Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

A two-coordinate Ni(I) silyl complex: CO_2 insertion and oxidatively-induced silyl migrations

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1) Experimental details, synthetic procedures, and characterization

General Considerations. Unless otherwise noted, all experiments were conducted with dry, oxygen-free solvents using standard Schlenk techniques or VAC Atmosphere or MBRAUN nitrogen-filled gloveboxes. Toluene (ACS grade) and pentane (HPLC grade) were purchased from Fischer Scientific. Diethyl ether (HPLC grade) was purchased from Honeywell. Tetrahydrofuran (ChromAR®) (THF) was purchased from Macron Fine Chemicals. *Ortho*-difluorobenzene (*o*-$C_6H_4F_2$) was purchased from Oakwood. Toluene, pentane, diethyl ether, tetrahydrofuran, and *ortho*-difluorobenzene were dried and deaerated using a JC Meyers Phoenix SDS solvent purification system. Benzene-d_6, THF-d_8, toluene-d_8, and bromobenzene-d_5 were purchased from Cambridge Isotope Laboratory and dried over 3 Å molecular sieves. Carbon dioxide was purchased from Praxair at a purity of 99.9%. Unless otherwise noted, reagents were obtained from commercial suppliers and used as received. Potassium tert-butoxide was purchased from Sigma Aldrich and sublimed before use. $[(IPr)Ni(\mu\text{-}Cl)]_2$,[1] $[(IPr)NiCl(\mu\text{-}Cl)]_2$,[2] $[(dtbpe)Ni(\mu\text{-}Cl)]_2$,[3] $(THF)_2KSi(SiMe_3)_3$,[4] $(THF)_2LiC(SiMe_3)_3$,[5] and potassium graphite[6] were prepared by standard literature procedures.

Analytical Methods All ^{1}H NMR spectra were taken at ambient temperature (ca. 21 °C) on Bruker AV-300, AVB-400, AVQ-400, AV-500, DRX-500, or AV-600 spectrometers each equipped with a 5 mm BB probe, and referenced to the residual proteo-solvent signals. Solution magnetic susceptibilities were determined by Evans method using ^{1}H NMR spectroscopy.[7] GC-MS analysis was performed with an Agilent Technologies 6890 GC system with a HP-5MS column. Elemental analyses were conducted by the UC Berkeley College of Chemistry Microanalytical Facility. Infrared spectra were collected on a Thermo Scientific Nicolet iS10 FTIR spectrophotometer using either a solution in C_6D_6 between NaCl plates or KBr pellets. The following abbreviations have been used to describe infrared features: “s” for strong, “m” for medium, “w” for weak, and “br” for broad. UV-visible spectra were collected on a Varian Cary 300 Bio UV-Visible spectrophotometer.

Electrochemistry. All electrochemical experiments were performed inside an MBRAUN glovebox using a pass-through consisting of gold plated tellurium copper binding posts connected to tinned copper conductors shielded with Beldfoil® and tinned copper braid. Experiments used a glassy carbon working electrode (polished with 0.30 then 0.05 μm alumina slurries, rinsed with water, and dried *in vacuo*), a platinum wire counter electrode, and a silver wire reference electrode. All voltammograms were referenced to $[Cp_2Fe]^{0/1+}$ in the same cell. Measurements were made with a BASi EC Epsilon pontentiostat/galvanostat and a PWR-3 Power Module. Cyclic voltammograms for **1** and **2** were recorded in a 0.1 M tetrabutylammonium tetrakis(pentafluorophenyl)borate ($[^nBu_4N][B(C_6F_5)_4]$) solution in *ortho*-difluorobenzene at 22 °C with software-determined *iR* compensation applied. Cyclic voltammograms for **7** used tetrabutylammonium hexafluorophosphate ($[^nBu_4N][PF_6]$) as the electrolyte. Data analysis was performed with Excel 2013.

X-Ray Diffraction Experiments Single crystal X-ray diffraction experiments for **1**, **2**, **5**, and **6** were performed at the UC Berkeley CHEXRAY crystallographic facility. Measurements of these compounds were performed on either a Bruker APEX-I CCD or a Bruker APEX-II CCD area detector using Mo Kα radiation (λ = 0.71073 Å) monochromated with QUAZAR multilayer mirrors. The temperature of the crystals was maintained at 100(2) K throughout collection. Data collection, refinement, and reduction were performed with Bruker APEX2 or APEX3 software. The structures were solved using SHELXT-2014 and refined with SHELXL-2014, with refinement of F^2 on all data by full-matrix least squares.[8–10] In all structures, non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included at the geometrically-calculated positions and refined using a riding model. The 3D molecular structure figures were visualized with Olex2.[11]

Single crystal X-ray diffraction experiments for **8** were performed at the UC Berkeley CHEXRAY crystallographic facility. Measurements of this compound were done on a Rigaku XtaLAB P200 equipped with a MicroMax 007HF rotating anode and a Pilatus 200K hybrid pixel array detector using Mo Kα radiation (λ = 0.71073 Å). The temperature of the crystal was maintained at 100(2) K throughout collection. Data collection, refinement, and reduction were performed with CrysAlisPro (version 1.171.39.46e, Rigaku Corporation, Oxford, UK). A multi-scan absorption correction was applied using the SCALE3 ABSPACK scaling algorithm within CrysAlisPro. The structure was solved using Olex2.solve and refined with SHELXL-2015, with refinement of F^2 on all data by full-matrix least squares. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included at the geometrically–calculated positions and refined using a riding model. The hydrogen atoms on C1 were found in the electron difference map. The 3D molecular structure figures were visualized with Olex2.

Single crystal X-ray diffraction experiments for **3** were performed at beamline 11.3.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory. Frames were collected on a PHOTON100 CMOS running shutterless using radiation with a wavelength of 0.7749 Å selected by a Si(111) monochromator and focused to 200 μm^2 with a toroidal mirror. Crystal was kept at 100(2) K throughout collection. Data collection, integration, scaling, and space group determination were performed with Bruker APEX3 (v. 2016.5-0) software. Structure was solved by SHELXT-2014 and refined with SHELXL-2014, with refinement of F^2 on all data by full-matrix least squares.[8–10] The 3D molecular structure figures were visualized with Olex2.[11]

Single crystal X-ray diffraction experiments for **4** were performed at beamline 12.2.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory. Frames were collected on a PHOTON II detector running shutterless using radiation with a wavelength of 0.7288 Å selected by a Si(111) monochromator and focused to 200 µm 2 with a toroidal mirror. Crystal was kept at 100(2) K throughout collection. Data collection, integration, scaling, and space group determination were performed with Bruker APEX3 (v. 2016.5-0) software. Structure was solved by SHELXT-2014 and refined with SHELXL-2014, with refinement of F 2 on all data by full-matrix least squares.[8–10] The 3D molecular structure figures were visualized with Olex2.[11]

Crystallographic data for the structures in this work have been deposited in the Cambridge Crystallographic Data Centre. The CCDC numbers are 1881708-1881713 and 1896672.

(IPr)Ni–Si(SiMe$_3$)$_3$ (1). To a 20 mL scintillation vial was added 244.8 mg (0.253 mmol) of [(IPr)Ni(μ-Cl)]$_2$. The yellow-green solid was dissolved in 5 mL of toluene. In a separate vial, 218.5 mg (0.507 mmol) of (THF)$_2$KSi(SiMe$_3$)$_3$ was dissolved in 2 mL of toluene. Both vials were cooled to -35 °C before the silyl reagent was added dropwise to the solution containing Ni. There was an immediate color change to dark red-orange and also precipitate formation in the vial (KCl). The reaction mixture was stirred for 1 h before the solvent was removed under reduced pressure. The resulting crude solid was then redissolved in 8 mL of pentane and stirred for an additional 15 min. The solution was then filtered to remove KCl. Finally, concentration of the pentane solution followed by cooling to -35 °C for 18 h resulted in red, X-ray quality crystals of **1**. Collecting three successive crops of crystals yielded 198.4 mg of **1** (56.3%). ^{1}H NMR (600.13 MHz, C$_6$D$_6$) δ 75.37 (2H), 43.04 (4H), 4.18 (12H), 0.50 (27H), -14.74 (2H), -19.25 (4H), -73.15 (12H). μ_{eff} = 2.90 μ_{B} (C$_6$D$_6$, 22 °C, Evans method). UV-Vis (pentane): λ_{max} 403 nm (ε = 4725 M^{-1}cm^{-1}), 381 nm (ε = 8324 M^{-1}cm^{-1}), 324 nm (ε = 5480 M^{-1}cm^{-1}), 292 nm (ε = 7343 M^{-1}cm^{-1}). Anal. Calcd. for C$_{36}$H$_{63}$N$_2$NiSi$_4$: C, 62.22%; H, 9.14%; N, 4.03%. Found: C, 62.24%; H, 8.87%; N, 4.18%.

(IPr)Ni–C(SiMe$_3$)$_3$ (2). To a 20 mL scintillation vial was added 137.3 mg (0.142 mmol) of [(IPr)Ni(μ-Cl)]$_2$, which was dissolved in 3 mL of toluene. In a separate vial, 108.9 mg (0.284 mmol) of (THF)$_2$LiC(SiMe$_3$)$_3$ was dissolved in 2 mL of toluene. Both vials were cooled to -35 °C before the ligand was added dropwise to the Ni solution. There was an immediate color change from yellow-green to dark red-orange. The reaction mixture was stirred for 45 min, and then was filtered and the solvent was removed under reduced pressure. Yellow X-ray quality crystals were grown from a concentrated pentane solution cooled to -35 °C for 18 h. This method resulted in a yield of 57.6 mg (29.8%). ^{1}H NMR (300.13 MHz, C$_6$D$_6$) δ 59.13 (2H), 23.98 (4H), 10.24 (12H), -10.23 (2H), -12.86 (4H), -13.53 (27H), -28.69 (12H). μ_{eff} = 3.01 μ_{B} (C$_6$D$_6$, 22 °C, Evans method). Anal. Calcd. for C$_{37}$H$_{63}$N$_2$NiSi$_3$: C, 65.46%; H, 9.35%; N, 4.13%. Found: C, 65.42%; H, 9.28%; N, 4.46%.

(IPr)Ni[κ^2-O$_2$CSi(SiMe$_3$)$_3$] (3). A 50 mL PTFE-stoppered flask was charged with 31.2 mg (0.0449 mmol) of **1** and 3 mL of pentane. The resulting solution was then degassed and an atmosphere of CO$_2$ (approx. 1.92 mmol) was added to the flask. An immediate color change from yellow-green to yellow-orange was observed. The reaction mixture was stirred for 1 h before the excess CO$_2$ and solvent were removed under vacuum. The crude reaction mixture was then dissolved in minimal pentane and the resulting solution was cooled to -35 °C. After 12 h, yellow-orange crystals of **3** were obtained in a yield of 23.0 mg (69.3%). ^{1}H NMR (400.13 MHz, C$_6$D$_6$) δ 12.57 (2H), 6.38 (4H), 5.85 (12H), 5.15 (4H), 4.28 (2H), 1.91 (12H), 0.11 (27H). μ_{eff} = 2.09 μ_{B} (C$_6$D$_6$, 22 °C, Evans method). Anal. Calcd. for C$_{37}$H$_{63}$N$_2$O$_2$NiSi$_4$: C, 60.14%; H, 8.59%; N, 3.79%. Found: C, 60.14%; H, 8.53%; N, 3.88%. FTIR (C$_6$D$_6$): 2962 (br m), 2892 (m), 2870 (m), 1618 (m), 1453 (br m), 1401 (m), 1385 (m), 1364 (w), 1329 (m), 1243 (m).

[(IPr)Ni(μ-η^2-SiHPh$_2$)]$_2$ (4). In a 20 mL scintillation vial, 26.0 mg (0.0374 mmol) of **1** was dissolved in 3 mL of pentane. Then, 6.9 mg (0.0374 mmol) of Ph_2SiH_2 in 1 mL of pentane was added. A red-orange solid immediately precipitated from solution. After 2 h of stirring the reaction solution was filtered and the orange-red solid was washed with pentane (2 x 5 mL) to yield 15.0 mg (63.6%) of **4**. Due to the complex's insolubility, characterization by NMR spectroscopy was not possible. FTIR (KBr pellet): 2958 (s), 2928 (m), 2868 (w), 1701 (m), 1459 (m), 1427 (m), 1117 (m), 1008 (br m), 700 (m), 550 (m).

κ^2-[1-(η^6-C$_6$H$_3$^{i}Pr$_2$),2-(η^1-SiMe$_2$)-3-(DIPP)-C$_3$H$_2$N$_2$]Ni[SiMe(SiMe$_3$)$_2$][B(C$_6$F$_5$)$_4$] (5). Method 1: A 20 mL scintillation vial was charged with 47.7 mg (0.0686 mmol) of **1** and 1 mL of *o*-difluorobenzene. Separately, 59.4 mg (0.0686 mmol) of $[Cp_2Fe][B(C_6F_5)_4]$ was dissolved in 1 mL of *o*-difluorobenzene and then added dropwise to the vial containing dissolved **1**. Upon completion of the addition, the color of the reaction solution had changed from yellow-green to orange. The reaction was stirred for an addition hour prior to removal of the solvent under reduced pressure. The resulting orange solids were washed twice with 5 mL of pentane to remove Cp_2Fe. The crude product was then dissolved in minimal *o*-difluorobenzene, layered with pentane, and then cooled to -35 °C overnight to yield 73.2 mg of **5** (77.6%). Method 2: A 20 mL scintillation vial was charged with 15.2 mg (0.0208 mmol) of **6** and 2 mL of toluene. One equivalent of solid $(Et_2O)_3LiB(C_6F_5)_4$ (18.9 mg, 0.0208 mmol) was added to the reaction solution, which resulted in a color change from purple to yellow-orange. After stirring for one hour, the solvent was removed under reduced pressure. The resulting orange solid was triturated three times with pentane, then dissolved in minimal *o*-difluorobenzene, filtered, layered with pentane, and cooled to -35 °C to yield 15.3 mg (53.5%) of **5**. ^{1}H NMR (600.13 MHz, THF-d_8) δ 8.45 (s, 1H, NCH), 8.26 (s, 1H, NCH), 7.65 (t, *J* = 7.9 Hz, 1H, para-CH), 7.50 (d, *J* = 8.0 Hz, 2H, meta-CH), 7.32 (d, *J* = 7.1 Hz, 2H, meta-CH), 6.70 (t, *J* = 7.0 Hz, 1H, para-CH), 2.38 (m, 4H, $C\underline{H}(CH_3)_2$), 1.53 (d, *J* = 7.0, 6H, $CH(C\underline{H}_3)_2$), 1.37 (d, *J* = 6.9, 12H, $CH(C\underline{H}_3)_2$), 1.19 (d, *J* = 6.9, 12H, $CH(C\underline{H}_3)_2$), 0.18 (s, 6H, $Si(CH_3)_2$), 0.16 (s, 18H, $SiCH_3(Si(C\underline{H}_3)_3)_2$), 0.05 (s, 3H, $SiC\underline{H}_3(Si(CH_3)_3)_2$). ^{13}C NMR (150.2 MHz, THF-d_8) δ 146.4, 133.4, 133.2, 132.2, 125.7, 124.9, 106.1, 103.3, 30.5, 30.1, 26.8, 23.1, 21.8, 3.7, 1.7, -5.6. Anal. Calcd. for $NiC_{60}H_{63}N_2Si_4BF_{20}$: C, 52.40%; H, 4.60%; N, 2.00%. Found: C, 52.65%; H, 4.73%; N, 2.19%.

