Electronic Supplementary Material (ESI) for Dalton Transactions.


**Supporting Information**

# Alkaline Earth Metal-Assisted Dinitrogen Bond Activation at Nickel

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## 1. Materials and Methods

All experiments were carried out in a dry box under an atmosphere of dry dinitrogen using a VAC glovebox and/or standard Schlenk techniques. All anhydrous solvents were purchased from Acros Organics and further dried over activated 4 Å molecular sieves and were freeze/pump/thaw degassed (3x). All deuterated solvents were sparged with anhydrous dinitrogen, dried over activated 4 Å molecular sieves and stored under dinitrogen inside of a dry box for at least 24h. Celite® 545 was dried overnight at 200 °C under vacuum. Proton nuclear magnetic resonance ($^1$H NMR) spectra were collected on a JEOL 400 SS spectrometer at 400 MHz and are calibrated to the residual protio solvent peak (cyclohexane-$d_{12}$: 1.38 ppm). Coupling constants were extracted assuming first-order coupling, and peak multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad signal. Carbon nuclear magnetic resonance ($^{13}$C NMR) spectra were collected on the same instrument at 101 MHz and calibrated to the deuterated solvent peak ($CDCl_3$: 77.16; $C_6D_6$: 128.06; THF-d8: 25.31 and 67.21 ppm).[1] Infrared (IR) spectra for both solids and oils were recorded on a Thermo Scientific Nicolet iS10 spectrometer using an ATR accessory. Mass spectra (HRMS) were recorded on a VG 7070E spectrometer (VG Analytical Ltd., Altrincham, Cheshire, England, UK) or a SX102a mass spectrometer (JEOL, Tokyo, Japan). EPR spectra were collected on a JEOL continuous wave spectrometer JES−FA200 equipped with an X−band Gunn oscillator bridge, a cylindrical mode cavity, and a liquid nitrogen cryostat. EPR measurements were performed in sealed quartz tubes. All spectra were obtained on freshly prepared solutions in toluene (at least two independently synthesized batches) and were checked carefully for reproducibility. Background spectra were obtained on clean solvents at the same measurement conditions.

Elemental magnesium, calcium, and strontium were purchased from MilliporeSigma and used without further purification. [$^{i}Pr_2NN$]H ligand and [$^{i}Pr_2NN$]Ni($\mu$-Br)$_2$Li(thf)$_2$] (**1**) were prepared according to the literature methods.[2–3]

## 2. Synthesis and Characterization of Complexes

### 2.1. Synthesis of $\{{}^{i}Pr_2NNNi(\mu\text{-}N_2)\}_2Mg(thf)_4$ (2)

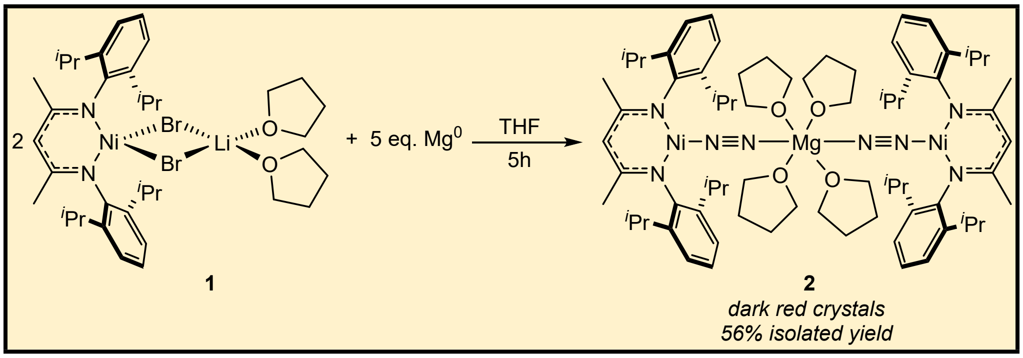



**Figure S1.** Synthesis of complex $\{{}^{i}Pr_2NNNi(\mu\text{-}N_2)\}_2Mg(thf)_4$ (**2**).

Inside a dry box filled with dry dinitrogen, $[{}^{i}Pr_2NN]Ni(\mu\text{-}Br)_2Li(thf)_2]$ (551 mg, 0.700 mmol) was dissolved in anhydrous THF (15 mL) to give a dark violet-blue solution. To this solution was added Mg turnings (97.9 mg, 3.5 mmol, 5 equiv.) and the mixture was stirred at room temperature. A dark red color was observed after 30-45 min. The stirring was continued for 5 h and then the dark red mixture was filtered through a pad of celite. The cherry red solution was dried under reduced pressure to yield the crude product. As much of the crude product as possible was dissolved in anhydrous *n*-pentane (~ 15 mL), and the mixture was filtered through syringe filter to remove a small amount of insoluble brownish material. The dark red solution was stored at –35 °C freezer inside the dry box to give dark red crystals that were suitable for X-ray crystallography (274 mg, 0.197 mmol, 56 %).

**Stability:** Unstable in air (within seconds)

**Elemental analysis:** $C_{79}H_{126}MgN_8Ni_2O_4$ (1390.85): calcd. C, 68.09; H, 9.11; N, 8.04; found C 67.93, H 9.19, N 8.09. To obtain satisfactory results, the EA was collected using crystals of **2** after several rounds of extraction/recrystallization with *n*-pentane to remove the $[{}^{i}Pr_2NNNiBr]$ impurity.

**UV-Vis (nm)** = 521 nm (ε/$M^{-1}$ $cm^{-1}$, 570)

**$^{1}$H NMR** (400 MHz, Cyclohexane-$d_{12}$) $\delta$ 7.04–6.90 (m, 9H), 6.76 (t, 4H), 4.22 (s, 2H), 3.63–3.57 (m, 24 H), 1.70–1.65 (m, 16 H), 1.44 (d, 12 H), 1.19 (d, 24H).

**$^{13}$C NMR** (101 MHz, Cyclohexane-$d_{12}$) $\delta$ 156.14, 151.95, 140.02, 121.87, 121.66, 92.60, 66.87, 27.64, 26.91, 26.15, 24.00, 23.92, 22.63, 21.84.

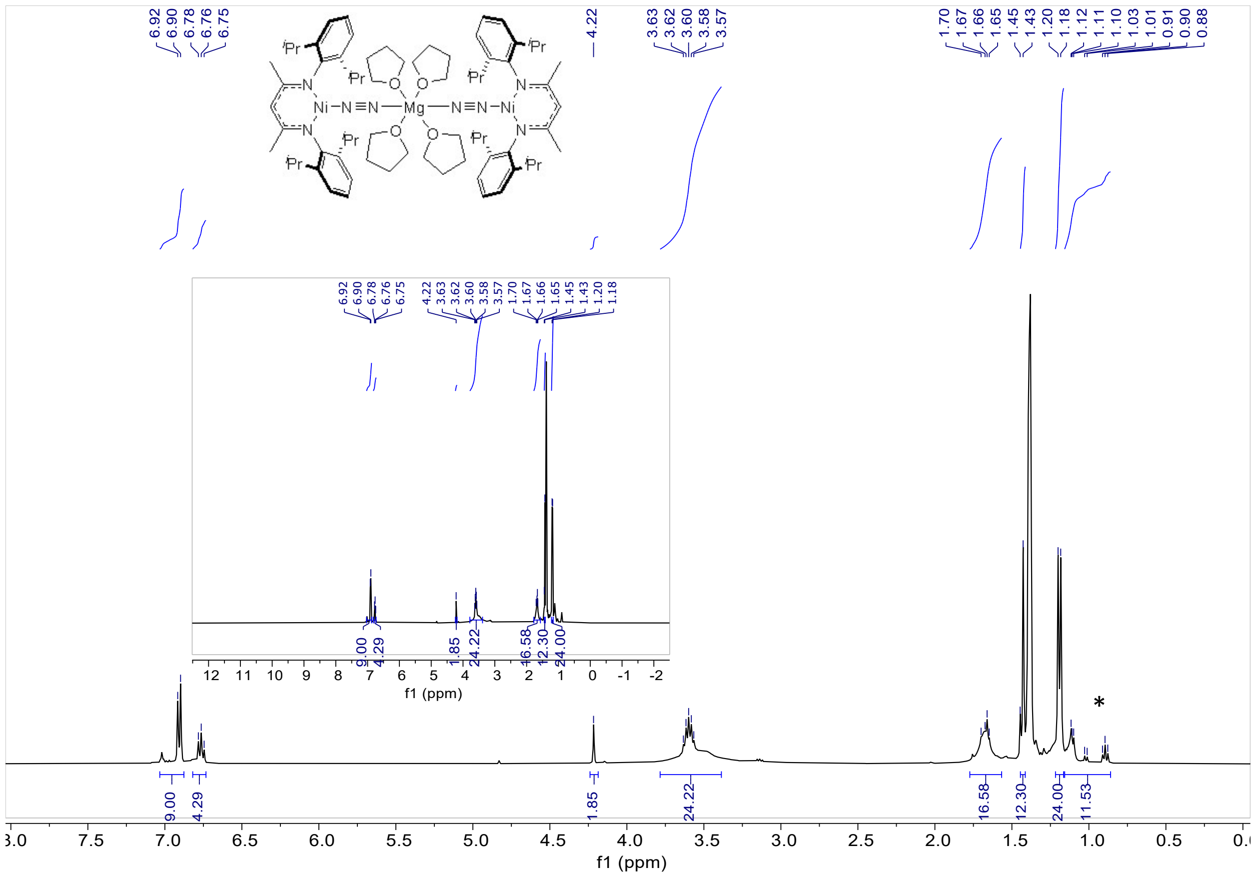


**Figure S2.** $^{1}$H NMR (cyclohexane-$d_{12}$) spectrum of crystalline $\{^{i}Pr_2NNNi(\mu\text{-}N_2)\}_2Mg(thf)_4$ (**2**). *Signals between 0.88-1.12 ppm represent the pentane solvent co-crystallized with **2**.

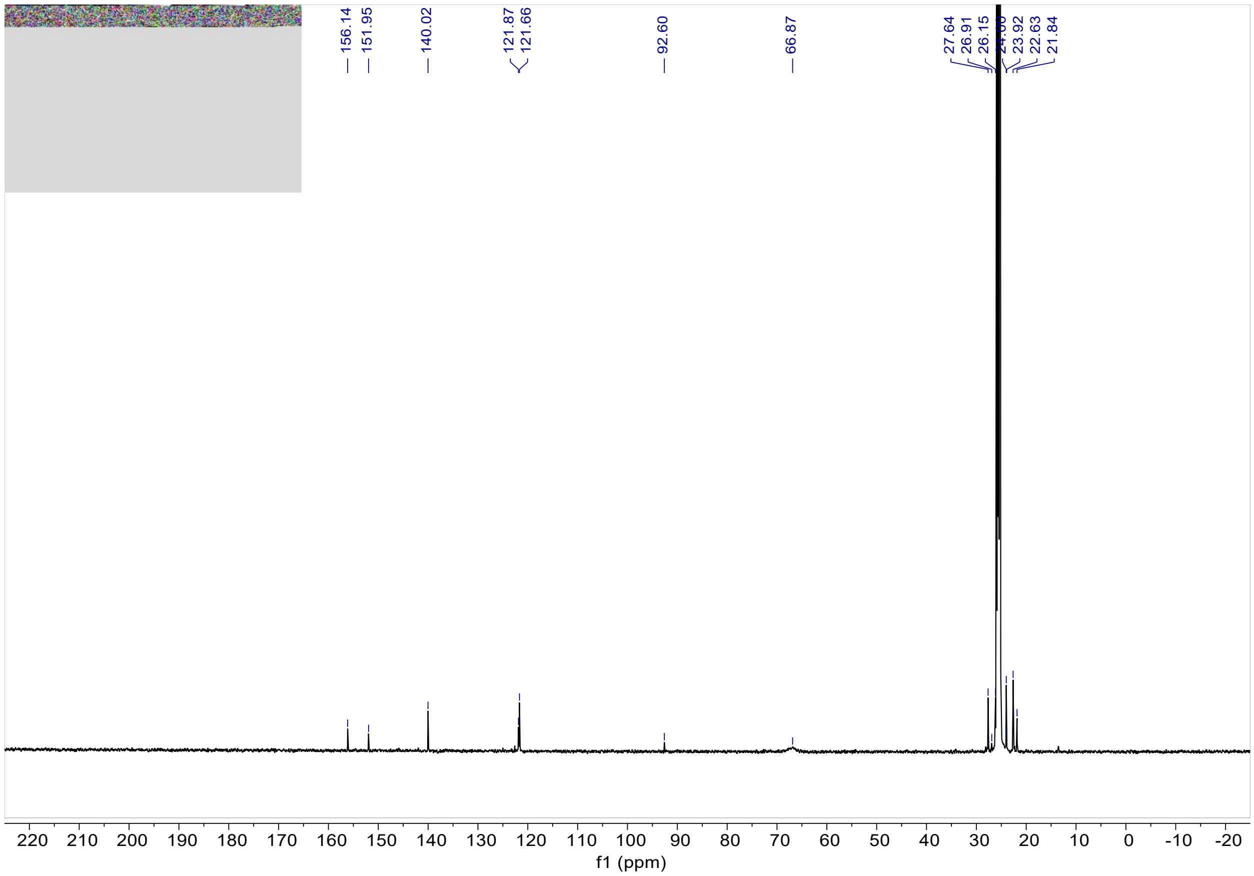



**Figure S3.** $^{13}C$ NMR (cyclohexane-$d_{12}$) spectrum of crystalline $\{^{i}Pr_2NNNi(\mu\text{-}N_2)\}_2Mg(thf)_4$ (**2**).

