Isolated Organometallic Nickel(III) and Nickel(IV) Complexes Relevant to Carbon-Carbon Bond Formation Reactions

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I. General specifications

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk and glove box techniques if not indicated otherwise. All reagents for which synthesis is not given were commercially available from Aldrich, Acros, STREM or Pressure Chemical and were used as received without further purification. Solvents were purified prior to use by passing through a column of activated alumina using an MBRAUN SPS. $Mg(CD_3)I$,[1] N,N'-methyl-2,11-diaza[3,3](2,6)pyridinophane ($^{Me}N4$),[2] $(PMe_3)_2Ni^{II}$(cycloneophyl),[3] and $FcPF_6$[4] were prepared according to the literature procedures.

^1H NMR spectra were recorded on a Varian Mercury-300 spectrometer (300.121 MHz), Agilent DD2-500 spectrometer (499.885 MHz) or Agilent DD2-600 spectrometer (599.736 MHz). Chemical shifts are reported in ppm and referenced to residual solvent resonance peaks.[5] Abbreviations for the multiplicity of NMR signals are s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). UV-visible spectra were recorded on a Varian Cary 50 Bio spectrophotometer and are reported as λ_{max}, nm (ε, $M^{-1}*cm^{-1}$). EPR spectra were recorded on a Bruker EMX-PLUS EPR or a JEOL JES-FA EPR spectrometer at X-band (~9.2 GHz) frequency in frozen solution at 77 K. The purchase of the Bruker EMX-PLUS EPR spectrometer was supported by the National Science Foundation (MRI, CHE-1429711). ESI-MS experiments were performed using a Thermo FT or Bruker Maxis Q-TOF mass spectrometer with an electrospray ionization source. ESI mass-spectrometry was provided by the Washington University Mass Spectrometry Resource, an NIH Research Resource (Grant No. P41RR0954). Elemental analyses were carried out by the Intertek Pharmaceutical Services.

Electrochemical-grade electrolytes from Fluka were used as the supporting electrolyte for electrochemical measurements. Cyclic voltammetry and controlled potential electrolysis experiments were performed with a BASi EC Epsilon electrochemical workstation or a CHI 660D Electrochemical Analyzer. The electrochemical measurements were performed under a blanket of nitrogen, and the analyzed solutions were deaerated by purging with nitrogen. A glassy carbon disk electrode (d = 1.6 mm) was used as the working electrode for cyclic voltammetry. The auxiliary electrode was a Pt wire for cyclic voltammetry measurements. Two different non-aqueous references electrodes were used: Ag/filled with 0.01M $AgNO_3$/0.1M Bu_4NClO_4/MeCN solution or silver wire. The reference electrodes were calibrated against Cp_2Fe (Fc).

II. Synthesis of Ni Complexes

Preparation of (^{Me}N4)Ni^{II}Br$_2$.

$$(^{Me}N4) + (DME)NiBr_2 \xrightarrow{DCM} (^{Me}N4)NiBr_2$$

(DME)NiBr$_2$ (0.345 g, 1.12 mmol) and ^{Me}N4 (0.300 grams, 1.12 mmol) were dissolved in 60 ml of CH_2Cl_2 at RT under N_2. The solution turned from orange to green. After 24 hours, the solvent was evaporated under vacuum and the solid residue was recrystallized from CH_2Cl_2 with slow ether diffusion to afford green paramagnetic crystals (0.341 grams, 0.70 mmol, 63%).

UV-Vis, λ, nm (ε, $M^{-1}\cdot cm^{-1}$), DCM: 259 (2305), 315 (sh, 680), 405 (281), 623 (22), 980 (33).

Evans method (CD_3CN): $\mu_{eff} = 3.05\mu_b$.

^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 68.45 (br), 56.41 (br), 13.23 (br), 1.58 (br).

Anal. Found: C, 37.18; H, 4.03; N, 10.41. Calculated for $C_{16}H_{20}Br_2N_4Ni\cdot 1/2CH_2Cl_2$: C, 37.44; H, 4.00; N, 10.58.

Preparation of (^{Me}N4)Ni^{II}Me$_2$, 1.

$$(^{Me}N4)NiBr_2 + MeMgCl \xrightarrow{THF} (^{Me}N4)NiMe_2$$

To a stirred suspension of (^{Me}N4)NiBr$_2$ (177 mg, 0.364 mmol) in THF (5 mL), cooled at -50°C under N_2, was added 0.56 mL of a ca. 1.94 M solution of MeMgCl in THF solution. The mixture was stirred at this temperature for 30 min, and then slowly warmed up to -5°C overnight. Then dioxane (5 mL) was added to the deep red solution. The resulting suspension was let stand for 1 hour in the -35°C freezer. Then the suspension was filtered and the solvent was completely removed under vacuum at -50°C and the residue was extracted with precooled diethyl ether (100 mL). The deep red solution was filtered and dried under vacuum. A red solid was obtained (84.1 mg, 0.235 mmol, 65%). X-ray quality crystals were obtained by slow pentane diffusion into a diethyl ether solution at -35°C. Several attempts to obtain elemental analysis data proved unsuccessful, likely due to the oxidation of **1** during transportation and handling.

UV-Vis, λ, nm (ε, $M^{-1}\cdot cm^{-1}$), THF: 400 (3100).

^{1}H-NMR (300 MHz, d_3-MeCN), δ (ppm): 7.42 (t, 2H, Py-H), 7.00 (d, 4H, Py-H), 6.77 (d, 2H, -CH_2-), 4.22 (d, 2H, -CH_2-), 2.25 (s, 18H, -CH_3), -0.91 (s, 6H, Ni-CH_3).

