Supporting Information for:

A Terminal Ni(III)-Imide with Diverse Reactivity Pathways

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Contents

General Experimental Details

Preparation of Compounds

EPR Spectra of Compounds 2 and 8 (Figures S1 – S2)

Plots of $\mu_{\text{eff}}$ vs. T in Solid State for 4 and 8 (Figure S3)

Computational Details (Tables S1 – S3; Figures S4 – S5; Scheme S1)

Fully labeled ORTEP diagrams for compounds 2 - 5, 7 and 8 (Figures S6 – S11)

General Experimental Details

All experiments were carried out in a dry nitrogen atmosphere using an MBraun glovebox and/or standard Schlenk techniques. 4A molecular sieves were activated in vacuo at 180 °C for 24 h. Dry dioxane was purchased from Aldrich and was stored over activated 4A molecular sieves. Diethyl ether and tetrahydrofuran (THF) were first sparged with nitrogen and then dried by passage through activated alumina columns.¹ Pentane was first washed with conc. HNO₃ / H₂SO₄ to remove olefins, stored over CaCl₂ and then distilled before use from sodium/benzophenone. All deuterated solvents were sparged with nitrogen, dried over activated 4A molecular sieves and stored under nitrogen. ¹H and ¹³C NMR spectra were recorded on a Mercury Varian 300 MHz spectrometer (300 and 75.4 MHz, respectively). All NMR spectra, including Evans method data, were recorded at room temperature unless otherwise noted and were indirectly referenced to TMS using residual solvent signals as internal standards. ³¹P NMR spectra were recorded at 121.4 MHz using an external reference of 85% H₃PO₄. X-band EPR spectra were recorded in toluene at RT or as a glass at 77K in a quartz tube.
using a Bruker EMX-A spectrometer control system equipped with a Bruker B-E2549 10-inch magnet and a built-in microwave frequency meter. Elemental analyses were performed on a Perkin-Elmer PE2400 microanalyzer in our laboratories.

Ethylmagnesium chloride, potassium hydride, thallium(I) acetate, 1-adamantylazide, and trimethylsilyl azide were purchased from Aldrich and used as received. Potassium hydride was obtained from Aldrich as a dispersion in mineral oil; it was filtered and washed with pentane to afford a dry powder. Hydrogen gas was purchased from MG Industries and used as received. \([\text{Me}_2\text{NN}]\text{Ni(Et)(2,4-lutidine)},^2\) and \(2,4\text{-bis(2,4,6-trimethylphenylimido)pentane}^3\) \((\text{H}[\text{Me}_3\text{NN}])\) were synthesized according to literature procedures.

**Synthesis of 2 – 8 with spectroscopic and analytical details.**

\([\text{Me}_2\text{NN}]\text{Ni(2,4-lutidine)}\) (2). \([\text{Me}_2\text{NN}]\text{Ni(Et)(2,4-lutidine)}\) (3.68 g, 7.35 mmol) was dissolved in 50 mL ether and transferred to a 150 mL high pressure vessel and charged with 80 psi \(\text{H}_2\). The solution was stirred for 1 h over which time the solution turned deep red. After carefully exhausting excess \(\text{H}_2\) gas, the solution was filtered through Celite. The filtrate was concentrated and left overnight to crystallize at -35 °C. Deep red crystals were collected on a frit, washed with cold ether (2 × 2 mL), and dried in vacuo to afford 2.22 g (64 %) of the product. \(\mu_{\text{eff}} = 1.81\) B.M. \((\text{C}_6\text{D}_6\) with ca. 10 equiv. added \(2,4\text{-lutidine})\). EPR (toluene, 77K, frozen glass) \(g_1 = 2.433, g_2 = 2.134, g_3 = 2.067\). Anal. Caled for \(\text{C}_{28}\text{H}_{34}\text{N}_3\text{Ni}: \text{C}, 71.36; \text{H}, 7.27; \text{N}, 8.92. \) Found C, 70.98; H, 6.98; N, 8.65.