(IPr)NiCl[SiMe$_2$SiMe(SiMe$_3$)$_2$] (6). Method 1: 53.1 mg (0.0764 mmol) of **1** and 21.3 mg (0.0764 mmol) of trityl chloride were added to separate 20 mL scintillation vials. **1** was then dissolved in 4 mL of pentane. This solution was pipetted into the vial containing trityl chloride and the resulting solution was stirred for 1.5 h. Over that time the reaction solution became purple. The reaction mixture was then filtered and cooled to -35 °C. After 12 h, 21.9 mg of purple crystals of **6** were obtained for a yield of 39.2%. Method 2: 17.1 mg (0.0124 mmol) of **5** was added to a 20 mL scintillation vial and dissolved in 2 mL of Et_2O. In a separate vial 3.5 mg (0.0124 mmol) of Bu_4NCl was dissolved in 2 mL of Et_2O and the resulting solution was added to the vial containing **5**. Over 5 min the color of the reaction solution changed from orange to purple. The reaction mixture was allowed to stir for 1 h before the solvent was removed under reduced pressure. 10

mL of pentane was then added to the reaction vial, the resulting mixture was stirred for 10 min before filtration to remove $[Bu_4N][B(C_6F_5)_4]$. The purple solution was then concentrated and cooled to -35 °C for 18 h to yield 7.7 mg of **6** (84 %). Method 3: A J-Young tube was charged with 7.0 mg (0.0068 mmol) of $[(IPr)Ni(\mu\text{-}Cl)Cl]_2$ dissolved in 0.5 mL of C_6D_6. Hexaethylbenzene was also added as an internal standard. Upon addition of 5.8 mg (0.0068 mmol) of $(THF)_2KSi(SiMe_3)_3$ there was a gradual color change over 20 min to a purple solution. After 1 h the ^1H NMR spectrum revealed that there was an observed yield of 52.2%. ^1H NMR (500.23 MHz, C_6D_6) δ 7.32 (t, J = 7.4 Hz, 2H, para-CH), 7.25 (d, J = 7.8 Hz, 4H, meta-CH), 6.53 (s, 2H, NCH), 3.08 (m, 4H, $C\underline{H}(CH_3)_2$), 1.51 (d, J = 6.6 Hz, 12H, $CH(C\underline{H}_3)_2$), 0.93 (d, J = 6.8 Hz, 12H, $CH(C\underline{H}_3)_2$), 0.30 (s, 3H, $SiC\underline{H}_3(Si(CH_3)_3)_2$), 0.26 (s, 18H, $SiCH_3(Si(C\underline{H}_3)_3)_2$), 0.07 (s, 6H, $Si(CH_3)_2$). ^{13}C NMR (150.92 MHz, C_6D_6) δ 185.42, 145.68, 136.34, 130.60, 125.00, 124.81, 29.80, 26.51, 22.92, 5.07, 1.32, -9.46. Anal. Calcd. for $NiC_{36}H_{63}N_2Si_4Cl$: C, 59.20%; H, 8.70%; 3.84%. Found: C, 59.14%; H, 8.53%; N, 3.68%.

(dtbpe)Ni-Si(SiMe$_3$)$_3$ (7). To a 20 mL scintillation vial was added 388.7 mg (0.471 mmol) of $[(dtbpe)Ni(\mu\text{-}Cl)]_2$ and 15 mL of toluene to form a red solution. To a separate 20 mL scintillation vial was added 406.0 mg (0.942 mmol) of $(THF)_2KSi(SiMe_3)_3$ and 2 mL of toluene to form a yellow solution. Both vials were cooled to -35 °C before the silyl reagent was added dropwise to the stirred solution containing Ni. There was an immediate color change to blue and formation of precipitate (KCl). The reaction was stirred for 1 h before the solvent was removed under reduced pressure. The resulting maroon solids were triturated with 2 mL of pentane. Then 60 mL of pentane was used to dissolve the product (blue in solution). This suspension was then filtered to remove KCl. Finally, the pentane solution was cooled to -35 °C for 18 h to yield maroon crystals of **7**. Collecting 2 successive crops yielded 361.8 mg of **7** (61.5%). ^1H NMR (600.13 MHz, C_6D_6) δ 8.96 (36H), 2.65 (27H), -7.87 (4H). μ_{eff} = 1.42 μ_B (C_6D_6, 22 °C, Evans method). UV-Vis (pentane): λ_{max} 587 nm (ε = 877 $M^{-1}cm^{-1}$), 392 nm (ε = 6016 $M^{-1}cm^{-1}$), 307 nm (ε = 4565 $M^{-1}cm^{-1}$), 261 nm (ε = 21104 $M^{-1}cm^{-1}$). Anal. Calcd. for $C_{27}H_{67}NiP_2Si_4$: C, 51.90%; H, 10.81%; N, 0.00%. Found: C, 51.11%; H, 10.57%; N, -0.04%. FTIR (KBr pellet): 2944 (br s), 2892 (br s), 1479 (m), 1390 (m), 1366 (m), 1234 (s), 1179 (w), 1019 (w), 830 (br s), 650 (m), 622 (m).

(dtbpe)Ni[SiMe$_2$SiMe(SiMe$_3$)$_2$] (8). To a 20 mL scintillation vial was added 86.2 mg (0.138 mmol) of **7** and 5 mL of *o*-difluorobenzene to form a purple solution. To a separate 20 mL scintillation vial was added 119.3 mg (0.138 mmol) of $[Cp_2Fe][B(C_6F_5)_4]$ and 3 mL of *o*-difluorobenzene. The $[Cp_2Fe][B(C_6F_5)_4]$ solution was added dropwise to the solution containing Ni. There was an immediate color change to red/orange upon completion of the addition. After stirring for 1 h the solvent was removed under reduced pressure. The resulting orange solids were washed three times with 5 mL of pentane to remove Cp_2Fe. The crude product was then dissolved in minimal *o*-difluorobenzene, layered with pentane, and the resulting mixture was shaken and then cooled to -35 °C for 18 h to yield 138.7 mg (77.1 %) of **8** as orange crystals. ^1H NMR (600.13 MHz, C_6D_5Br) δ 1.69 (br. s, 3H), 1.60 (br. s, 3H), 1.06 (d, J = 13.6 Hz, 36H), 0.24 (d, obscured, 4H), 0.19 (s, 18H), -0.47 (br. s, 3H). ^{13}C NMR (150.92 MHz, C_6D_5Br) δ 150.09, 148.52, 139.92, 138.02, 136.32, 36.31, 34.87, 30.71, 23.21, 14.98, 0.95. Anal. Calcd. for $C_{51}H_{67}BF_{20}NiP_2Si_4$: C, 46.98%; H, 5.18%; N, 0.00%. Found: C, 46.69%; H, 4.94%; N, 0.02%. FTIR (KBr pellet): 2956 (br m), 2897 (br m), 1644 (m), 1514 (s), 1464 (s), 1411 (w), 1396 (m), 1275 (m), 1248 (m), 1176 (w), 1020 (s), 980 (s), 805 (s), 760 (s), 684 (m), 661 (m), 610 (w), 574 (w). Attempts were made to observe the agostic C–H–Ni interaction by variable temperature ^1H NMR spectroscopy, but they were unsuccessful. The observed temperature range was -73 to 77 °C. Due to the broadness and proximity of the resonances to one another, identification and integration of individual resonances proved difficult.

(IPr)Ni(C_2H_4)$_2$. A J-Young tube was charged with 5.3 mg (0.0076 mmol) of **1** dissolved in 0.5 mL of C_6D_6. Hexamethylbenzene was also added as an internal standard. The solution was then degassed before 1 atm of ethylene (approx. 0.0818 mmol) was added. No immediate color change occurred and no reaction was observed by ^1H NMR spectroscopy. After 24 h the solution changed color from yellow-green to a pale yellow. The ^1H NMR spectrum showed that there was a 93.3 % yield. The spectrum matched that reported previously in the literature.[12]

(IPr)Ni(CO)$_3$. A J-Young tube was charged with 6.0 mg (0.0086 mmol) of **1** dissolved in 0.5 mL of C_6D_6. Hexamethylbenzene was also added as an internal standard. The solution was degassed before 1 atm of CO (approx. 0.0818 mmol) was added. No immediate reaction was observed by ^1H NMR spectroscopy. After 24 h the ^1H NMR spectrum indicated an observed yield of 64.9 %. The spectrum matched that reported previously in the literature.[12]

[(IPr)Ni]$_2$(μ-CO)(μ-η^2,η^2-CO$_2$). A J-Young tube was charged with 11.0 mg (0.0149 mmol) of **3** dissolved in 0.5 mL of C_6D_6. Hexamethylbenzene was used as an internal standard. The sample was then heated to 70 °C for 24 h. This resulted in a color change from yellow to a darker orange. The ^1H NMR spectrum revealed a yield of 24.0 %. The spectrum matched that reported previously in the literature.[13]

Treatment of 1 with KC_8. To a scintillation vial was added 64.6 mg (0.0930 mmol) of **1** and 3 mL of pentane. The resulting solution was cooled to -130 °C. Then 13.8 mg (0.102 mmol) of KC_8 was added and the reaction solution was allowed to warm to ambient temperature. Upon addition there was an immediate color change to red. After stirring for 1 h the solution was filtered, concentrated, and cooled to -35 °C. Thermally unstable red crystals grew overnight, but this product could not be characterized given its rate of decomposition.

General procedure for attempts to trap intermediates of oxidation with [Cp_2Fe][B(C_6F_5)$_4$]. To a 20 mL scintillation vial was added 10.9 mg (0.0157 mmol) of **1**, 3.4 µL (0.0158 mmol) of bis(trimethylsilyl)acetylene, and 2 mL of Et_2O. Then 13.6 mg (0.0157 mmol) of [Cp_2Fe][B(C_6F_5)$_4$] was added. The ferrocenium gradually dissolved over 20 min, coinciding with a slow color change to orange. Upon workup **5** was observed by ^1H NMR spectroscopy to be the sole product. Similar attempts with dimethylaminopyridine (DMAP) and diphenylacetylene also did not trap any intermediates.

Treatment of 2 with CO_2. A J-Young tube was charged with 12.0 mg (0.0177 mmol) of **2** dissolved in 0.5 mL of C_6D_6. The solution was degassed before 1 atm of CO_2 (approx. 0.0818 mmol) was added. No immediate reaction was observed by ^{1}H NMR spectroscopy. Upon heating to 60 °C for 1 h, decomposition of **2** was observed.

Treatment of 2 with C_2H_4. A J-Young tube was charged with 10.0 mg (0.0147 mmol) of **2** dissolved in 0.5 mL of C_6D_6. The solution was degassed and 1 atm of C_2H_4 (approx. 0.0818 mmol) was added. No reaction was observed after 24 h, by ^{1}H NMR spectroscopy.

Treatment of 2 with Ph_2SiH_2. A J-Young tube was charged with 5.5 mg (0.0081 mmol) of **2** dissolved in 0.5 mL of C_6D_6. Then one equivalent of Ph_2SiH_2 was added via microsyringe (1.8 µL, 0.0081 mmol). No reaction was observed by ^{1}H NMR spectroscopy after 20 min at ambient temperature, or after heating to 90 °C for 2 days.

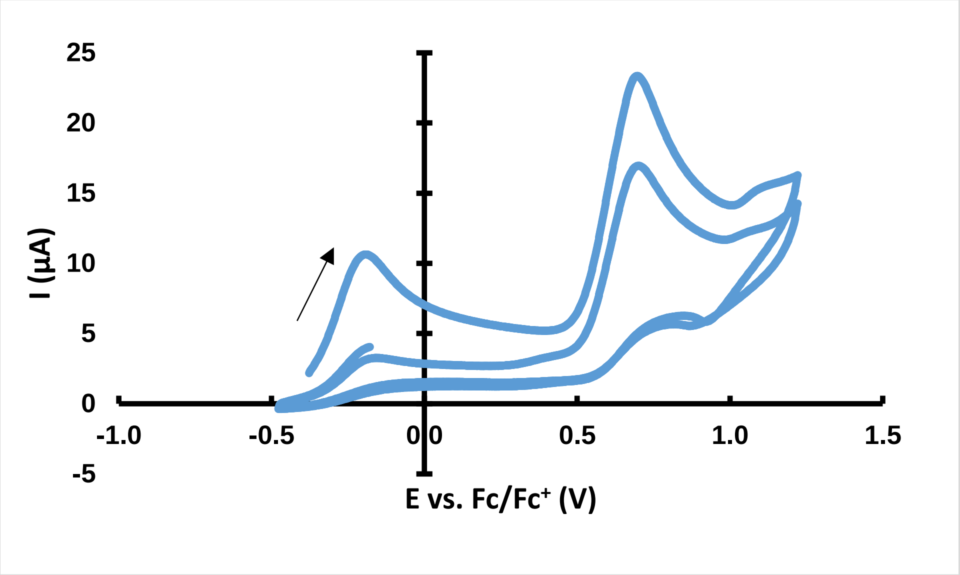
Treatment of 2 with KC_8. To a 20 mL scintillation vial was added 51.6 mg (0.0760 mmol) of **2** and 2 mL of THF. The solution was then cooled to -35 °C before 11.3 mg (0.0836 mmol) of KC_8 was added. The addition caused the color of the solution to turn red. After stirring for an additional 30 min the color became darker. After removal of graphite via filtration and THF via vacuum transfer, a crystallization from Et_2O layered with pentane was attempted, but this was ultimately unsuccessful. The crude ^{1}H NMR spectrum was inconclusive.

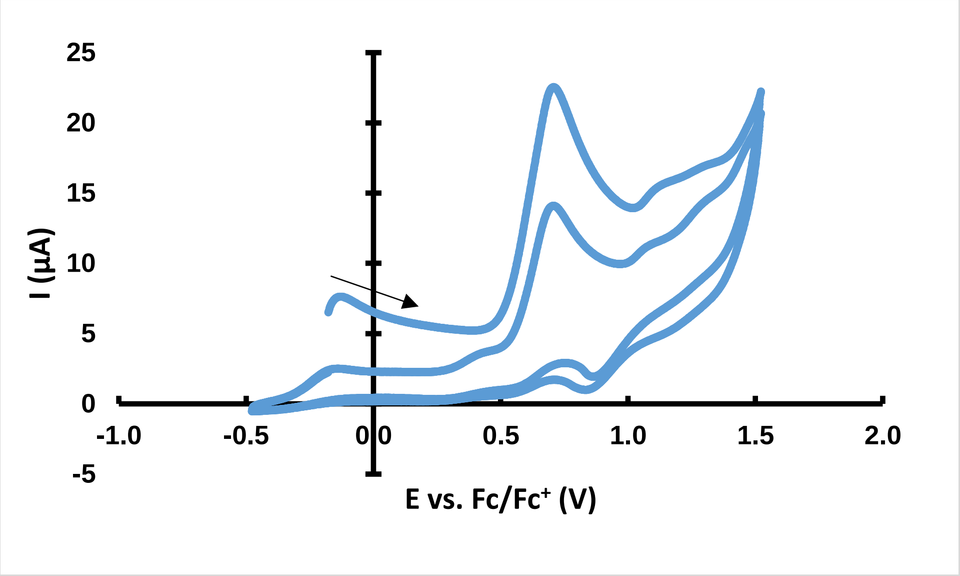
Treatment of 2 with $[Cp_2Fe][B(C_6F_5)_4]$. To a 20 mL scintillation vial was added 26.1 mg (0.0384 mmol) of **2** and 2 mL of *o*-difluorobenzene. To another 20 ml scintillation vial was added 33.3 mg (0.0385 mmol) of $[Cp_2Fe][B(C_6F_5)_4]$ and 2 mL of *o*-difluorobenzene. Both vials were cooled to -35 °C before the $[Cp_2Fe][B(C_6F_5)_4]$ solution was added dropwise to the solution of **2**. There was an immediate color change to red that later faded to black over 5-10 min. The product was an insoluble black powder.