^{13}C-NMR (600 MHz, d_8-THF), δ (ppm): 159.22, 134.46, 124.58, 63.94, 63.94, 38.48, -9.65.

Preparation of [(^{Me}N4)Ni^{III}Me$_2$]PF$_6$, 2.

$$(^{Me}N4)NiMe_2 + FcPF_6 \xrightarrow{THF} (^{Me}N4)NiMe_2(PF_6)$$

A solution of **1** (32.8 mg, 0.092 mmol) and $FcPF_6$ (30.4 mg, 0.092 mmol) in pre-cooled THF was stirred at -50 ºC for 3 hours under N_2 and then resulting solution was then filtered at -50 ºC. To the filtrate was added pre-cooled pentane producing a precipitated immediately. After filtration, an orange-red solid was isolated and dried under vacuum (17.6 mg, 0.035 mmol, 38%). X-ray quality crystals were obtained by slow pentane diffusion into a tetrahydrofuran solution at -35°C in the presence of $NaBPh_4$. Elemental analysis sample was obtained using similar X-ray quality crystals obtained under the same conditions.

Evans method (CD_3CN): $\mu_{eff} = 1.70\mu_b$.

UV-Vis, λ, nm (ε, $M^{-1}\cdot cm^{-1}$), MeCN: 240 (10800), 465 (470).

ESI-MS (HR) in Acetonitrile: m/z 356.1501; Calculated for [(^{Me}N4)Ni^{III}Me$_2$]$^+$: m/z 356.1511.

Anal. Found: C, 73.31; H, 6.89; N, 7.55. Calculated for $C_{42}H_{46}BN_4Ni\cdot C_4H_8O$: C, 73.82; H, 7.27; N, 7.49.

Preparation of (^{Me}N4)Ni^{II}(CD$_3$)$_2$, 1-d$_6$.

$$(^{tBu}N4)NiBr_2 + CD_3MgCl \xrightarrow{THF} (^{tBu}N4)Ni(CD_3)_2$$

To a stirred suspension of (^{Me}N4)NiBr$_2$ (220 mg, 0.452 mmol) in THF (6 mL), cooled at -50°C, was added 1.35 mL of the CD_3MgI solution. The mixture was stirred at this temperature for 30 min, and then slowly warmed up to -5°C overnight. Then dioxane (6 mL) was added to the deep red solution. The resulting suspension was let stand for 1 hour in the -35°C freezer. Then the suspension was filtered and the solvent was completely removed under vacuum and the residue was extracted with precooled diethyl ether (150 mL). The deep red solution was filtered and dried under vacuum. A red solid was obtained (150 mg, 0.413 mmol, 91%). The ^{1}H NMR spectrum of the product is identical to that of (^{Me}N4)Ni^{II}Me$_2$ except for the missing singlet for the Ni-Me group.

Preparation of (^{Me}N4)Ni^{II}(cycloneophyl), 5.

$$(^{Me}N4) + (PMe_3)Ni(cycloneophyl) \xrightarrow{Et_2O} (^{Me}N4)Ni(cycloneophyl)$$

A solution of ^{Me}N4 (0.2300 grams, 0.86 mmol) and $(PMe_3)_2Ni^{II}$(cycloneophyl) (0.2940 grams, 0.86 mmol) in diethyl ether was stirred at room temperature overnight. The red precipitate was then separated by filtration, washed with pentane (3 mL), and dried under vacuum. Yield: 0.2473 grams, 0.54 mmol, 63%.

UV-vis (MeCN, RT), λ_{max} (ε, M^{-1} cm^{-1}): 247 (17500), 302 (5900), 367 (5530), 490 (350).

^{1}H-NMR (300 MHz, CDCl3), δ (ppm): 7.54 (t, 1H, Py-H), 7.46 (t, 1H, Py-H), 7.11 (d, 2H, Py-H), 7.04 (d, 2H, Py-H), 6.66 (m, 6H, Cycle/-CH_2-), 6.38 (t, 1H, Cycle), 5.86 (d, 1H, Cycle), 4.22 (dd, 4H, -CH_2-), 2.24 (s, 6H, N-CH_3), 1.32 (s, 6H, CH_3), 1.24 (s, 2H, Ni-CH_2-Cycle).

^{13}C-NMR (600 MHz, d_3-MeCN), δ (ppm): 159.21, 158.49, 136.35, 136.16, 136.05, 135.88, 125.59, 125.48, 123.89, 123.24, 122.95, 121.91, 66.70, 64.07, 63.95, 49.09, 38.87, 34.21.

Several attempts to obtain elemental analysis data proved unsuccessful, likely due to the oxidation of **5** during transportation and handling.

Preparation of [(^{Me}N4)Ni^{III}(cycloneophyl)]PF_6, 6.

$$(^{Me}N4)Ni(cycloneophyl) + FcPF_6 \xrightarrow{THF} (^{Me}N4)Ni(cycloneophyl)PF_6$$

A THF solution of (^{Me}N4)Ni^{II}(cycloneophyl) (0.1581 grams, 0.34 mmol) and $FcPF_6$ (0.1140 grams, 0.34 mmol) was stirred at -50 ºC for 2 hours. The resulting solution was then precipitated with excess pentane. The orange precipitate was separated by filtration, washed with pentane (3 mL), and dried under vacuum. Yield: 0.1658 grams, 0.27 mmol, 79%. X-ray quality crystals were obtained by slow pentane diffusion into a tetrahydrofuran solution in the presence of $NaBPh_4$ at -35°C.

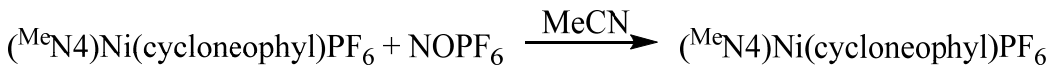
Evans method (CD_3CN): μ_{eff} = 1.894 μ_b.