**Synthesis of \([\text{Me}_2\text{NN}]\text{Ni(2,4-lutidine)}\) (2) from \(\text{Tl}[\text{Me}_2\text{NN}]\) and \(\text{NiCl}_2(2,4\text{-lutidine})_2\).** A solution of \(\text{Tl}[\text{Me}_2\text{NN}]\) (2.00 g, 3.92 mmol) in THF was added to a stirring solution of \(\text{NiCl}_2(2,4\text{-lutidine})_2\) (1.35 g, 3.92 mmol) in THF. The dark purple solution darkened immediately as was allowed to stir an additional 20 min. The solid \(\text{TlCl}\) precipitate was filtered away through a pad of Celite. To the purple filtrate was added 0.5 wt% Na/Hg amalgam (23.5 g, 5.10 mmol Na). During the course of stirring this mixture for an hour, the purple solution gradually turned deep red. The Hg and NaCl were allowed to settle, and the red solution was decanted, filtered, and concentrated in vacuo. Recrystallization
of the residue from ether at -35 °C afforded 1.50 g (81%) of brick red blocks in two
crops.

**Tl[Me₃NN].** Prepared by an identical method used for Tl[Me₂NN].⁴ Dry, powdered KH (1.71 g, 42.5 mmol) was added with stirring to a solution of H[2,4,6-Me₃NN] (9.49 g, 28.4 mmol) in 50 mL THF. Slow evolution of H₂ ensued and the reaction mixture was stirred overnight. After filtering through Celite to remove excess KH, TlOAc (7.47 g, 28.4 mmol) was added to the clear yellow filtrate and the solution turned dark immediately. After stirring overnight, the volatiles were removed in vacuo and the residue was extracted with ether (30 mL) and filtered through Celite. The filtrate was concentrated and kept overnight at -35°C. Yellow crystals that had formed were collected on a frit, washed with cold ether and dried in vacuo to afford 8.24 g (54%) of the product. 

\[^1\text{H} \text{NMR (C}_6\text{D}_6): \delta 6.863 \text{ (s, 4, Ar-H)}, 4.837 \text{ (s, 1, backbone-CH), 2.217 (s, 6, Ar-p-CH}_3\text{), 2.144 (s, 12, Ar-o-CH}_3\text{), 1.705 (s, 6, backbone-CH}_3\text{);} \]^\text{13C} \{^1\text{H}\} \text{ NMR (C}_6\text{D}_6): \delta 161.87, 147.28, 132.15, 130.39, 129.31, 100.12 \text{ (backbone-CH), 24.93 (Ar-o-CH}_3\text{), 21.36 (Ar-p-CH}_3\text{), 19.59 (backbone-CH}_3\text{).} \]

**[Me₃NN]Ni(Et)(2,4-lutidine).** Prepared by an identical method used for [Me₂NN]Ni(Et)(2,4-lutidine):² Tl[Me₃NN] (3.28 g, 6.10 mmol) was dissolved in 5 mL THF and added with stirring to a suspension of NiCl₂(2,4-lutidine)₂ (2.10 g, 6.10 mmol) in 15 mL THF. The initially purple solution deepened in color over 5 min and became cloudy. The precipitate was allowed to settle and the solution was filtered through Celite to remove TlCl that had formed. A chilled (-35 °C) solution of EtMgCl (2.63 mL, 6.10 mmol, 2.32 M) in 5 ml THF was added to the chilled filtrate. The purple solution turned orange-red immediately, becoming deeper in color over 5 minutes. All volatiles were removed in vacuo and the remaining solids were extracted with 20 mL ether. Magnesium salts were precipitated by addition of dioxane (0.54 g, 6.1 mmol) with stirring. After allowing the solids to settle, the solution was filtered through Celite, and the filtrate was concentrated in vacuo. Crystallization occurred as the solution was concentrated, and the solution was left to stand at -35 °C overnight. The red-orange crystals that had formed were collected on a frit, washed with cold ether (5 mL), and dried in vacuo to afford 2.45 g (76 % yield) of the product. 

