480a -> 487a  :     0.084948 (c=  0.29145877)
   480a -> 488a  :     0.421777 (c=  0.64944362)
   482a -> 490a  :     0.015207 (c= -0.12331754)
   482a -> 491a  :     0.011534 (c= -0.10739518)
   483a -> 491a  :     0.068055 (c=  0.26087334)
   484a -> 502a  :     0.015988 (c=  0.12644474)

STATE 42:  E=   0.121047 au      3.294 eV    26566.8 cm**-1 <S**2> =   0.000000 Mult 1
   481a -> 488a  :     0.020188 (c= -0.14208345)
   481a -> 490a  :     0.651140 (c=  0.80693234)
   481a -> 491a  :     0.019448 (c= -0.13945661)
   482a -> 490a  :     0.015436 (c= -0.12424051)
```

```
  483a -> 492a  :     0.011028 (c=  0.10501197)
  484a -> 502a  :     0.193295 (c=  0.43965330)

STATE 43:  E=   0.121532 au      3.307 eV    26673.1 cm**-1 <S**2> =   0.000000 Mult 1
  476a -> 485a  :     0.132456 (c= -0.36394442)
  478a -> 486a  :     0.021450 (c=  0.14645799)
  480a -> 487a  :     0.033720 (c= -0.18363009)
  480a -> 488a  :     0.060832 (c= -0.24664080)
  481a -> 490a  :     0.180336 (c= -0.42466042)
  483a -> 492a  :     0.031564 (c=  0.17766356)
  484a -> 500a  :     0.027584 (c=  0.16608314)
  484a -> 502a  :     0.367841 (c=  0.60649882)
  484a -> 504a  :     0.014608 (c=  0.12086509)

STATE 44:  E=   0.122244 au      3.326 eV    26829.6 cm**-1 <S**2> =   0.000000 Mult 1
  476a -> 485a  :     0.200331 (c=  0.44758312)
  478a -> 486a  :     0.188309 (c= -0.43394585)
  478a -> 488a  :     0.037582 (c= -0.19386061)
  479a -> 486a  :     0.036941 (c= -0.19220011)
  479a -> 487a  :     0.025989 (c=  0.16121163)
  480a -> 488a  :     0.057162 (c=  0.23908659)
  483a -> 492a  :     0.081162 (c=  0.28488879)
  484a -> 502a  :     0.108077 (c=  0.32875114)
  484a -> 503a  :     0.081795 (c=  0.28599770)
  484a -> 504a  :     0.079613 (c=  0.28215764)

STATE 45:  E=   0.122361 au      3.330 eV    26855.2 cm**-1 <S**2> =   0.000000 Mult 1
  478a -> 486a  :     0.014967 (c=  0.12233885)
  481a -> 492a  :     0.063208 (c=  0.25141173)
  482a -> 492a  :     0.012536 (c= -0.11196440)
  483a -> 491a  :     0.019861 (c= -0.14092921)
  483a -> 492a  :     0.665023 (c=  0.81548950)
  484a -> 502a  :     0.066150 (c= -0.25719578)
  484a -> 504a  :     0.079128 (c= -0.28129630)
  484a -> 506a  :     0.021232 (c= -0.14571312)

STATE 46:  E=   0.122650 au      3.337 eV    26918.5 cm**-1 <S**2> =   0.000000 Mult 1
  482a -> 489a  :     0.959512 (c= -0.97954704)
  482a -> 491a  :     0.014318 (c= -0.11965719)

STATE 47:  E=   0.123148 au      3.351 eV    27027.9 cm**-1 <S**2> =   0.000000 Mult 1
  478a -> 486a  :     0.010364 (c= -0.10180601)
  483a -> 492a  :     0.015776 (c=  0.12560157)
  484a -> 503a  :     0.392305 (c= -0.62634295)
  484a -> 504a  :     0.072464 (c=  0.26919227)
  484a -> 505a  :     0.449760 (c=  0.67064171)

STATE 48:  E=   0.123375 au      3.357 eV    27077.7 cm**-1 <S**2> =   0.000000 Mult 1
  478a -> 486a  :     0.031658 (c= -0.17792642)
  482a -> 491a  :     0.109649 (c=  0.33113333)
  484a -> 502a  :     0.017379 (c= -0.13183049)
  484a -> 503a  :     0.242166 (c= -0.49210350)
  484a -> 504a  :     0.085641 (c=  0.29264415)
  484a -> 505a  :     0.417829 (c= -0.64639681)
  484a -> 506a  :     0.014077 (c=  0.11864838)
  484a -> 507a  :     0.011758 (c= -0.10843491)

STATE 49:  E=   0.123447 au      3.359 eV    27093.4 cm**-1 <S**2> =   0.000000 Mult 1
  479a -> 487a  :     0.015135 (c=  0.12302315)
  481a -> 491a  :     0.033108 (c=  0.18195589)
  482a -> 489a  :     0.011847 (c=  0.10884479)
```

482a -> 490a : 0.010034 (c= -0.10017069)
482a -> 491a : 0.705668 (c= -0.84004067)
483a -> 491a : 0.028209 (c= -0.16795465)
484a -> 503a : 0.062666 (c= -0.25033105)
484a -> 504a : 0.029325 (c= 0.17124398)
484a -> 505a : 0.046656 (c= -0.21600026)

STATE 50: E= 0.123909 au 3.372 eV 27194.8 cm**-1 <S**2> = 0.000000 Mult 1
476a -> 485a : 0.021548 (c= 0.14679366)
479a -> 487a : 0.049284 (c= -0.22199950)
479a -> 491a : 0.013091 (c= -0.11441553)
481a -> 489a : 0.079588 (c= -0.28211309)
481a -> 490a : 0.041300 (c= -0.20322438)
481a -> 491a : 0.429368 (c= -0.65526198)
481a -> 492a : 0.032713 (c= -0.18086600)
482a -> 491a : 0.042209 (c= -0.20544924)
483a -> 491a : 0.019750 (c= 0.14053535)
484a -> 503a : 0.019501 (c= -0.13964580)
484a -> 504a : 0.149406 (c= -0.38653011)
484a -> 505a : 0.014360 (c= -0.11983189)
484a -> 506a : 0.010151 (c= -0.10075393)

STATE 51: E= 0.124431 au 3.386 eV 27309.5 cm**-1 <S**2> = 0.000000 Mult 1
478a -> 486a : 0.099187 (c= 0.31493960)
479a -> 486a : 0.020437 (c= 0.14295721)
480a -> 487a : 0.016926 (c= 0.13010181)
481a -> 489a : 0.336210 (c= -0.57983658)
481a -> 490a : 0.018743 (c= 0.13690457)
481a -> 491a : 0.069777 (c= -0.26415307)
482a -> 490a : 0.010184 (c= 0.10091588)
483a -> 492a : 0.018119 (c= 0.13460528)
484a -> 502a : 0.014298 (c= -0.11957329)
484a -> 503a : 0.043971 (c= 0.20969232)
484a -> 504a : 0.244002 (c= 0.49396532)

STATE 52: E= 0.124562 au 3.390 eV 27338.3 cm**-1 <S**2> = 0.000000 Mult 1
478a -> 486a : 0.033139 (c= -0.18204083)
479a -> 487a : 0.035244 (c= 0.18773277)
481a -> 489a : 0.560084 (c= -0.74838751)
481a -> 491a : 0.190659 (c= 0.43664537)
484a -> 503a : 0.014996 (c= -0.12245856)
484a -> 504a : 0.071684 (c= -0.26773816)

STATE 53: E= 0.124785 au 3.396 eV 27387.1 cm**-1 <S**2> = 0.000000 Mult 1
476a -> 485a : 0.015738 (c= 0.12545104)
478a -> 487a : 0.027047 (c= 0.16446032)
478a -> 488a : 0.010407 (c= -0.10201449)
479a -> 486a : 0.016303 (c= -0.12768234)
479a -> 487a : 0.606609 (c= -0.77885095)
479a -> 488a : 0.077482 (c= 0.27835620)
480a -> 490a : 0.048564 (c= 0.22037165)
481a -> 491a : 0.057191 (c= 0.23914638)
481a -> 492a : 0.018821 (c= 0.13719022)
482a -> 491a : 0.015712 (c= -0.12534913)
484a -> 503a : 0.011119 (c= 0.10544687)

STATE 54: E= 0.125776 au 3.423 eV 27604.7 cm**-1 <S**2> = 0.000000 Mult 1
476a -> 485a : 0.011845 (c= -0.10883584)
478a -> 486a : 0.013736 (c= -0.11720241)
478a -> 487a : 0.011239 (c= 0.10601607)
479a -> 487a : 0.017324 (c= 0.13162024)