UV-vis (MeCN, RT), λ_{max} (ε, M^{-1} cm^{-1}): 246 (18000), 473 (630), 964 (50).

ESI-MS of [(^{Me}N4)Ni^{III}(cycloneophyl)]PF_6, m/z 458.1969; calculated for [(^{Me}N4)Ni^{III}(cycloneophyl)]$^+$, 458.1980.

Anal. Found: C, 53.32; H, 5.79; N, 7.96. Calculated for $C_{26}H_{32}F_6N_4NiP$▪C_4H_8O: C, 53.28; H, 5.96; N, 8.28.

Preparation of [(^{Me}N4)Ni^{IV}(cycloneophyl)](PF$_6$)$_2$, 7.



A d$_3$-MeCN solution of [(^{Me}N4)Ni^{III}(cycloneophyl)]PF$_6$ (20 mg, 0.03 mmol) and NOPF$_6$ (29 mg, 0.17 mmol) was stirred at -40 ºC for 15 minutes. The resulting orange-red solution was then transferred to a pre-cooled NMR tube. NMR experiments were conducted at -15°C. An X-ray structure was not obtained due to decomposition of X-ray quality crystals during data collection. X-ray quality crystals were however obtained by slow pentane diffusion into a tetrahydrofuran solution at -35°C. Elemental analysis proved unsuccessful due to instability and decomposition of the complex.

UV-vis (MeCN, RT), λ_{max} (ε, M^{-1} cm^{-1}): 258 (8825), 305 (1400), 457 (525).

^{1}H-NMR (500 MHz, CDCl3, -15°C), δ (ppm): 8.05 (t, 1H, Py-H), 7.97 (t, 1H, Py-H), 7.51 (d, 2H, Py-H), 7.41 (d, 2H, Py-H), 7.25 (t, 1H, Cyc-H), 7.19 (d, 1H, Cyc-H), 6.92 (t, 1H, Cyc-H), 6.55 (d, 1H, Cyc-H), 5.33 (s, 2H, Ni-CH$_2$-Cyc), 5.01 (d, 2H, -CH$_2$-), 4.56 (d, 2H, -CH$_2$-), 4.22 (d, 2H, -CH$_2$-), 4.08 (d, 2H, -CH$_2$-), 2.38 (s, 6H, N-CH$_3$), 1.67 (s, 6H, -CH$_3$).

^{13}C-NMR (500 MHz, CDCl3, -15°C), δ (ppm): 159.42, 158.44, 156.25, 154.50, 144.89, 133.85, 132.31, 131.31, 131.15, 125.82, 125.07, 79.77, 77.38, 57.31, 36.00.

III. Cyclic Voltammograms (CVs) of Isolated Ni Complexes

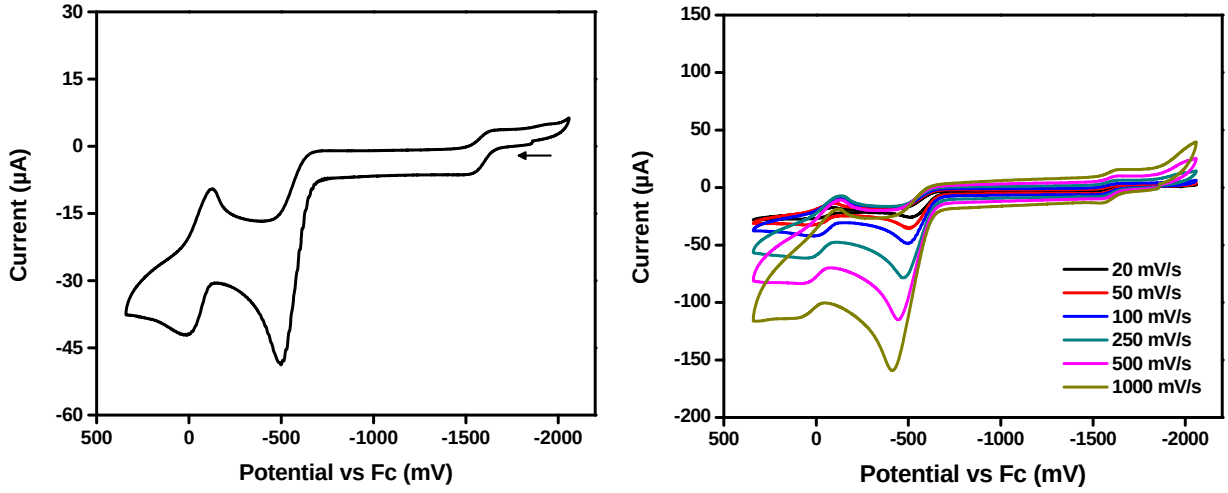


Figure S1: CVs of (^{Me}N4)NiMe$_2$ in MeCN at RT ([Bu$_4$NPF$_6$] = 0.1 M, glassy carbon disk electrode), at 100 mV/s scan rate (left) and variable scan rates (right). Potentials vs Fc/Fc$^+$ (V): E_{pa} = -1.50, -0.50 and 0.03, E_{pc} = -0.10, -0.70 and -1.65.

