

## Supporting Information

### Synthesis and Reactivity of an Easily Prepared, Strictly Two-Coordinate Nickel(II) bis(amido) Complex

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#### Experimental

**General Considerations.** Unless stated otherwise, all reactions and procedures were carried out in a VAC Atmosphere Nexus glovebox or using standard Schlenk techniques under a nitrogen atmosphere. Solvents were received from Sigma Aldrich, degassed and dried using a Vac Atmosphere Solvent Purifier system and stored over 3Å molecular sieves. Prior to drying, toluene, benzene and pentane were treated to remove thiophenes and olefins as appropriate, using standard techniques.<sup>1</sup> Acetonitrile was dried by stirring over CaH<sub>2</sub> and was then distilled under a nitrogen atmosphere. C<sub>6</sub>D<sub>6</sub> was purchased from Cambridge Isotope Laboratories, dried over Na/K alloy, and then degassed by several freeze-pump-thaw cycles. All silanes were purchased from Gelest, stored under nitrogen and used as received. 2,6-dimethylphenylisocyanide and 4-(N,N-dimethylamino)pyridine were purchased from Sigma Aldrich and used as received. Oxygen gas was purchased from Praxair and used without additional purification or drying. Lithium (trimethylsilyl)(2,6-diisopropylphenyl) amide<sup>2</sup> was prepared according to a literature procedure. Molecular sieves were activated by evacuation overnight at approximately 200°C. GC-MS analysis was performed using an Agilent Technologies 6890N GC system equipped with an HP-5MS column and an Agilent Technologies 5973 Network Mass Selective detector. All NMR spectra were collected at ambient temperature (ca. 23°C) on Bruker AVB-400, AV-500, AV-600 or AVQ-400 NMR spectrometers equipped with a 5 mm BB probe, as appropriate and referenced to the residual proteo solvent signals. Solution magnetic susceptibilities were determined by <sup>1</sup>H NMR spectroscopy using Evans' method.<sup>3</sup> X-ray analyses were carried out at UC Berkeley CHEXRAY crystallographic facility. Measurements of **1-5** were made on an APEX CCD area detector with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). IR spectra were collected on a Bruker Alpha-P FT-IR Spectrometer equipped with a "Platinum" Attenuated Total Reflection sample module. The abbreviation "IPr" refers to N,N'-1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene.

**Ni[N(SiMe<sub>3</sub>)(DIPP)]<sub>2</sub> (**1**).** To a 100 mL round bottom Schlenk flask was added lithium (trimethylsilyl)(2,6-diisopropylphenyl)amide (1.005 g, 3.935 mmol) and nickel(II) bromide dimethoxyethane adduct (0.640 g, 2.077 mmol). Approximately 25 mL of benzene was added to form a dark suspension which quickly became dark purple. The mixture was stirred at ambient temperature for 6 hours. The volatile components were then removed under reduced pressure, and to the resulting residue was added 50 mL of hexanes and the mixture was stirred for 1 hour. The mixture was filtered, and the filtrate cooled to -78°C for 17 hours, yielding 0.945 g (86%) of **1** as dark purple block-like crystals. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 23°C)  $\delta$  65.63 (m-Ar-H or Me<sub>2</sub>C-H, 4H), 56.28 (m-Ar-H or Me<sub>2</sub>C-H, 4H), 41.27 (HC(CH<sub>3</sub>)<sub>2</sub>, 12H), 11.79 (HC(CH<sub>3</sub>)<sub>2</sub>, 12H), 6.40 (Si(CH<sub>3</sub>)<sub>3</sub>, 18H), -91.70 (p-Ar-H, 2H).  $\mu_{\text{eff}} = 2.67\mu_{\text{B}}$  (C<sub>6</sub>D<sub>6</sub>, 22°C, Evans' method). MP = 164.5-

<sup>1</sup> Armarego, W. L. F.; Chai, C. L. L. Purification of Organic Chemicals. *Purification of Laboratory Chemicals*, 6<sup>th</sup>

<sup>2</sup> Chao, Y.-W.; Wexler, P. A.; Wigley, D. E. *Inorg. Chem.* **1989**, *28*, 3860.