\[^1\text{H} \text{NMR (toluene-}d_8, -40 °C): \delta 7.42 \text{ (d, 1, lut), 6.85, 6.82,} \]
6.67, 6.03, 5.85 (aromatic), 5.48 (d, 1, lut), 4.99 (s, 1, H-backbone), 3.76 (s, 3, lut-CH3), 3.18 (s, 3, Ar-CH3), 2.76 (s, 3, Ar-CH3), 2.49 (s, 3, Ar-CH3), 2.18 (s, 3, Ar-CH3), 2.02 (s, 3, Ar-CH3), 1.58, 1.49, 1.47, 1.44 (s, 3, CH3 – 1 Ar-Me, 1 lut-Me, 2 backbone Me), 0.11 (q, 1, NiCH2CH3), 0.05 (q, 1, NiCH2CH3), -0.50 (t, 3, NiCH2CH3); 13C NMR (toluene-d8, -40 °C) δ 159.20, 159.10, 158.77, 149.36, 148.58, 145.32, 133.22, 132.96, 132.53, 132.11, 131.69, 131.00, 97.71 (backbone C), 27.66, 26.39, 24.41, 21.78, 21.40, 21.18, 20.66, 20.36, 19.99, 18.14, 16.34 (Ni-CH2CH3), 9.75 (Ni-CH2CH3); Anal. Calcd for C32H43N3Ni: C, 72.74; H, 8.20; N, 7.95. Found: C, 72.41; H, 8.57; N, 7.73.

[Me3NN]Ni(2,4-lutidine) (3). [Me3NN]Ni(Et)(2,4-lutidine) (1.67 g, 3.16 mmol) was dissolved in 40 mL ether and transferred to a 150 mL high pressure vessel and charged with 80 psi H2. The solution was stirred for 1 h over which time the solution turned deep red. After carefully exhausting excess H2 gas, the solution was filtered through Celite. The filtrate was concentrated and left overnight to crystallize at -35 °C. Deep red crystals were collected on a frit, washed with cold ether (2 x 2 mL), and dried in vacuo to afford 0.930 g (59 %) of the product. μeff = 2.00 B.M. (C6D6 with ca. 10 equiv. added 2,4-lutidine). EPR (toluene, 77K, frozen glass) g1 = 2.437, g2 = 2.131, g3 = 2.068. Anal. Calcd for C30H38N3Ni: C, 72.16; H, 7.67; N, 8.42. Found C, 71.80; H, 7.88; N, 8.23.

{[Me2NN]Ni}2(µ-NAd) (4). 1-Adamantylazide (0.088 g, 0.495 mmol) was dissolved in 5 mL ether and added to a stirring solution of [Me2NN]Ni(2,4-lutidine) (0.467 g, 0.991 mmol) in 5 mL ether at room temperature. The solution immediately turned green and vigorous bubbling of N2 gas was observed. The solution was stirred for 30 minutes, filtered through Celite and the filtrate was concentrated in vacuo to ca. 3 mL. The solution was left to crystallize at -35°C overnight. The crystals that formed were collected on a frit, washed with ether (1 mL), and dried in vacuo to afford a total yield of 0.148 g (34%) of army-green crystals. μeff = 0.95 B.M. (C6D6). Anal. Calcd for C52H64N5Ni2: C, 71.26; H, 7.36; N, 7.99. Found C, 70.88; H, 7.19; N, 8.12.

[Me3NN]Ni=NAd (5). 1-Adamantylazide (0.071 g, 0.40 mmol) was dissolved in 5 mL ether and added to a stirring solution of [Me3NN]Ni(2,4-lutidine) (0.200 g, 0.401 mmol) in 5 mL ether at room temperature. The solution immediately turned green and vigorous bubbling of N2 gas was observed. The solution was stirred for 30 minutes, filtered through Celite and the filtrate was concentrated in vacuo to ca. 3 mL.
left to crystallize at –35°C overnight. The crystals that formed were collected on a frit, washed with ether (1 mL), and dried in vacuo to afford a total yield of 0.113g (52%) of green crystals. EPR (toluene, 77K, frozen glass) g1 = 2.162, g2 = 2.039 (A = 22 G), g3 = 1.936. Anal. Calcd for C33H43N3Ni: C, 73.34; H, 8.02; N, 7.78. Found: C, 72.98; H, 7.89; N, 7.83.