```
   480a -> 488a  :     0.015865 (c= -0.12595615)
   480a -> 490a  :     0.152898 (c=  0.39102135)
   482a -> 492a  :     0.679132 (c=  0.82409486)
   482a -> 493a  :     0.014459 (c= -0.12024649)
   484a -> 504a  :     0.014633 (c= -0.12096811)

STATE 55:  E=   0.126139 au      3.432 eV    27684.4 cm**-1 <S**2> =   0.000000 Mult 1
   476a -> 485a  :     0.017151 (c= -0.13096068)
   478a -> 486a  :     0.075979 (c= -0.27564232)
   478a -> 487a  :     0.036169 (c=  0.19018249)
   479a -> 486a  :     0.019801 (c=  0.14071479)
   479a -> 488a  :     0.190799 (c= -0.43680489)
   480a -> 486a  :     0.011277 (c= -0.10619410)
   480a -> 488a  :     0.031848 (c= -0.17845886)
   480a -> 490a  :     0.255035 (c=  0.50500966)
   481a -> 491a  :     0.017357 (c= -0.13174477)
   481a -> 492a  :     0.020202 (c=  0.14213435)
   482a -> 492a  :     0.153654 (c= -0.39198713)
   482a -> 493a  :     0.017850 (c=  0.13360426)
   484a -> 506a  :     0.019417 (c=  0.13934652)

STATE 56:  E=   0.126337 au      3.438 eV    27727.7 cm**-1 <S**2> =   0.000000 Mult 1
   479a -> 487a  :     0.013209 (c= -0.11493180)
   479a -> 488a  :     0.025968 (c= -0.16114538)
   480a -> 490a  :     0.012934 (c= -0.11372781)
   481a -> 492a  :     0.047755 (c=  0.21852810)
   481a -> 493a  :     0.015792 (c=  0.12566721)
   482a -> 492a  :     0.010307 (c=  0.10152367)
   483a -> 493a  :     0.664723 (c=  0.81530527)
   484a -> 504a  :     0.021292 (c= -0.14591885)
   484a -> 506a  :     0.118456 (c=  0.34417490)
   484a -> 507a  :     0.016738 (c= -0.12937686)

STATE 57:  E=   0.126576 au      3.444 eV    27780.3 cm**-1 <S**2> =   0.000000 Mult 1
   478a -> 486a  :     0.012878 (c= -0.11348086)
   478a -> 487a  :     0.010420 (c=  0.10207793)
   479a -> 487a  :     0.034615 (c= -0.18605075)
   479a -> 488a  :     0.034599 (c= -0.18600930)
   480a -> 490a  :     0.246064 (c= -0.49604845)
   481a -> 492a  :     0.080164 (c=  0.28313171)
   481a -> 493a  :     0.019237 (c= -0.13869592)
   482a -> 492a  :     0.024741 (c=  0.15729428)
   483a -> 493a  :     0.218855 (c= -0.46781897)
   484a -> 504a  :     0.029871 (c= -0.17283097)
   484a -> 506a  :     0.210921 (c=  0.45926118)
   484a -> 507a  :     0.023494 (c= -0.15327807)

STATE 58:  E=   0.126864 au      3.452 eV    27843.4 cm**-1 <S**2> =   0.000000 Mult 1
   478a -> 486a  :     0.064337 (c=  0.25364740)
   478a -> 488a  :     0.032196 (c= -0.17943154)
   479a -> 486a  :     0.015015 (c= -0.12253507)
   479a -> 487a  :     0.055099 (c=  0.23473206)
   479a -> 488a  :     0.275387 (c=  0.52477301)
   480a -> 490a  :     0.080212 (c=  0.28321757)
   481a -> 492a  :     0.014902 (c=  0.12207192)
   482a -> 492a  :     0.037576 (c= -0.19384523)
   484a -> 504a  :     0.025881 (c= -0.16087466)
   484a -> 506a  :     0.283671 (c=  0.53260815)
   484a -> 507a  :     0.020322 (c= -0.14255651)

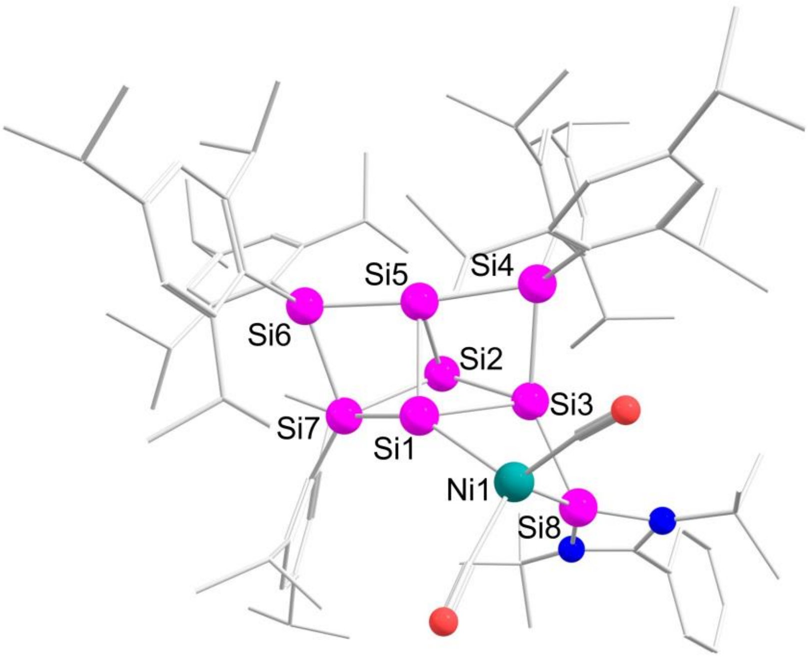
STATE 59:  E=   0.126979 au      3.455 eV    27868.8 cm**-1 <S**2> =   0.000000 Mult 1
```