## 2.2. Synthesis of $\{^{i}Pr_2NNNi(\mu\text{-}N_2)\}_2Ca(thf)_4$ (3)

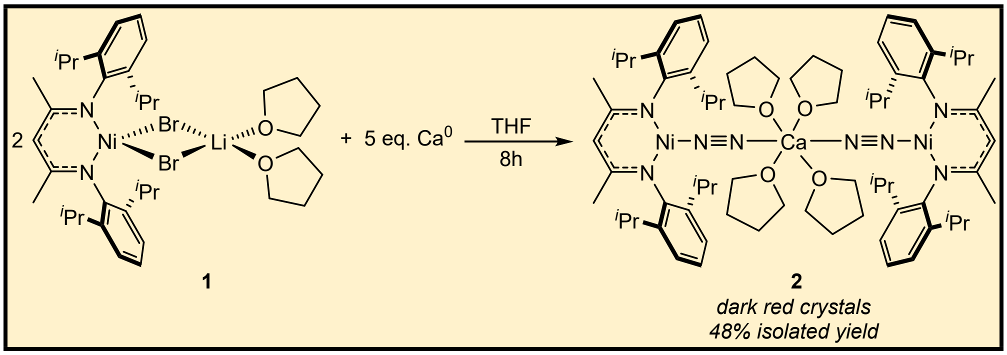



**Figure S4.** Synthesis of complex $\{^{i}Pr_2NNNi(\mu\text{-}N_2)\}_2Ca(thf)_4$ (**3**).

Inside a dry box filled with dry dinitrogen, $[^{i}Pr_2NN]Ni(\mu\text{-}Br)_2Li(thf)_2]$ (551 mg, 0.700 mmol) was dissolved in anhydrous THF (15 mL) to give a dark violet-blue solution. To this solution was added Ca turnings (140 mg, 3.5 mmol, 5 equiv.) and the mixture was stirred at room temperature. A dark red color was observed after 3–4 h. The stirring was continued for 8 h before the dark red mixture was filtered through a pad of celite. The red solution was then dried under dynamic vacuum to yield the crude product. As much of the residue as possible was dissolved in anhydrous *n*-pentane (~ 15 mL), and the mixture was filtered through syringe filter to remove a small amount of insoluble brownish material. The dark red solution was stored at –35 °C freezer inside the dry box to furnish dark red crystals that were suitable for X-ray crystallography (237 mg, 0.168 mmol, 48 %).

**Stability:** Unstable in air (within seconds)

**Elemental analysis:** $C_{79}H_{126}CaN_8Ni_2O_4$ (1406.82): calcd. C, 67.32; H, 9.01; N, 7.95; found C 67.44, H 9.08, N 8.03.

**UV-Vis (nm)** = 498 nm ($\varepsilon$/M$^{-1}$ cm$^{-1}$, < 100), 658 nm ($\varepsilon$/M$^{-1}$ cm$^{-1}$, < 100)

**$^1$H NMR** (400 MHz, Cyclohexane-$d_{12}$) $\delta$ 6.98 – 6.92 (m, 8H), 6.82 – 6.87 (m, 2H), 6.79 – 6.75 (m, 2H), 4.59 (s, 1H), 4.17 (s, 1H), 3.64 (sept, 4H), 3.16 (sept, 4H), 3.04 (br, 16H), 1.52 (br, 16H), 1.52 (d, 7H), 1.20–1.16 (m, 24H), 1.01 (d, 11H).

**$^{13}$C NMR** (101 MHz, Cyclohexane-$d_{12}$) $\delta$ 162.64, 148.93, 140.41, 140.18, 122.41, 122.17, 121.93, 92.20, 67.43, 27.50, 26.16, 24.12, 23.75, 22.74, 22.02.

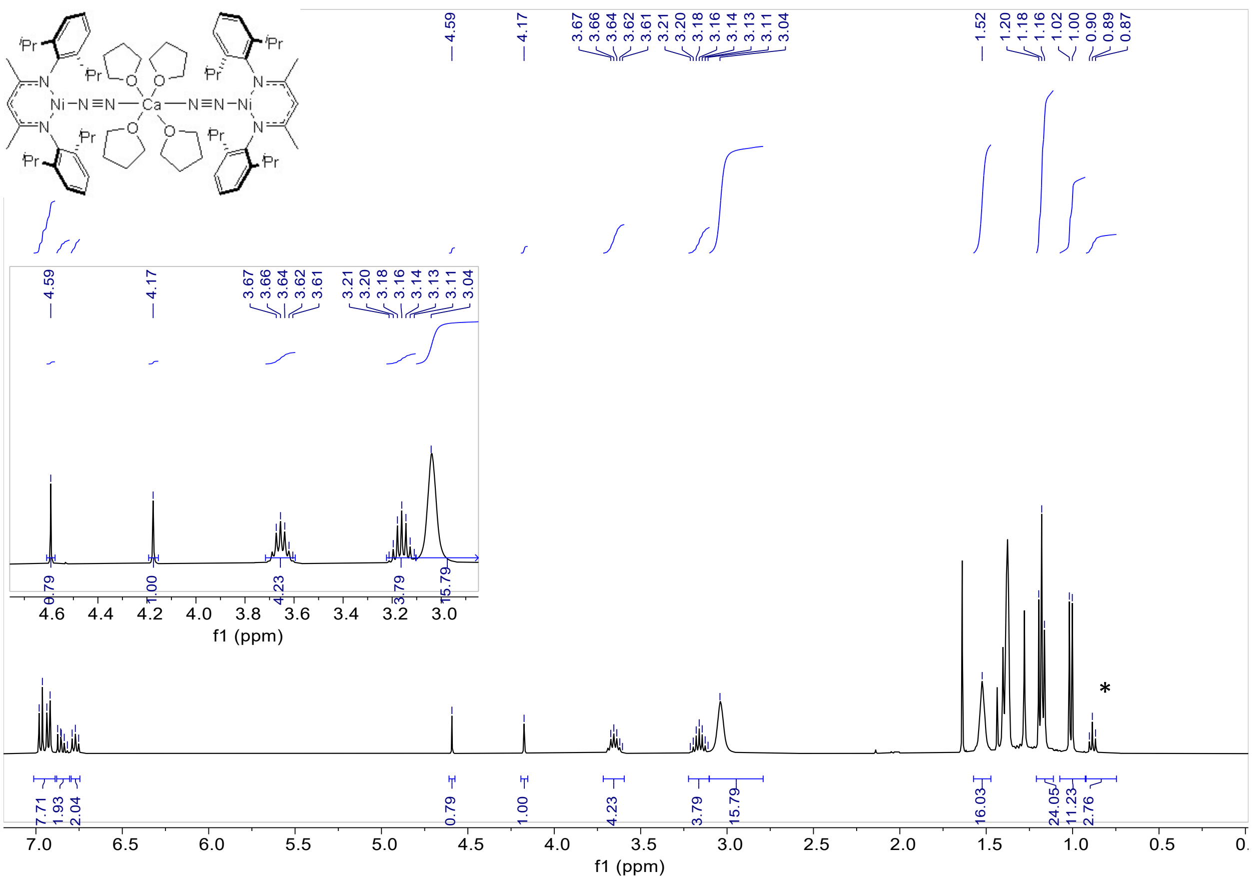


**Figure S5.** $^1$H NMR (cyclohexane-$d_{12}$) spectrum of crystalline $\{^i\mathrm{Pr}_2\mathrm{NNNi}(\mu\text{-}\mathrm{N}_2)\}_2\mathrm{Ca(thf)}_4$ (**3**). *Signals between 0.88-1.12 ppm represent the pentane solvent co-crystallized with **3**.

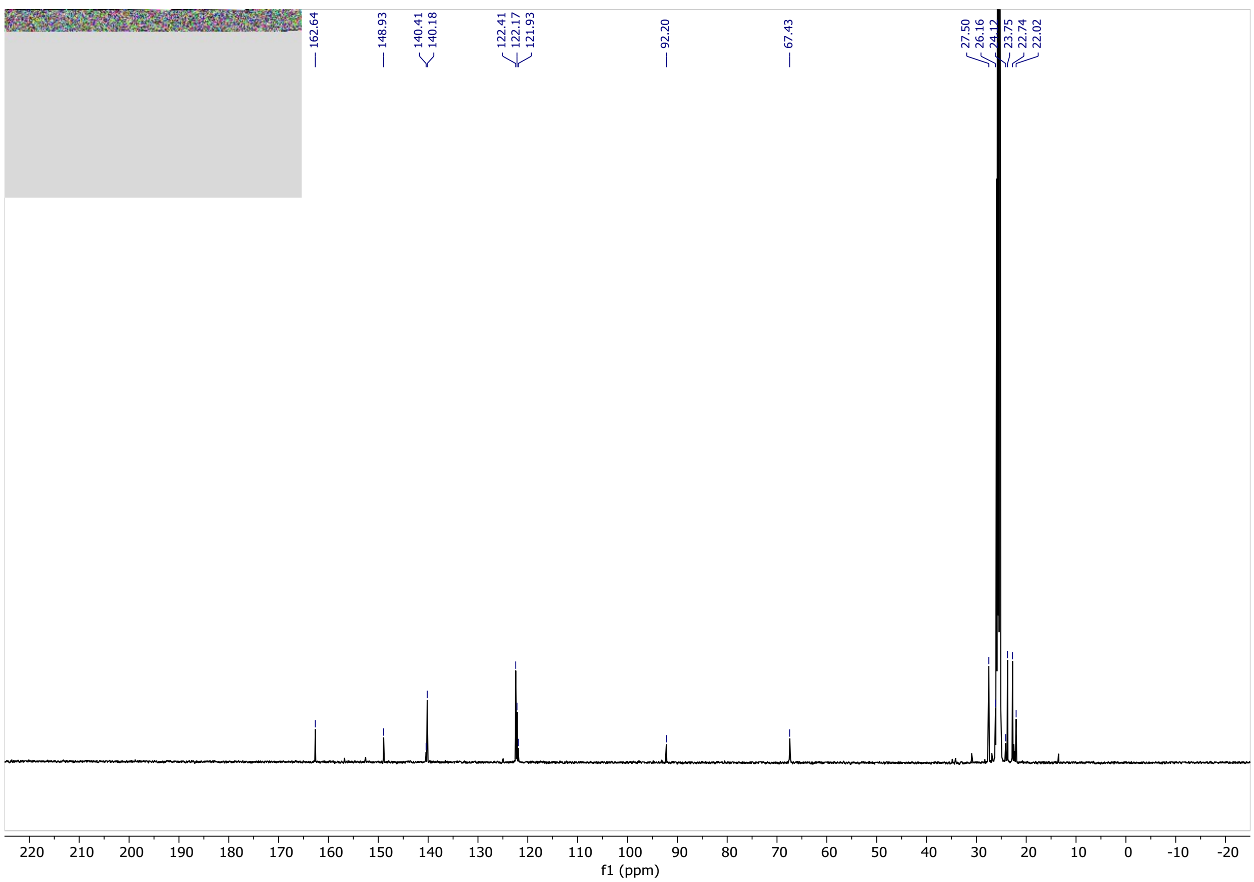



**Figure S6.** $^{13}$C NMR (cyclohexane-$d_{12}$) spectrum of crystalline $\{^{i}Pr_2NNNi(\mu\text{-}N_2)\}_2Ca(thf)_4$ (**3**).