**Reaction of [Me₃NN]Ni=NAd with carbon monoxide.** [Me₃NN]Ni=NAd (0.021 g, 0.039 mmol) was dissolved in 5 mL of Et₂O, transferred into the pressure Schlenk flask, removed from the drybox to a Schlenk line and kept under excess carbon monoxide, which was bubbled through the solution. There was immediate color change to black. A portion of the solution was analyzed by GC-MS and clear formation of O=C=NAd (m/z = 177.27) in 76% yield was observed, authenticated and quantified by GC-MS against an internal standard (mesitylene).

$$\{[\text{Me}_3\text{NN}]\text{Ni}(\mu-\text{CO})\}_2 \text{ (9)}.$$ [Me₃NN]Ni=NAd (0.330 g, 0.611 mmol) was dissolved in 10 mL of Et₂O, transferred into a Schlenk flask, removed from the drybox and excess CO was bubbled through the solution. There was immediate color change from green to black. The reaction mixture was filtered through Celite and the filtrate was concentrated in vacuo to ca. 3 mL. The solution was left to crystallize at –35°C overnight. The crystals that formed were collected on a frit, washed with Et₂O (1 mL), and dried in vacuo to afford a total yield of 0.202g (85%) of black crystals. ¹H NMR (toluene-d₈) at -90°C: δ 6.873 (br, 1, Ar-H), 6.767 (br, 2, Ar-H), 6.527 (br, 1, Ar-H), 4.992 (s, 1, backbone-CH), 3.365 (s, 6, Ar-o-CH₃), 2.374 (s, 12, Ar-o-CH₃ and Ar-p-CH₃), 2.138 (s, 6, Ar-p-CH₃), 2.024 (s, 6, Ar-o-CH₃), 1.695 (s, 6, Ar-o-CH₂), 1.601 (s, 12, backbone-CH₃); ¹³C{¹H} NMR (toluene-d₈) at -60°C: δ 160.55, 149.19, 137.44, 133.45, 131.68, 129.94, 98.22 (backbone-CH), 23.70, 21.27 (backbone-CH₃), 20.27, 18.79. IR (thin film on NaCl plate) νCO = 1931, 1893 cm⁻¹. Anal. Calcd for C₄₈H₅₈N₄O₂Ni₂: C, 68.59; H, 6.97; N, 6.67. Found: C, 68.21; H, 6.94; N, 6.84.

**Reaction of [Me₃NN]Ni=NAd with CN'Bu.** t-butyli isocyanide (0.015 g, 0.178 mmol) solution in 2 mL toluene was added to a stirring solution of [Me₃NN]Ni=NAd (0.096 g, 0.178 mmol) in 10 mL toluene at room temperature. There was immediate color change to red. Portion of the solution was analyzed by GC-MS and clear formation of...
'BuN=C=NAd (m/z = 232.41) in 84% yield was observed, authenticated and quantified by GC-MS against an internal standard (mesitylene).

**Reaction of [Me3NN]Ni=NAd with PMe3.** A solution of PMe3 (0.004 g, 0.108 mmol) in 0.5 mL C₆D₆ was added to a stirring solution of [Me3NN]Ni=NAd (0.029 g, 0.054 mmol) in 1 mL C₆D₆. A color change to red was observed within minutes. The reaction mixture was analyzed by ³¹P NMR and clear formation of Me₃P=NAd (δ -13.7 ppm) in 89% yield was observed and quantified by ³¹P with the use of PhN=PPh₃ as internal standard. An authentic sample of Me₃P=NAd was prepared via the facile Staudinger reaction between PMe₃ and N₃Ad.

[Me₃NN]NiNAd(η⁵-C₅H₅CoCp) (7). Cobaltocene (0.139 g, 0.736 mmol) was dissolved in 5 mL ether and added to a stirring solution of [Me₃NN]Ni=NAd (0.398 g, 0.736 mmol) in 10 mL ether at room temperature. The solution immediately turned red. The reaction mixture was stirred for 30 minutes, filtered through Celite and the filtrate was concentrated in vacuo to ca. 3 mL. The solution was left to crystallize at −35 °C overnight. The crystals that formed were collected on a frit, washed with ether (1 mL), and dried in vacuo to afford a total yield of 0.350 g (65%) of red crystals. ¹H NMR (THF-d₈): δ 6.83 (s, 2, Ar-H), 6.71 (s, 2, Ar-H), 5.17 (s, 2, Cp), 4.63 (s, 5, free Cp), 4.20 (s, 1, backbone-CH), 3.00 (s, 2, Cp), 2.93 (s, 6, Ar-o-CH₃), 2.62 (s, 6, Ar-p-CH₃), 2.26 (s, 6, Ar-o-CH₃), 2.10 (s, 1, Cp), 2.02, 1.90, 1.56 (br, Ad), 1.04 (s, 6, backbone-CH₃); ¹³C {¹H} NMR (THF-d₈): δ 153.71, 134.33, 134.08, 132.95, 132.72, 128.36, 127.93, 102.34 (backbone-CH), 78.64, 75.26, 72.57, 60.56, 51.37, 44.16, 37.01, 36.71, 30.51, 25.29, 24.23, 23.94, 22.48, 20.11, 19.43, 18.61. Anal. Calcd for C₄₃H₅₄N₃NiCo: C, 70.68; H, 7.46; N, 5.75. Found: C, 70.56; H, 7.76; N, 5.74.