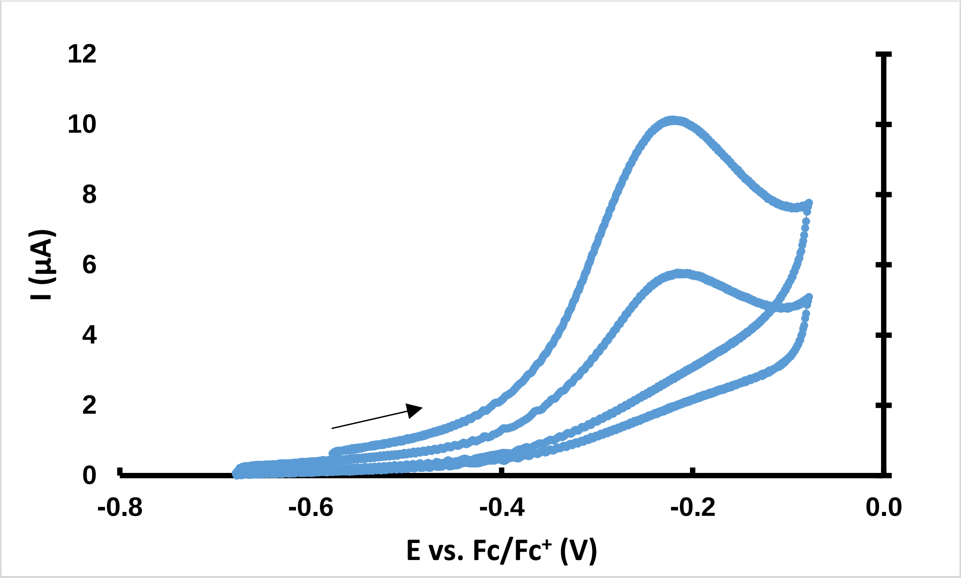
Treatment of 2 with trityl chloride. To a 20 mL scintillation vial was added 20.4 mg (0.0301 mmol) of **2** and 5 mL of pentane. Then 8.4 mg (0.0301 mmol) of trityl chloride was added to the vial. No immediate color change was observed upon addition, nor after 5 h of stirring. The ^{1}H NMR spectrum confirmed that no reaction had occurred.

2) Electrochemical data

Figure S1. Cyclic voltammagrams of a 0.5 mM solution of (IPr)Ni–Si(SiMe$_3$)$_3$ (**1**) in *ortho*-difluorobenzene with a 0.1 M [^{n}Bu$_4$N][B(C$_6$F$_5$)$_4$] supporting electrolyte.



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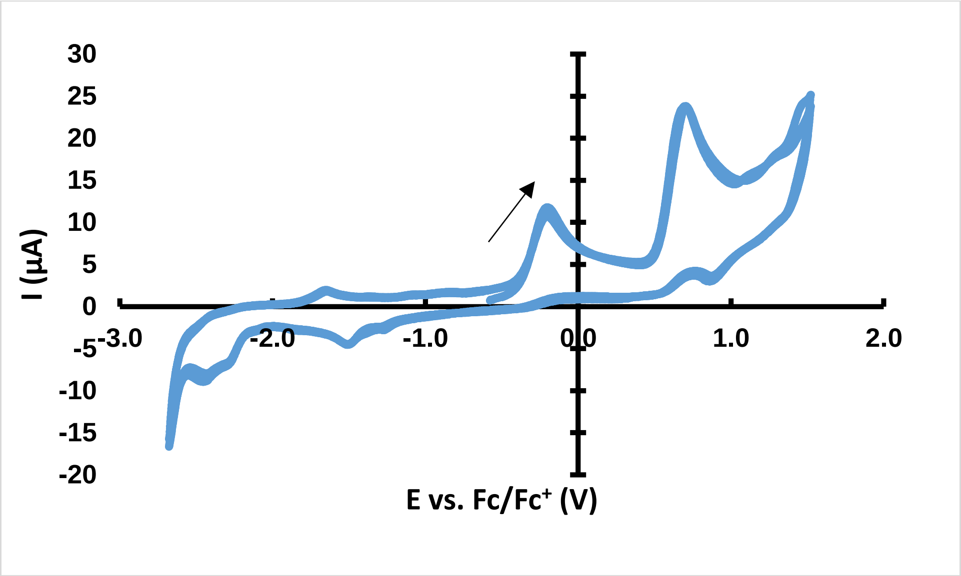
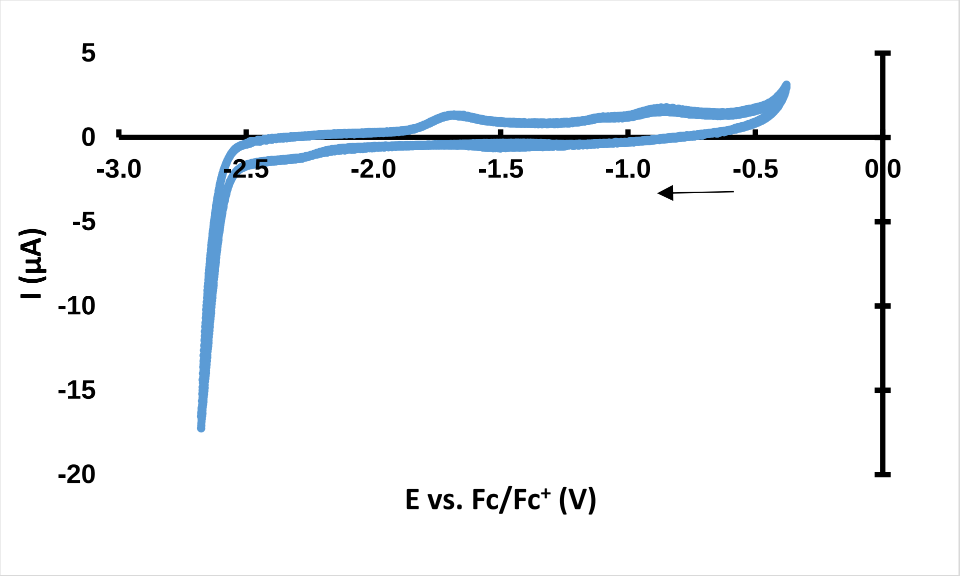
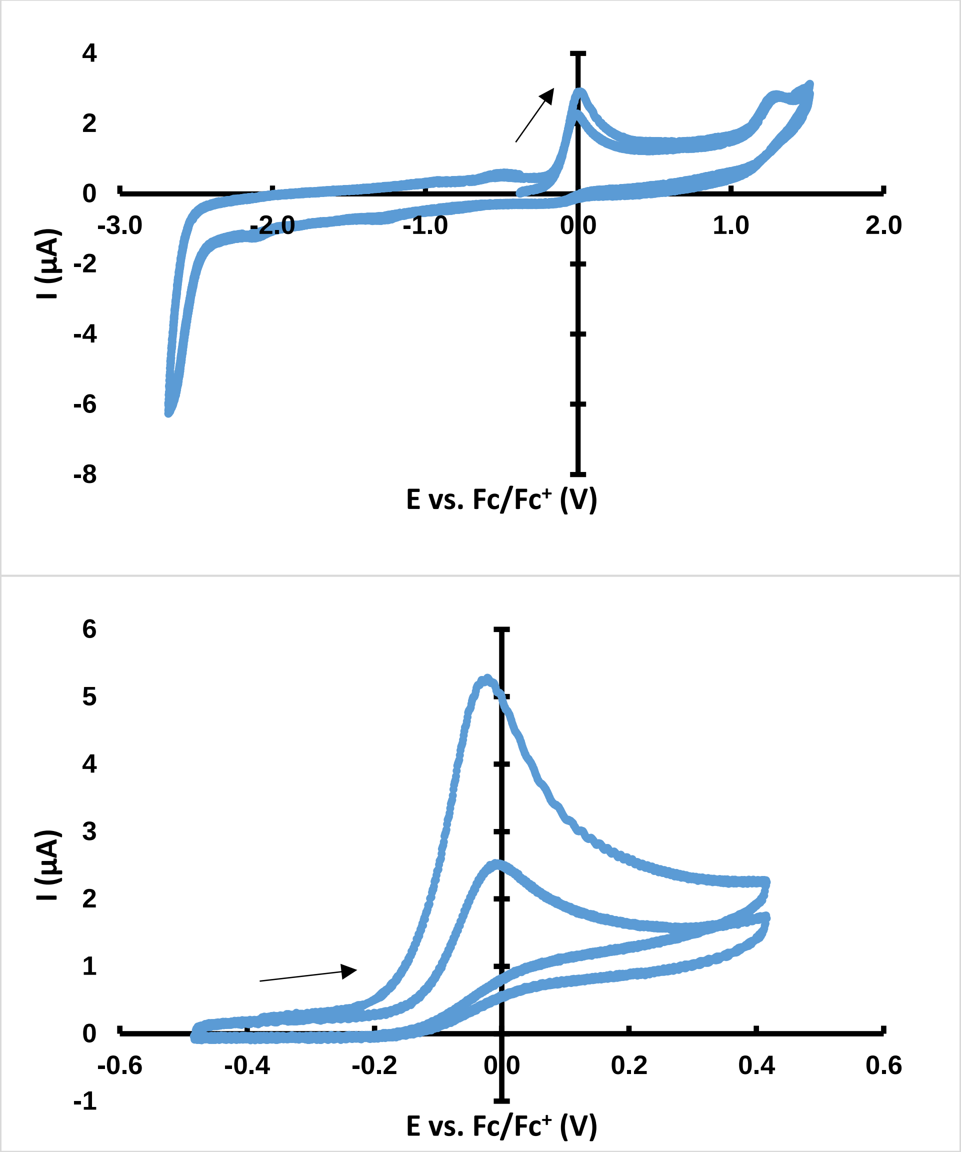
6
4
2
0
I (μA)
-0.8
-0.6
-0.4
-0.2
0.0
E vs. Fc/Fc⁺ (V)

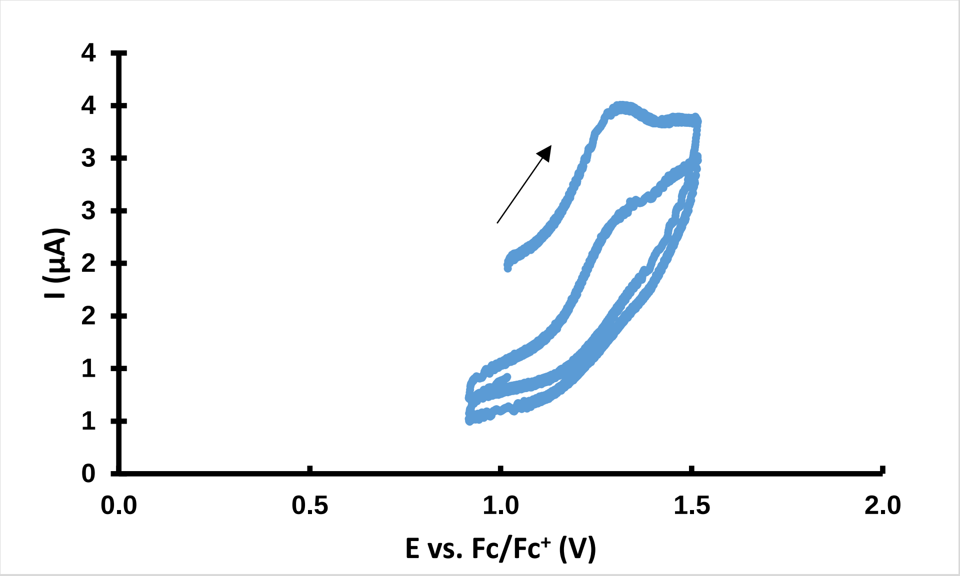

30
25
20
15
10
5
0
-5
-10
-15
-20
I (μA)
-3.0
-2.0
-1.0
0.0
1.0
2.0
E vs. Fc/Fc⁺ (V)

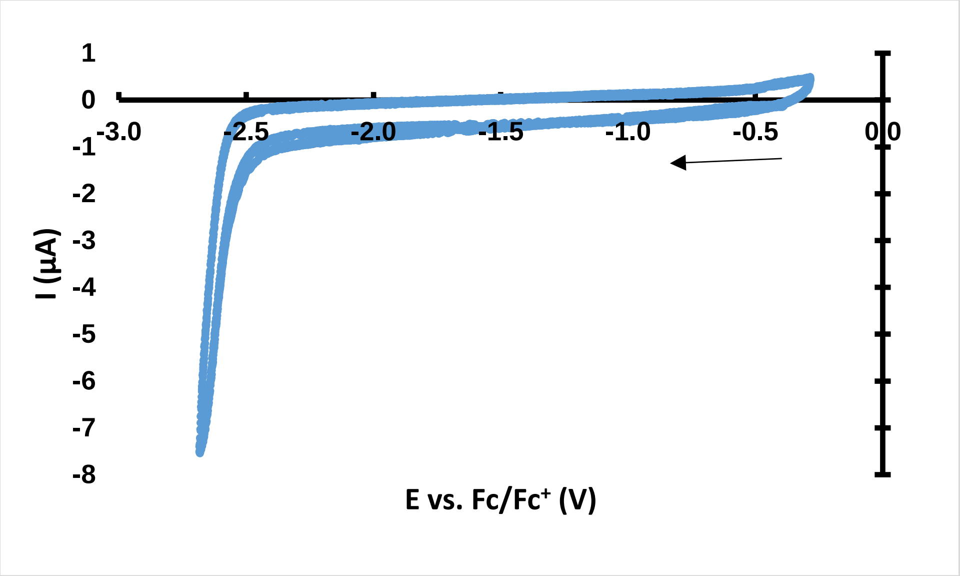


Details: The arrow indicates the initial potential and scanning direction. The scan rate was 100 mV/s, and two complete cycles are displayed on each voltammagram. They show two irreversible oxidations at -0.32 and 0.60 V. No reduction events are observed. The oxidations give rise to reductions at 0.90, -1.50, and -2.41 V.

Figure S2. Cyclic voltammagrams of a 0.5 mM solution of (IPr)Ni–C(SiMe$_3$)$_3$ (**2**) in *ortho*-difluorobenzene with a 0.1 M [^{n}Bu$_4$N][B(C$_6$F$_5$)$_4$] supporting electrolyte.