```
   478a -> 487a  :     0.029339 (c=  0.17128772)
   479a -> 487a  :     0.018317 (c= -0.13534177)
   479a -> 488a  :     0.019024 (c= -0.13792859)
   479a -> 492a  :     0.015500 (c= -0.12449912)
   481a -> 491a  :     0.030330 (c=  0.17415643)
   481a -> 492a  :     0.633339 (c= -0.79582623)
   483a -> 492a  :     0.070536 (c=  0.26558585)
   484a -> 506a  :     0.116209 (c=  0.34089393)

 STATE 60:  E=   0.127855 au      3.479 eV    28060.9 cm**-1 <S**2> =   0.000000 Mult 1
   476a -> 485a  :     0.028151 (c= -0.16778264)
   478a -> 486a  :     0.093655 (c= -0.30603183)
   478a -> 487a  :     0.487824 (c= -0.69844416)
   478a -> 488a  :     0.072614 (c=  0.26946983)
   479a -> 486a  :     0.012500 (c= -0.11180271)
   479a -> 488a  :     0.048297 (c=  0.21976620)
   480a -> 491a  :     0.049260 (c=  0.22194649)
   483a -> 492a  :     0.012200 (c=  0.11045360)
   483a -> 494a  :     0.015290 (c=  0.12365331)
   484a -> 506a  :     0.025478 (c=  0.15961977)
```

4.4 Ni(CO)$_2$ siliconoid/silylene 3c

4.4.1 Optimization and molecular orbitals



Supplementary Figure S56. Calculated structure of Ni(CO)$_2$ siliconoid/silylene **3c** at the B3LYP/def2-TZVP level of theory.[23–29] Hydrogen atoms are omitted for clarity.

Supplementary Table S18. Coordinates of Ni(CO)$_2$) siliconoid/silylene **3c** at the B3LYP/def2-TZVP level of theory.[23–29]

Ni	9.710638	16.765035	10.0919
Si	8.737086	15.609136	8.302706
Si	7.279631	16.049883	10.225285
Si	8.10697	18.073091	10.948841
C	10.344276	15.785786	11.468736

C	11.038791	17.681304	9.302116
Si	6.065646	15.60913	8.246405
Si	7.389753	13.689203	8.396245
Si	7.47064	15.83611	6.38638
Si	7.146311	13.710909	10.7459
N	6.985322	19.465753	10.500391
N	7.43699	18.816725	12.4863
C	6.728644	19.713221	11.787349
O	10.758063	15.271994	12.401638
O	11.911261	18.288857	8.88341
Si	7.486771	13.43487	6.059948
C	7.091108	17.284233	5.217181
C	8.396826	12.890338	11.930234
C	5.386155	13.042899	11.099703
C	6.360002	19.981936	9.267294
C	7.665697	18.659945	13.930712
C	5.806098	20.731459	12.33464
C	8.938804	12.302838	5.522588
C	5.996822	13.123336	4.91776
C	5.742214	17.599085	4.925428
C	8.090344	18.196448	4.831612
C	9.573819	12.246047	11.480077
C	8.051564	12.759024	13.294148
C	4.247134	13.826385	11.400532
C	5.20057	11.649127	10.952212
C	4.921824	19.464938	9.15627
C	7.191046	19.438697	8.107517
C	6.385311	21.513639	9.219724
C	8.856605	17.70998	14.065549
C	6.428943	18.031249	14.581385
C	8.008098	19.992991	14.603954
C	4.501844	20.363871	12.657741
C	6.220174	22.046911	12.530091
C	8.713027	10.905427	5.421294
C	10.249795	12.766069	5.290182
C	4.722722	12.665288	5.317836
C	6.212386	13.392547	3.547248
C	5.432264	18.837266	4.37596
C	4.590265	16.633766	5.151015
C	7.729983	19.42797	4.289073
C	9.568544	17.89635	4.983858
C	10.272078	11.411928	12.348085
C	10.142939	12.416808	10.07964
C	8.794225	11.929279	14.126619
C	6.908116	13.526628	13.939111
C	2.993153	13.226071	11.471966
C	4.278042	15.317244	11.705409

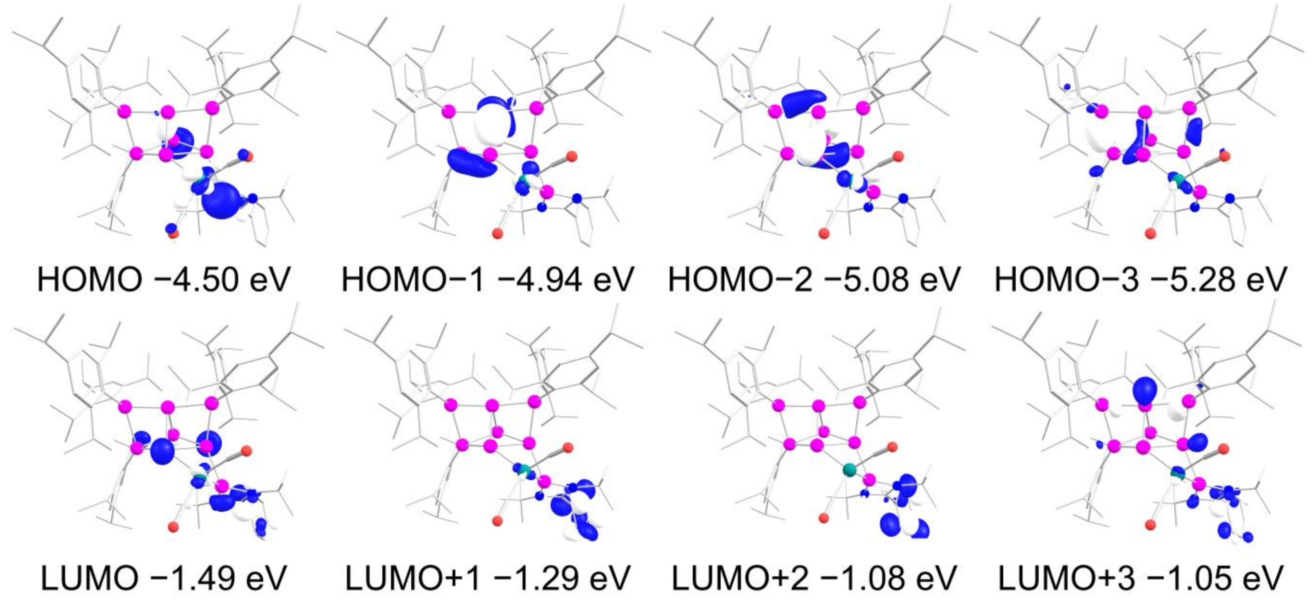
C	3.927467	11.094873	11.045118
C	6.34772	10.682337	10.718056
H	4.491491	19.771433	8.201985
H	4.295752	19.86372	9.954589
H	4.906438	18.37675	9.203603
H	6.761081	19.746384	7.155567
H	7.213838	18.349976	8.121978
H	8.215035	19.806559	8.161102
H	6.067979	21.843045	8.229262
H	7.395963	21.885931	9.394869
H	5.71504	21.960398	9.950623
H	8.659918	16.7709	13.55122
H	9.042348	17.486929	15.115849