[Me₃NN]Ni-NHAd (8). A solution of 1,4-cyclohexadiene (0.024 g, 0.301 mmol) in 2 mL pentane was added to a stirring solution of [Me₃NN]Ni=NAd (0.325 g, 0.601 mmol) in 10 mL pentane at room temperature. The solution turned red within 5 minutes. The reaction mixture was stirred for 30 minutes, filtered through Celite and the filtrate was concentrated in vacuo to ca. 3 mL. The solution was left to crystallize at −35 °C for 2 days. The crystals that formed were collected on a frit, washed with pentane (1 mL), and dried in vacuo to afford a total yield of 0.103 g (32%) of red crystals. This reaction proceeds in > 90% yield as monitored by ¹H NMR, but its isolation is hindered owing to
its high solubility. $^1$H NMR (toluene-$d_8$) at -50°C: $\delta$ 7.363 (s, 2, Ar-H), 7.221 (s, 2, Ar-H), 5.661 (s, 1, NH), 5.283 (s, 1, backbone-CH), 3.090 (s, 6, Ar-o-CH$_3$), 2.586 (s, 6, Ar-p-CH$_3$), 1.754, 1.545, 1.467 (br, adamantyl-H’s), 0.871 (s, 6, Ar-o-CH$_3$), 0.593 (s, 6, backbone-CH$_3$); $^{13}$C($^1$H) NMR (toluene-$d_8$) at -50°C: $\delta$ 172.61, 151.68, 140.89, 140.53, 137.41, 132.46, 126.26, 112.77 (backbone-CH), 36.66, 34.74, 34.59, 30.28, 19.79, 19.63, 19.49, 17.17. Anal. Caled for C$_{33}$H$_{45}$N$_3$Ni: C, 73.06; H, 8.38; N, 7.75. Found: C, 73.26; H, 8.55; N, 7.67.

References for Synthetic Procedures

Figure S1. X-band EPR spectrum of [Me$_2$NN]Ni(2,4-lutidine) (2) in toluene at 77K as a frozen glass.

\[ g_1 = 2.433 \quad g_2 = 2.134 \quad g_3 = 2.067 \]
**Figure S2.** X-band EPR spectra of [2,4,6-Me₃NN]Ni=NAd (8) at room temperature in toluene (top) and as a frozen glass in toluene at 77K (bottom). (An isotropic impurity at $g = 2.008$ is observed in each spectrum.)

- $g_{\text{iso}} = 2.046$
- $g_1 = 2.162$
- $g_2 = 2.038$
- $g_3 = 1.937$
- $A = 22$ Gauss
Figure S3. Plots of $\mu_{\text{eff}}$ (B.M.) vs $T$ (K) for solid state samples of $\{[\text{Me}_2\text{NN}]\text{Ni}\}_2(\mu\text{-NAd})$ (4) (top) and $[\text{Me}_3\text{NN}]\text{Ni-NHAd}$ (8) (bottom).
Computational Details

The DFT calculations mentioned in the text employed the Becke-Perdew exchange correlation functional\textsuperscript{1} using the Amsterdam Density Functional suite of programs (ADF 2002.03).\textsuperscript{2} Slater-type orbital (STO) basis sets employed for H, C, and N atoms were of triple-\(\zeta\) quality augmented with two polarization functions (TZP2 / ADF basis V) while an improved triple-\(\zeta\) basis set with two polarization functions (TZP2+) was employed for the Ni atom. The 1s electrons of C and N as well as the 1s – 2p electrons of Ni were treated as frozen core. The VWN (Vosko, Wilk, and Nusair) functional was used for LDA (local density approximation).\textsuperscript{3} The calculation was performed in spin-unrestricted mode with an excess of 1 electron (\(\alpha - \beta\)) placed into the AA manifold of MOs.