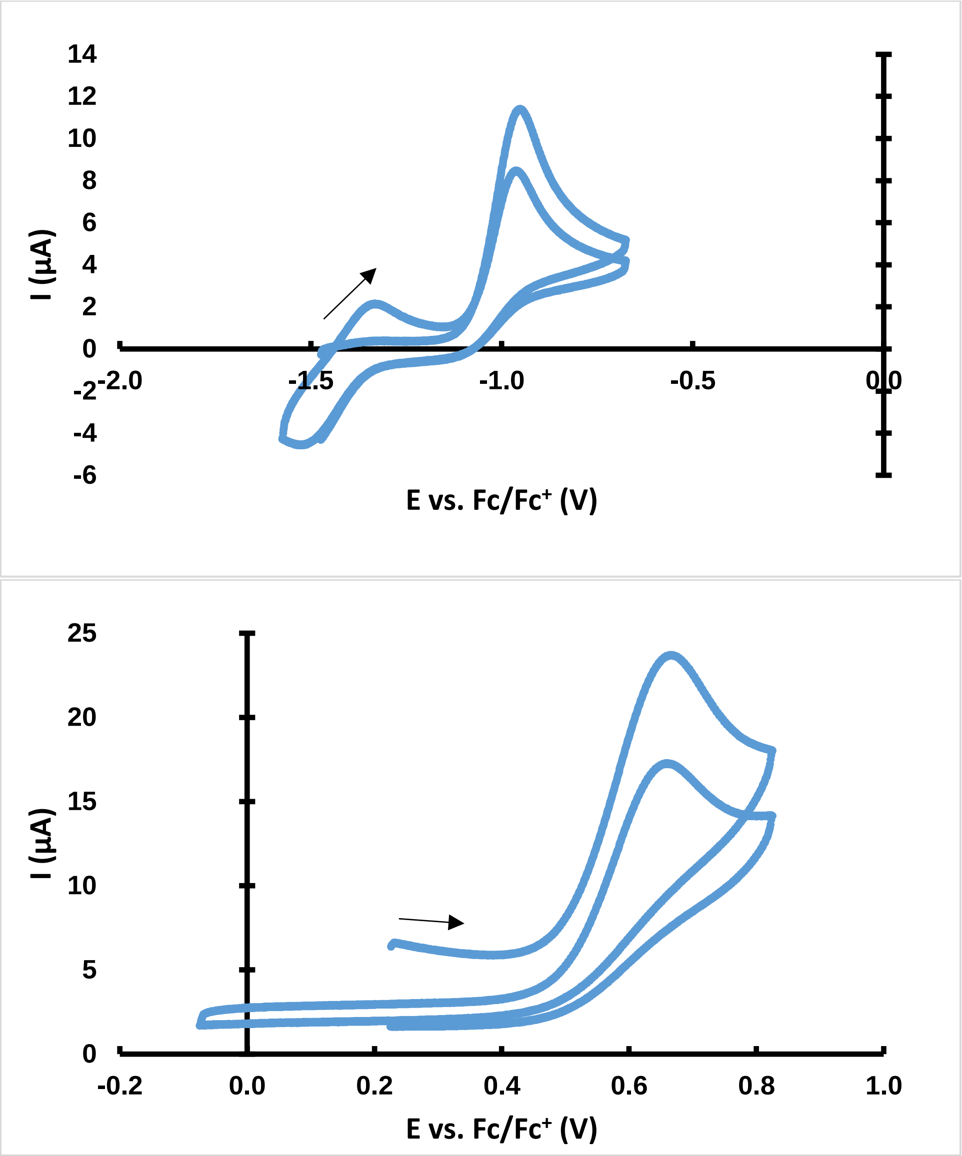


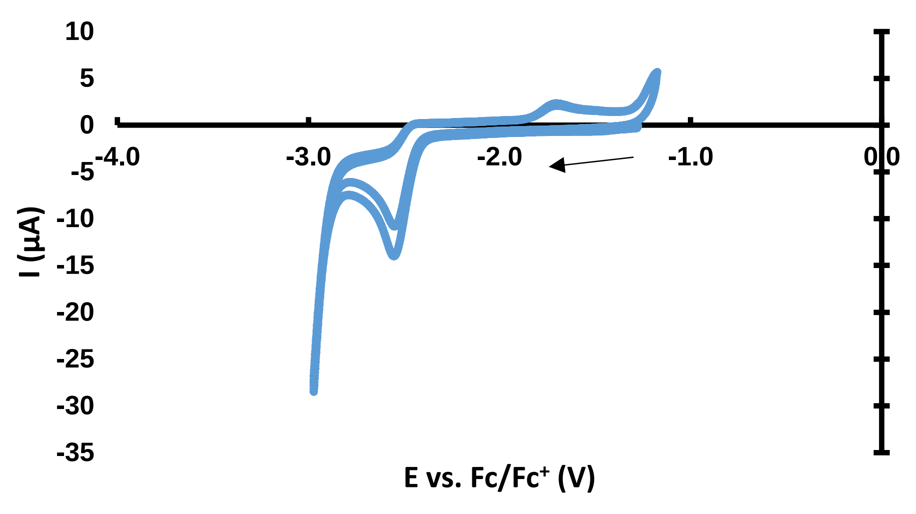


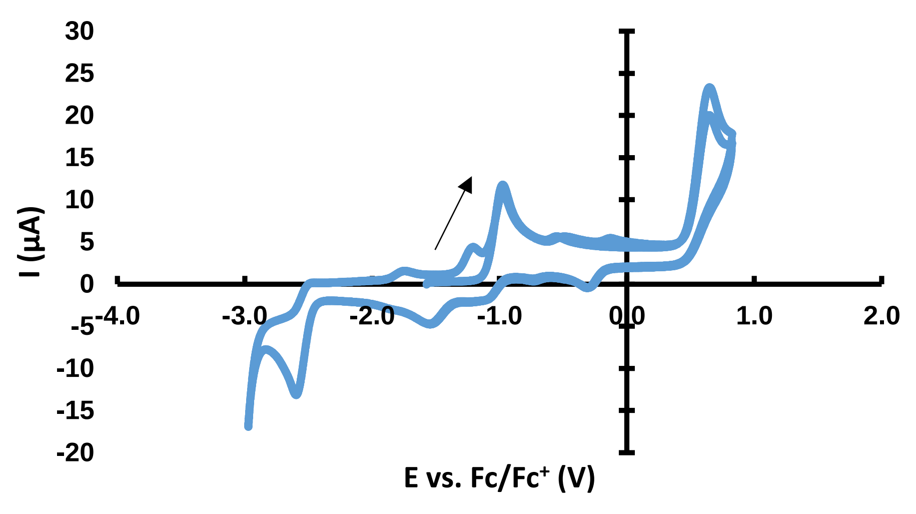


Details: The arrow indicates the initial potential and scanning direction. The scan rate was 100 mV/s, and two complete cycles are displayed on each voltammagram. They show two irreversible oxidations at -0.089 and 1.22 V. No reduction events are observed. The oxidations give rise to reductions at -0.040, -1.24, and -2.05 V.

Figure S3. Cyclic voltammagrams of a 0.5 mM solution of (dtbpe)Ni–Si(SiMe$_3$)$_3$ (**7**) in *ortho*-difluorobenzene with a 0.1 M [^{n}Bu$_4$N][PF$_6$] supporting electrolyte.



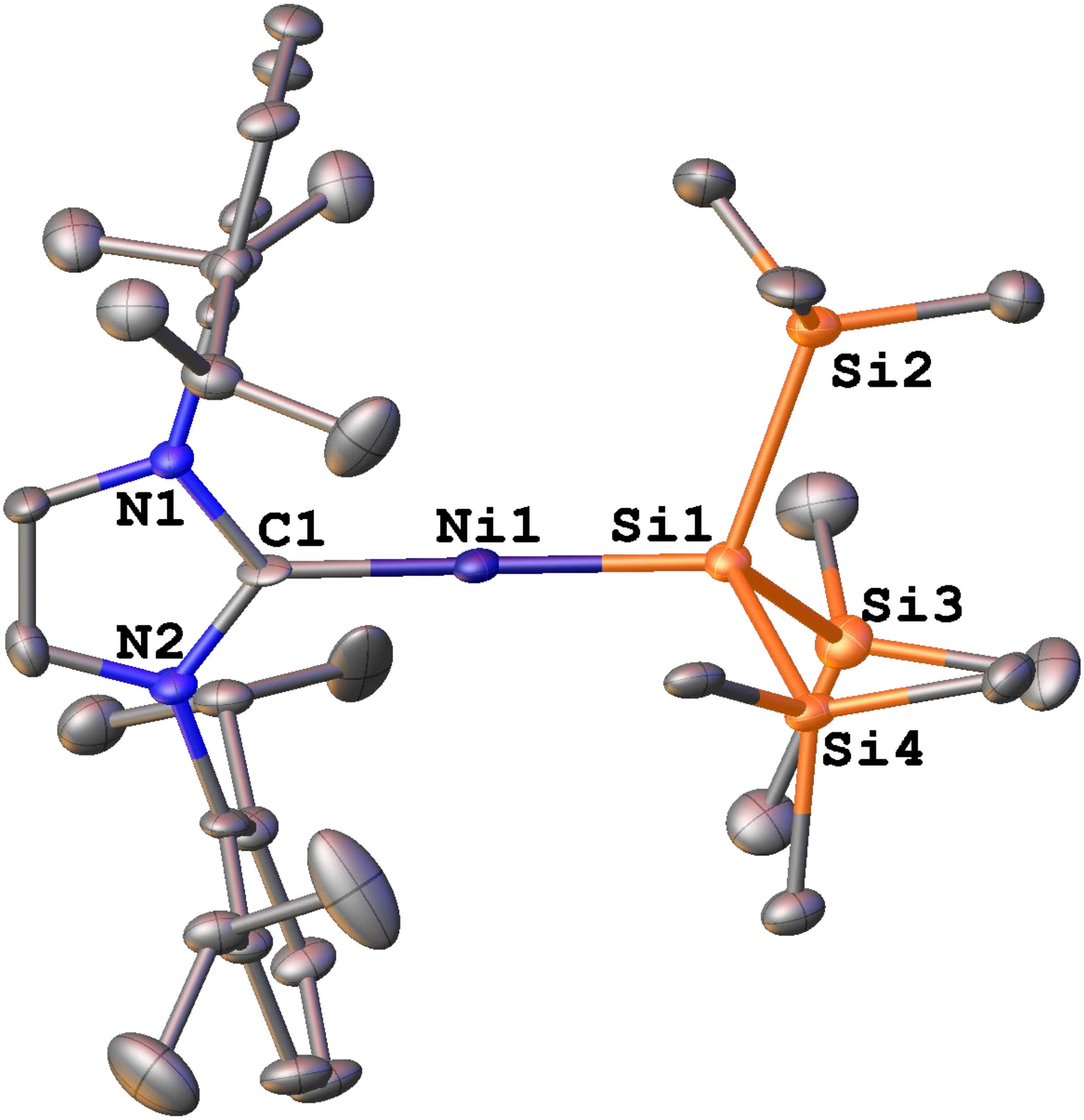




Details: The arrow indicates the initial potential and scanning direction. The scan rate was 100 mV/s, and two complete cycles are displayed on each voltammagram. They show two irreversible oxidations at -0.952 and 0.667 V. There is also one irreversible reduction at -2.55 V. The oxidations give rise to reductions at -0.289 and -1.51 V.

3) Single crystal X-ray diffraction crystal structure figures and data tables

Figure SC1. Solid state structure of (IPr)Ni–Si(SiMe_3)$_3$ (**1**) as determined by single crystal X-ray diffraction.

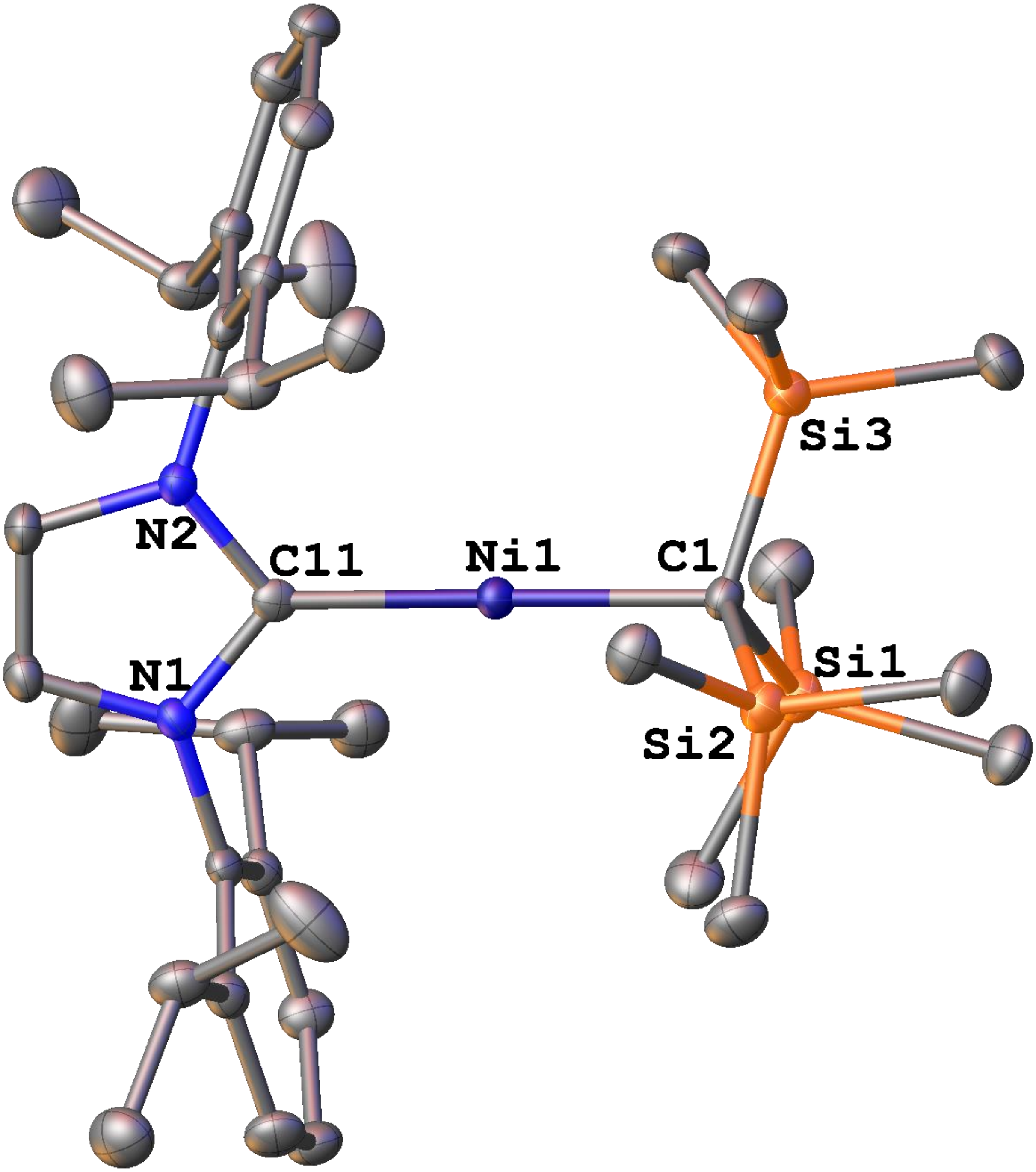


Details: Hydrogens have been eliminated for clarity and ellipsoids were set at 50% probability. Selected bond lengths [Å] and angles [°]: Ni1—Si1 = 2.283(1), Ni1—C1 = 1.935(1), Si1-Ni1-C1 = 175.8(1).

Table SC1.

Empirical formula	$C_{36}H_{63}N_2NiSi_4$
Formula weight	694.95
Temperature/K	99.98
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.9291(11)
b/Å	18.3739(18)
c/Å	21.345(2)
α/°	90
β/°	97.886(2)
γ/°	90
Volume/Å^3	4245.7(7)
Z	4
ρ_{calc}g/cm^3	1.087
μ/mm^{-1}	0.594
F(000)	1508.0
Crystal size/mm^3	0.1 × 0.08 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.936 to 51.772
Index ranges	$-13 \le h \le 13$, $-22 \le k \le 22$, $-26 \le l \le 26$
Reflections collected	115097
Independent reflections	8175 [R_{int} = 0.2168, R_{sigma} = 0.1183]
Data/restraints/parameters	8175/0/405
Goodness-of-fit on F^2	1.113
Final R indexes [I>=2σ (I)]	R_1 = 0.0849, wR_2 = 0.1931
Final R indexes [all data]	R_1 = 0.1583, wR_2 = 0.2283
Largest diff. peak/hole / e Å^{-3}	1.80/-0.52

Figure SC2. Solid state structure of (IPr)Ni–C(SiMe$_3$)$_3$ (**2**) as determined by single crystal X-ray diffraction.

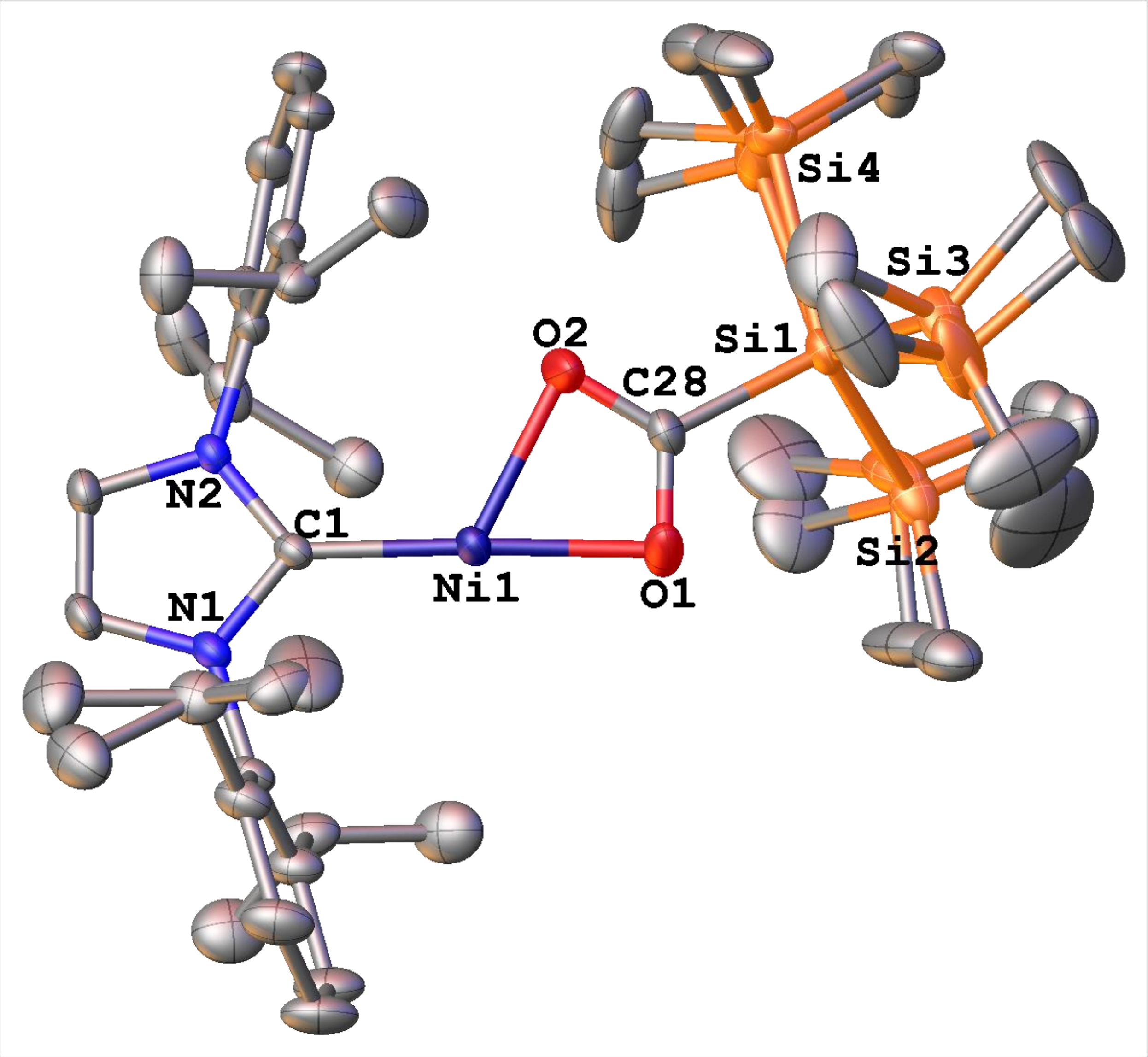


Details: Hydrogens have been eliminated for clarity and ellipsoids were set at 50% probability. Selected bond lengths [Å] and angles [°]: Ni1—C1 = 1.989(3), Ni1—C11 = 1.918(3), C1-Ni1-C11 = 175.9(1).