## 3. IR Spectra of Complexes 1, 2 and 3

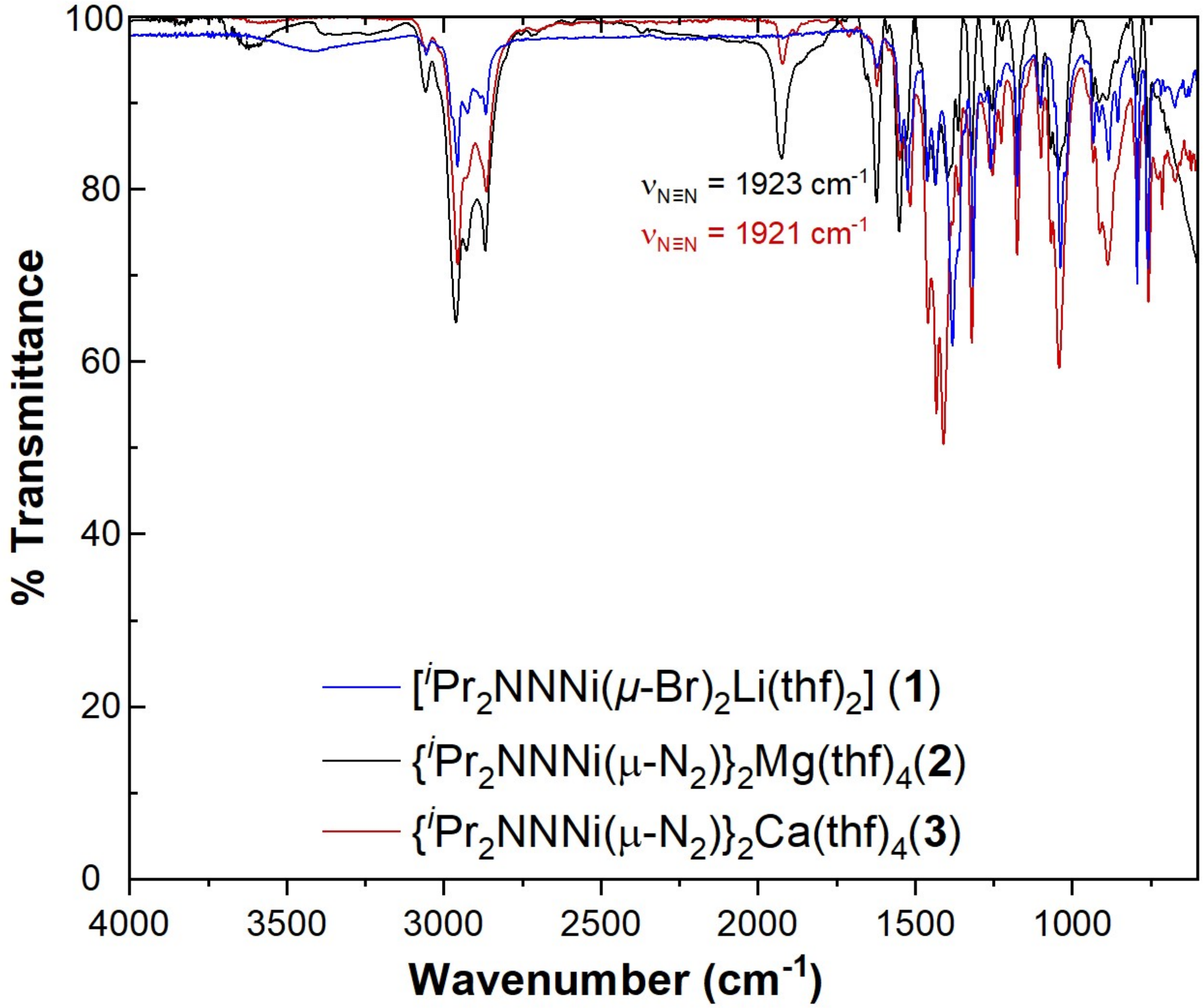



**Figure S7.** FT-IR spectra of **1** (KBr pellet, blue trace), **2** (THF solution, black trace), and **3** (THF solution, red trace).

Complex **2** FT-IR (THF Solution, cm$^{-1}$): 3055, 2960, 2925, 2866, 1923, 1622, 1551, 1460, 1436, 1395, 1382, 1362, 1319, 1259, 1254, 1192, 1175, 1100, 1051, 1044, 934, 912, 888, 795, 758.

Complex **3** FT-IR (THF Solution, cm$^{-1}$): 3050, 2954, 2863, 1921, 1621, 1530, 1515, 1439, 1414, 1409, 1360, 1320, 1254, 1249, 1175, 1099, 1055, 1041, 923, 897, 886, 762, 758, 714.

## 4. UV-Vis Spectra of Complexes 2 and 3

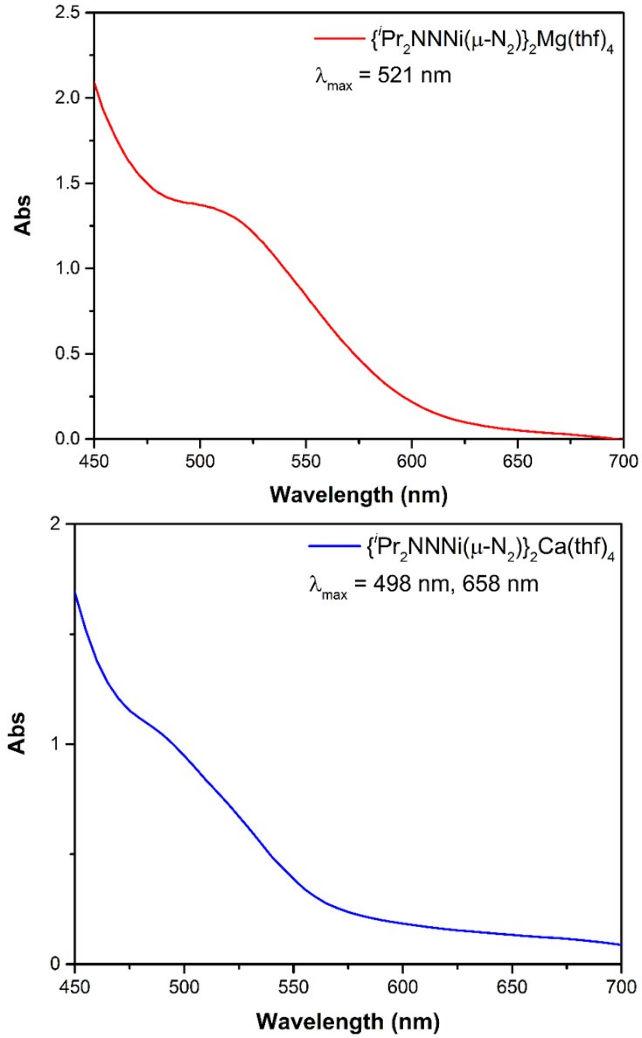



**Figure S8.** UV-Vis spectra of complexes **2** (red trace), and **3** (blue trace) in THF (0.1 mM) at RT.

## 5. Crystallographic Details

Single crystals of each compound **2** and **3** (CCDC 2283060 and 2283061) were mounted under mineral oil on glass slides and immediately placed in a cold nitrogen stream at 100(2) K prior to data collection. Data were collected on a Bruker D8 Quest equipped with a Photon100 CMOS detector and a Mo ImS source ($\lambda$ = 0.7107 Å). Data were integrated with the Bruker SAINT program. Structure solutions were performed using the SHELXTL/PC suite.[4] 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.[5] Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in idealized positions. Structures were rendered with POV-Ray in X-SEED [6] using 50% probability ellipsoids. Further comments on the refinement details are below.

$\{^i Pr_2NNNi(\mu\text{-}N_2)\}_2Mg(thf)_4$ (**2**): There is 5% substitutional disorder of a ($^i Pr_2NN$)NiBr species co-crystallized with the Ni-NN-Mg-NN-Ni complex. Due to the nature of this disorder and positional disorder of the THF molecules coordinating to the Mg atom, it was refined as three part disorder. The Mg1/Mg1B, N3/N3B, and N4/N4B atom pairs were constrained to have equal x,y,z positions and equal anisotropic displacement parameters. The like Mg-O, O-C, and C-C distances were restrained to be similar. The pentane molecule is also disordered over two orientations. The like C-C distances restrained to be similar. Similar displacement amplitudes (esd 0.01) were imposed on disordered sites overlapping by less than the sum of van der Waals radii.

$\{^i Pr_2NNNi(\mu\text{-}N_2)\}_2Ca(thf)_4$ (**3**): One THF molecule is disordered over two orientations. The like O–C, C–C, and Ca–O distances were restrained to be similar. The pentane solvent molecule is also disordered over two orientations. The like C–C distances were restrained to be similar.

Similar displacement amplitudes were imposed on disordered sites overlapping by less than the sum of van der Waals radii.

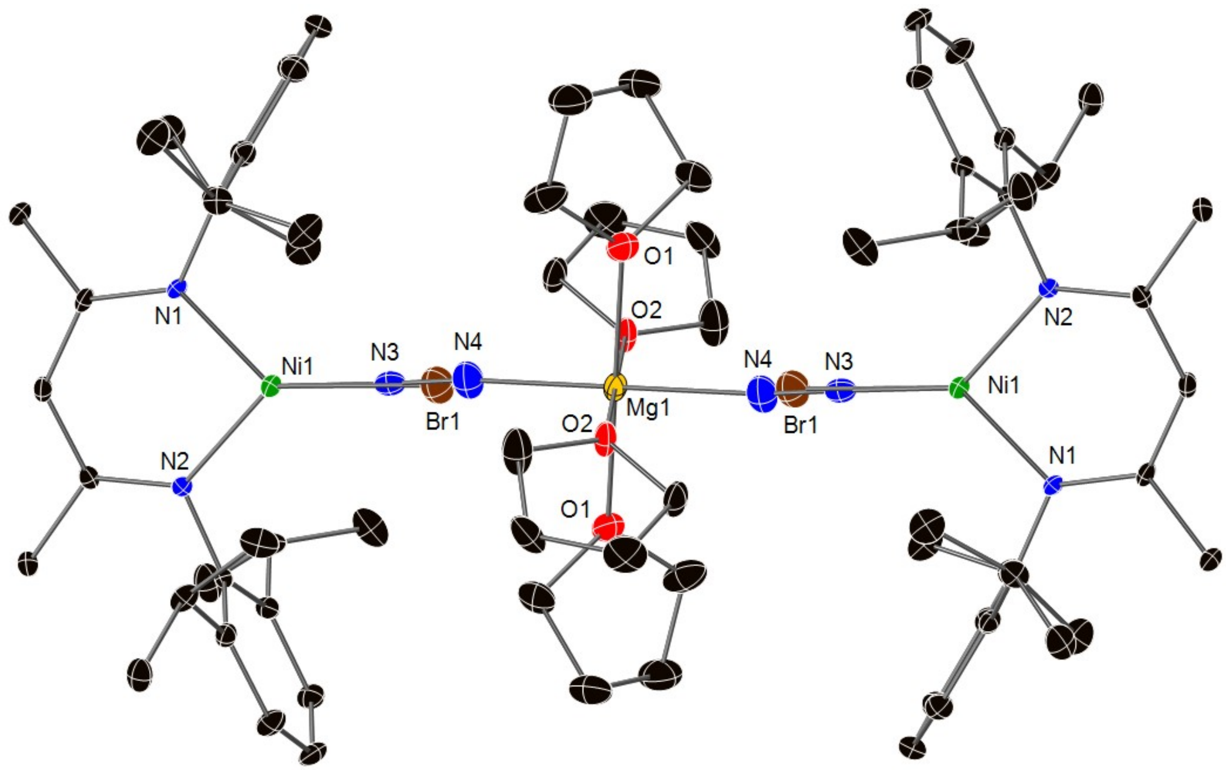



**Figure S9.** Molecular structure of $\{^{i}Pr_2NNNi(\mu\text{-}N_2)\}_2Mg(thf)_4$ (**2**). The thermal ellipsoid plots are drawn at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ni1–N1 1.9122(18), Ni1–N2 1.9114(18), Ni1–N3 1.688(5), N3–N4 1.115(9), N4–Mg1 2.082(6), Mg1–N4–N3 173.5(7), N4-N3-Ni1 178.4(6).

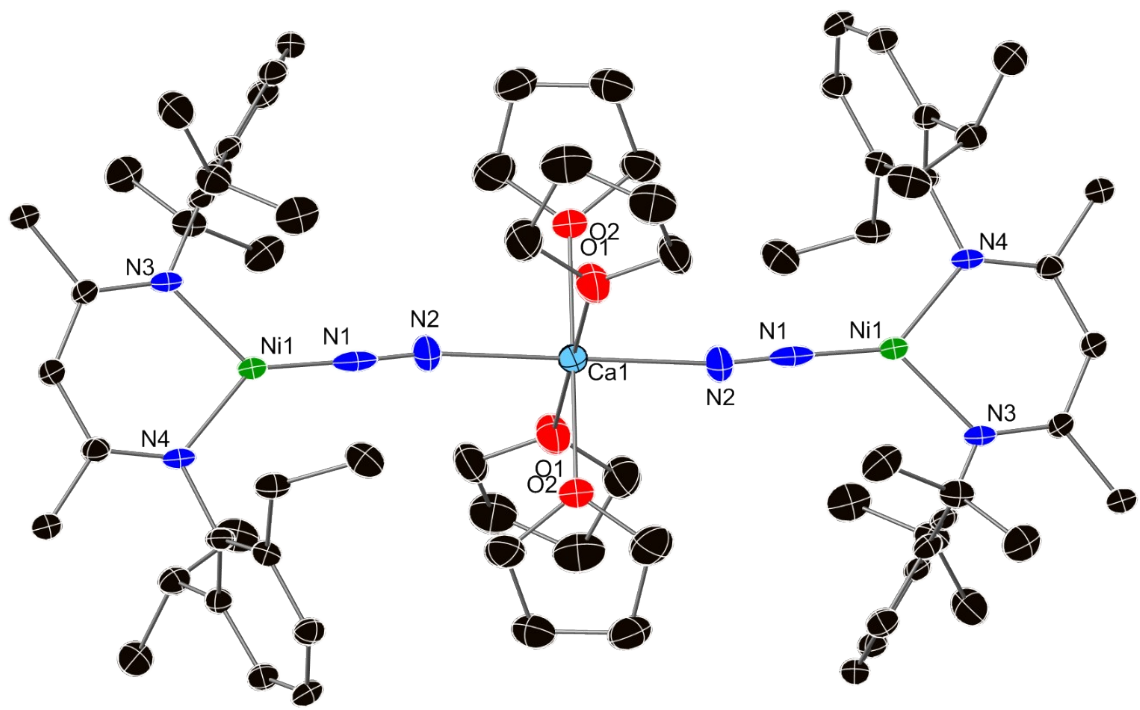



**Figure S10.** Molecular structure of $\{^{i}Pr_2NNNi(\mu\text{-}N_2)\}_2Ca(thf)_4$ (**3**). The thermal ellipsoid plots are drawn at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ni1–N3 1.906(2), Ni1–N4 1.900(2), Ni1–N1 1.646(3), N1–N2 1.163(4), N2–Ca1 2.299(3), Ca1–N2–N1 169.9(3), N2-N1-Ni1 178.0(3).