H	9.757686	18.148456	13.636799
H	5.570318	18.698736	14.518969
H	6.621213	17.822274	15.634826
H	6.178377	17.095596	14.085161
H	8.829648	20.48683	14.082419
H	8.320929	19.806896	15.632541
H	7.155263	20.667652	14.631449
H	4.179533	19.343196	12.500912
C	3.618554	21.305255	13.169627
C	5.337809	22.984816	13.045978
H	7.233138	22.331765	12.279612
C	9.76091	10.052009	5.097149
C	7.357658	10.250413	5.643937
C	11.275332	11.864456	5.009292
C	10.638367	14.230511	5.302699
C	3.731229	12.472752	4.360668
C	4.356698	12.353857	6.761034
C	5.19623	13.158938	2.625987
C	7.539913	13.901974	3.000945
H	4.394627	19.070301	4.174413
C	6.406952	19.781454	4.078174
H	4.998967	15.702705	5.543031
C	3.578933	17.172257	6.167235
C	3.883108	16.285031	3.836124
H	8.502872	20.140122	4.026441
H	9.664107	16.846285	5.264128
C	10.203022	18.724296	6.101151
C	10.319349	18.09399	3.661923
H	11.155109	10.899973	11.98723
C	9.890435	11.216472	13.665997
H	9.686792	13.302811	9.644336
C	11.655875	12.670684	10.083662
C	9.81692	11.23075	9.163453
H	8.502621	11.832743	15.164804

H	6.487841	14.200957	13.191525
C	5.781886	12.611377	14.433808
C	7.423044	14.398861	15.09146
H	2.133524	13.848499	11.68407
C	2.802127	11.865772	11.282147
H	5.302319	15.6711	11.589761
C	3.865909	15.605514	13.155474
C	3.401644	16.127506	10.744868
H	3.808445	10.02487	10.9239
H	7.258784	11.256475	10.58241
C	6.166816	9.854849	9.449981
C	6.58633	9.774444	11.930398
H	2.605678	21.013515	13.414331
C	4.035542	22.616005	13.365506
H	5.666533	24.004628	13.197403
H	9.560445	8.993043	5.011378
C	11.058168	10.503646	4.902713
H	6.728602	10.950035	6.194161
C	7.458834	8.975252	6.490408
C	6.659706	9.922751	4.317185
H	12.279706	12.240439	4.857266
H	9.729008	14.812099	5.439779
C	11.56726	14.567432	6.471962
C	11.261329	14.660973	3.97023
H	2.758969	12.122188	4.682593
C	3.94836	12.694241	3.007815
H	5.261731	12.433883	7.363337
C	3.808253	10.932692	6.935835
C	3.358602	13.372015	7.323505
H	5.380846	13.345038	1.574587
H	8.19073	14.139492	3.84199
C	8.251927	12.826027	2.171925
C	7.391489	15.200548	2.199918
C	6.0429	21.151449	3.548514
H	3.113256	18.09157	5.805475
H	4.056168	17.384478	7.122705
H	2.786407	16.441261	6.338521
H	3.400187	17.161851	3.399367
H	3.115755	15.532184	4.019056
H	4.578021	15.877994	3.104771
H	11.260111	18.480256	6.214581
H	9.709352	18.529739	7.050538
H	10.12336	19.792853	5.888629
H	9.899025	17.471321	2.871169
H	11.373137	17.837351	3.779629
H	10.274777	19.132671	3.331493
C	10.658062	10.275104	14.567919

H	12.218535	11.779962	10.369911
H	11.925565	13.473339	10.768585
H	11.982952	12.951032	9.081528
H	10.205696	11.403443	8.158235
H	8.743282	11.070863	9.076747
H	10.261318	10.310695	9.551015
H	5.326454	12.057789	13.616289
H	4.998861	13.195697	14.921105
H	6.161077	11.894638	15.165095
H	8.266191	15.011306	14.777593
H	7.755293	13.785338	15.93051
H	6.631745	15.056429	15.456548
C	1.42288	11.244592	11.310981
H	3.900993	16.678837	13.35335
H	4.522465	15.108538	13.867348
H	2.847644	15.263774	13.349353
H	3.655246	15.915743	9.707285
H	3.54188	17.197201	10.915064
H	2.342965	15.904132	10.891413
H	6.093555	10.495176	8.572579
H	5.269791	9.234829	9.487748
H	7.020574	9.19191	9.315698
H	5.726838	9.124954	12.111436
H	7.459437	9.142548	11.755829
H	3.347753	23.349384	13.765804
C	12.190283	9.54979	4.591694
H	7.8894	8.151798	5.918724
H	6.466421	8.658706	6.813234
H	8.075475	9.130392	7.373696
H	6.513658	10.806524	3.703164
H	5.680408	9.476307	4.501422