Employing typical bond distances and angles for the \(\beta\)-diketiminate ligand and the imido \(t\)-butyl substituent as well as Ni-N and N-Ni-N angles similar to those determined in the X-ray structure of [Me\textsubscript{3}NN]Ni=NAd (5), coordinates for a model of [Me\textsubscript{2}NN]Ni=NBu\textsuperscript{1} possessing \(C\textsubscript{s}\) symmetry (\(z \rightarrow -z\)) were developed in the coordinate system shown in Figure S3. These coordinates were optimized and converged to give a structure (Figure S3) whose Ni-N distances and N1-Ni-N2 angle are in good agreement with the experimentally determined structure of [Me\textsubscript{3}NN]Ni=NAd (Table S1). In this calculation to identify the electronic structure of a C\(_2\textsubscript{v}\)-like [Me\textsubscript{2}NN]Ni=NR species possessing a linear Ni=N-R linkage, bending of the imido substituent as well as the trigonal asymmetry (N1-Ni-N3 \(\neq\) N2-Ni-N3) observed in the X-ray structure of 5 were not considered.

Table S1. Selected calculated vs. experimentally determined distances (\(\text{Å}\)) and angles (\(^\circ\)).

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<th>Parameter</th>
<th>Calculated</th>
<th>Experiment</th>
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<td>Ni1-N2</td>
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<tr>
<td>N2-Ni-N3</td>
<td>132.7</td>
<td>122.7(1)</td>
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Figure S4. Chem3D model of final coordinates from DFT calculation.
Table S2. List of selected spin \( \alpha \) MOs for \([\text{Me}_2\text{NN}]\text{Ni}=\text{NBu}^i\) with the most significant SFO (>5%) gross populations.

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<th>Orbital</th>
<th>Energy (eV)</th>
<th>Symmetry</th>
<th>Occupancy</th>
<th>Composition</th>
<th>SFO</th>
<th>fragment (first member only; same atom labels as in Figure S4)</th>
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Figure S5. Contour density plots of spin \( \alpha \) HOMO (left) and LUMO (right) from DFT calculation for linear \([\text{Me}_2\text{NN}]\text{Ni}=\text{NBu}^i\) illustrating significant Ni-N(imide) \( \pi \)-antibonding interactions.
Table S3. Selected spin $\beta$ MOs for $[\text{Me}_2\text{NN}]\text{Ni}=\text{NBu}^t$ with the most significant SFO (>5%) gross populations.

<table>
<thead>
<tr>
<th>Orbital Energy (eV)</th>
<th>Symmetry</th>
<th>Occupancy</th>
<th>Composition</th>
<th>SFO</th>
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Scheme S1. Schematic representation of metal-imide multiple bonding for linear imides $[\text{Me}_2\text{NN}]\text{Ni}=\text{NR}$ based on DFT calculations (same coordinate system as in calculations). Relative energy levels taken from spin $\alpha$ energies.
References for DFT calculations


X-ray structure refinement details

Single crystals of each compound were mounted under mineral oil on glass fibers and immediately placed in a cold nitrogen stream at –90(2) °C on a Bruker SMART CCD system. Either full spheres (triclinic) or hemispheres (monoclinic or higher) of data were collected (0.3° ω-scans; 2θmax = 56°; monochromatic Mo Ka radiation, λ = 0.7107 Å) depending on the crystal system and integrated with the Bruker SAINT program. Structure solutions were performed using the SHELXTL/PC suite\(^a\) and XSEED.\(^b\) Intensities were corrected for Lorentz and polarization effects and an empirical absorption correction was applied using Blessing’s method as incorporated into the program SADABS.\(^c\) Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in idealized positions. Due to considerable solvent disorder in the X-ray structures of 4 and 8, the SQUEEZE subroutine of PLATON\(^d\) was employed. In 4, 509 solvent electrons were identified in the unit cell corresponding to 3 molecules of pentane / 4. In 8, 486 solvent electrons were identified corresponding to 1.5 molecules of pentane / 8. Despite multiple data collections on different crystals of 8 · 1.5 pentane, no data set with Rint < 10% could be obtained (reported data set Rint = 10.78%) which may somewhat limit the accuracy of reported bond distances and angles.