<sup>3</sup> Evans, D. F. *J. Chem. Soc.*, **1957**, 2003

166°C. Anal. Calcd. for  $C_{30}H_{52}N_2Ni$ : C, 64.85%; H, 9.43%; N, 5.04%. Found: C, 64.96%; H, 9.26%; N, 4.98%. Crystals suitable for X-ray diffraction were obtained from the workup described above.

**Ni[N(SiMe<sub>3</sub>)(DIPP)]<sub>2</sub>(DMAP) (2).** To a 20 mL scintillation vial was added **1** (0.0350 g, 0.063 mmol) which was dissolved in approximately 4 mL of pentane to form a dark purple solution. To this solution was added DMAP (4-(N,N-dimethylamino)pyridine) (0.0077 g, 0.063 mmol) and the mixture was manually shaken for approximately 3 minutes, during which the color changed to dark red. The volatile components were removed under reduced pressure and the resulting red solid residue was extracted with 2 mL of pentane and the extracts were filtered and placed in the freezer at -35°C overnight, yielding 0.038 g (89%) of **2** as dark red crystals.  $\mu_{\text{eff}} = 3.07 \mu_B$  ( $C_6D_6$ , 21°C, Evans' method) Anal. Calcd. for  $C_{37}H_{62}N_4NiSi_2$ : C, 65.57%; H, 9.22%; N, 8.27%. Found: C, 65.42%; H, 9.25%; N, 8.19%. Crystals suitable for X-ray diffraction were obtained from the workup described above. <sup>1</sup>H NMR spectra of **2** exhibited extremely broad signals which were difficult to integrate. We attribute this to the paramagnetism of **2**.

**Ni[N(SiMe<sub>3</sub>)(DIPP)]<sub>2</sub>(MeCN) (3).** To a 20 mL scintillation vial was added **1** (0.0996 g, 0.174 mmol) which was dissolved in approximately 4 mL of pentane forming a dark purple solution. To this solution was added 10 drops of acetonitrile and the solution was stirred vigorously for 20 minutes, during which the color changed to dark red. The volatile components were removed under reduced pressure and the resulting red solid residue was redissolved in approximately 1 mL of hexanes and the resulting solution was placed in the freezer at -20°C overnight, yielding 0.080g (77%) of **3** as dark red crystals.  $\mu_{\text{eff}} = 2.86 \mu_B$  ( $C_6D_6$ , 20°C, Evans' method) Anal. Calcd. for  $C_{32}H_{55}N_3NiSi_2$ : C, 64.42%; H, 9.29%; N, 7.04%. Found: C, 64.47%; H, 9.26%; N, 6.96%. IR (neat solid,  $cm^{-1}$ ) 2959 m, 1424 m sh, 1310 w sh, 1239 m sh, 1189 m sh, 899 m sh, 878 m sh, 822 s, 783 s sh, Crystals suitable for X-ray diffraction were obtained from the workup described above. <sup>1</sup>H NMR spectra of **3** exhibited extremely broad signals which were difficult to integrate. We attribute this to the paramagnetism of **3**.