H	7.256716	9.205032	3.749409
H	12.523639	14.048319	6.377941
H	11.119714	14.277893	7.422388
H	11.767496	15.640302	6.509513
H	10.573551	14.499599	3.139876
H	12.174372	14.103518	3.756438
H	11.52136	15.717337	3.995735
C	2.865826	12.439224	1.981107
H	2.861682	10.803486	6.408121
H	3.628805	10.731891	7.992805
H	4.503395	10.182607	6.55895
H	3.738517	14.387913	7.227954
H	3.178133	13.182691	8.382975
H	2.403243	13.31504	6.795519
H	7.643411	12.533463	1.313538
H	8.453007	11.936259	2.766113

H	9.20519	13.200927	1.794041
H	8.375303	15.561552	1.892033
H	6.920408	15.982727	2.79248
H	6.798373	15.049327	1.296294
H	6.980572	21.66282	3.310252
C	5.322206	21.97712	4.623036
C	5.213158	21.076514	2.262054
H	11.475282	9.857505	13.971979
C	11.280865	11.009647	15.761094
C	9.77684	9.109922	15.035118
H	1.558761	10.161921	11.226921
C	0.689389	11.520425	12.627929
C	0.589969	11.704152	10.106938
H	13.099	10.151946	4.494765
C	12.412602	8.550304	5.733748
C	11.966599	8.824767	3.259281
H	3.299647	12.655943	1.000036
C	2.426033	10.970228	1.980079
C	1.66671	13.37499	2.174029
H	5.104995	22.984148	4.259629
H	5.932512	22.062559	5.523945
H	4.376169	21.508218	4.902796
H	5.024702	22.077293	1.867154
H	4.245814	20.603598	2.443037
H	5.730112	20.496709	1.49586
H	11.878821	10.324203	16.366065
H	11.924274	11.825068	15.426975
H	10.509001	11.43611	16.405529
H	9.354354	8.572104	14.184851
H	10.354759	8.404244	15.636332
H	8.946679	9.469999	15.646785
H	0.496913	12.587678	12.756826
H	1.276809	11.181292	13.482756
H	-0.273832	11.005673	12.646781
H	1.099048	11.479102	9.168648
H	0.419577	12.782583	10.141363
H	-0.383955	11.209251	10.098114
H	11.540273	7.906475	5.864848
H	12.589316	9.067751	6.678037
H	13.272844	7.910166	5.525061
H	11.833253	9.536865	2.44326
H	11.075124	8.195204	3.301654
H	1.698851	10.78494	1.186205
H	1.959727	10.699436	2.929829
H	3.279132	10.307235	1.827531
H	1.973254	14.420597	2.126177
H	1.191819	13.210393	3.144003

H	0.914379	13.20248	1.400872
H	12.817618	8.182814	3.02044
H	6.771224	10.356192	12.830232



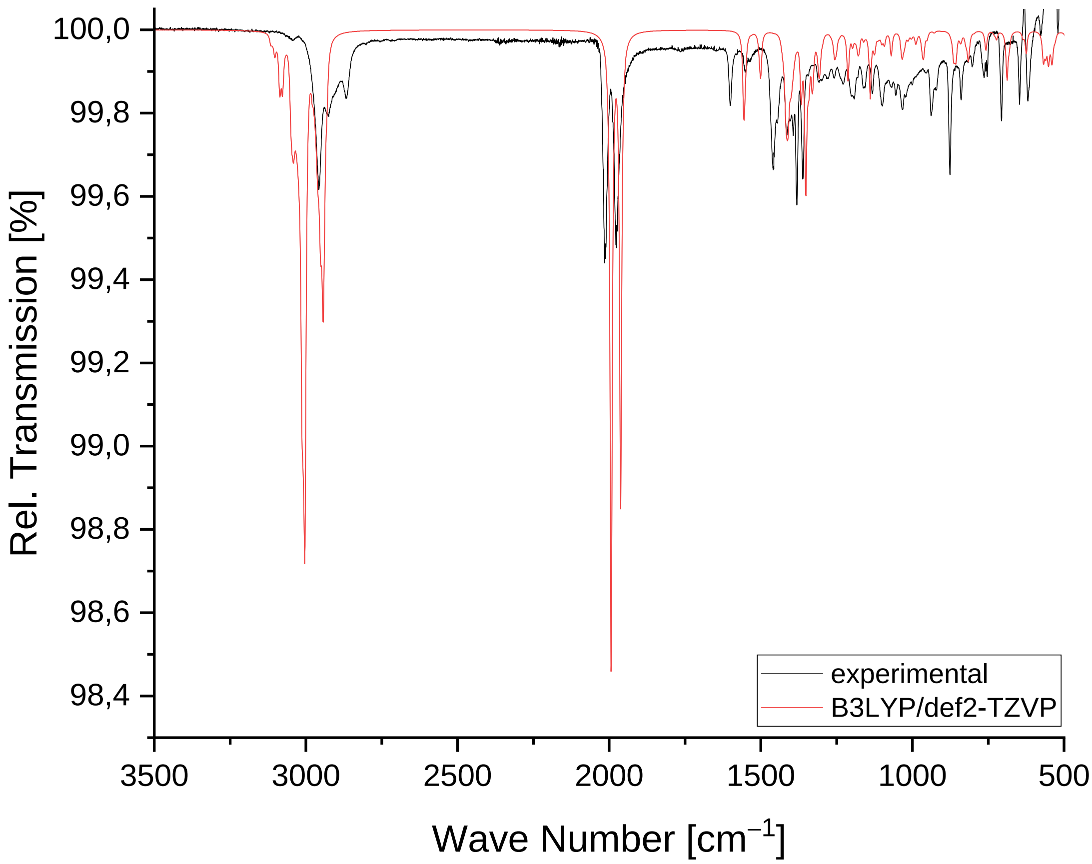
Supplementary Figure S57. Selected frontier orbitals of $Ni(CO)_2$ siliconoid/silylene **3c** at B3LYP/def2-TZVP level of theory (contour value 0.05).[23–29] Hydrogen atoms are omitted for clarity.

4.4.2 Experimental vs. calculated NMR shifts

Supplementary Table S19. Comparison of experimental vs. calculated NMR chemical shifts for compound $Ni(CO)_2$ siliconoid/silylene **3c** at the TPSSh/def2-TZVP level of theory.[26–29,33]

	Exp. **3c** $\delta(^{29}Si)$ [ppm]	Calc. **3c** $\delta(^{29}Si)$ [ppm]
Si3 (*Si*NHSi)	−4.0	−7.0
Si8 (NH*Si*)	96.5	93.1
Si7 (*Si*Tip)	70.9	80.1
Si6 (*Si*Tip_2)	44.6	37.1
Si4 (*Si*Tip_2)	−10.1	−11.6
Si5 (unsubstituted)	−81.9	−78.5
Si1 (*Si*Ni)	−160.5	−160.9
Si2 (unsubstituted)	−342.2	−354.4

4.4.3 Experimental vs. calculated FT-IR shifts



Supplementary Figure S58. Experimental vs. theoretical FT-IR spectrum of $Ni(CO)_2$ siliconoid/silylene **3c** at the B3LYP/def2-TZVP level of theory.[23–29]

4.4.4 TD-DFT calculations

Supplementary Table S20. Transition Energy. wavelength. and oscillator strengths of the electronic transition of $Ni(CO)_2$ siliconoid/silylene **3c** calculated at the TD-TPSSh/def2-TZVP level of theory.[26–29,33,34] (the 429th orbital is the highest occupied orbital (HOMO). the 430th orbital is the lowest unoccupied orbital (LUMO) shown in Supplementary Figure S57).