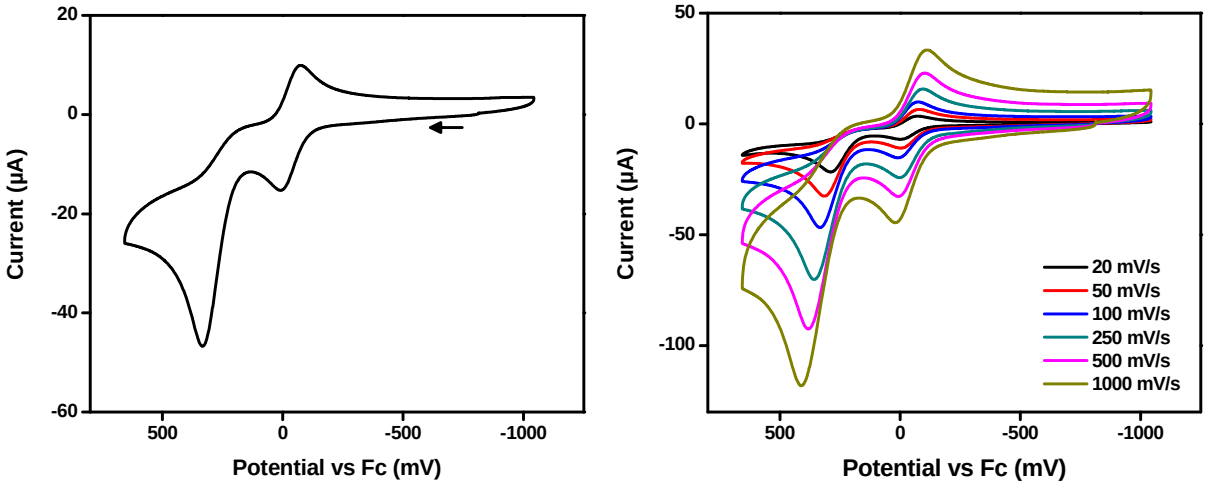


Figure S2: CVs of [(^{Me}N4)NiMe$_2$]PF$_6$ in MeCN under N$_2$ at RT ([Bu$_4$NPF$_6$] = 0.1 M, glassy carbon disk electrode), at 100 mV/s scan rate (left) and variable scan rates (right). Potentials vs Fc/Fc$^+$ (V): E_{pa} = 0.01 and 0.36 V, E_{pc} = -0.07.

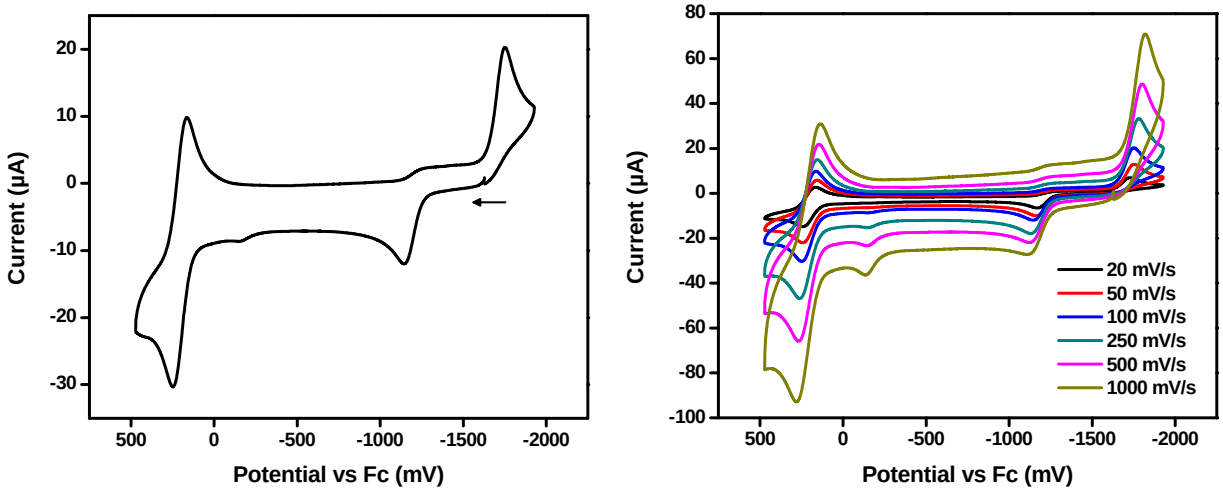


Figure S3: CVs of (^{Me}N4)Ni(cycloneophyl) in MeCN under N_2 at RT ([Bu_4NPF_6] = 0.1 M, glassy carbon disk electrode), at 100 mV/s scan rate (left) and variable scan rates (right). Potentials vs Fc/Fc^+ (V): E_{pa} = -1.17 and 0.25, E_{pc} = 0.17 and -1.75.