**[N,N-(SiMe<sub>3</sub>)(2,6-dimethylphenyl)-N'-(DIPP)carbamiimidoyl]Ni[N(SiMe<sub>3</sub>)(DIPP)][CN(2,6-dimethylphenyl)] (4).** To a 20 mL scintillation vial was added **1** (0.100 g, 0.180 mmol), 2,6-dimethylphenylisocyanide (0.0472 g, 0.360 mmol) and 8 mL of benzene, to form a dark red solution. The mixture was stirred at ambient temperature for 30 minutes, during which the color changed to a lighter red. The volatile components were removed under reduced pressure, yielding 0.147 g of **4** as a red powder which was 96% pure by <sup>1</sup>H NMR spectroscopy. Extremely pure samples of **4** were obtained by recrystallization of this red powder from 2 mL of hexanes at -35°C, to yield 0.032 g (22%) of **4** as red crystals. <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ , 23°C)  $\delta$  7.04 (d, 7.4Hz, 2H, Ar-H), 6.94 (m, 4H, Ar-H), 6.71 (m, 1H, Ar-H), 6.63 (m, 4H, Ar-H), 6.45 (t, 7.6Hz, 1H, Ar-H), 4.47 (spt, 5.3Hz, 2H, Me<sub>2</sub>C-H), 3.22 (spt, 5.3Hz, 2H, Me<sub>2</sub>C-H), 2.42 (s, 6H, Ar-CH<sub>3</sub>), 1.94 (s, 6H, Ar-CH<sub>3</sub>), 1.68 (d, 6.8Hz, 6H, HC(CH<sub>3</sub>)<sub>2</sub>), 1.46 (d, 6.9Hz, 6H, HC(CH<sub>3</sub>)<sub>2</sub>), 1.38 (d, 6.9Hz, 6H, HC(CH<sub>3</sub>)<sub>2</sub>), 1.07 (d, 6.9Hz, 6H, HC(CH<sub>3</sub>)<sub>2</sub>), 0.18 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), -0.23 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (600 MHz,  $C_6D_6$ , 22°C)  $\delta$  159.55, 159.03, 146.16, 145.28, 142.30, 138.67, 134.39, 132.66, 128.74, 128.35, 127.71, 127.57, 127.51, 126.17, 124.17, 122.68, 119.58, 28.79, 27.83, 25.89, 25.55, 25.03, 23.44, 19.71, 19.60, 4.92, 1.52. Anal. Calcd. for  $C_{48}H_{70}N_4NiSi_2$ : C, 70.48%; H, 8.63%; N, 6.85%. Found: C, 70.42%; H, 8.31%; N, 7.22%. IR (neat solid,  $cm^{-1}$ ) 2958 m, 2138 m sh, 1656 m sh, 1461 m sh, 1421 m sh, 1236 m sh, 837 s sh,

766 s sh. Crystals suitable for X-ray diffraction were obtained by slow cooling of a saturated solution in hexanes at -35°C.

**(DIPP)<sub>2</sub>N<sub>2</sub> (5).** To a 50 mL Chemglass Air-Free teflon-stoppered flask was added **1** (0.106 g, 0.191 mmol) and 15 mL of benzene, to form a dark purple solution. The solution was frozen with liquid nitrogen, and the headspace of the flask was evacuated and refilled with oxygen gas. The flask was sealed and the solution was allowed to thaw and was stirred for 20 minutes, by which time the solution had changed to dark orange. The volatile materials were removed under reduced pressure, to leave a dark orange residue. The residue was extracted with two portions of 4 mL of pentane and the extracts were filtered. The filtrate was combined and the volatile materials were removed under reduced pressure to give a gooey orange solid. Recrystallization of this solid from hexanes at -35°C yielded orange crystals of **5** (0.08g, 24%). Crystals suitable for X-ray diffraction were obtained by the method described above. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>, 23°C) δ 7.24-7.14 (m, 6H, Ar-H), 3.49 (spt, 6.7Hz, 4H, Me<sub>2</sub>C-H), 1.21 (d, 6.7Hz, 24H, HC(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>, 22°C) δ 141.26, 129.13, 128.59, 124.28, 28.00, 28.45. HRMS *m/z* Calcd. for C<sub>24</sub>H<sub>34</sub>N<sub>2</sub>: 350.2722. Found: 350.2732.