```
STATE  1:  E=   0.090101 au      2.452 eV    19775.0 cm**-1 <S**2> =   0.000000 Mult 1
   427a -> 430a  :     0.015750 (c=  0.12549942)
   428a -> 430a  :     0.048770 (c=  0.22083919)
   429a -> 430a  :     0.784327 (c= -0.88562242)
   429a -> 431a  :     0.031754 (c=  0.17819762)
   429a -> 432a  :     0.078200 (c=  0.27964340)

STATE  2:  E=   0.097680 au      2.658 eV    21438.2 cm**-1 <S**2> =   0.000000 Mult 1
   428a -> 430a  :     0.237174 (c= -0.48700512)
   429a -> 430a  :     0.012157 (c=  0.11025795)
   429a -> 431a  :     0.639359 (c=  0.79959910)
   429a -> 432a  :     0.079818 (c=  0.28252063)
   429a -> 435a  :     0.013073 (c=  0.11433638)

STATE  3:  E=   0.100007 au      2.721 eV    21949.1 cm**-1 <S**2> =   0.000000 Mult 1
```

427a -> 430a : 0.209767 (c= 0.45800339)
428a -> 430a : 0.360491 (c= -0.60040866)
429a -> 431a : 0.239800 (c= -0.48969426)
429a -> 432a : 0.154545 (c= 0.39312152)

STATE 4: E= 0.100737 au 2.741 eV 22109.3 cm**-1 <S**2> = 0.000000 Mult 1
427a -> 430a : 0.110944 (c= 0.33308251)
428a -> 430a : 0.110421 (c= -0.33229665)
429a -> 430a : 0.058475 (c= -0.24181590)
429a -> 431a : 0.019977 (c= 0.14134001)
429a -> 432a : 0.639126 (c= -0.79945385)

STATE 5: E= 0.104423 au 2.841 eV 22918.2 cm**-1 <S**2> = 0.000000 Mult 1
426a -> 430a : 0.030007 (c= 0.17322640)
427a -> 430a : 0.593019 (c= 0.77007731)
428a -> 430a : 0.198124 (c= 0.44511165)
429a -> 430a : 0.064628 (c= 0.25421991)
429a -> 431a : 0.041119 (c= 0.20277862)

STATE 6: E= 0.110528 au 3.008 eV 24258.1 cm**-1 <S**2> = 0.000000 Mult 1
425a -> 430a : 0.023527 (c= 0.15338594)
426a -> 430a : 0.012842 (c= -0.11332107)
429a -> 434a : 0.057400 (c= 0.23958281)
429a -> 435a : 0.814421 (c= -0.90245267)
429a -> 436a : 0.017847 (c= -0.13359448)
429a -> 437a : 0.021769 (c= -0.14754476)

STATE 7: E= 0.111102 au 3.023 eV 24384.2 cm**-1 <S**2> = 0.000000 Mult 1
429a -> 433a : 0.990609 (c= 0.99529333)

STATE 8: E= 0.111538 au 3.035 eV 24479.9 cm**-1 <S**2> = 0.000000 Mult 1
426a -> 430a : 0.809643 (c= -0.89980186)
427a -> 430a : 0.018324 (c= 0.13536519)
429a -> 434a : 0.125937 (c= -0.35487659)

STATE 9: E= 0.113061 au 3.077 eV 24814.0 cm**-1 <S**2> = 0.000000 Mult 1
426a -> 430a : 0.024360 (c= -0.15607536)
427a -> 432a : 0.012657 (c= 0.11250199)
428a -> 431a : 0.257348 (c= 0.50729493)
428a -> 432a : 0.542571 (c= 0.73659407)
429a -> 434a : 0.117140 (c= 0.34225763)

STATE 10: E= 0.114297 au 3.110 eV 25085.3 cm**-1 <S**2> = 0.000000 Mult 1
424a -> 430a : 0.046676 (c= 0.21604598)
426a -> 430a : 0.057089 (c= -0.23893230)
427a -> 432a : 0.020347 (c= -0.14264149)
428a -> 431a : 0.248398 (c= -0.49839585)
429a -> 434a : 0.495817 (c= 0.70414242)
429a -> 435a : 0.027301 (c= 0.16523091)
429a -> 436a : 0.029102 (c= 0.17059327)
429a -> 437a : 0.010409 (c= 0.10202426)

STATE 11: E= 0.116308 au 3.165 eV 25526.6 cm**-1 <S**2> = 0.000000 Mult 1
424a -> 430a : 0.021189 (c= 0.14556355)
427a -> 431a : 0.046627 (c= -0.21593401)
427a -> 432a : 0.049408 (c= -0.22228000)
428a -> 431a : 0.440742 (c= 0.66388367)
428a -> 432a : 0.309610 (c= -0.55642642)
429a -> 434a : 0.058994 (c= 0.24288693)
429a -> 436a : 0.024573 (c= 0.15675750)

STATE 12: E= 0.117162 au 3.188 eV 25714.0 cm**-1 <S**2> = 0.000000 Mult 1
424a -> 430a : 0.076921 (c= -0.27734714)
425a -> 430a : 0.780892 (c= -0.88368084)
426a -> 431a : 0.010011 (c= -0.10005595)
426a -> 432a : 0.024497 (c= -0.15651419)
429a -> 435a : 0.029589 (c= -0.17201533)

STATE 13: E= 0.118507 au 3.225 eV 26009.2 cm**-1 <S**2> = 0.000000 Mult 1
424a -> 430a : 0.041103 (c= 0.20273775)
427a -> 431a : 0.452221 (c= 0.67247391)
427a -> 432a : 0.211764 (c= 0.46017772)
427a -> 435a : 0.010976 (c= 0.10476627)
428a -> 431a : 0.011080 (c= 0.10526066)
428a -> 432a : 0.089000 (c= -0.29832934)
429a -> 434a : 0.020882 (c= 0.14450678)
429a -> 436a : 0.101090 (c= -0.31794588)

STATE 14: E= 0.118821 au 3.233 eV 26078.1 cm**-1 <S**2> = 0.000000 Mult 1
424a -> 430a : 0.018531 (c= -0.13612786)
425a -> 430a : 0.010808 (c= 0.10396080)
427a -> 431a : 0.044881 (c= 0.21185192)
427a -> 432a : 0.173892 (c= 0.41700420)
429a -> 435a : 0.022736 (c= -0.15078509)
429a -> 436a : 0.596047 (c= 0.77204060)
429a -> 437a : 0.084618 (c= 0.29089141)

STATE 15: E= 0.121014 au 3.293 eV 26559.6 cm**-1 <S**2> = 0.000000 Mult 1
426a -> 432a : 0.012976 (c= 0.11391224)
427a -> 431a : 0.387397 (c= -0.62241239)
427a -> 432a : 0.490025 (c= 0.70001779)
429a -> 434a : 0.014348 (c= 0.11978235)
429a -> 436a : 0.020824 (c= -0.14430524)

STATE 16: E= 0.123391 au 3.358 eV 27081.1 cm**-1 <S**2> = 0.000000 Mult 1
429a -> 435a : 0.010434 (c= 0.10214465)
429a -> 436a : 0.144017 (c= 0.37949551)
429a -> 437a : 0.800862 (c= -0.89490893)
429a -> 438a : 0.010854 (c= 0.10418214)

STATE 17: E= 0.124565 au 3.390 eV 27338.8 cm**-1 <S**2> = 0.000000 Mult 1
423a -> 430a : 0.032007 (c= -0.17890541)
424a -> 430a : 0.556050 (c= -0.74568792)
425a -> 430a : 0.058778 (c= 0.24244124)
426a -> 430a : 0.019458 (c= -0.13949257)
426a -> 431a : 0.015709 (c= 0.12533439)
428a -> 434a : 0.084428 (c= -0.29056576)
428a -> 435a : 0.015547 (c= 0.12468617)
429a -> 434a : 0.027014 (c= 0.16435838)
429a -> 437a : 0.013650 (c= -0.11683214)
429a -> 438a : 0.024323 (c= -0.15595771)
429a -> 439a : 0.023165 (c= 0.15220190)
429a -> 441a : 0.019387 (c= 0.13923822)

STATE 18: E= 0.126712 au 3.448 eV 27810.1 cm**-1 <S**2> = 0.000000 Mult 1
423a -> 430a : 0.016516 (c= -0.12851385)
424a -> 430a : 0.032402 (c= -0.18000692)
425a -> 430a : 0.011033 (c= 0.10503780)
426a -> 431a : 0.029344 (c= -0.17130213)
426a -> 432a : 0.235891 (c= -0.48568611)
428a -> 435a : 0.276639 (c= -0.52596457)
428a -> 436a : 0.014692 (c= -0.12121170)

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   429a -> 435a  :     0.010011 (c=  0.10005726)
   429a -> 436a  :     0.012309 (c= -0.11094489)