Table SC2.

Empirical formula	$C_{37}H_{63}N_2NiSi_3$
Formula weight	678.87
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.9273(6)
b/Å	18.0527(11)
c/Å	20.2837(13)
α/°	90
β/°	98.521(3)
γ/°	90
Volume/Å^3	3957.1(4)
Z	4
ρ_{calc}g/cm^3	1.140
μ/mm^{-1}	0.607
F(000)	1476
Crystal size/mm^3	0.100 × 0.070 × 0.030
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.036 to 50.70
Index ranges	$-13 \le h \le 13$, $-21 \le k \le 21$, $-23 \le l \le 24$
Reflections collected	60000
Independent reflections	7247 [R_{int} = 0.0576]
Data/restraints/parameters	7247/0/405
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	R_1 = 0.0532, wR_2 = 0.1264
Final R indexes [all data]	R_1 = 0.0731, wR_2 = 0.1368
Largest diff. peak/hole / e Å^{-3}	1.683/-0.277

Figure SC3. Solid state structure of (IPr)Ni(κ^2-$O_2CSi(SiMe_3)_3$) (**3**) as determined by single crystal X-ray diffraction.

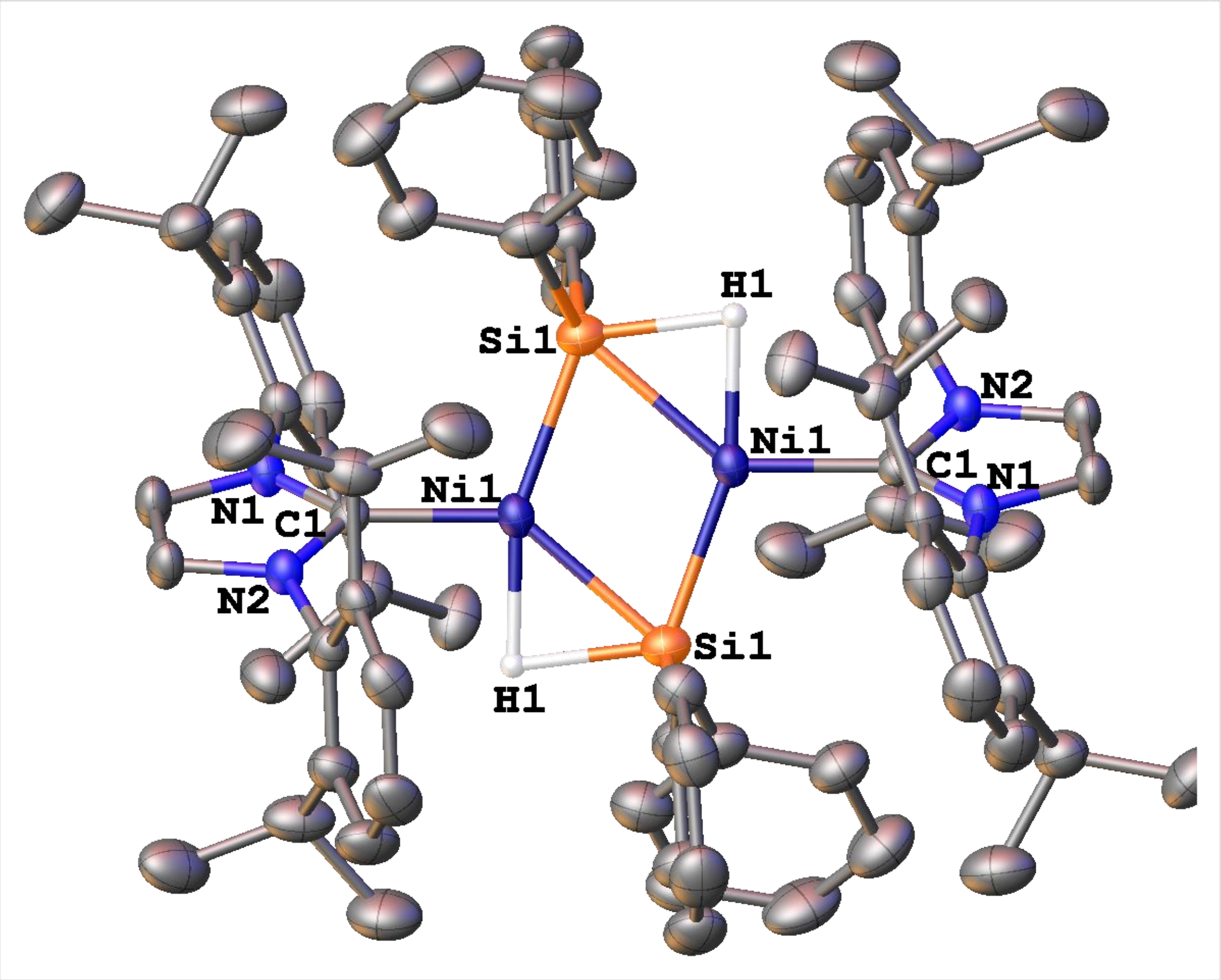


Details: Hydrogens have been eliminated for clarity and ellipsoids were set at 50% probability. The rotational disorder about –$Si(SiMe_3)_3$ and an isopropyl group have been modelled appropriately. Selected bond lengths [Å] and angles [°]: Ni1—O1 = 1.978(1), Ni1—O2 = 2.078(1), Ni1—C28 = 2.361(1), Ni1—C1 = 1.872(1), C28—O1 = 1.263(1), C28—O2 = 1.252(2), C28—Si1 = 1.931(1), C1-Ni1-O1 = 174.2(1), C1-Ni1-O2 = 117.4(1), O1-Ni1-O2 = 64.1(1), O1-C28-O2 = 117.8(1).

Table SC3.

Empirical formula	$C_{37}H_{63}N_2O_2Si_4Ni$
Formula weight	738.96
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	10.3727(4)
b/Å	14.3391(6)
c/Å	15.0287(6)
α/°	100.925(2)
β/°	91.647(2)
γ/°	96.645(2)
Volume/Å^3	2177.09(15)
Z	2
ρ_{calc}g/cm^3	1.127
μ/mm^{-1}	0.737
F(000)	798.0
Crystal size/mm^3	? × ? × ?
Radiation	synchrotron (λ = 0.7749)
2Θ range for data collection/°	5.662 to 78.318
Index ranges	$-16 \leq h \leq 16$, $-23 \leq k \leq 23$, $-24 \leq l \leq 24$
Reflections collected	38875
Independent reflections	19211 [R_{int} = 0.0302, R_{sigma} = 0.0510]
Data/restraints/parameters	19211/306/548
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0502, wR_2 = 0.1111
Final R indexes [all data]	R_1 = 0.0687, wR_2 = 0.1191
Largest diff. peak/hole / e Å^{-3}	1.14/-0.86

Figure SC4. Solid state structure of [(IPr)NiH(μ-SiPh$_2$)]$_2$ (**4**) as determined by single crystal X-ray diffraction.

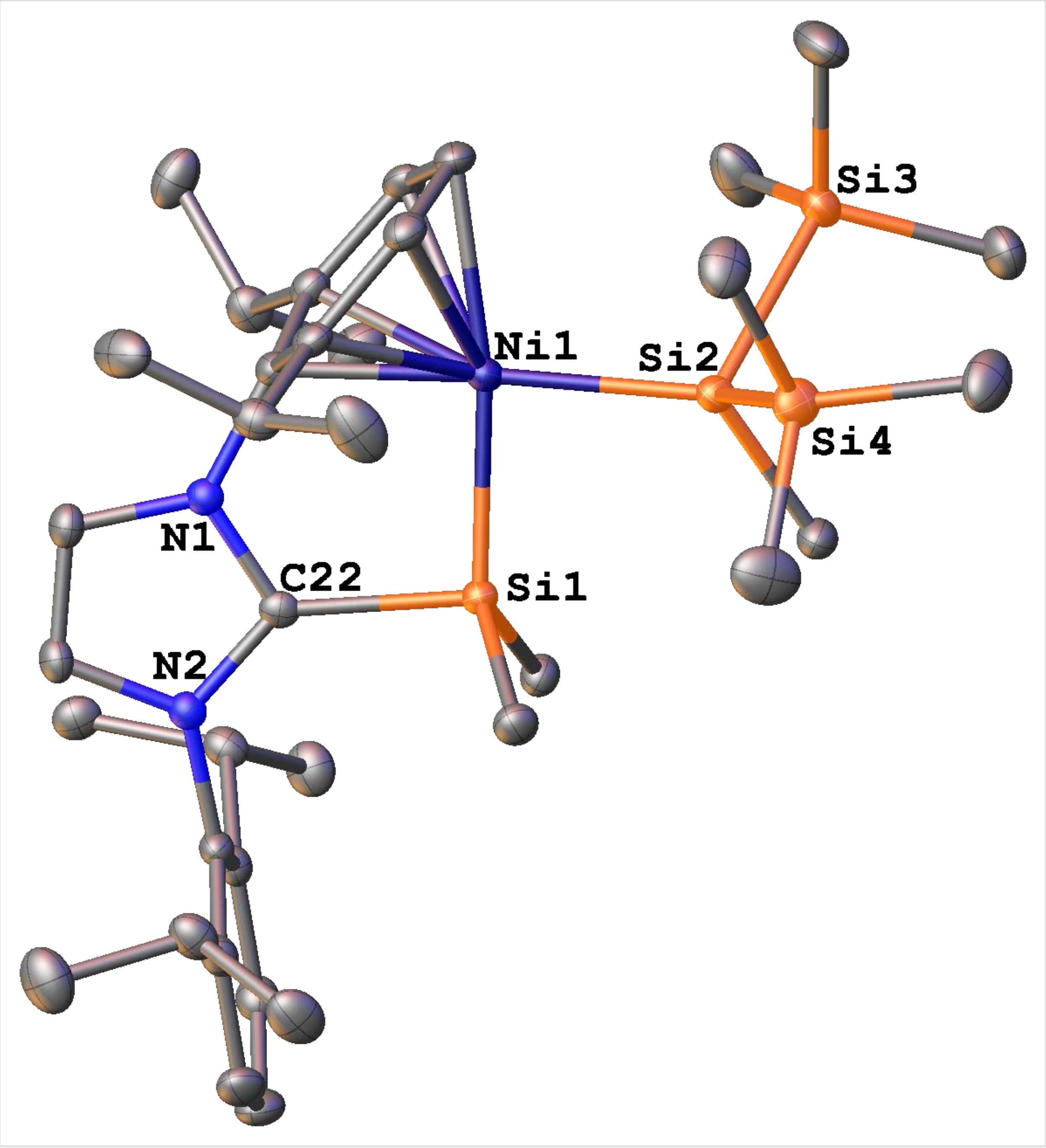


Details: Hydrogens have been eliminated for clarity and ellipsoids were set at 50% probability. Two disordered molecules of toluene were removed using SQUEEZE. Total solvent accessible volume / cell = 401.4 Å^3. Total electron count / cell = 104.4 electrons. Selected bond lengths [Å] and angles [°]: Ni1···Ni1 = 2.533(1), Ni1—Si1(μ-H1) = 2.257(1), Ni1—Si1 = 2.200(1), Ni1—C1 = 1.890(1), Ni1—H1 = 1.720(1), Si1—H1 = 1.792(1), C1-Ni1-Si1 = 109.5(1), Ni1-Si1-Ni1 = 69.3(1), Si1-Ni1-Si1 = 110.7(1), C1-Ni1-Si1(μ-H1) = 139.4(1), C1-Ni1-H1 = 89.0(1), Si1-Ni1-H1 = 51.4(1).

Table SC4.

Empirical formula	$C_{78}H_{94}N_4Ni_2Si_2$
Formula weight	1261.17
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.6870(7)
b/Å	13.8918(8)
c/Å	20.3891(11)
α/°	90
β/°	98.800(2)
γ/°	90
Volume/Å^3	3551.2(3)
Z	2
ρ_{calc}g/cm^3	1.179
μ/mm^{-1}	0.648
F(000)	1348.0
Crystal size/mm^3	0.04 × 0.04 × 0.04
Radiation	synchrotron (λ = 0.7288)
2Θ range for data collection/°	4.488 to 55.08
Index ranges	$-15 \leq h \leq 16$, $-17 \leq k \leq 17$, $-25 \leq l \leq 25$
Reflections collected	37354
Independent reflections	7578 [R_{int} = 0.0767, R_{sigma} = 0.0510]
Data/restraints/parameters	7578/0/400
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0531, wR_2 = 0.1490
Final R indexes [all data]	R_1 = 0.0677, wR_2 = 0.1611
Largest diff. peak/hole / e Å^{-3}	1.05/-0.69

Figure SC5. Solid state structure of κ^2-[1-(η^6-$C_6H_3(^iPr)_2$),2-(η^1-$SiMe_2$)-3-(DIPP)-$C_3H_2N_2$]Ni[SiMe($SiMe_3$)$_2$][B(C_6F_5)$_4$] (**5**) as determined by single crystal X-ray diffraction.