**Procedure for reaction of Ni[N(SiMe<sub>3</sub>)(DIPP)]<sub>2</sub> (1) with 1 equiv of O<sub>2</sub> gas.** To a 20 mL scintillation vial was added **1** (0.0350 g, 0.063 mmol) and Si(SiMe<sub>3</sub>)<sub>4</sub> (0.0040 g, 0.012 mmol) as an internal standard. The contents of the vial were dissolved in approximately 0.7 mL of C<sub>6</sub>D<sub>6</sub> and transferred to a J-Young NMR tube equipped with a Teflon valve. The tube was attached to a 45 mL calibrated bulb and the entire apparatus was attached to a Schlenk line. The solution was frozen and the headspace above the tube was evacuated along with the calibrated bulb. The tube was then isolated from the bulb via a Teflon valve. The vacuum manifold of the Schlenk line and the bulb were isolated from the vacuum pump and refilled with O<sub>2</sub> gas to a pressure of 6-7 mm Hg. The bulb was then isolated from the Schlenk line via a Teflon valve, and the valve was isolated the J-young tube from the bulb was opened. The tube was then submerged in liquid nitrogen for 2 hours, after which the tube was sealed and allowed to thaw. When melted, the contents of the tube were shaken for several minutes. The solution was then filtered and analysis of the products was conducted by <sup>1</sup>H NMR spectroscopy.

**Procedure for reaction of Ni[N(SiMe<sub>3</sub>)(DIPP)]<sub>2</sub> (1) with 1 atm of O<sub>2</sub> gas and isolation of the insoluble precipitate.** To a 100 mL Chemglass Air-Free Teflon-stoppered flask was added **1** (0.4010 g, 0.720 mmol) and 50 mL of benzene, to form a purple solution. The flask was attached to a Schlenk line, the solution was frozen with liquid nitrogen and the headspace was evacuated. The vacuum manifold was isolated from the vacuum pump and refilled with 1 atm of O<sub>2</sub> gas. The solution was then thawed and upon fully melting, the flask was sealed and the solution was stirred for 2 days, during which the color changed from purple to brown. After 2 days, the solution was filtered through a Bucher funnel and the dark brown powder was collected on the filter. The powder was washed three times with 10 mL of hexanes and then dried under vacuum, to give 0.165 g of a tan/brown powder. Anal. Found: C, 39.08%; H, 6.30%; N, 3.29%.

### X-ray Data

#### Compound 1:

Identification code  
Empirical formula

shelxl  
C30 H52 N2 Ni Si2

Formula weight	555.62
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 8.9248(4) Å      a = 102.092(2)°. b = 9.1680(4) Å      b = 92.571(2)°. c = 10.9493(5) Å      g = 114.391(2)°.
Volume	789.11(6) Å <sup>3</sup>
Z	1
Density (calculated)	1.169 Mg/m <sup>3</sup>
Absorption coefficient	0.711 mm <sup>-1</sup>
F(000)	302
Crystal size	0.12 x 0.08 x 0.08 mm <sup>3</sup>
Theta range for data collection	1.92 to 25.39°.
Index ranges	-10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -13 ≤ l ≤ 13
Reflections collected	15509
Independent reflections	2891 [R(int) = 0.0307]
Completeness to theta = 25.00°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9453 and 0.9196
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2891 / 0 / 167
Goodness-of-fit on F <sup>2</sup>	1.061
Final R indices [I > 2σ(I)]	R1 = 0.0241, wR2 = 0.0645
R indices (all data)	R1 = 0.0260, wR2 = 0.0658
Largest diff. peak and hole	0.380 and -0.199 e.Å <sup>-3</sup>

**Compound 2:**

Identification code	shelxl
Empirical formula	C <sub>37</sub> H <sub>62</sub> N <sub>4</sub> Ni Si <sub>2</sub>
Formula weight	677.80
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 10.5555(4) Å      a = 84.922(2)°. b = 12.6703(5) Å      b = 74.854(2)°. c = 16.2859(6) Å      g = 69.522(2)°.
Volume	1969.57(13) Å <sup>3</sup>
Z	2
Density (calculated)	1.143 Mg/m <sup>3</sup>
Absorption coefficient	0.582 mm <sup>-1</sup>
F(000)	736
Crystal size	0.18 x 0.10 x 0.06 mm <sup>3</sup>
Theta range for data collection	1.30 to 25.40°.