## 6. XAS Measurements and Calculations

### 6.1. Measurements

[($^i$Pr$_2$NNNi)$_2$(μ-η$^3$:η$^3$-$C_6H_5$Me)] (complex **4**) [3], {$^i$Pr$_2$NNNi(μ-Br)$_2$}Li(thf)$_2$ (complex **1**) [3], and {$^i$Pr$_2$NNNi(μ-$N_2$)}$_2$Mg(thf)$_4$ (complex **2**) were prepared in house. For Ni K-edge measurements, samples were ground with boron nitride (BN) to a final concentration of 5 wt % Ni, pressed into 1 mm Al spacers, and sealed with 38 μm Kapton tape.

Ni K-edge XAS spectra were collected at the Stanford Synchrotron Radiation Lightsource at beamline 9-3 under ring conditions of 3 GeV and 300 mA. Beamline 9-3 is equipped with a 16-pole, 2-Tesla wiggler source. Incident X-ray radiation was monochromated using a double Si(220) crystal monochromator; samples were maintained at 10 K in a liquid He cryostat during data collection. Data were collected in fluorescence mode, with X-rays detected by a passivated implanted planar silicon (PIPS) detector placed at a 90° angle to the sample. Inelastic scatter was attenuated using a Soller slits fitted with a Co filter. A Ni foil and a third ionization chamber upstream of the sample were used for internal energy calibration, setting the first inflection point of a Ni foil spectrum to 8331.6 eV. Data were collected from 8010 to 8730 eV. Four scans were measured and averaged for each compound. Spectra were processed using EXAFSPAK.[7] A smooth pre-edge background was removed from each averaged spectrum by fitting a second-order polynomial to the pre-edge region and subtracting this polynomial from the entire spectrum. A polynomial spline was subtracted above $E_0$ = 8400 eV and the data normalized in the post-edge absorption to 1.0. Pre-edge data were fit using Igor Pro 7.0. Pre-edge peak positions were identified by calculating second derivatives of the spectra.

### 6.2. Calculations

All electronic structure and spectroscopic calculations were performed using version 4.20 of the ORCA computational chemistry package [8] using crystallographic coordinates. It should be noted that the revised crystal structure for **3** was used. When Br disorder is considered, the N–N distance is 1.116 Å relative to 0.998 Å in the uncorrected structure. Single point calculations were performed using the B3LYP [9] functional, the zeroth-order regular approximation for relativistic effects (ZORA)[10] as implemented by van Wüllen,[11] CP(PPP) basis on Ni[12], and the scalar-relativistically recontracted ZORA-def2-TZVP(-f) basis set on all other atoms.[13] A more dense integration grid (ORCA GRID7) was used on Ni. Solvation was modeled with the conductor-like polarizable continuum model (CPCM)[14] in an infinite dielectric.

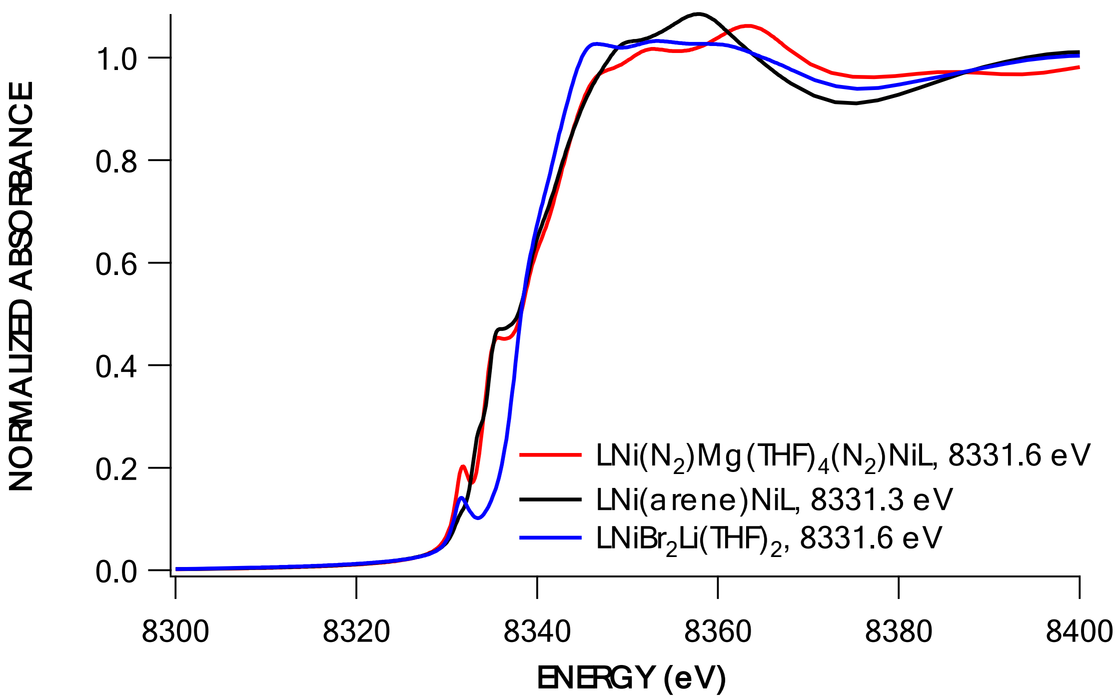



**Figure S11.** Ni K-edge XAS of compounds [($^{i}$Pr$_2$NNNi)$_2$(μ-η$^3$:η$^3$-C$_6$H$_5$Me)] as Ni(I) reference (**4**), {$^{i}$Pr$_2$NNNi(μ-Br)$_2$}Li(thf)$_2$ **(1)** as Ni(II) reference, and {$^{i}$Pr$_2$NNNi(μ-N$_2$)}$_2$Mg(thf)$_4$ (**2**).

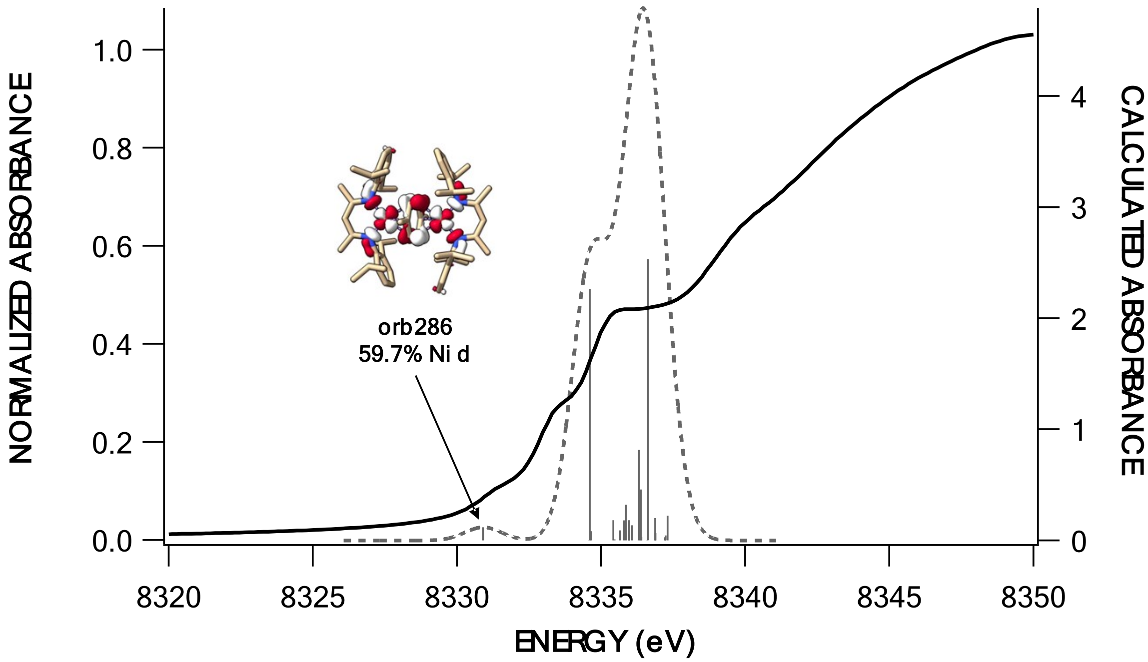



**Figure 12.** Experimental (black) and TDDFT-calculated (gray, dashed) Ni K-edge XAS of $\{[LNi]_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-}C_6H_5\text{-Me})]$ (**4**). Dominant acceptor molecular orbitals contributing to individual transitions (sticks) are plotted at an isovalue of 0.03 au.

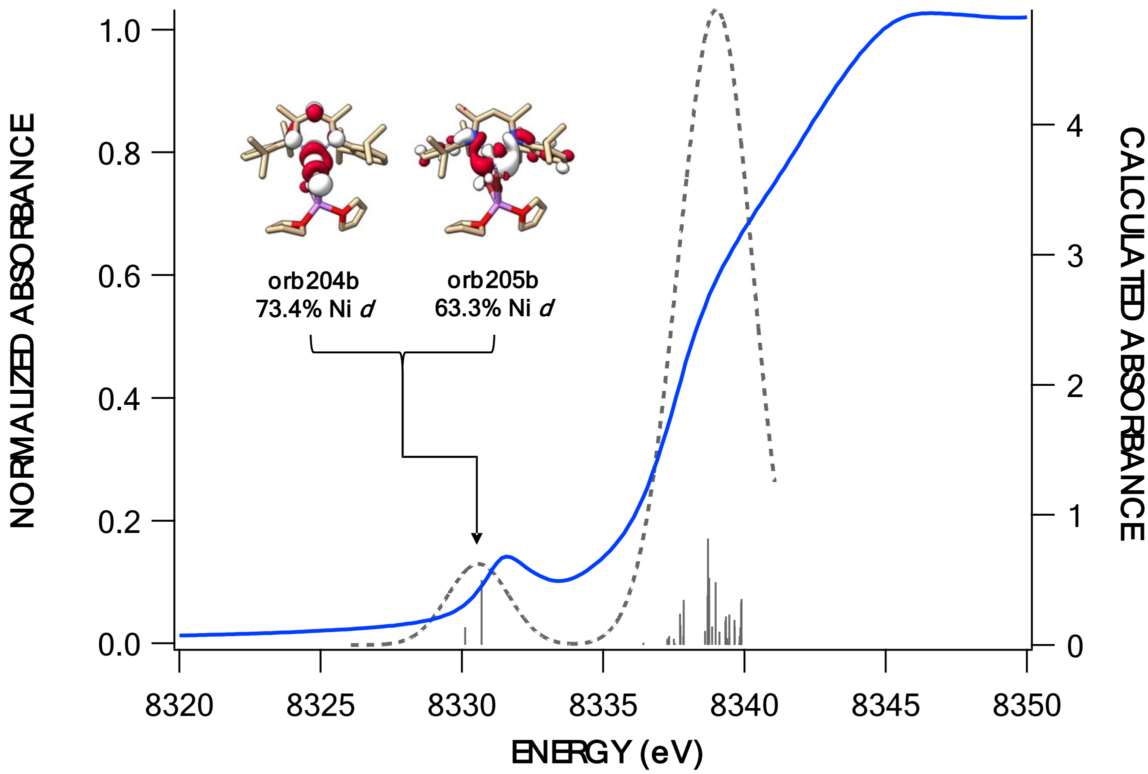



**Figure 13.** Experimental (black) and TDDFT-calculated (gray, dashed) Ni K-edge XAS of $\{^{i}Pr_2NNNi(\mu\text{-}Br)_2\}Li(thf)_2$ **(1)**. Dominant acceptor molecular orbitals contributing to individual transitions (sticks) are plotted at an isovalue of 0.03 au.