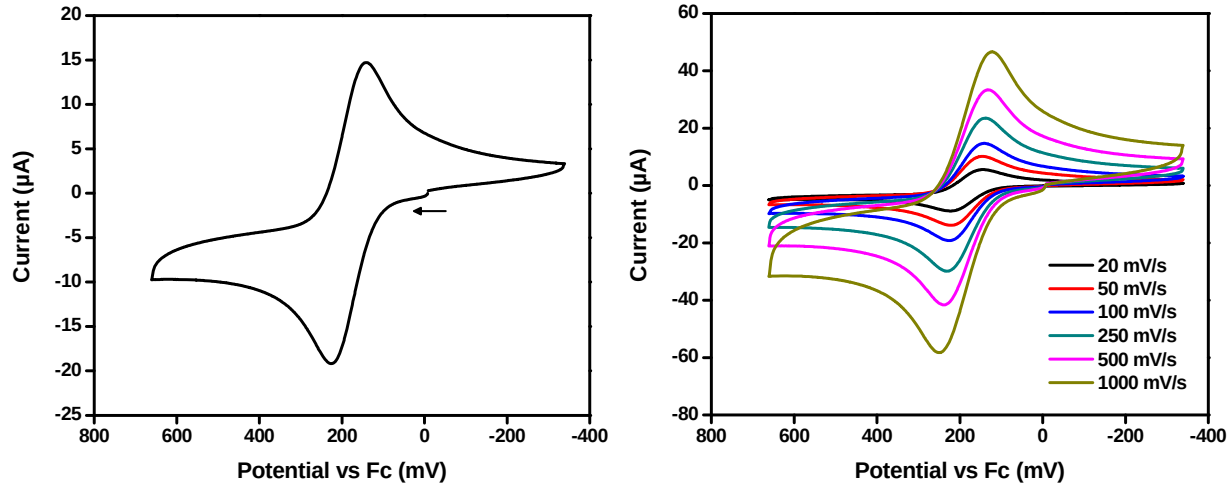


Figure S4: CVs of [(^{Me}N4)Ni(cycloneophyl)]PF_6 in MeCN under N_2 at RT ([Bu_4NPF_6] = 0.1 M, glassy carbon disk electrode), at 100 mV/s scan rate (left) and variable scan rates (right). Potentials vs Fc/Fc^+ (V): E_{pa} = 0.25, E_{pc} = 0.17.

IV. UV-Vis spectra of Isolated Ni Complexes

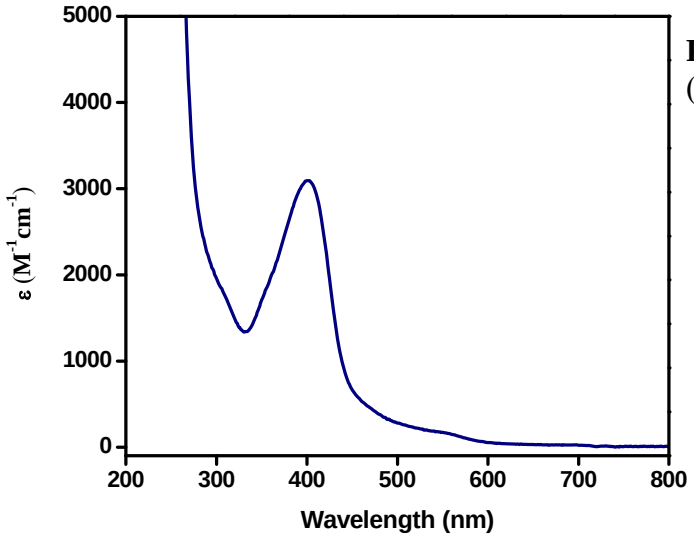


Figure S5. UV-visible spectrum of (^{Me}N4)Ni^{II}Me$_2$ in THF (5.0*10^{-4} M).

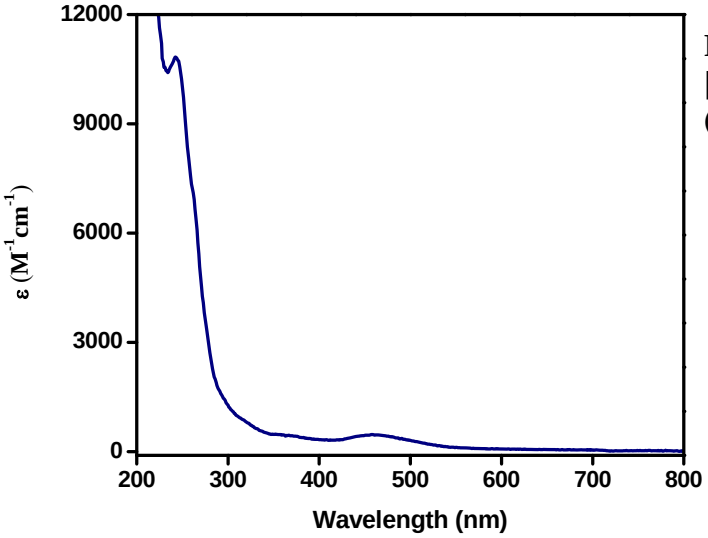


Figure S6. UV-visible spectrum of [(^{Me}N4)Ni^{III}Me$_2$]PF$_6$ in MeCN (1.25*10^{-4} M).

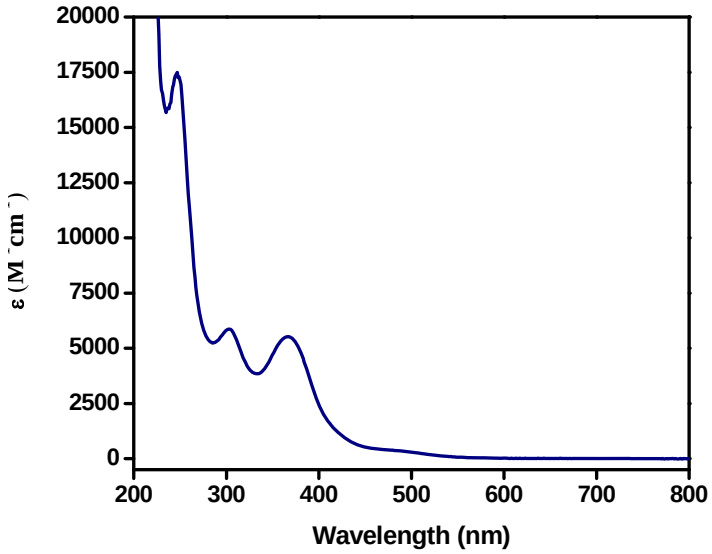


Figure S7. UV-visible spectrum of (^{Me}N4)Ni^{II}(cycloneophyl) in MeCN (1.25*10^{-4} M).