Index ranges	-12<=h<=12, -15<=k<=14, -19<=l<=19
Reflections collected	37916
Independent reflections	7213 [R(int) = 0.0479]
Completeness to theta = 25.00°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9659 and 0.9025
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	7213 / 0 / 398
Goodness-of-fit on F <sup>2</sup>	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0333, wR2 = 0.0788
R indices (all data)	R1 = 0.0423, wR2 = 0.0839
Largest diff. peak and hole	0.314 and -0.275 e.Å <sup>-3</sup>

**Compound 3:**

Identification code	shelxl	
Empirical formula	C32 H55 N3 Ni Si2	
Formula weight	596.68	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.6047(3) Å	a = 97.4630(10)°.
	b = 11.1888(4) Å	b = 97.333(2)°.
	c = 17.6838(5) Å	g = 110.211(2)°.
Volume	1737.61(10) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.140 Mg/m <sup>3</sup>	
Absorption coefficient	0.650 mm <sup>-1</sup>	
F(000)	648	
Crystal size	0.16 x 0.07 x 0.06 mm <sup>3</sup>	
Theta range for data collection	1.97 to 25.36°.	
Index ranges	-11<=h<=11, -13<=k<=13, -21<=l<=21	
Reflections collected	29585	
Independent reflections	6356 [R(int) = 0.0279]	
Completeness to theta = 25.00°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9620 and 0.9031	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	6356 / 0 / 358	
Goodness-of-fit on F <sup>2</sup>	1.034	
Final R indices [I>2sigma(I)]	R1 = 0.0280, wR2 = 0.0666	
R indices (all data)	R1 = 0.0337, wR2 = 0.0694	
Largest diff. peak and hole	0.359 and -0.224 e.Å <sup>-3</sup>	

**Compound 4:**

Identification code	shelxl
Empirical formula	C <sub>48</sub> H <sub>70</sub> N <sub>4</sub> Ni Si <sub>2</sub>
Formula weight	817.97
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pna2(1)
Unit cell dimensions	a = 16.3178(4) Å      a = 90°. b = 20.8353(5) Å      b = 90°. c = 13.7272(3) Å      g = 90°.
Volume	4667.06(19) Å <sup>3</sup>
Z	4
Density (calculated)	1.164 Mg/m <sup>3</sup>
Absorption coefficient	0.503 mm <sup>-1</sup>
F(000)	1768
Crystal size	0.24 x 0.18 x 0.15 mm <sup>3</sup>
Theta range for data collection	1.59 to 25.34°.
Index ranges	-19<=h<=19, -23<=k<=25, -16<=l<=16
Reflections collected	39140
Independent reflections	8159 [R(int) = 0.0265]
Completeness to theta = 25.00°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9284 and 0.8889
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	8159 / 1 / 514
Goodness-of-fit on F <sup>2</sup>	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0268, wR2 = 0.0636
R indices (all data)	R1 = 0.0305, wR2 = 0.0658
Absolute structure parameter	-0.007(8)
Largest diff. peak and hole	0.297 and -0.159 e.Å <sup>-3</sup>

**Compound 5:**

Identification code	shelxl
Empirical formula	C <sub>24</sub> H <sub>34</sub> N <sub>2</sub>
Formula weight	350.53
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 16.2978(9) Å    alpha = 90 deg. b = 9.4465(5) Å    beta = 100.003(2) deg. c = 13.7560(8) Å    gamma = 90 deg.
Volume	2085.6(2) Å <sup>3</sup>
Z, Calculated density	4, 1.116 Mg/m <sup>3</sup>
Absorption coefficient	0.065 mm <sup>-1</sup>

F(000)	768
Crystal size	0.15 x 0.06 x 0.04 mm
Theta range for data collection	2.50 to 25.37 deg.
Limiting indices	-19<=h<=19, -11<=k<=11, -16<=l<=16
Reflections collected / unique	13521 / 1914 [R(int) = 0.0448]
Completeness to theta = 25.00	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9974 and 0.9904
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	1914 / 0 / 122
Goodness-of-fit on F <sup>2</sup>	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0392, wR2 = 0.0901
R indices (all data)	R1 = 0.0553, wR2 = 0.0991
Largest diff. peak and hole	0.177 and -0.180 e.A <sup>-3</sup>