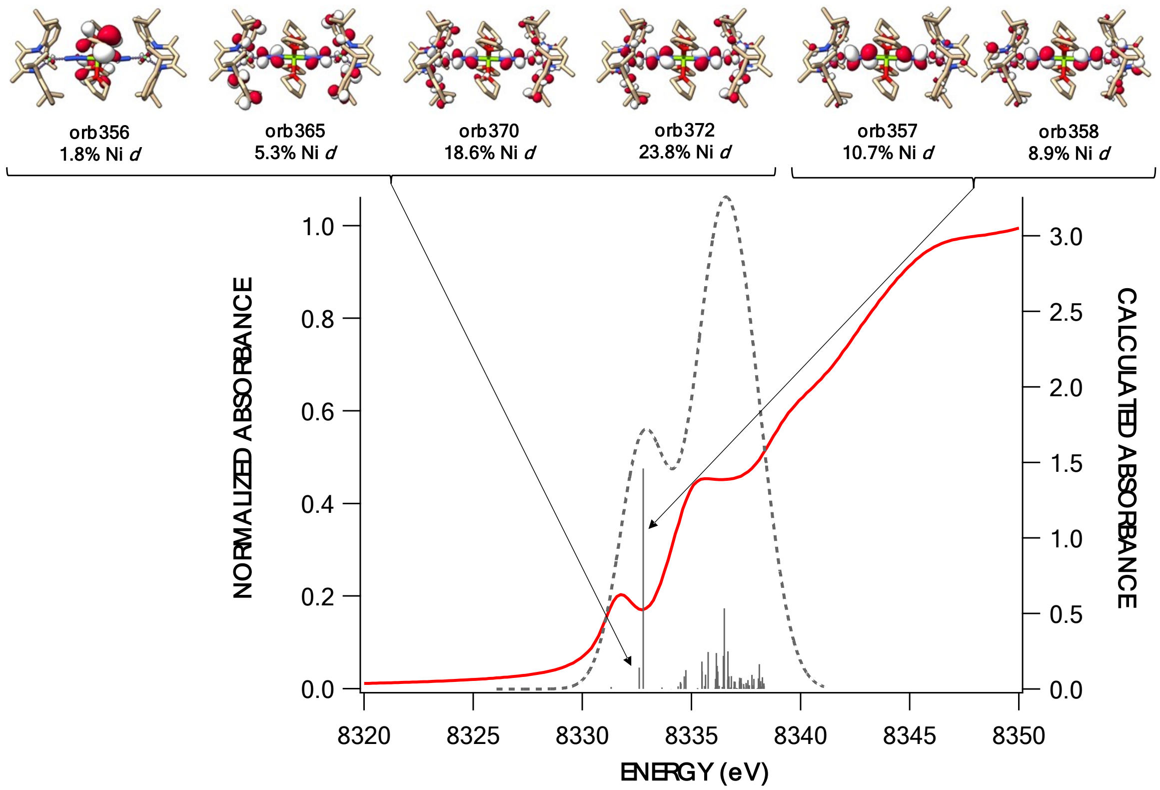



**Figure 14.** Experimental (black) and TDDFT-calculated (gray, dashed) Ni K-edge XAS of $\{^{i}Pr_2NNNi(\mu\text{-}N_2)\}_2Mg(thf)_4$ **(2)**. Dominant acceptor molecular orbitals contributing to individual transitions (sticks) are plotted at an isovalue of 0.03 au.

{$^{i}Pr_2NNNi(\mu\text{-}N_2)\}_2Mg(thf)_4$

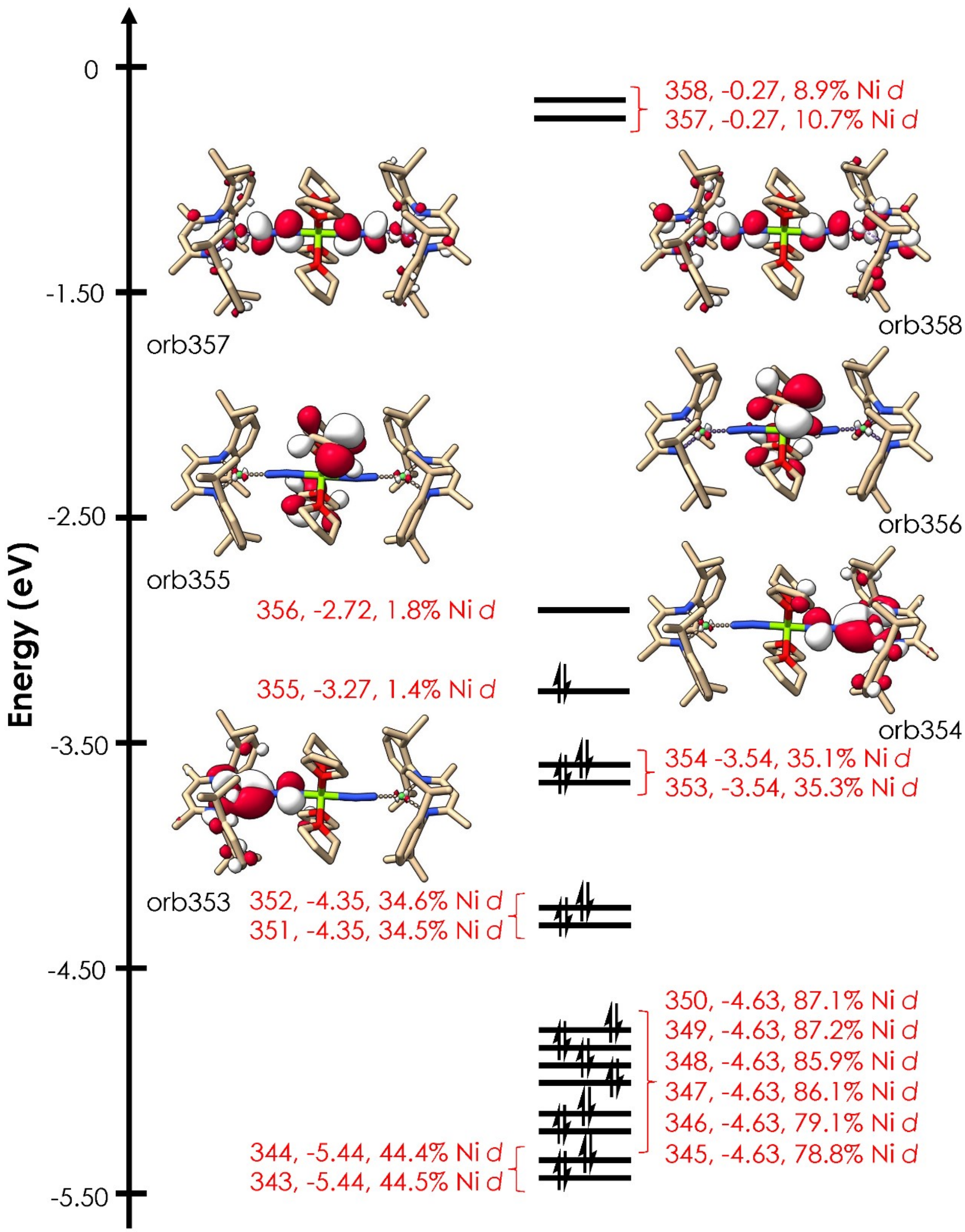


**Figure 15.** Frontier molecular orbital diagram for **2**. Orbitals are plotted at an isovalue of 0.03 au.

## 7. Mg 1s XPS Measurements

Mg 1s XPS data were obtained at the Cornell Center for Materials Research. The value obtained for the Mg 1s excitation in complex **2** is 1304.17 eV. This value is consistent with divalent Mg.[15] Reported values for $Mg^0$ (as Mg metal) range from 1303 eV to 1303.6 eV. $Mg^{II}$ as MgO ranges from 1304.2–1305.3. $MgCO_3$ appears at 1305 eV.

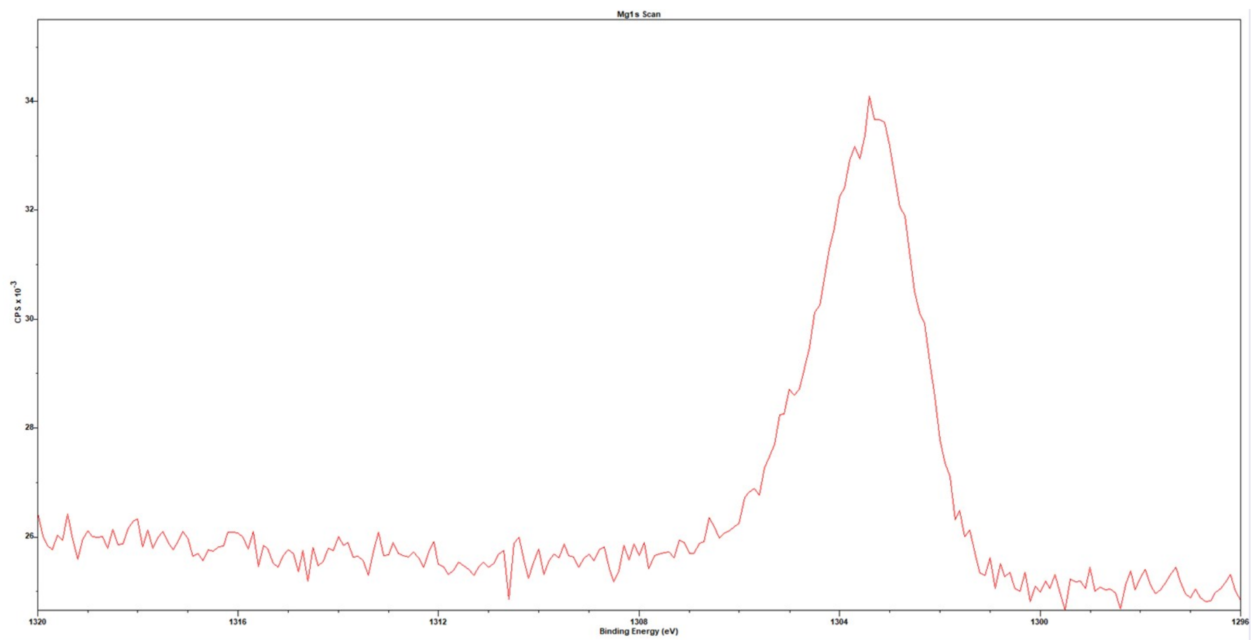



**Figure S17.** Mg 1s XPS measurement of $\{^i Pr_2 NNNi(\mu\text{-}N_2)\}_2 Mg(thf)_4$ (**2**) that was collected using the Nexsa XPS, with the survey spectrum and the high-resolution scans collected at 50 eV.

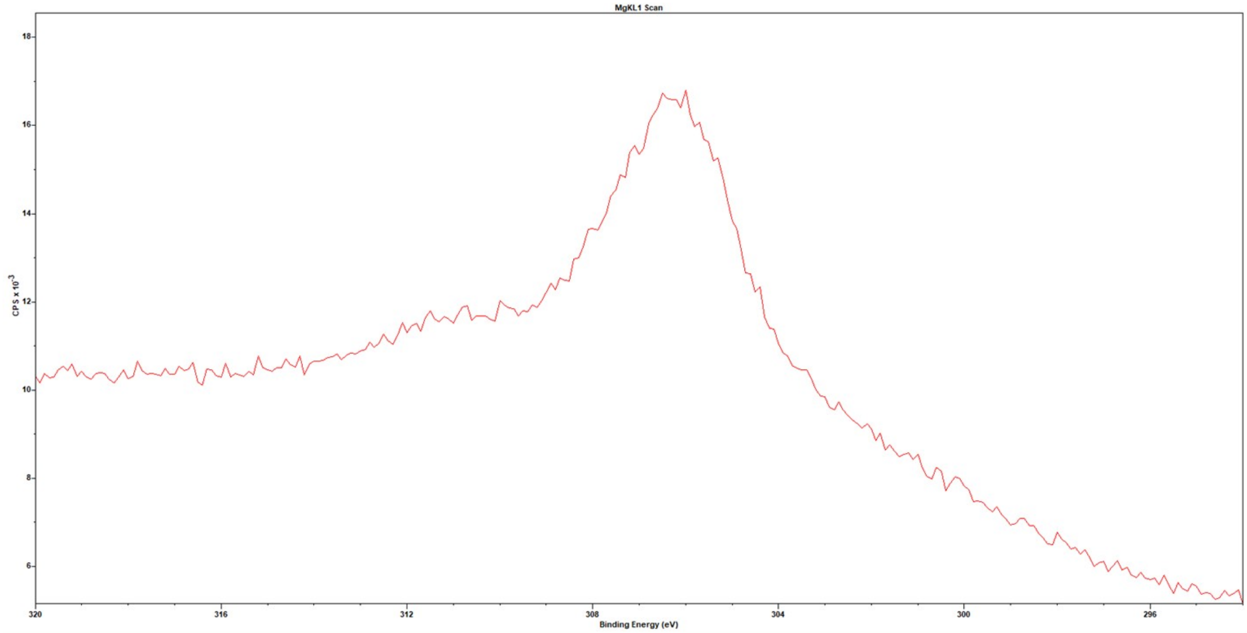



**Figure S18.** Mg KL1 XPS measurement of $\{^i Pr_2NNNi(\mu\text{-}N_2)\}_2Mg(thf)_4$ (**2**) that was collected using the Nexsa XPS, with the survey spectrum and the high-resolution scans collected at 50 eV.