References for X-ray structure refinement details

(a) SHELXTL-PC, Vers. 5.10; 1998, Bruker-Analytical X-ray Services, Madison, WI; G. M. Sheldrick, SHELX-97, Universität Göttingen, Göttingen, Germany.

(b) L. Barbour, XSEED, 1999.


Figure S6. Fully labeled ORTEP diagram of [Me$_2$NN]$\text{Ni}(2,4$-lutidine) (2) (all H atoms omitted). Selected bond distances (Å) and angles (°): Ni-N1 1.873(2), Ni-N2 1.925(2), Ni-N3 1.946(2), N1-Ni-N2 97.44(8), N1-Ni1-N3 153.63(9), N2-Ni-N3 108.80(8).
Figure S7. Fully labeled ORTEP diagram of [Me₃NN]Ni(2,4-lutidine) (3) (all H atoms omitted). Selected bond distances (Å) and angles (°): Ni-N1 1.872(2), Ni-N2 1.930(2), Ni-N3 1.945(2), N1-Ni-N2 97.28(8), N1-Ni-N3 154.30(8), N2-Ni-N3 108.35(8).
Figure S8. Fully labeled ORTEP diagram of \{[\text{Me}_2\text{NN}]\text{Ni}_2(\mu-\text{NAd})\} \cdot 3 \text{pentane from SQUEEZE refinement (molecules of solvation and all H atoms omitted). Selected bond distances (Å) and angles (°): Ni1-N5 1.752(4), Ni2-N5 1.732(4), Ni1-Ni2
2.5057(12), Ni1-N1 1.929(4), Ni1-N2 1.933(4), Ni1-N3 1.944(4), Ni2-N4 1.928(4), Ni1-N5-Ni2 91.97(18), Ni1-N5-C43 144.8(3), Ni2-N5-C43 122.8(3), N1-Ni1-N2 93.61(15), N3-Ni2-N2 93.22(15).}
Figure S9. Fully labeled ORTEP diagram of [Me₃NN]Ni=NAd (5) (all H atoms omitted). Selected bond distances (Å) and angles (°): Ni1-N3 1.662(2), Ni1-N1 1.873(2), Ni1-N2 1.883(2), Ni1-N3-C18 164.5(2), N1-Ni1-N2 94.43(9), N1-Ni1-N3 122.71(10), N2-Ni1-N3 142.85(11).
Figure S10. Fully labeled ORTEP diagram of [Me$_3$NN]NiNAd(η$^4$-C$_5$H$_5$)CoCp (7) (all H atoms omitted). Selected bond distances (Å) and angles (°): Ni-N3 1.812(3), Ni-N1 1.881(3), Ni-N2 1.879(3), N3-C24 1.481(4), N3-C34 1.473(4), Co···C34 2.561, Co-C35 2.026(4), Co-C36 1.962(4), Co-C37 1.963(4), Co-C38 2.037(4), Co-C39 2.042(4), Co-C40 2.031(4), Co-C41 2.090(4), Co-C42 2.077(4), Co-C43 2.042(4), Ni-N3-C24 123.9(2), Ni-N3-C34 122.4(2), C24-N3-C34 113.6(3), N1-Ni-N2 93.95(12), N1-Ni-N3 132.79(13), N2-Ni-N3 133.17(12).
Figure S11. Fully labeled ORTEP diagram of [Me₃NN]Ni-NHAd (8) • 1.5 pentane from SQUEEZE refinement (all H atoms and molecules of solvent omitted). Selected bond distances (Å) and angles (°): Ni1-N3 1.742(4), Ni1-N1 1.839(5), Ni1-N2 1.834(5), N3-H3 (not shown) 0.90, Ni-N3-C24 132.2(3), Ni-N3-H3 135.5, C24-N3-H3 92.3, N1-Ni-N2 94.92(19), N1-Ni-N3 137.4(2), N2-Ni-N3 127.6(2).