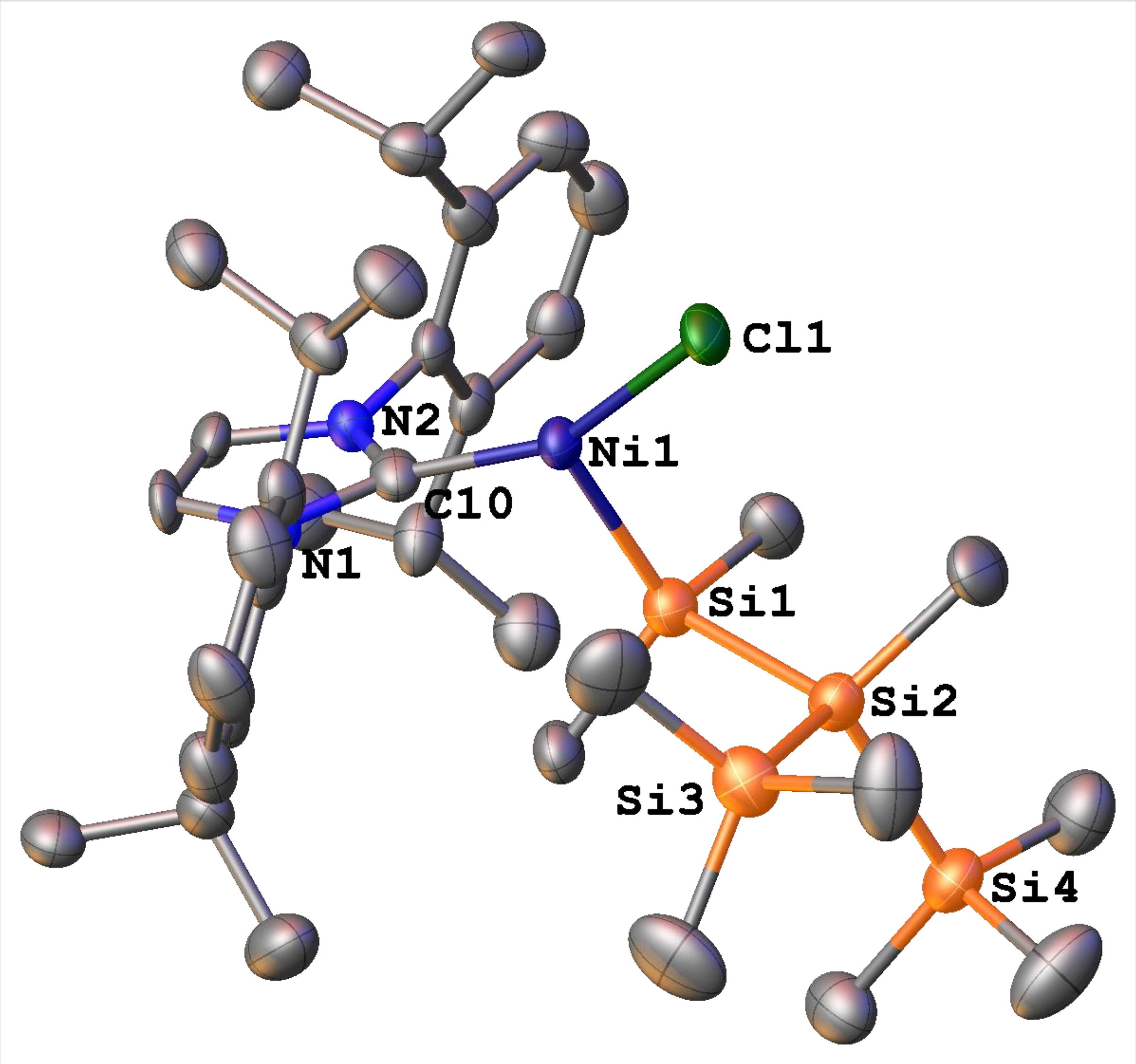


Details: Hydrogens and B(C_6F_5)$_4^-$ anion have been eliminated for clarity and ellipsoids were set at 50% probability. Selected bond lengths [Å] and angles [°]: Ni1—Si1 = 2.223(5), Ni1—Si2 = 2.276(6), Ni1—DIPP = 1.662, C22—Si1 = 1.968(2), C22—N1 = 1.350(2), C22—N2 = 1.354(2), C22-Si1-Ni1 = 95.3(1), Si1-Ni1-Si2 = 87.6(1).

Table SC5.

Empirical formula	$C_{60}H_{63}BF_{20}N_2NiSi_4$
Formula weight	1374.00
Temperature/K	100
Crystal system	triclinic
Space group	P -1
a/Å	10.7613(5)
b/Å	17.1090(8)
c/Å	28.0799(8)
α/°	97.169(2)
β/°	98.893(2)
γ/°	106.986(2)
Volume/Å^3	3094.0(2)
Z	2
ρ_{calc}g/cm^3	1.475
μ/mm^{-1}	0.492
F(000)	1412
Crystal size/mm^3	0.200 × 0.120 × 0.120
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.318 to 50.808
Index ranges	$-12 \le h \le 12$, $-20 \le k \le 20$, $-21 \le l \le 21$
Reflections collected	96364
Independent reflections	11374 [R_{int} = 0.0270]
Data/restraints/parameters	11374/0/810
Goodness-of-fit on F^2	1.074
Final R indexes [I>=2σ (I)]	R_1 = 0.0291, wR_2 = 0.0732
Final R indexes [all data]	R_1 = 0.0314, wR_2 = 0.0747
Largest diff. peak/hole / e Å^{-3}	0.289/-0.262

Figure SC6. Solid state structure of (IPr)NiCl[$SiMe_2SiMe(SiMe_3)_2$] (**6**) as determined by single crystal X-ray diffraction.

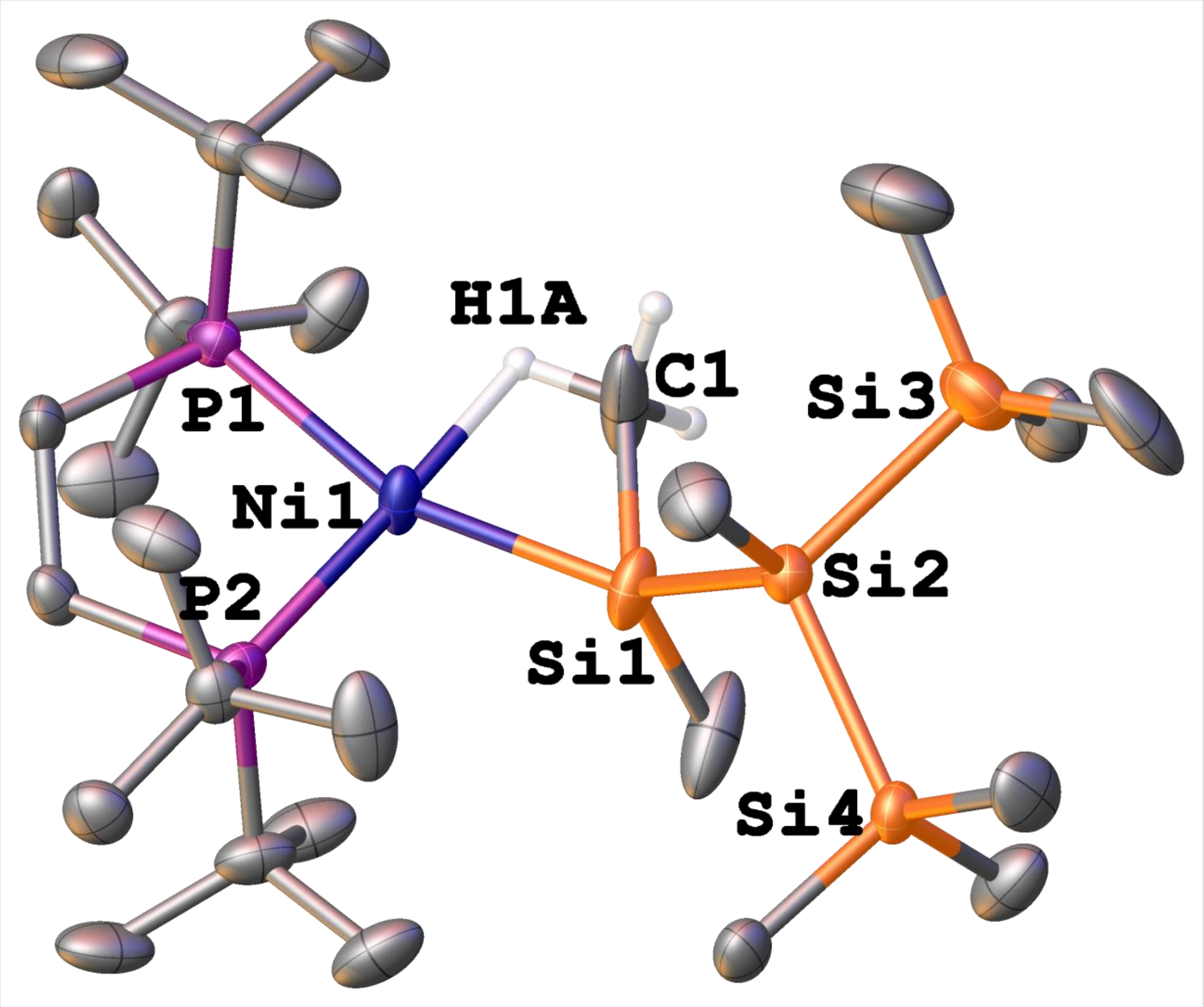


Details: Hydrogens have been eliminated for clarity and ellipsoids were set at 50% probability. Selected bond lengths [Å] and angles [°]: Ni1—C10 = 1.850(7), Ni1—Si1 = 2.231(3), Ni1—Cl1 = 2.129(1), C10-Ni1-Si1 = 94.5(3), Si1-Ni1-Cl1 = 107.9(1), Cl1-Ni1-C10 = 156.8(3).

Table SC6.

Empirical formula	$C_{36}H_{63}ClN_2NiSi_4$
Formula weight	730.40
Temperature/K	100
Crystal system	orthorhombic
Space group	P b c a
a/Å	16.488(2)
b/Å	18.790(3)
c/Å	27.260(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	8446(3)
Z	8
ρ_{calc}g/cm^3	1.149
μ/mm^{-1}	0.661
F(000)	3152
Crystal size/mm^3	0.150 × 0.040 × 0.020
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.610 to 50.722
Index ranges	$-19 \leq h \leq 19$, $-22 \leq k \leq 18$, $-32 \leq l \leq 19$
Reflections collected	40472
Independent reflections	7714 [R_{int} = 0.1730]
Data/restraints/parameters	7714/0/414
Goodness-of-fit on F^2	1.007
Final R indexes [I>=2σ (I)]	R_1 = 0.0831, wR_2 = 0.1933
Final R indexes [all data]	R_1 = 0.2029, wR_2 = 0.2541
Largest diff. peak/hole / e Å^{-3}	1.895/-0.524

Figure SC7. Solid state structure of (dtbpe)Ni[$SiMe_2SiMe(SiMe_3)_2$] (**8**) as determined by single crystal X-ray diffraction.



Details: The $B(C_6F_5)_4$ anion and most hydrogens have been eliminated for clarity and ellipsoids were set at 50% probability. The hydrogen atoms displayed were located in the electron difference map. Selected bond lengths [Å] and angles [°]: Ni1—Si1 = 2.231(1), Ni1—P1 = 2.263(1), Ni1—P2 = 2.159(1), Ni1—C1 = 2.210(1), Ni1—H1A = 1.737(1), Si1—C1 = 1.899(1), C1—H1A = 0.997(1), P1-Ni1-P2 = 92.9(1), P2-Ni1-Si1 = 107.1(1), Si1-Ni1-H1A = 76.5(1), P1-Ni1-H1A = 83.5(1), P1-Ni1-Si1 = 159.1.

Table SC7.

Empirical formula	$C_{51}H_{67}BF_{20}NiP_2Si_4$
Formula weight	1303.86
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.5880(5)
b/Å	27.7435(9)
c/Å	17.8008(6)
α/°	90
β/°	105.410(4)
γ/°	90
Volume/Å^3	5993.2(4)
Z	4
ρ_{calc}g/cm^3	1.445
μ/mm^{-1}	0.554
F(000)	2688.0
Crystal size/mm^3	0.198 × 0.167 × 0.136
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.664 to 50.698
Index ranges	$-15 \leq h \leq 15$, $-33 \leq k \leq 29$, $-17 \leq l \leq 21$
Reflections collected	50009
Independent reflections	10967 [R_{int} = 0.0844, R_{sigma} = 0.0879]
Data/restraints/parameters	10967/0/744
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0562, wR_2 = 0.1202
Final R indexes [all data]	R_1 = 0.1011, wR_2 = 0.1352
Largest diff. peak/hole / e Å^{-3}	1.03/-0.37

4) NMR Spectra

Note: Most spectra contain resonances for THF, Et_2O, pentane, and toluene.

Figure SN1.

(IPr)Ni–Si($SiMe_3$)$_3$ (**1**)

^1H NMR, 500.13 MHz, C_6D_6

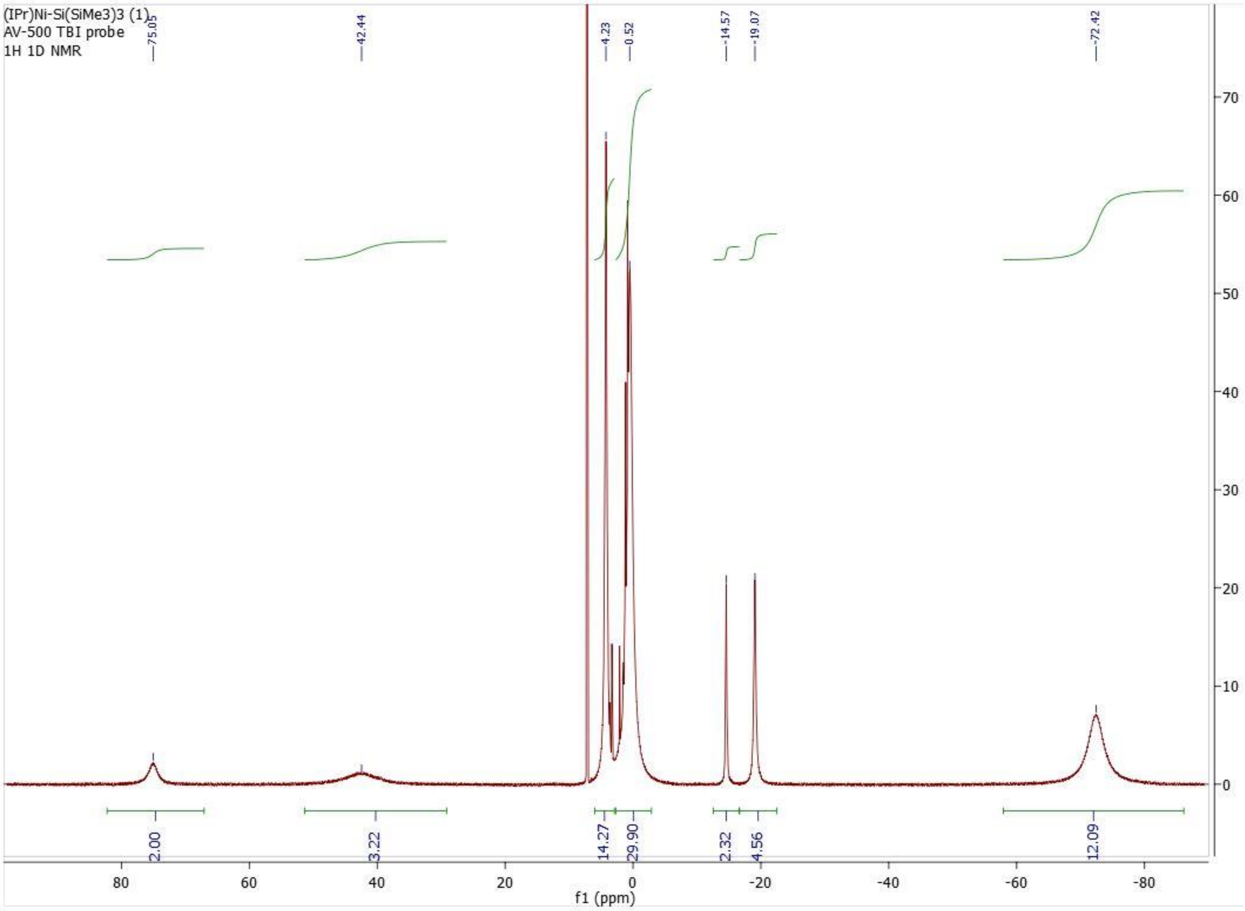


Figure SN2.