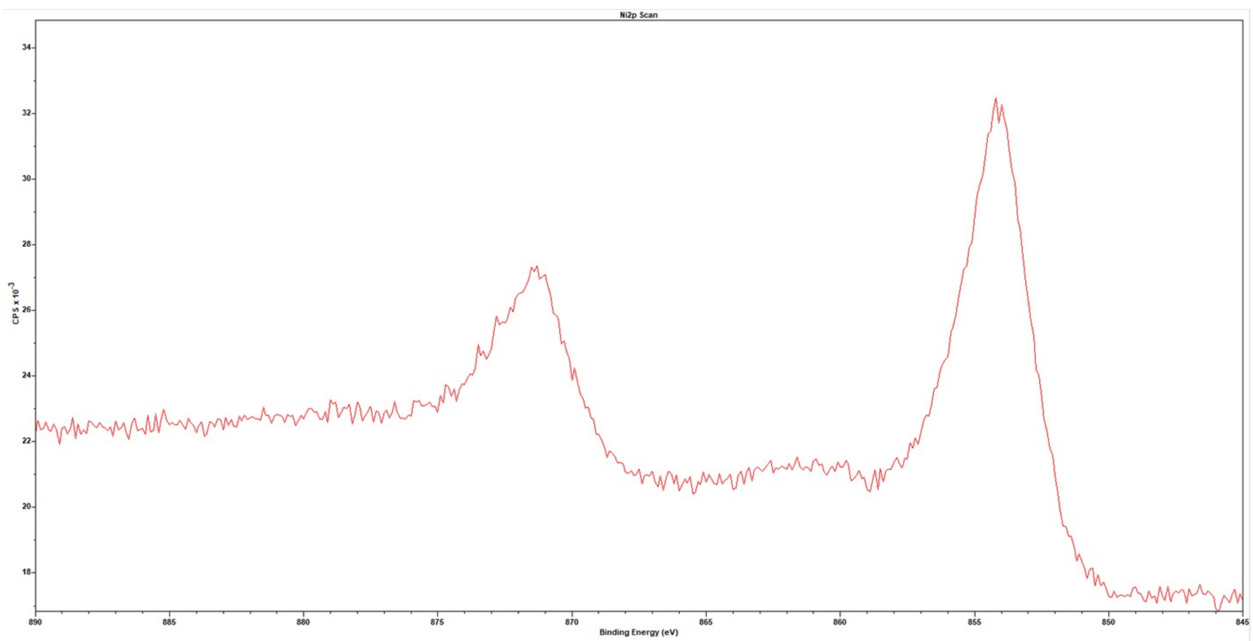



**Figure S19.** Ni 2p XPS measurement of $\{^i Pr_2NNNi(\mu\text{-}N_2)\}_2Mg(thf)_4$ (**2**) that was collected using the Nexsa XPS, with the survey spectrum and the high-resolution scans collected at 50 eV.

| Sample Identifier | Name | Position | FWHM | Raw Area | %At Conc |
|---|---|---|---|---|---|
| NiMgN2 | O 1s | 532.13 | 2.98 | 187166.67 | 6.40 |
| | C 1s | 285.45 | 2.65 | 957301.91 | 81.89 |
| | N 1s | 399.39 | 2.76 | 103312.57 | 5.25 |
| | Mg 1s | 1304.17 | 2.78 | 69975.21 | 3.02 |
| | Ni 2p3/2 | 855.05 | 3.41 | 243437.36 | 2.31 |
| | Br 3p | 182.16 | 2.74 | 14185.68 | 0.23 |
| | Ca 2p | 352.30 | 4.11 | 51809.52 | 0.91 |

Peak Area Results Compact form (Atomic Concentrations)

| Name | %Conc St.Dev. | Sample Identifier |
|---|---|---|
| O 1s | 6.40 | NiMgN2 |
| C 1s | 81.89 | |
| N 1s | 5.25 | |
| Mg 1s | 3.02 | |
| Ni 2p3/2 | 2.31 | |
| Br 3p | 0.23 | |
| Ca 2p | 0.91 | |

Peak Area Results (RSF Corrected Intensities and St.Dev.)

| NiMgN2 | O 1s | C 1s | N 1s | Mg 1s | Ni 2p3/2 | Br 3p | Ca 2p |
|---|---|---|---|---|---|---|---|
| Area | 75371.6 | 965012 | 61817.2 | 35576.8 | 27192.9 | 2697.78 | 10696.4 |
| St.Dev. | | | | | | | |

| NiMgN2 | O 1s | C 1s | N 1s | Mg 1s | Ni 2p3/2 | Br 3p | Ca 2p |
|---|---|---|---|---|---|---|---|
| %Conc | 5.22 | 87.35 | 4.87 | 0.57 | 1.17 | 0.18 | 0.63 |
| CPS | 55566.7 | 317045 | 31826.5 | 23095.1 | 62075.2 | 3373.51 | 11672.8 |

## 8. Computational Methods

To perform bonding analysis, all structures were fully optimized at PBE0[16-18]/def2-SVP[19-20] computational level by Gaussian 16, Rev. C01.[21] Complexes $\{^{i}Pr_2NNNi(\mu\text{-}N_2)\}_2Ca(thf)_4$ and $\{^{i}Pr_2NNNi(\mu\text{-}N_2)\}_2Mg(thf)_4$ were optimized at their singlet, triplet, and broken-symmetry singlet electronic states. For the broken-symmetry initial guess, we started with two doublet Ni(nacnac) fragments corresponding to Ni(I) and singlet $M(N_2)_2(THF)_4$ (M = Ca or Mg) fragments. The wavefunctions of the optimized structure were analyzed for assessing the bonding properties of the complexes, within the context of the quantum theory of atoms in molecules, QTAIM [22], by AIMAll [23] suite of programs.

Cartesian Coordinates of optimized structures at PBE0/def2-SVP computational level:

**$\{^{i}Pr_2NNNi(\mu\text{-}N_2)\}_2Ca(thf)_4$**
203
E (PBE0/def2-SVP) = -7313.96765838 a.u.
symmetry c1

| | | | |
|---|---|---|---|
| Ni | 3.757426000 | 11.493657000 | 9.584159000 |
| N | 3.201307000 | 10.486303000 | 8.037286000 |
| N | 2.537157000 | 10.652805000 | 10.813779000 |
| N | 4.925848000 | 12.718526000 | 9.666605000 |
| N | 5.734115000 | 13.555523000 | 9.661686000 |
| C | 1.882931000 | 8.873033000 | 6.740437000 |
| H | 1.058858000 | 8.163725000 | 6.887216000 |
| H | 2.742164000 | 8.328504000 | 6.318522000 |
| H | 1.583844000 | 9.609645000 | 5.979125000 |
| C | 2.253252000 | 9.557701000 | 8.033308000 |
| C | 1.552818000 | 9.169029000 | 9.191862000 |
| H | 0.807129000 | 8.384831000 | 9.060338000 |
| C | 1.681770000 | 9.686897000 | 10.493760000 |
| C | 0.787032000 | 9.107455000 | 11.561123000 |
| H | 0.147522000 | 8.312302000 | 11.158059000 |
| H | 0.144681000 | 9.885900000 | 12.002124000 |
| H | 1.382142000 | 8.695104000 | 12.391030000 |
| C | 3.862071000 | 10.848855000 | 6.842290000 |
| C | 4.983357000 | 10.104713000 | 6.394776000 |
| C | 5.638650000 | 10.507947000 | 5.228915000 |
| H | 6.498914000 | 9.936550000 | 4.872312000 |
| C | 5.215380000 | 11.621180000 | 4.506395000 |
| H | 5.731510000 | 11.910052000 | 3.587002000 |
| C | 4.127847000 | 12.357283000 | 4.963620000 |
| H | 3.797236000 | 13.234573000 | 4.399440000 |
| C | 3.441109000 | 11.994861000 | 6.126868000 |

| | | | |
|---|---|---|---|
| C | 5.507157000 | 8.940817000 | 7.218295000 |
| H | 4.647606000 | 8.503054000 | 7.749432000 |
| C | 6.149451000 | 7.830780000 | 6.392049000 |
| H | 6.394430000 | 6.971303000 | 7.035417000 |
| H | 7.090751000 | 8.155033000 | 5.919616000 |
| H | 5.478996000 | 7.476156000 | 5.593684000 |
| C | 6.464487000 | 9.461989000 | 8.294012000 |
| H | 6.805437000 | 8.646384000 | 8.952484000 |
| H | 5.956374000 | 10.218512000 | 8.912123000 |
| H | 7.352039000 | 9.927995000 | 7.834050000 |
| C | 2.276334000 | 12.840157000 | 6.610864000 |
| H | 1.953024000 | 12.409609000 | 7.570750000 |
| C | 1.090500000 | 12.792333000 | 5.646252000 |
| H | 0.239995000 | 13.370728000 | 6.041805000 |
| H | 0.745817000 | 11.760462000 | 5.481112000 |
| H | 1.352484000 | 13.215721000 | 4.662620000 |
| C | 2.706524000 | 14.282749000 | 6.884954000 |
| H | 1.868622000 | 14.864513000 | 7.303027000 |
| H | 3.035256000 | 14.791826000 | 5.963606000 |
| H | 3.537202000 | 14.311707000 | 7.606432000 |
| C | 2.584517000 | 11.161264000 | 12.132210000 |
| C | 1.758977000 | 12.253789000 | 12.495861000 |
| C | 1.885720000 | 12.799239000 | 13.776288000 |
| H | 1.255135000 | 13.644626000 | 14.063614000 |
| C | 2.791569000 | 12.281155000 | 14.697528000 |
| H | 2.869115000 | 12.714465000 | 15.698178000 |
| C | 3.582115000 | 11.192952000 | 14.340381000 |
| H | 4.282648000 | 10.778047000 | 15.069984000 |
| C | 3.491289000 | 10.613306000 | 13.071572000 |
| C | 0.792875000 | 12.859803000 | 11.492704000 |
| H | 0.596446000 | 12.091412000 | 10.729348000 |
| C | -0.548940000 | 13.258704000 | 12.102172000 |
| H | -1.246885000 | 13.579441000 | 11.312809000 |
| H | -0.452739000 | 14.100107000 | 12.807240000 |
| H | -1.013325000 | 12.420723000 | 12.644844000 |
| C | 1.450359000 | 14.037466000 | 10.769169000 |
| H | 0.778889000 | 14.456989000 | 10.002007000 |
| H | 2.376554000 | 13.704772000 | 10.274668000 |
| H | 1.704472000 | 14.842359000 | 11.479326000 |
| C | 4.392372000 | 9.451363000 | 12.692461000 |
| H | 3.940229000 | 8.968165000 | 11.812714000 |
| C | 4.516318000 | 8.395543000 | 13.788641000 |
| H | 5.085474000 | 7.527115000 | 13.421057000 |
| H | 3.529244000 | 8.037712000 | 14.120263000 |
| H | 5.047617000 | 8.776521000 | 14.675719000 |
| C | 5.764440000 | 9.968715000 | 12.253848000 |

| | | | |
|---|---|---|---|
| H | 6.418064000 | 9.140632000 | 11.933879000 |
| H | 6.265700000 | 10.502292000 | 13.079178000 |
| H | 5.648843000 | 10.663921000 | 11.408178000 |
| Ni | 10.823116000 | 19.043644000 | 10.313800000 |
| N | 11.349809000 | 20.060299000 | 11.864855000 |
| N | 12.002982000 | 19.939792000 | 9.083738000 |
| N | 9.659412000 | 17.815635000 | 10.209448000 |
| N | 8.852090000 | 16.977695000 | 10.196418000 |
| C | 12.537373000 | 21.784736000 | 13.145154000 |
| H | 13.270959000 | 22.584056000 | 12.981784000 |
| H | 11.616427000 | 22.228306000 | 13.553497000 |
| H | 12.923587000 | 21.109543000 | 13.924737000 |
| C | 12.251036000 | 21.034567000 | 11.867385000 |
| C | 12.968223000 | 21.421605000 | 10.718678000 |
| H | 13.691235000 | 22.226159000 | 10.853775000 |
| C | 12.847430000 | 20.912268000 | 9.412672000 |
| C | 13.723581000 | 21.523250000 | 8.347499000 |
| H | 14.375843000 | 22.300802000 | 8.764226000 |
| H | 14.351257000 | 20.756175000 | 7.867353000 |
| H | 13.115036000 | 21.967742000 | 7.544274000 |
| C | 10.645443000 | 19.726455000 | 13.043266000 |
| C | 9.348370000 | 20.249834000 | 13.257903000 |
| C | 8.653443000 | 19.884142000 | 14.415124000 |
| H | 7.655932000 | 20.297557000 | 14.591948000 |
| C | 9.207382000 | 19.013385000 | 15.347072000 |
| H | 8.656276000 | 18.749401000 | 16.253536000 |
| C | 10.474957000 | 18.483247000 | 15.117168000 |
| H | 10.904167000 | 17.792485000 | 15.846829000 |
| C | 11.209516000 | 18.821359000 | 13.978042000 |
| C | 8.698903000 | 21.179150000 | 12.247969000 |
| H | 9.394236000 | 21.254342000 | 11.398190000 |
| C | 8.486040000 | 22.584418000 | 12.812587000 |
| H | 8.060548000 | 23.253755000 | 12.047528000 |
| H | 7.792412000 | 22.574703000 | 13.669449000 |
| H | 9.431849000 | 23.028660000 | 13.157480000 |
| C | 7.390306000 | 20.596137000 | 11.710553000 |
| H | 6.970083000 | 21.246539000 | 10.925850000 |
| H | 7.556987000 | 19.598465000 | 11.276880000 |
| H | 6.630167000 | 20.501464000 | 12.503700000 |
| C | 12.553809000 | 18.171749000 | 13.698775000 |
| H | 13.138134000 | 18.878475000 | 13.089225000 |
| C | 13.369157000 | 17.861982000 | 14.950462000 |
| H | 14.373965000 | 17.507902000 | 14.671822000 |
| H | 13.488273000 | 18.750526000 | 15.589919000 |
| H | 12.908667000 | 17.068965000 | 15.561573000 |
| C | 12.351336000 | 16.920145000 | 12.839917000 |