   429a -> 438a  :     0.198402 (c=  0.44542338)
   429a -> 439a  :     0.039682 (c= -0.19920437)
   429a -> 440a  :     0.055004 (c= -0.23452950)

STATE 19:  E=   0.127172 au      3.461 eV    27911.0 cm**-1 <S**2> =   0.000000 Mult 1
   426a -> 431a  :     0.080139 (c= -0.28308875)
   426a -> 432a  :     0.019770 (c= -0.14060567)
   428a -> 434a  :     0.096677 (c=  0.31092931)
   428a -> 435a  :     0.189089 (c= -0.43484398)
   429a -> 438a  :     0.186244 (c= -0.43155946)
   429a -> 439a  :     0.206047 (c=  0.45392391)
   429a -> 440a  :     0.152454 (c=  0.39045380)

STATE 20:  E=   0.127376 au      3.466 eV    27955.8 cm**-1 <S**2> =   0.000000 Mult 1
   425a -> 430a  :     0.013633 (c=  0.11676056)
   425a -> 432a  :     0.018016 (c=  0.13422186)
   426a -> 431a  :     0.133527 (c= -0.36541279)
   426a -> 432a  :     0.308418 (c= -0.55535366)
   428a -> 434a  :     0.036249 (c=  0.19039189)
   428a -> 435a  :     0.335390 (c=  0.57912853)
   429a -> 438a  :     0.054961 (c= -0.23443781)
   429a -> 439a  :     0.030222 (c= -0.17384456)

STATE 21:  E=   0.128235 au      3.489 eV    28144.2 cm**-1 <S**2> =   0.000000 Mult 1
   426a -> 431a  :     0.541675 (c= -0.73598580)
   426a -> 432a  :     0.094653 (c=  0.30765714)
   428a -> 434a  :     0.080061 (c= -0.28294998)
   428a -> 435a  :     0.013374 (c=  0.11564496)
   429a -> 438a  :     0.155080 (c=  0.39380201)
   429a -> 439a  :     0.023225 (c=  0.15239795)
   429a -> 440a  :     0.030784 (c=  0.17545397)

STATE 22:  E=   0.128614 au      3.500 eV    28227.6 cm**-1 <S**2> =   0.000000 Mult 1
   423a -> 430a  :     0.044680 (c= -0.21137712)
   424a -> 430a  :     0.030112 (c= -0.17352876)
   425a -> 432a  :     0.024803 (c= -0.15748834)
   426a -> 431a  :     0.055839 (c= -0.23630204)
   426a -> 432a  :     0.160569 (c=  0.40071084)
   428a -> 433a  :     0.283647 (c=  0.53258507)
   428a -> 434a  :     0.226242 (c=  0.47564949)
   429a -> 438a  :     0.010470 (c= -0.10232263)
   429a -> 439a  :     0.028887 (c= -0.16996264)
   429a -> 440a  :     0.073557 (c= -0.27121319)

STATE 23:  E=   0.128715 au      3.503 eV    28249.7 cm**-1 <S**2> =   0.000000 Mult 1
   423a -> 430a  :     0.010419 (c= -0.10207255)
   426a -> 431a  :     0.043884 (c= -0.20948513)
   426a -> 432a  :     0.060152 (c=  0.24525883)
   428a -> 433a  :     0.554358 (c= -0.74455231)
   428a -> 435a  :     0.016784 (c= -0.12955263)
   429a -> 438a  :     0.121766 (c= -0.34894962)
   429a -> 439a  :     0.064028 (c= -0.25303664)
   429a -> 440a  :     0.079944 (c= -0.28274450)

STATE 24:  E=   0.128866 au      3.507 eV    28282.8 cm**-1 <S**2> =   0.000000 Mult 1
   423a -> 430a  :     0.012124 (c= -0.11010981)
   425a -> 432a  :     0.011593 (c= -0.10767066)
   426a -> 431a  :     0.035505 (c=  0.18842748)
   428a -> 433a  :     0.153020 (c= -0.39117738)
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  428a -> 434a  :     0.351863 (c=  0.59318080)
  428a -> 435a  :     0.066762 (c=  0.25838391)
  429a -> 438a  :     0.198847 (c=  0.44592315)
  429a -> 439a  :     0.065849 (c=  0.25661154)
  429a -> 440a  :     0.023374 (c=  0.15288541)
  429a -> 441a  :     0.016692 (c=  0.12919858)

STATE 25:  E=   0.131415 au      3.576 eV    28842.2 cm**-1 <S**2> =   0.000000 Mult 1
  423a -> 430a  :     0.070095 (c= -0.26475510)
  427a -> 434a  :     0.158507 (c=  0.39812962)
  429a -> 439a  :     0.323882 (c= -0.56910619)
  429a -> 440a  :     0.355148 (c=  0.59594265)
  429a -> 441a  :     0.018214 (c=  0.13495777)

STATE 26:  E=   0.131733 au      3.585 eV    28912.0 cm**-1 <S**2> =   0.000000 Mult 1
  423a -> 430a  :     0.102057 (c= -0.31946304)
  425a -> 431a  :     0.340653 (c=  0.58365460)
  425a -> 432a  :     0.372997 (c=  0.61073484)
  427a -> 434a  :     0.010326 (c=  0.10161763)
  427a -> 435a  :     0.049020 (c=  0.22140487)
  429a -> 439a  :     0.024424 (c=  0.15628094)
  429a -> 440a  :     0.024360 (c= -0.15607833)

STATE 27:  E=   0.132096 au      3.595 eV    28991.6 cm**-1 <S**2> =   0.000000 Mult 1
  425a -> 431a  :     0.014395 (c= -0.11997896)
  427a -> 434a  :     0.131445 (c= -0.36255368)
  427a -> 435a  :     0.588147 (c=  0.76690734)
  429a -> 439a  :     0.014598 (c= -0.12082119)
  429a -> 440a  :     0.052391 (c=  0.22889003)
  429a -> 441a  :     0.116552 (c= -0.34139646)
  429a -> 442a  :     0.011698 (c=  0.10815822)

STATE 28:  E=   0.132420 au      3.603 eV    29062.8 cm**-1 <S**2> =   0.000000 Mult 1
  423a -> 430a  :     0.163145 (c=  0.40391183)
  425a -> 431a  :     0.013986 (c= -0.11826160)
  427a -> 433a  :     0.035675 (c=  0.18887794)
  427a -> 434a  :     0.373712 (c=  0.61132017)
  427a -> 435a  :     0.190185 (c=  0.43610186)
  428a -> 436a  :     0.032681 (c=  0.18077885)
  429a -> 440a  :     0.063246 (c= -0.25148792)
  429a -> 441a  :     0.042638 (c=  0.20648881)
  429a -> 443a  :     0.014796 (c=  0.12163722)

STATE 29:  E=   0.132787 au      3.613 eV    29143.4 cm**-1 <S**2> =   0.000000 Mult 1
  423a -> 430a  :     0.023922 (c= -0.15466785)
  427a -> 433a  :     0.893869 (c=  0.94544637)
  429a -> 441a  :     0.036091 (c= -0.18997575)

STATE 30:  E=   0.132922 au      3.617 eV    29173.1 cm**-1 <S**2> =   0.000000 Mult 1
  423a -> 430a  :     0.166163 (c= -0.40763113)
  425a -> 431a  :     0.016251 (c= -0.12748081)
  425a -> 432a  :     0.067881 (c= -0.26053947)
  427a -> 433a  :     0.063076 (c= -0.25115003)
  427a -> 434a  :     0.225408 (c=  0.47477108)
  428a -> 434a  :     0.014606 (c= -0.12085605)
  428a -> 436a  :     0.021298 (c= -0.14593800)
  429a -> 439a  :     0.098759 (c=  0.31425897)
  429a -> 441a  :     0.196369 (c= -0.44313530)
  429a -> 442a  :     0.030553 (c=  0.17479293)
  429a -> 443a  :     0.012506 (c= -0.11182809)
```