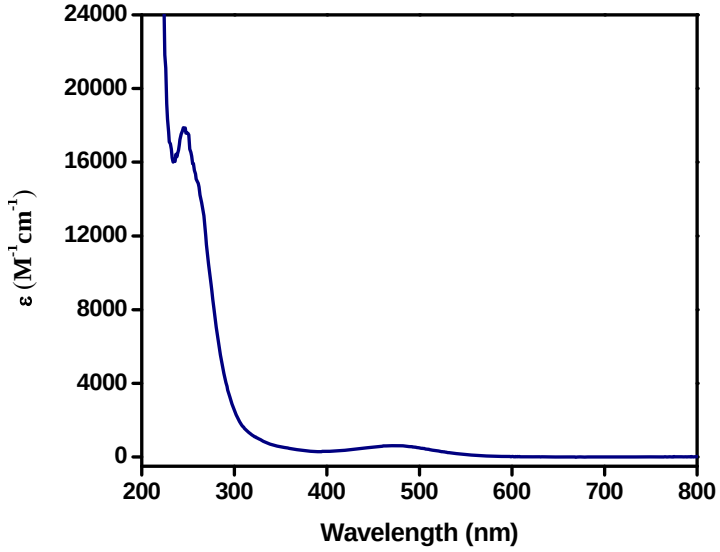


Figure S8. UV-visible spectrum of [(^{Me}N4)Ni^{III}(cycloneophyl)]PF_6 in MeCN (1.25*10^{-4} M).

V. Simulation of EPR spectra of Isolated Ni^{III} Complexes

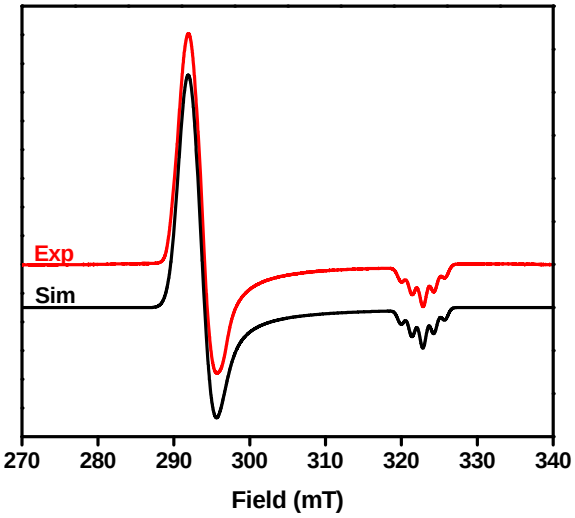


Figure S9. Experimental and simulated EPR spectra of isolated $[(^{Me}N4)Ni^{III}Me_2]PF_6$ in frozen PrCN (77 K).

Experimental conditions: frequency ≈ 9.097 GHz, power = 1mW, modulation frequency = 100 kHz, modulation amplitude = 3 G, time constant = 0.3 s.

Simulation parameters: $g_x = 2.2283$, $g_y = 2.2100$, $g_z = 2.0137$ ($A_N = 14.30$ G).

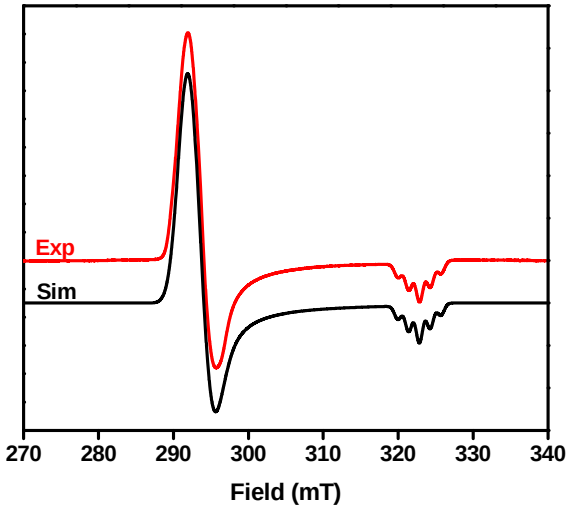


Figure S10. Experimental and simulated EPR spectra of isolated $[(^{Me}N4)Ni^{III}Me_2]BPh_4$ in frozen PrCN (77 K).

Experimental conditions: frequency ≈ 9.097 GHz, power = 1mW, modulation frequency = 100 kHz, modulation amplitude = 3 G, time constant = 0.3 s.

Simulation parameters: $g_x = 2.2283$, $g_y = 2.2100$, $g_z = 2.0137$ ($A_N = 14.30$ G).

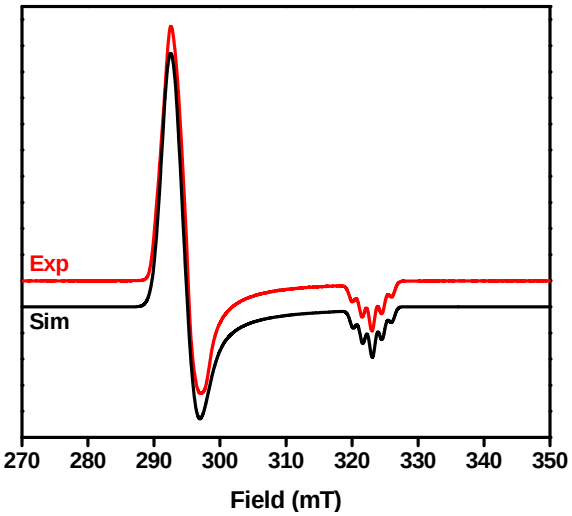


Figure S11. Experimental and simulated EPR spectra of $[(^{Me}N4)Ni^{III}(cycloneophyl)]PF_6$ in frozen PrCN (77 K).

Experimental conditions: frequency ≈ 9.097 GHz, power = 1mW, modulation frequency = 100 kHz, modulation amplitude = 3 G, time constant = 0.3 s.