| | | | |
|---|---|---|---|
| H | 13.316969000 | 16.466951000 | 12.562014000 |
| H | 11.760537000 | 16.164770000 | 13.385117000 |
| H | 11.812476000 | 17.183001000 | 11.916253000 |
| C | 11.900946000 | 19.501796000 | 7.743328000 |
| C | 12.690358000 | 18.417273000 | 7.289636000 |
| C | 12.506864000 | 17.947010000 | 5.986139000 |
| H | 13.110207000 | 17.107946000 | 5.629607000 |
| C | 11.579335000 | 18.531856000 | 5.129203000 |
| H | 11.457395000 | 18.157214000 | 4.109491000 |
| C | 10.823008000 | 19.611902000 | 5.575305000 |
| H | 10.104936000 | 20.078901000 | 4.896112000 |
| C | 10.970791000 | 20.117369000 | 6.869891000 |
| C | 13.680372000 | 17.737515000 | 8.218911000 |
| H | 13.894346000 | 18.445985000 | 9.033878000 |
| C | 15.006661000 | 17.390897000 | 7.546271000 |
| H | 15.723563000 | 17.006946000 | 8.289131000 |
| H | 14.892014000 | 16.610566000 | 6.776675000 |
| H | 15.458556000 | 18.271020000 | 7.063014000 |
| C | 13.039480000 | 16.506121000 | 8.863570000 |
| H | 13.730525000 | 16.025826000 | 9.575733000 |
| H | 12.129926000 | 16.800314000 | 9.409299000 |
| H | 12.761909000 | 15.760997000 | 8.098955000 |
| C | 10.106692000 | 21.271051000 | 7.348623000 |
| H | 10.611208000 | 21.710665000 | 8.222563000 |
| C | 9.935604000 | 22.376211000 | 6.309077000 |
| H | 9.401222000 | 23.233938000 | 6.747107000 |
| H | 10.907115000 | 22.736738000 | 5.936931000 |
| H | 9.348506000 | 22.042042000 | 5.438456000 |
| C | 8.753516000 | 20.751111000 | 7.839870000 |
| H | 8.132274000 | 21.571483000 | 8.235375000 |
| H | 8.197757000 | 20.266151000 | 7.019476000 |
| H | 8.903846000 | 20.012802000 | 8.643231000 |
| Ca | 7.290697000 | 15.268585000 | 9.928386000 |
| O | 7.909491000 | 15.154774000 | 7.608564000 |
| C | 7.319136000 | 14.299312000 | 6.630130000 |
| H | 6.387971000 | 13.889368000 | 7.042755000 |
| H | 8.007477000 | 13.458479000 | 6.426170000 |
| C | 7.148969000 | 15.186538000 | 5.399351000 |
| H | 7.252733000 | 14.607093000 | 4.471463000 |
| H | 6.145418000 | 15.637000000 | 5.388886000 |
| C | 8.239999000 | 16.264987000 | 5.568553000 |
| H | 8.983815000 | 16.256079000 | 4.759843000 |
| H | 7.803882000 | 17.274148000 | 5.589572000 |
| C | 8.888406000 | 15.926816000 | 6.912755000 |
| H | 9.795789000 | 15.311127000 | 6.773151000 |
| H | 9.154540000 | 16.793392000 | 7.531638000 |

| | | | |
|---|---|---|---|
| H | 10.537587000 | 14.850203000 | 11.138517000 |
| H | 10.728289000 | 14.144609000 | 9.513372000 |
| C | 10.083531000 | 11.597132000 | 10.614701000 |
| H | 10.297938000 | 11.360782000 | 9.559866000 |
| H | 10.146821000 | 10.662059000 | 11.188840000 |
| C | 8.725580000 | 12.264658000 | 10.742476000 |
| H | 7.975207000 | 11.905832000 | 10.023499000 |
| H | 8.309444000 | 12.147305000 | 11.758445000 |
| O | 6.577569000 | 15.463581000 | 12.218545000 |
| C | 7.162108000 | 16.325723000 | 13.195051000 |
| H | 8.048146000 | 16.799892000 | 12.752594000 |
| H | 6.435821000 | 17.118627000 | 13.451824000 |
| C | 7.443072000 | 15.421298000 | 14.395282000 |
| H | 7.303008000 | 15.962472000 | 15.341397000 |
| H | 8.484368000 | 15.068544000 | 14.377042000 |
| C | 6.455408000 | 14.248813000 | 14.215591000 |
| H | 5.768522000 | 14.125334000 | 15.064347000 |
| H | 6.991522000 | 13.296152000 | 14.093839000 |
| C | 5.695085000 | 14.602264000 | 12.938139000 |
| H | 4.764658000 | 15.153525000 | 13.167433000 |
| H | 5.438743000 | 13.748908000 | 12.297270000 |
| O | 5.614783000 | 16.876627000 | 9.389690000 |
| C | 4.304135000 | 16.882212000 | 9.971561000 |
| H | 3.891645000 | 15.864148000 | 9.916283000 |
| H | 4.391125000 | 17.167425000 | 11.034453000 |
| C | 3.522369000 | 17.912506000 | 9.175225000 |
| H | 3.097786000 | 17.452629000 | 8.268255000 |
| H | 2.694930000 | 18.349553000 | 9.751726000 |
| C | 4.611802000 | 18.916104000 | 8.808929000 |
| H | 4.836370000 | 19.573405000 | 9.664334000 |
| H | 4.355747000 | 19.553579000 | 7.950969000 |
| C | 5.792453000 | 18.003695000 | 8.522755000 |
| H | 6.770958000 | 18.459712000 | 8.734128000 |
| H | 5.788627000 | 17.648972000 | 7.477048000 |
| O | 8.969153000 | 13.658087000 | 10.498567000 |
| C | 10.376616000 | 13.942307000 | 10.539732000 |
| C | 11.018386000 | 12.692466000 | 11.117661000 |
| H | 11.011049000 | 12.729379000 | 12.219095000 |
| H | 12.061053000 | 12.569119000 | 10.792689000 |

**{$^{i}$Pr$_2$NNNi($\mu$-N$_2$)}$_2$Mg(thf)$_4$**

203

E (PBE0/def2-SVP) = -6836.53336094 a.u.

symmetry c1

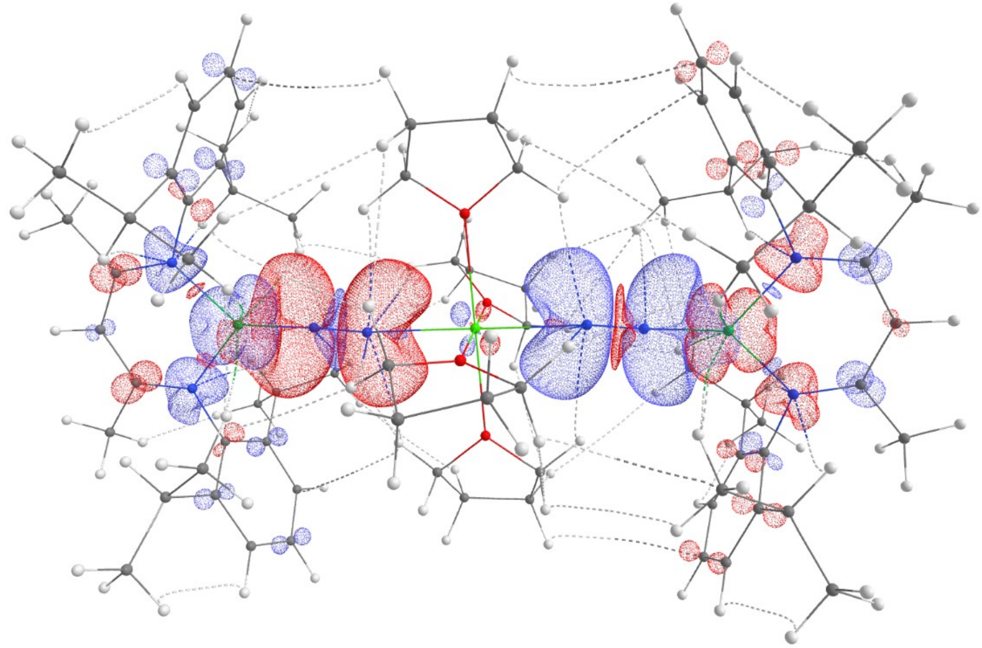
| | | | |
|---|---|---|---|
| Ni | -0.040480000 | -4.937116000 | -0.025039000 |
| N | 0.001441000 | -3.243786000 | 0.036958000 |
| N | 0.021429000 | -2.082444000 | 0.079062000 |
| N | 1.308771000 | -6.278309000 | -0.363831000 |
| N | -1.482782000 | -6.190098000 | 0.266879000 |
| C | 1.094047000 | -7.589888000 | -0.365827000 |
| C | -0.160397000 | -8.168206000 | -0.098165000 |
| H | -0.199896000 | -9.257330000 | -0.120336000 |
| C | -1.365288000 | -7.512157000 | 0.216579000 |
| C | 2.238445000 | -8.528622000 | -0.658462000 |
| H | 1.911757000 | -9.575714000 | -0.634451000 |
| H | 3.052717000 | -8.397314000 | 0.071429000 |
| H | 2.676628000 | -8.318692000 | -1.646795000 |
| C | -2.563442000 | -8.379440000 | 0.515820000 |
| H | -2.948926000 | -8.177034000 | 1.527070000 |
| H | -2.312087000 | -9.444884000 | 0.442848000 |
| H | -3.392992000 | -8.165898000 | -0.176104000 |
| C | 2.605669000 | -5.771251000 | -0.608602000 |
| C | 3.495884000 | -5.560005000 | 0.473313000 |
| C | 4.742019000 | -4.980481000 | 0.219368000 |
| H | 5.433908000 | -4.811621000 | 1.048477000 |
| C | 5.126273000 | -4.626345000 | -1.070821000 |
| H | 6.109852000 | -4.184660000 | -1.251047000 |
| C | 4.256583000 | -4.861065000 | -2.131418000 |
| H | 4.567044000 | -4.598632000 | -3.146221000 |
| C | 2.999707000 | -5.437976000 | -1.927238000 |
| C | 3.083509000 | -5.911794000 | 1.892226000 |
| H | 2.291447000 | -6.672856000 | 1.817935000 |
| C | 4.215117000 | -6.503797000 | 2.728712000 |
| H | 3.829827000 | -6.851799000 | 3.700027000 |
| H | 5.005239000 | -5.766053000 | 2.942679000 |
| H | 4.687188000 | -7.361314000 | 2.224557000 |
| C | 2.457851000 | -4.696041000 | 2.579406000 |
| H | 1.594166000 | -4.340461000 | 1.995867000 |
| H | 3.187103000 | -3.872421000 | 2.660882000 |
| H | 2.110716000 | -4.948103000 | 3.594879000 |
| C | 2.056751000 | -5.658012000 | -3.097063000 |
| H | 1.316162000 | -6.406745000 | -2.776351000 |
| C | 2.751057000 | -6.199081000 | -4.344838000 |
| H | 3.330986000 | -7.108632000 | -4.124088000 |
| H | 3.440971000 | -5.464014000 | -4.789796000 |