(IPr)Ni–C(SiMe$_3$)$_3$ (**2**)

^{1}H NMR, 300.13 MHz, C$_6$D$_6$

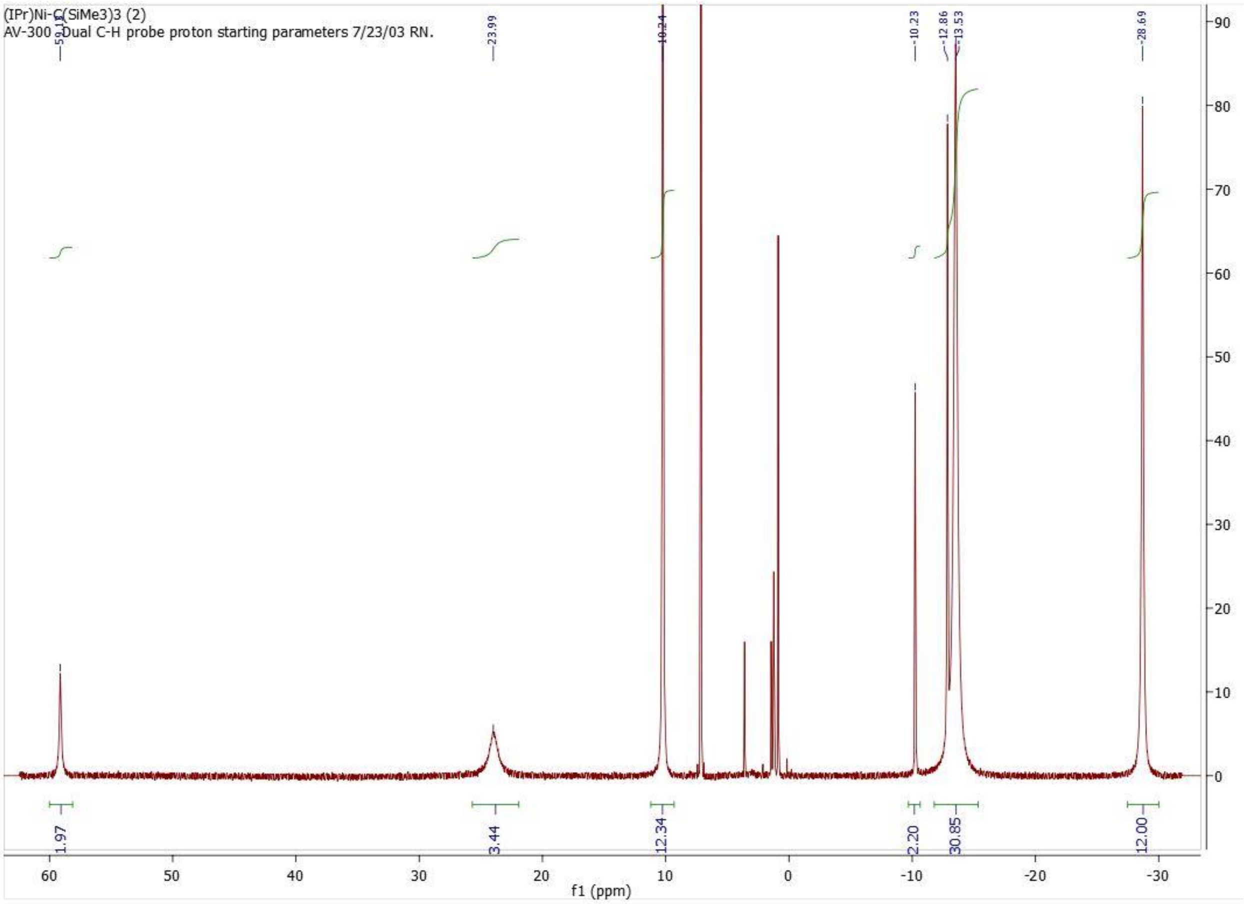


Figure SN3.

(IPr)Ni(κ^2-$O_2CSi(SiMe_3)_3$) (**3**)

^{1}H NMR, 400.13 MHz, C_6D_6

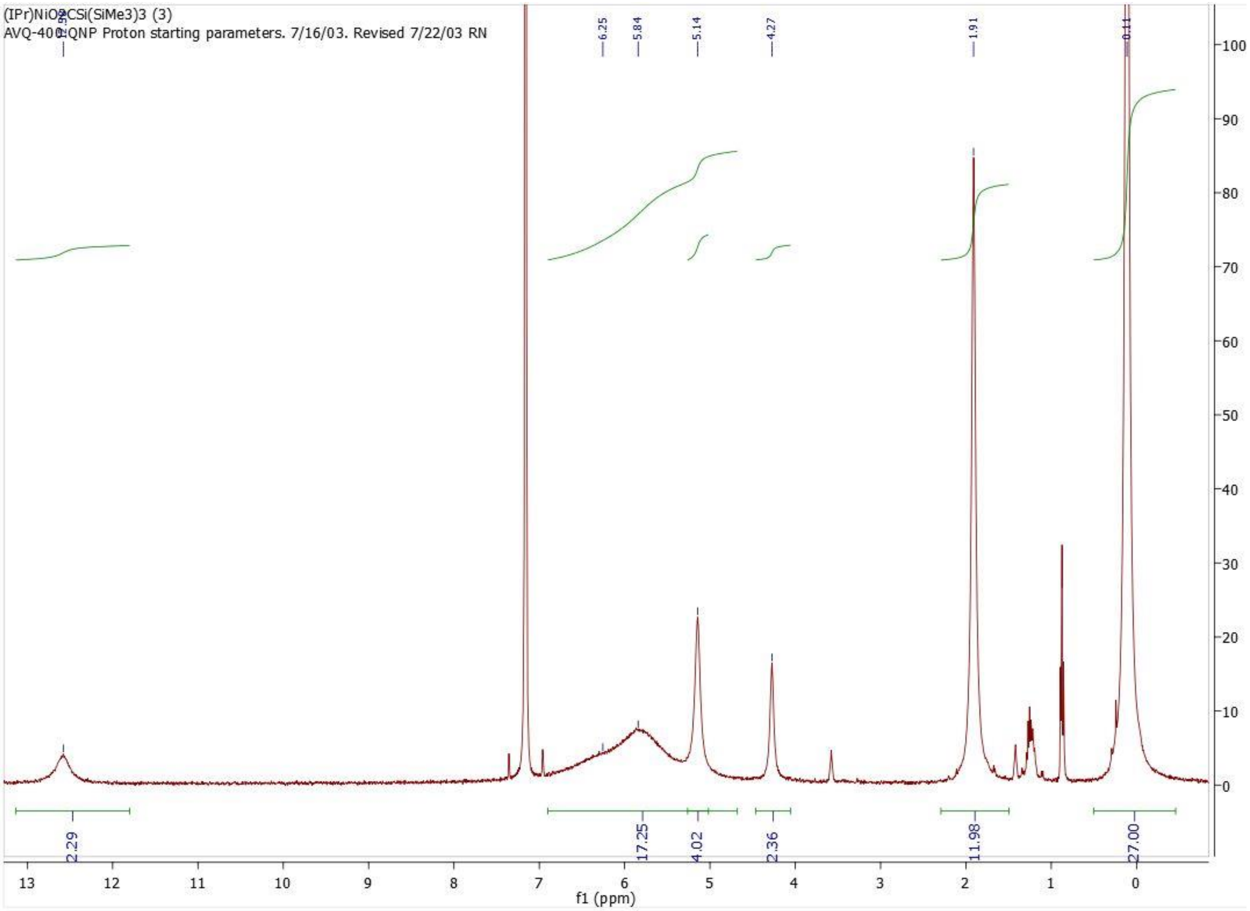


Figure SN4.

κ^2-[1-(η^6-C_6H_3(^{i}Pr)$_2$),2-(η^1-$SiMe_2$)-3-(DIPP)-$C_3H_2N_2$]Ni[SiMe($SiMe_3$)$_2$][B(C_6F_5)$_4$] (**5**)

^{1}H NMR, 600.13 MHz, THF-d$_8$

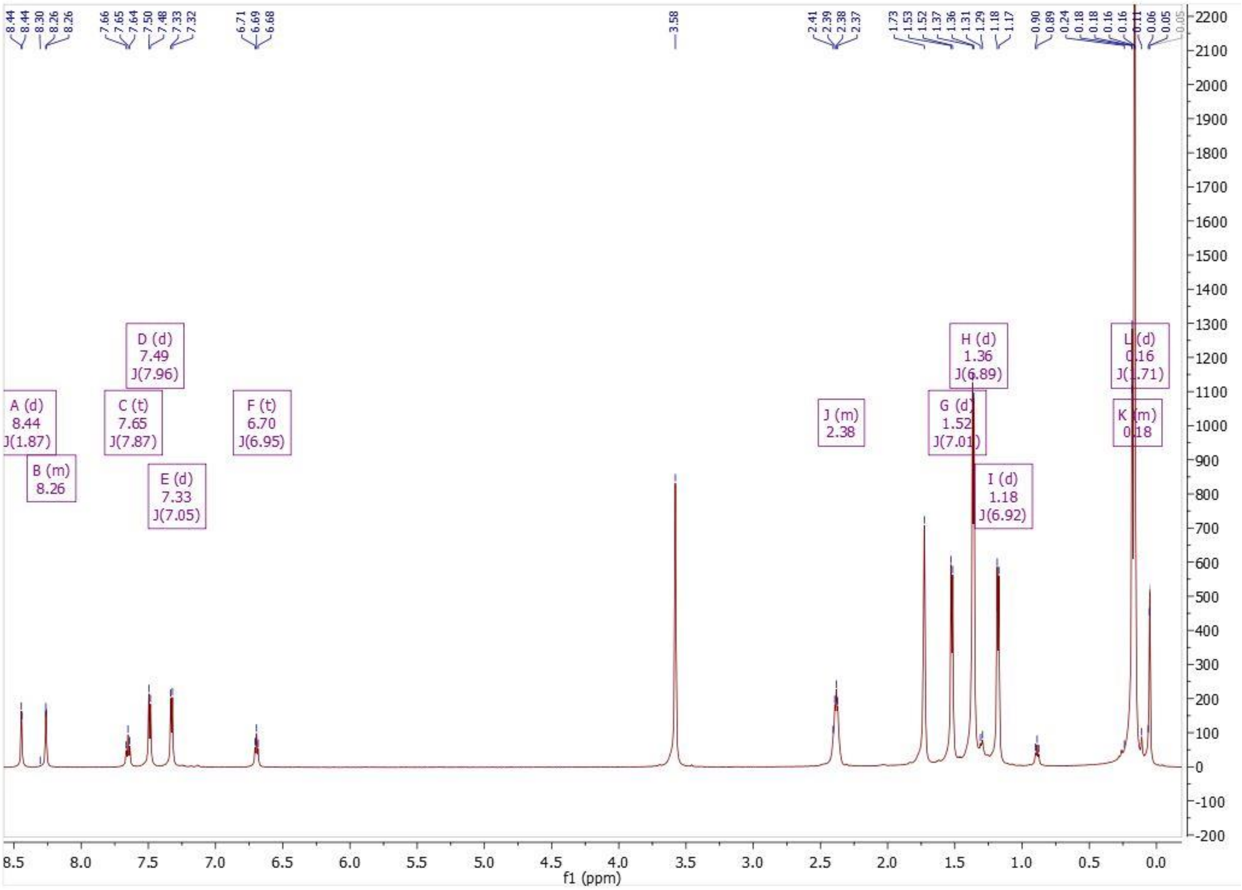


Figure SN5.

κ^2-[1-(η^6-C_6H_3(^{i}Pr)$_2$),2-(η^1-$SiMe_2$)-3-(DIPP)-$C_3H_2N_2$]Ni[SiMe($SiMe_3$)$_2$][B(C_6F_5)$_4$] (**5**)

^{13}C NMR, 150.2 MHz, THF-d_8

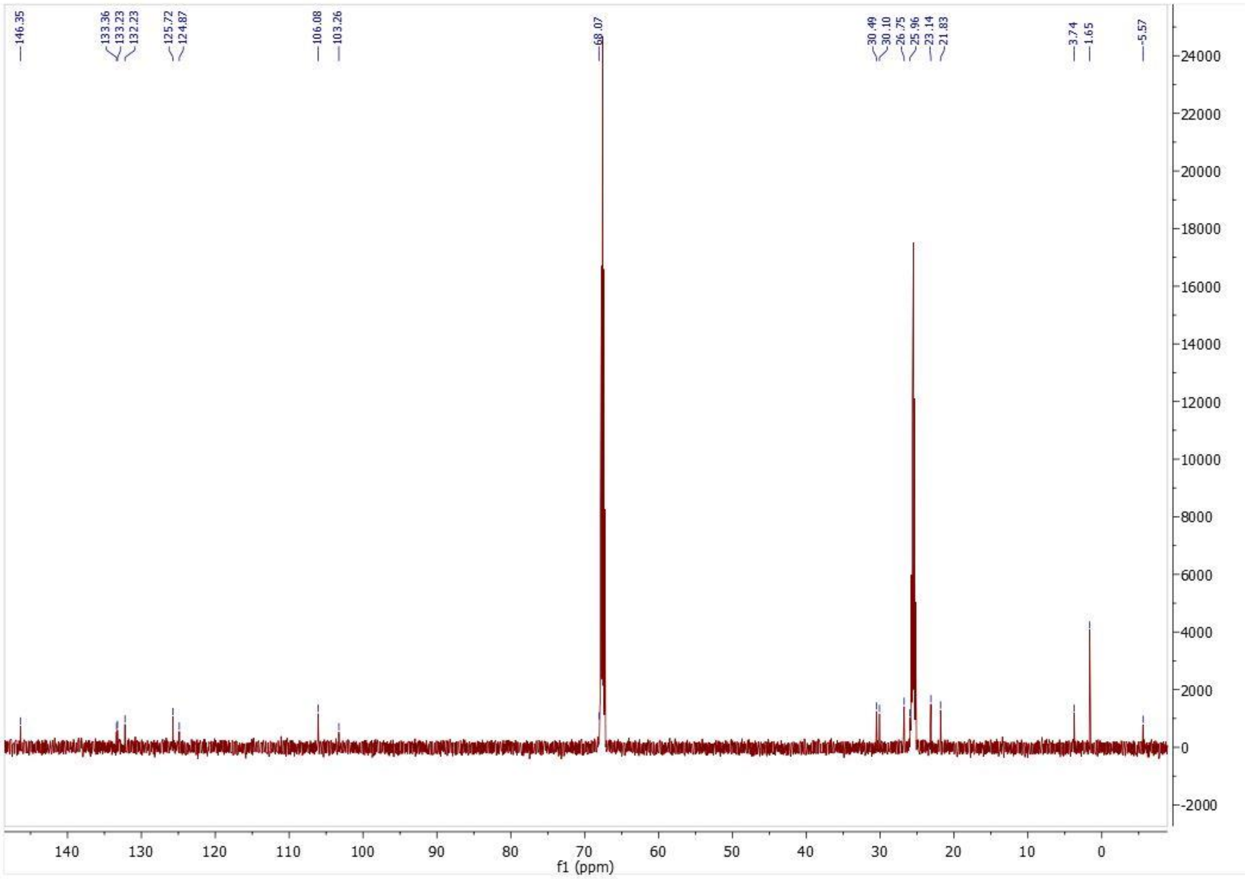
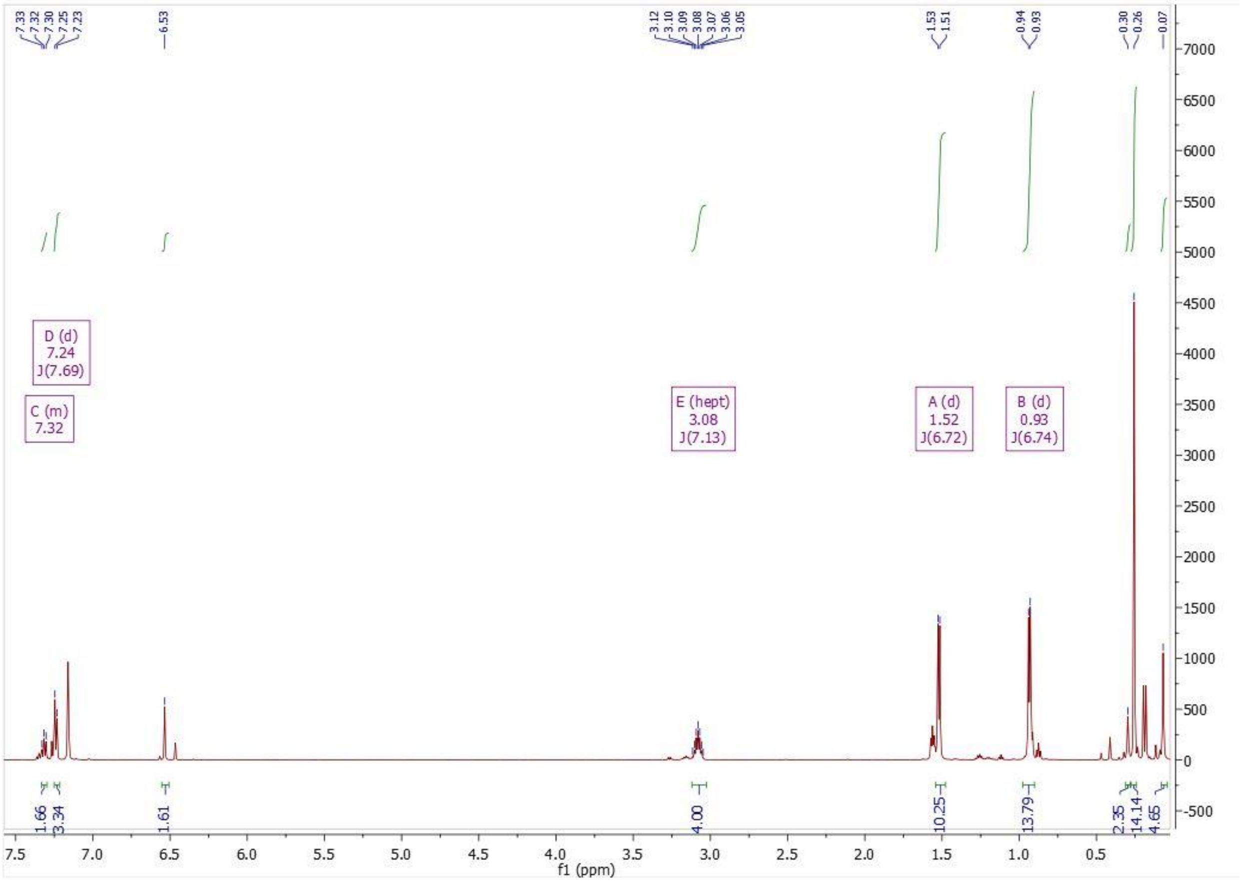


Figure SN6.