Simulation parameters: $g_x = 2.2225$, $g_y = 2.2012$, $g_z = 2.0116$ ($A_N = 14.50$ G).

VI. NMR Spectra of Ni^{IV} Complex $[(^{Me}N4)Ni^{IV}(cycloneophyl)](PF_6)_2$

A d_3-MeCN solution of $[(^{Me}N4)Ni^{III}(cycloneophyl)]PF_6$ (20.0 mg, 0.033 mmol) and $NOPF_6$ (29.0 mg, 0.166 mmol) was stirred at -40ºC for 5 minutes. The resulting solution was then transferred to a pre-cooled NMR tube at -40ºC. The NMR tube was then sealed and quickly removed from the glove box and placed in the NMR, which the temperature control was set at -15ºC for all NMR experiments.

^{1}H-NMR (300 MHz, CDCl3), δ (ppm): 8.05 (t, 1H, **F**), 7.97 (t, 1H, **G**), 7.51 (d, 2H, **I**), 7.41 (d, 2H, **H**), 7.25 (t, 1H, **L**), 7.19 (d, 1H, **K**), 6.92 (t, 1H, **M**), 6.55 (d, 1H, **N**), 5.33 (s, 2H, **O**), 5.01 (d, 2H, **E**), 4.56 (d, 2H, **B**), 4.22 (d, 2H, **D**), 4.08 (d, 2H, **C**), 2.38 (s, 6H, **A**), 1.67 (s, 6H, **J**).

^{13}C-NMR (600 MHz, CDCl3), δ (ppm): 159.42 (**p**, **k**), 158.44 (**i**), 156.25 (**g**), 154.50 (**c**), 144.89 (**e**), 133.85 (**o**), 132.31 (**n**), 131.31 (**l**), 131.15 (**m**), 125.82 (**d**), 125.07 (**f**), 79.77 (**h**), 77.38 (**b**), 57.31 (**a**), 36.00 (**j**).

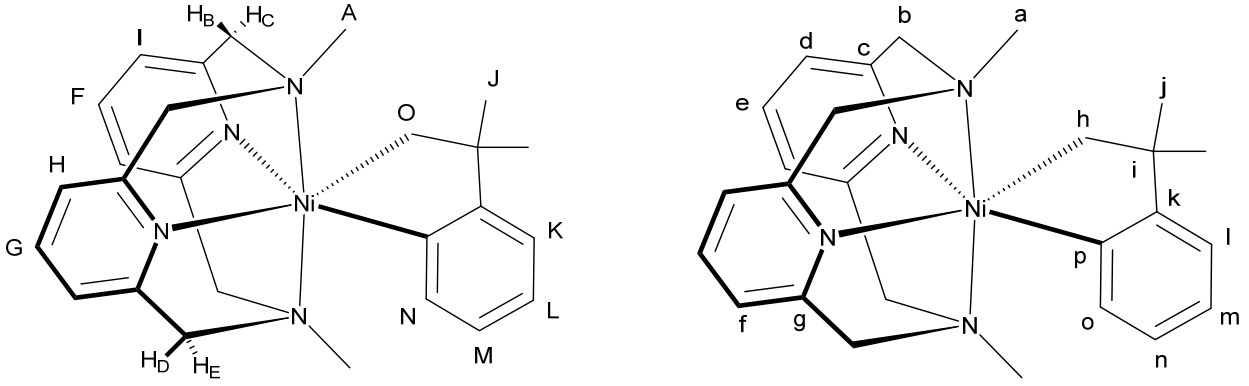


Figure S12. Proton (left) and carbon (right) structural assignments from NMR experiments.