| | | | |
|---|---|---|---|
| H | 2.007458000 | -6.450632000 | -5.117455000 |
| C | 1.279765000 | -4.374973000 | -3.400633000 |
| H | 0.563496000 | -4.529958000 | -4.224206000 |
| H | 1.963491000 | -3.558797000 | -3.689219000 |
| H | 0.717693000 | -4.060409000 | -2.507803000 |
| C | -2.721091000 | -5.599370000 | 0.605913000 |
| C | -3.687886000 | -5.347806000 | -0.400775000 |
| C | -4.884598000 | -4.720459000 | -0.045751000 |
| H | -5.637514000 | -4.527610000 | -0.813734000 |
| C | -5.144001000 | -4.344585000 | 1.270403000 |
| H | -6.094157000 | -3.870772000 | 1.531016000 |
| C | -4.189205000 | -4.591860000 | 2.250835000 |
| H | -4.393304000 | -4.299849000 | 3.285346000 |
| C | -2.976560000 | -5.217011000 | 1.943984000 |
| C | -3.392961000 | -5.694844000 | -1.849754000 |
| H | -2.700411000 | -6.551012000 | -1.844346000 |
| C | -4.622772000 | -6.103611000 | -2.654831000 |
| H | -5.182815000 | -6.913146000 | -2.161321000 |
| H | -4.322784000 | -6.458950000 | -3.653046000 |
| H | -5.317397000 | -5.262350000 | -2.810444000 |
| C | -2.648054000 | -4.535576000 | -2.516014000 |
| H | -3.280656000 | -3.632499000 | -2.547090000 |
| H | -2.358566000 | -4.788435000 | -3.549178000 |
| H | -1.735146000 | -4.302658000 | -1.946154000 |
| C | -1.948535000 | -5.447547000 | 3.037315000 |
| H | -1.105300000 | -5.981087000 | 2.573600000 |
| C | -1.402964000 | -4.118410000 | 3.563884000 |
| H | -2.197389000 | -3.514396000 | 4.033444000 |
| H | -0.965463000 | -3.533344000 | 2.740973000 |
| H | -0.619110000 | -4.287619000 | 4.320173000 |
| C | -2.489498000 | -6.315044000 | 4.174039000 |
| H | -3.322649000 | -5.823565000 | 4.702505000 |
| H | -1.701927000 | -6.518527000 | 4.917234000 |
| H | -2.858940000 | -7.282935000 | 3.802518000 |
| Ni | 0.000150000 | 4.940310000 | -0.057774000 |
| N | 0.041927000 | 3.246882000 | -0.010145000 |
| N | 0.091974000 | 2.086106000 | 0.026889000 |
| N | -1.433458000 | 6.233049000 | 0.017855000 |
| N | 1.422242000 | 6.243374000 | -0.174350000 |
| C | -1.273259000 | 7.551343000 | -0.034380000 |
| C | -0.014285000 | 8.173965000 | -0.118764000 |
| H | -0.019414000 | 9.263826000 | -0.139044000 |
| C | 1.251642000 | 7.560444000 | -0.169600000 |
| C | -2.485921000 | 8.448420000 | -0.001945000 |
| H | -2.200553000 | 9.506794000 | -0.047857000 |
| H | -3.157811000 | 8.228229000 | -0.846377000 |

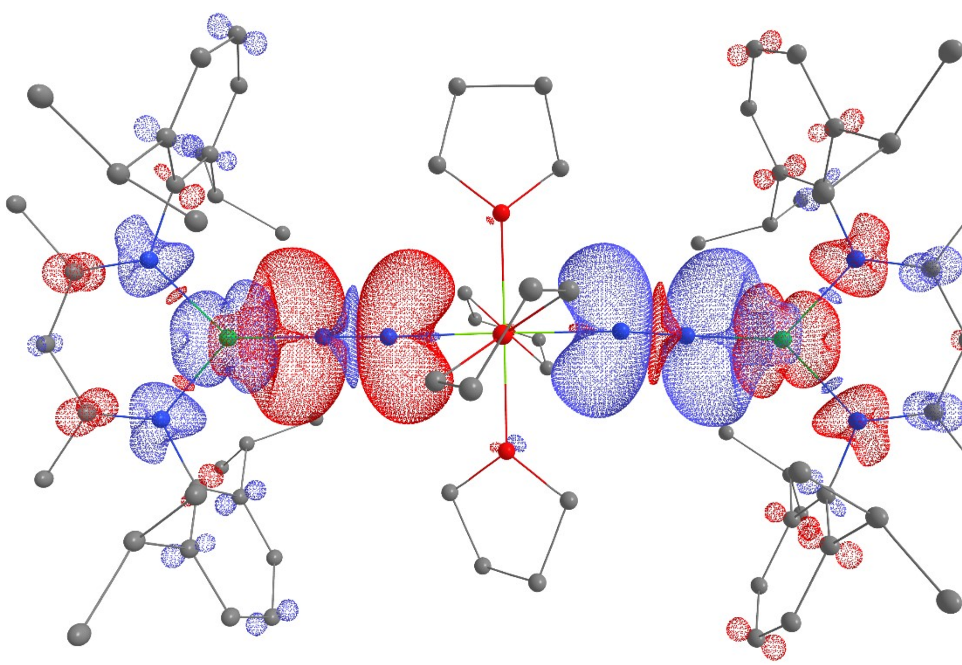
| | | | |
|---|---|---|---|
| H | -3.078014000 | 8.282457000 | 0.911595000 |
| C | 2.456020000 | 8.468725000 | -0.213333000 |
| H | 3.062768000 | 8.283155000 | -1.113220000 |
| H | 2.159045000 | 9.524835000 | -0.202432000 |
| H | 3.118269000 | 8.280648000 | 0.646063000 |
| C | -2.729313000 | 5.678580000 | 0.124383000 |
| C | -3.437770000 | 5.304732000 | -1.042534000 |
| C | -4.684616000 | 4.686627000 | -0.908267000 |
| H | -5.235777000 | 4.392523000 | -1.805841000 |
| C | -5.243671000 | 4.449704000 | 0.343478000 |
| H | -6.226879000 | 3.979342000 | 0.429036000 |
| C | -4.549909000 | 4.838514000 | 1.486656000 |
| H | -4.997902000 | 4.664582000 | 2.468123000 |
| C | -3.300134000 | 5.457756000 | 1.403046000 |
| C | -2.841911000 | 5.527419000 | -2.421361000 |
| H | -2.002769000 | 6.228768000 | -2.298571000 |
| C | -3.828658000 | 6.149809000 | -3.407795000 |
| H | -3.325323000 | 6.384779000 | -4.359062000 |
| H | -4.664719000 | 5.471432000 | -3.642630000 |
| H | -4.259610000 | 7.083243000 | -3.013972000 |
| C | -2.251923000 | 4.224645000 | -2.965979000 |
| H | -1.483166000 | 3.845494000 | -2.275320000 |
| H | -3.031637000 | 3.452688000 | -3.080343000 |
| H | -1.783014000 | 4.383248000 | -3.950998000 |
| C | -2.538094000 | 5.838063000 | 2.660672000 |
| H | -1.849114000 | 6.652047000 | 2.386536000 |
| C | -3.428449000 | 6.349112000 | 3.790058000 |
| H | -4.079138000 | 7.171790000 | 3.455017000 |
| H | -4.075280000 | 5.557475000 | 4.201480000 |
| H | -2.811231000 | 6.722746000 | 4.622095000 |
| C | -1.668062000 | 4.666947000 | 3.122792000 |
| H | -1.060247000 | 4.944351000 | 3.999575000 |
| H | -2.292609000 | 3.800399000 | 3.398107000 |
| H | -0.988521000 | 4.362916000 | 2.311083000 |
| C | 2.723372000 | 5.693523000 | -0.220047000 |
| C | 3.373850000 | 5.320573000 | 0.980006000 |
| C | 4.639079000 | 4.729067000 | 0.909173000 |
| H | 5.147988000 | 4.443393000 | 1.834463000 |
| C | 5.266668000 | 4.507256000 | -0.311830000 |
| H | 6.262137000 | 4.056998000 | -0.348212000 |
| C | 4.620649000 | 4.876988000 | -1.489221000 |
| H | 5.118039000 | 4.705157000 | -2.446805000 |
| C | 3.356358000 | 5.470967000 | -1.469537000 |
| C | 2.707085000 | 5.524056000 | 2.328714000 |
| H | 1.760153000 | 6.051471000 | 2.138354000 |
| C | 3.545192000 | 6.386224000 | 3.272850000 |

| | | | |
|---|---|---|---|
| H | 3.784478000 | 7.362153000 | 2.823697000 |
| H | 3.002582000 | 6.572782000 | 4.213438000 |
| H | 4.498597000 | 5.898713000 | 3.534089000 |
| C | 2.350094000 | 4.182201000 | 2.971245000 |
| H | 3.252393000 | 3.584845000 | 3.184505000 |
| H | 1.815507000 | 4.333733000 | 3.923334000 |
| H | 1.700661000 | 3.598783000 | 2.301383000 |
| C | 2.637657000 | 5.812848000 | -2.763327000 |
| H | 1.958828000 | 6.652144000 | -2.545472000 |
| C | 1.754499000 | 4.638246000 | -3.191193000 |
| H | 2.368777000 | 3.749549000 | -3.413800000 |
| H | 1.054208000 | 4.383469000 | -2.380430000 |
| H | 1.169573000 | 4.886610000 | -4.091978000 |
| C | 3.564910000 | 6.253031000 | -3.892131000 |
| H | 4.201420000 | 5.429252000 | -4.253566000 |
| H | 2.975148000 | 6.602902000 | -4.753792000 |
| H | 4.227296000 | 7.074977000 | -3.578754000 |
| Mg | 0.084007000 | 0.002025000 | 0.064344000 |
| O | -0.181479000 | -0.015034000 | -2.035733000 |
| O | 2.208442000 | -0.035774000 | -0.210433000 |
| C | -0.954184000 | -0.993633000 | -2.747542000 |
| H | -1.902561000 | -1.143245000 | -2.212544000 |
| H | -0.405282000 | -1.948712000 | -2.745286000 |
| C | -1.110528000 | -0.425473000 | -4.146942000 |
| H | -1.266129000 | -1.210001000 | -4.900646000 |
| H | -1.968346000 | 0.264975000 | -4.192300000 |
| C | 0.196303000 | 0.341879000 | -4.320721000 |
| H | 0.157676000 | 1.109207000 | -5.106538000 |
| C | 0.392426000 | 0.941065000 | -2.939048000 |
| H | 1.444605000 | 1.095546000 | -2.660590000 |
| H | -0.136161000 | 1.900758000 | -2.823001000 |
| C | 2.928161000 | -1.136642000 | -0.797541000 |
| H | 2.584721000 | -2.073825000 | -0.340684000 |
| H | 2.690193000 | -1.176380000 | -1.874901000 |
| C | 4.392906000 | -0.820620000 | -0.557829000 |
| H | 5.045714000 | -1.299439000 | -1.300526000 |
| H | 4.702811000 | -1.181111000 | 0.436441000 |
| C | 4.401779000 | 0.702570000 | -0.605849000 |
| H | 5.271956000 | 1.164379000 | -0.119481000 |
| H | 4.378054000 | 1.059774000 | -1.648314000 |
| C | 3.102840000 | 1.049790000 | 0.098583000 |
| H | 3.233530000 | 1.097086000 | 1.193849000 |
| H | 2.645926000 | 1.993000000 | -0.228266000 |
| O | 0.355030000 | 0.016986000 | 2.165391000 |
| O | -2.028230000 | 0.033103000 | 0.337360000 |
| C | -0.315633000 | 0.909313000 | 3.067126000 |

| | | | |
|---|---|---|---|
| H | -0.289800000 | 1.920838000 | 2.640577000 |
| H | -1.369751000 | 0.594391000 | 3.156069000 |
| C | 0.425662000 | 0.766211000 | 4.384298000 |
| H | -0.206379000 | 1.011700000 | 5.249239000 |
| H | 1.300898000 | 1.435265000 | 4.403877000 |
| C | 0.866267000 | -0.693588000 | 4.340036000 |
| C | 1.234746000 | -0.865929000 | 2.876927000 |
| H | 1.092797000 | -1.885067000 | 2.492892000 |
| H | 2.275923000 | -0.559349000 | 2.678497000 |
| C | -2.883885000 | 1.118093000 | -0.065395000 |
| H | -2.593534000 | 1.436064000 | -1.076490000 |
| H | -2.728111000 | 1.973962000 | 0.611133000 |
| C | -4.293061000 | 0.561701000 | 0.032717000 |
| H | -5.034336000 | 1.355519000 | 0.198524000 |
| H | -4.566103000 | 0.026406000 | -0.891625000 |
| C | -4.164288000 | -0.420700000 | 1.191750000 |
| H | -4.950285000 | -1.187958000 | 1.218041000 |
| H | -4.181298000 | 0.119654000 | 2.152594000 |
| C | -2.794517000 | -1.025074000 | 0.940164000 |
| H | -2.839414000 | -1.881960000 | 0.248304000 |
| H | -2.274785000 | -1.360945000 | 1.848377000 |
| H | 1.704725000 | -0.923132000 | 5.012536000 |
| H | 0.029283000 | -1.359972000 | 4.603884000 |
| H | 1.017403000 | -0.352168000 | -4.563006000 |



**{$^{i}$Pr$_2$NNNi($\mu$-N$_2$)}$_2$Ca(thf)$_4$**



**{$^{i}$Pr$_2$NNNi($\mu$-N$_2$)}$_2$Mg(thf)$_4$**

**Figure S20**. Spin density maps of the molecules depicted with an isodensity surface of 0.001 au.

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