(IPr)NiCl[SiMe$_2$SiMe(SiMe$_3$)$_2$] (**6**)

^{1}H NMR, 500.23 MHz, C_6D_6

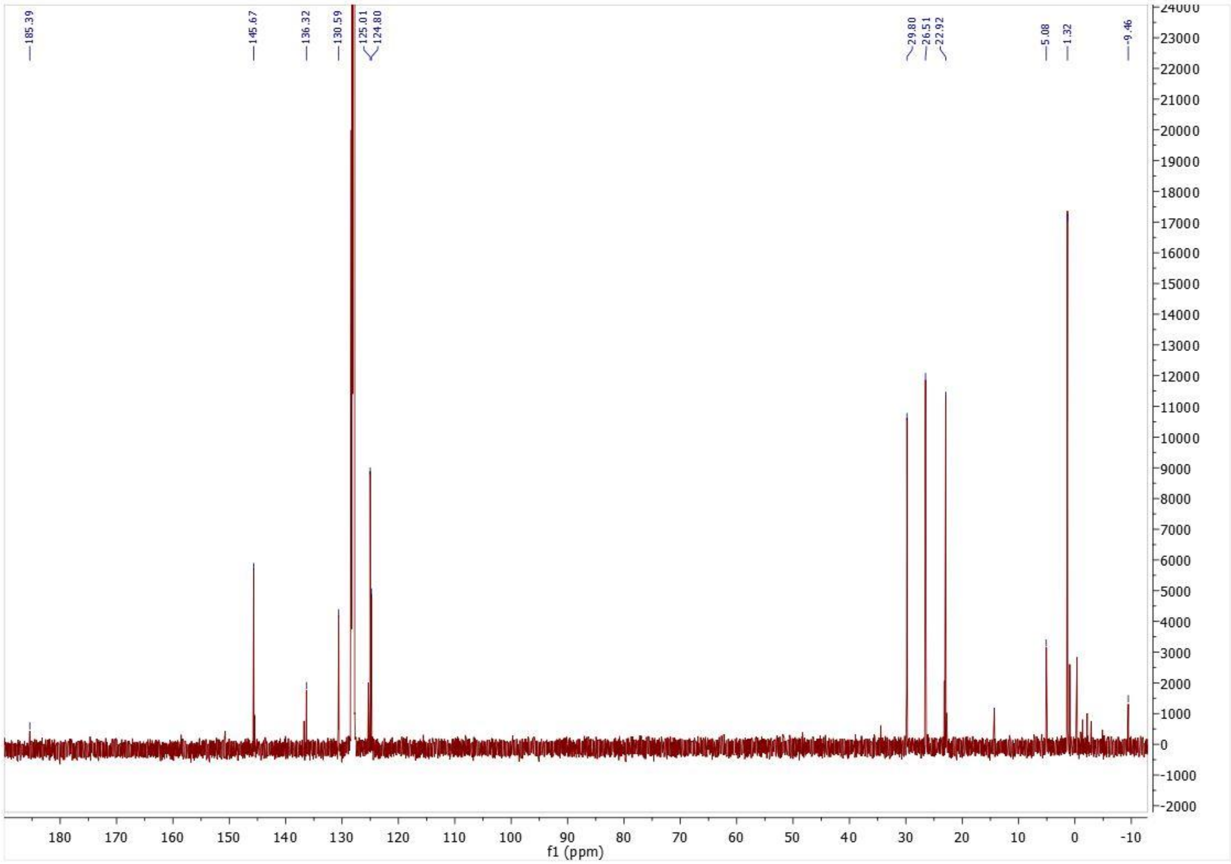


There is a minor unidentified impurity.

Figure SN7.

(IPr)NiCl[SiMe$_2$SiMe(SiMe$_3$)$_2$] (**6**)

^{13}C NMR, 150.92 MHz, C$_6$D$_6$



There is a minor unidentified impurity.

Figure SN8.

(dtbpe)Ni–Si(SiMe$_3$)$_3$ (**7**)

^{1}H NMR, 600.13 MHz, C$_6$D$_6$

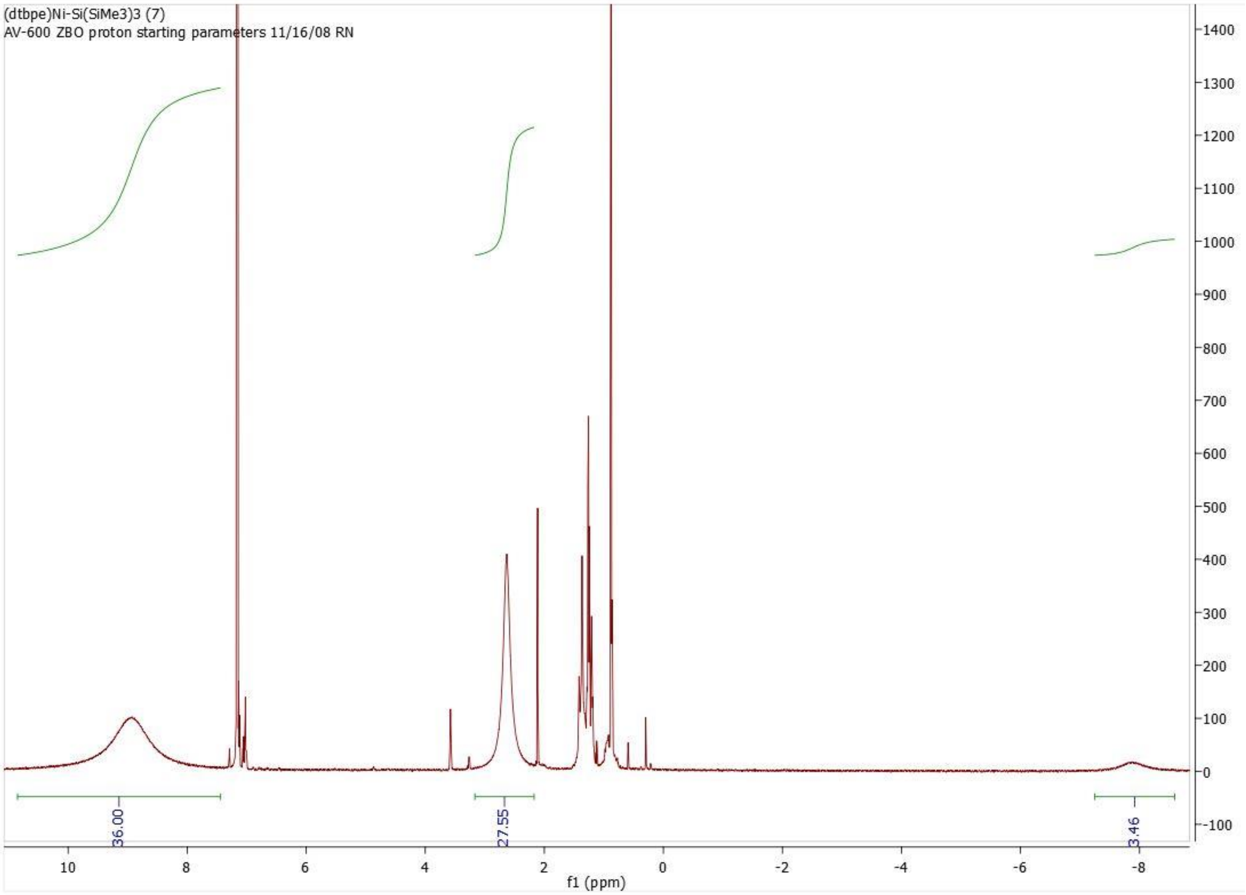


Figure SN9.

(dtbpe)Ni[SiMe$_2$SiMe(SiMe$_3$)$_2$] (**8**)

^{1}H NMR, 600.13 MHz, C$_6$D$_5$Br

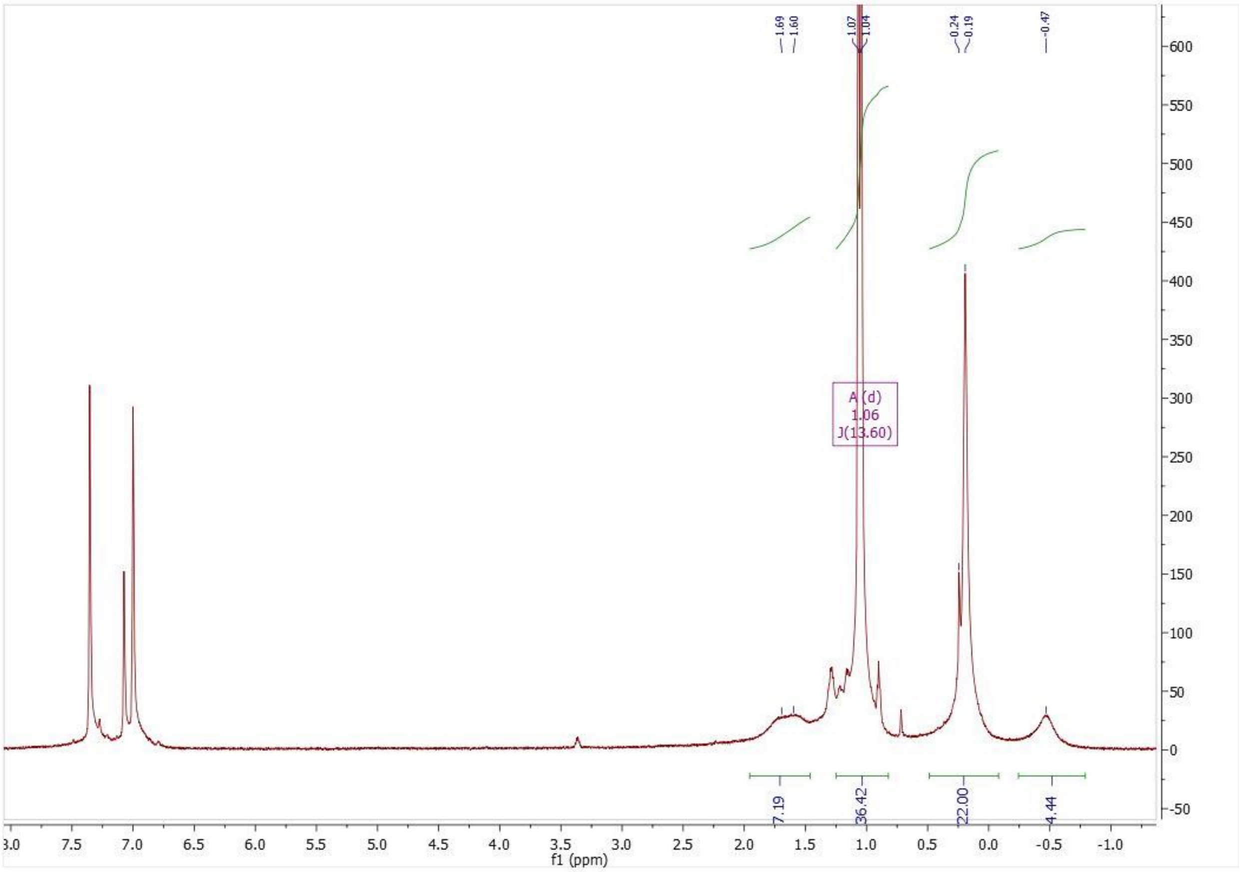
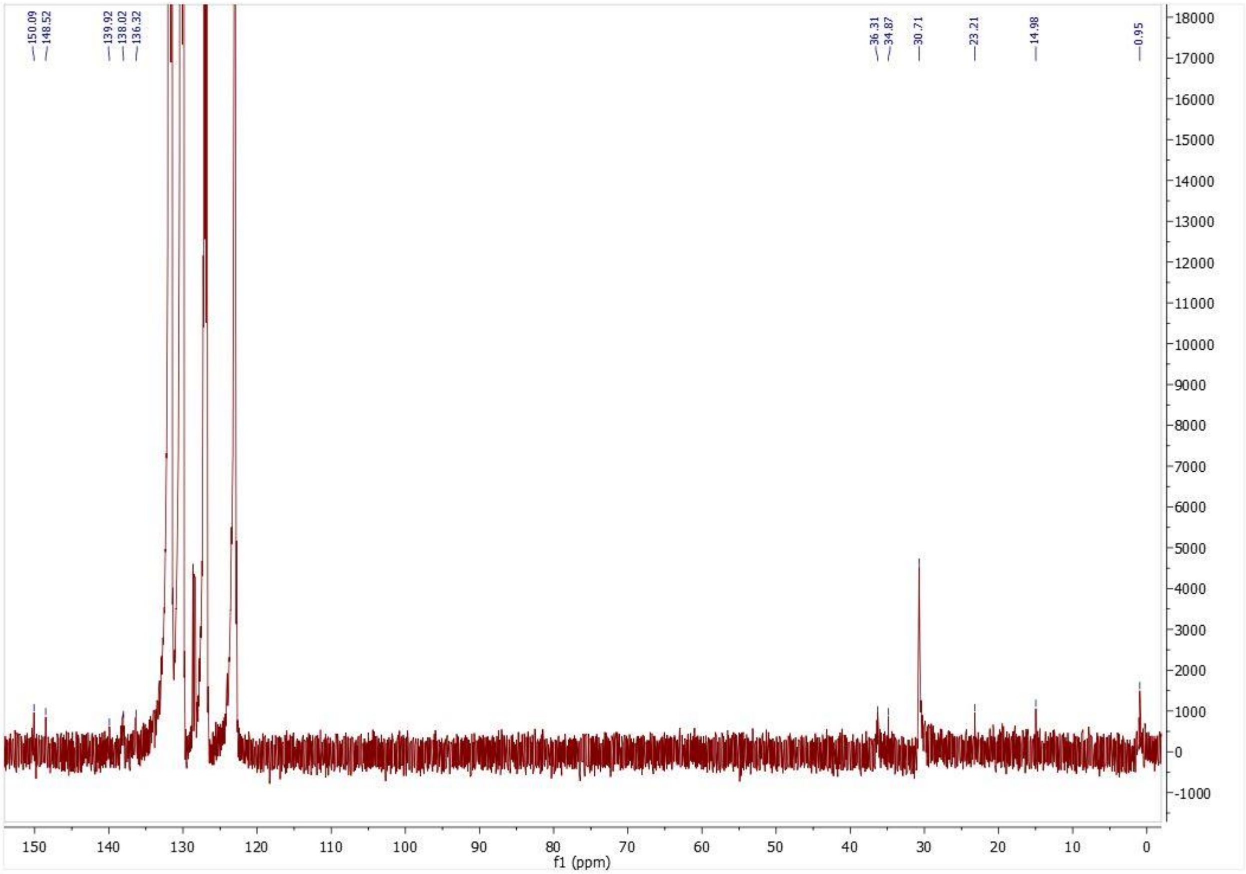


Figure SN10.

(dtbpe)Ni[$SiMe_2SiMe(SiMe_3)_2$] (**8**)

^{13}C NMR, 150.92 MHz, C_6D_5Br



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