4.5 TD-DFT Overview

Supplementary Table S21. Extended comparison of wavelengths λ_{max}, oscillator strengths f, and excitation energy E from experimental and TD-DFT calculations at TD-TPSSh/def2-TZVP[26–29,33,34] for transition metal complexes **2**-**3c**.

	Experimental		Calculated			
	λ_{max} (nm)	Excitation energy E (eV)	λ_{max} (nm)	Excitation energy E (eV)	Oscillator strength f	Transitions (% contribution)
2	525	2.362	528	2.349	0.00277	HOMO→LUMO (98.6)
	342	3.625	355	3.493	0.0365	HOMO−15→LUMO (5.9) HOMO−14→LUMO (1.6) HOMO−13→LUMO (27.7) HOMO−12→LUMO (5.0) HOMO−11→LUMO (25.8) HOMO−10→LUMO (3.7) HOMO−7→LUMO (1.3) HOMO−5→LUMO+1 (1.2) HOMO−3→LUMO+1 (5.1) HOMO−2→LUMO+1 (7.5) HOMO→LUMO+2 (10.6)
			353	3.516	0.0282	HOMO−15→LUMO (6.1) HOMO−13→LUMO (68.9) HOMO−11→LUMO (10.6) HOMO−10→LUMO (1.8) HOMO−5→LUMO+1 (1.1) HOMO−3→LUMO+1 (1.1) HOMO−2→LUMO+1 (4.2) HOMO→LUMO+2 (1.3)

			350	3.516	0.0054	HOMO−4→LUMO+1 (54.5) HOMO−4→LUMO+2 (2.5) HOMO−4→LUMO+7 (1.5) HOMO−3→LUMO+1 (2.9) HOMO−1→LUMO+1 (1.7) HOMO−1→LUMO+2 (26.8) HOMO−1→LUMO+7 (1.3)
3a	538	2.305	546	2.269	0.0416	HOMO−2→LUMO (1.1) HOMO−1→LUMO (18.9) HOMO→LUMO (52.6) HOMO→LUMO+1 (19.0) HOMO→LUMO+2 (4.8)
			520	2.386	0.0145	HOMO−2→LUMO (3.5) HOMO−1→LUMO (72.6) HOMO→LUMO (5.3) HOMO→LUMO+1 (13.6)
			516	2.402	0.0822	HOMO−2→LUMO (2.2) HOMO−1→LUMO (2.3) HOMO→LUMO (23.7) HOMO→LUMO+1 (65.4) HOMO→LUMO+2 (3.0)
			402	3.085	0.0108	HOMO−5→LUMO (2.1) HOMO−4→LUMO (5.5) HOMO−3→LUMO (1.3) HOMO−3→LUMO+1 (74.6) HOMO−3→LUMO+2 (6.7) HOMO−3→LUMO+4 (1.5) HOMO−1→LUMO+4 (2.9)

	392	3.163	399	3.105	0.0111	HOMO−5→LUMO (2.3) HOMO−4→LUMO (2.0) HOMO−1→LUMO+4 (7.1) HOMO→LUMO+6 (83.3) HOMO→LUMO+7 (1.0)
			395	3.136	0.0145	HOMO−5→LUMO (9.0) HOMO−4→LUMO (2.2) HOMO−3→LUMO+1 (1.6) HOMO−2→LUMO+2 (1.2) HOMO−1→LUMO+4 (72.1) HOMO−1→LUMO+5 (1.2) HOMO→LUMO+6 (4.2)
3b	596	2.080	740	1.675	0.0179	HOMO→LUMO (89.6) HOMO→LUMO+1 (4.2) HOMO→LUMO+3 (2.2)
			572	2.169	0.0439	HOMO−2→LUMO (2.7) HOMO−1→LUMO (2.5) HOMO→LUMO+1 (76.8) HOMO→LUMO+2 (3.6) HOMO→LUMO+3 (11.4)
			555	2.232/	0.0517	HOMO→LUMO (1.7) HOMO→LUMO+1 (3.1) HOMO→LUMO+2 (92.3)
	519	2.389	472	2.629	0.167	HOMO−6→LUMO (6.3) HOMO−5→LUMO (15.5) HOMO−4→LUMO (31.0) HOMO−3→LUMO (2.7) HOMO−2→LUMO (5.3)

						HOMO−1→LUMO (2.3) HOMO→LUMO (2.2) HOMO→LUMO+1 (4.6) HOMO→LUMO+3 (9.3) HOMO→LUMO+6 (4.1) HOMO→LUMO+7 (7.2)
	365	3.397	361	3.432	0.0115	HOMO−8→LUMO (1.7) HOMO−6→LUMO+1 (7.6) HOMO−6→LUMO+2 (3.6) HOMO−5→LUMO+1 (2.0) HOMO−5→LUMO+3 (19.1) HOMO−4→LUMO+1 (1.1) HOMO−4→LUMO+3 (3.1) HOMO−4→LUMO+5 (25.5) HOMO−3→LUMO+6 (1.7) HOMO−3→LUMO+7 (2.0) HOMO−2→LUMO+7 (15.4) HOMO−2→LUMO+8 (1.8) HOMO→LUMO+21 (1.9)
	523	2.371	506	2.45	0.0930	HOMO−2→LUMO (1.6) HOMO−1→LUMO (4.9) HOMO→LUMO (99.6) HOMO→LUMO+1 (3.2) HOMO→LUMO+2 (7.8)
	472	2.627	456	2.721	0.00234	HOMO−2→LUMO (21.0) HOMO−1→LUMO (36.0) HOMO→LUMO+1 (8.0) HOMO→LUMO+2 (1.3)

			452	2.741	0.1091	HOMO−2→LUMO (11.1) HOMO−1→LUMO (11.0) HOMO→LUMO (5.8) HOMO→LUMO+1 (2.0) HOMO→LUMO+2 (63.9)
3c	363	3.416	360	3.358	0.0061	HOMO−6→LUMO (1.7) HOMO−5→LUMO (3.2) HOMO−4→LUMO (1.1) HOMO−3→LUMO+1 (2.9) HOMO−3→LUMO+2 (23.6) HOMO−1→LUMO+5 (27.7) HOMO−1→LUMO+6 (1.5) HOMO→LUMO+5 (1.0) HOMO→LUMO+6 (1.2) HOMO→LUMO+8 (19.8) HOMO→LUMO+9 (4.0) HOMO→LUMO+10 (5.5)
			358	3.461	0.0086	HOMO−3→LUMO+1 (8.0) HOMO−3→LUMO+2 (2.0) HOMO−1→LUMO+4 (9.7) HOMO−1→LUMO+5 (18.9) HOMO→LUMO+8 (18.6) HOMO→LUMO+9 (20.6) HOMO→LUMO+10 (15.2)
			358	3.466	0.0689	HOMO−4→LUMO (1.3) HOMO−4→LUMO+2 (1.8) HOMO−3→LUMO+1 (13.4)

			HOMO−3→LUMO+2 (30.8)
			HOMO−1→LUMO+4 (3.6)
			HOMO−1→LUMO+5 (33.5)
			HOMO→LUMO+8 (5.5)
			HOMO→LUMO+9 (3.0)

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6 Author Contributions

L. Giarrana performed the synthetic work and data analysis with partial support by D. Welterlich; L. Giarrana. and D. Scheschkewitz designed the study. D. Scheschkewitz acquired the funding; B. Morgenstern performed the X-ray diffraction studies. M. Zimmer performed the solid state and variable temperature NMR measurements. L. Giarrana performed the DFT calculations. L. Giarrana wrote the initial manuscript draft. L. Giarrana and D. Scheschkewitz reviewed and edited the manuscript.