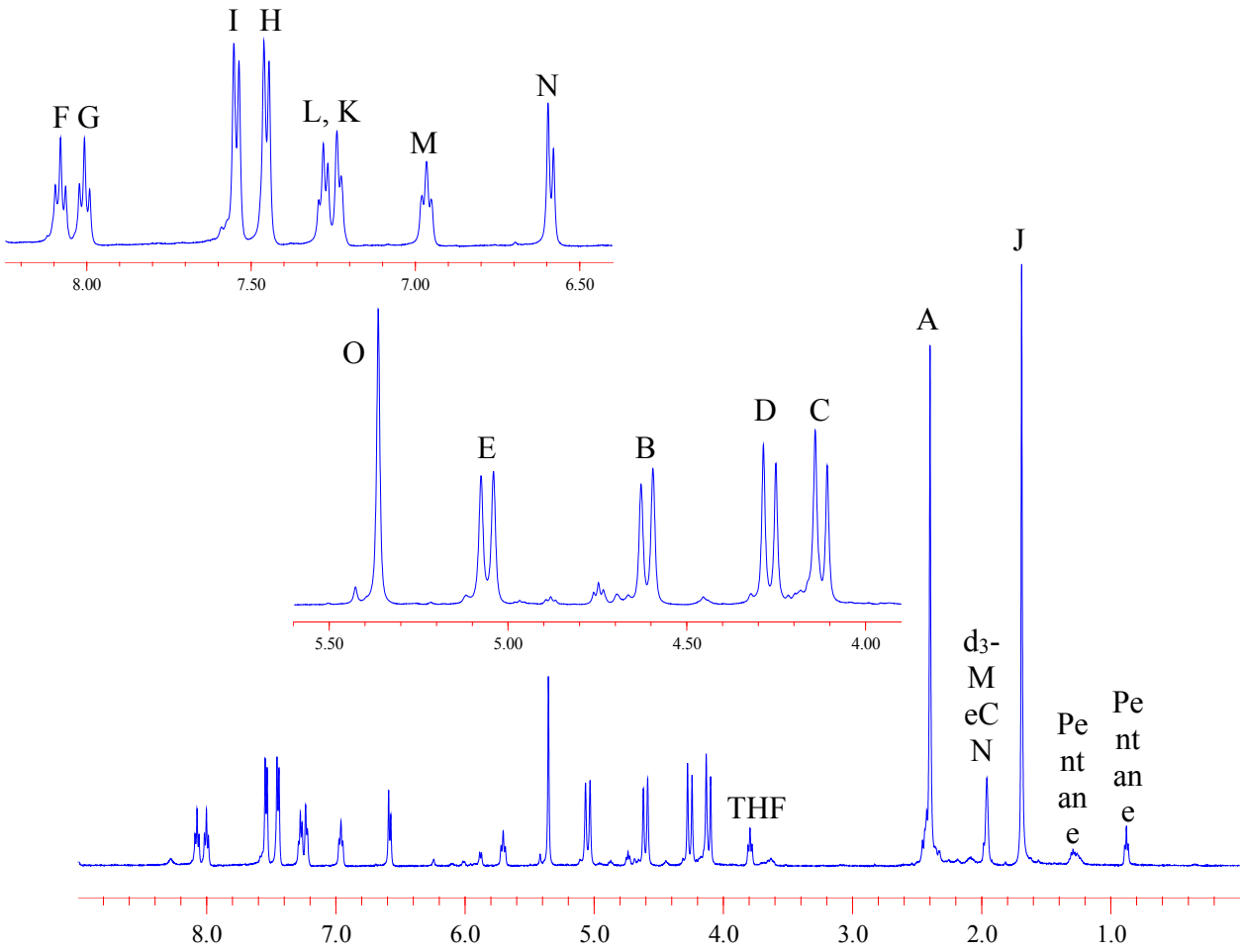


Figure S13. ^{1}H NMR spectrum of [(^{Me}N4)Ni^{IV}(cycloneophyl)](PF$_6$)$_2$ in d$_3$-MeCN at -15°C.

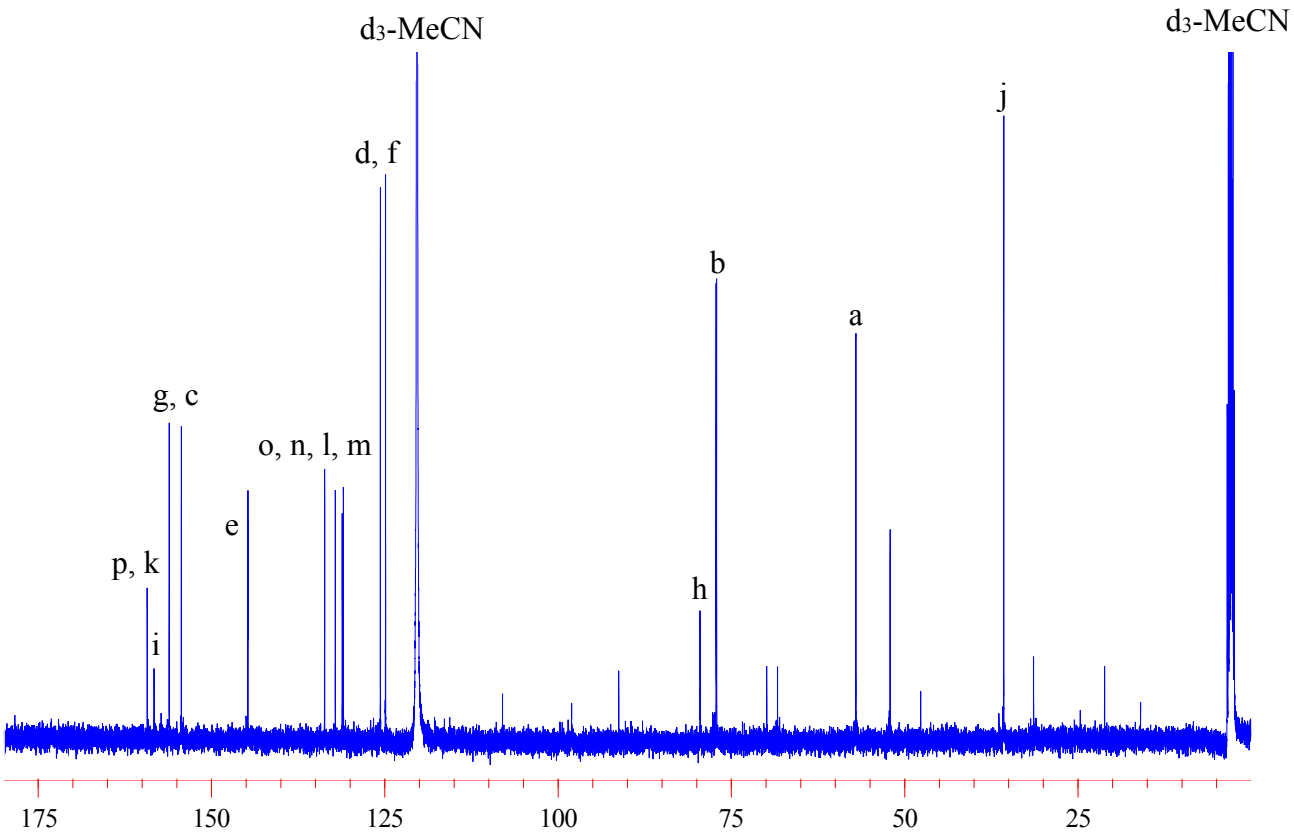


Figure S14. ^{13}C NMR spectrum of [(^{Me}N4)Ni^{IV}(cycloneophyl)](PF$_6$)$_2$ in d$_3$-MeCN at -15°C.

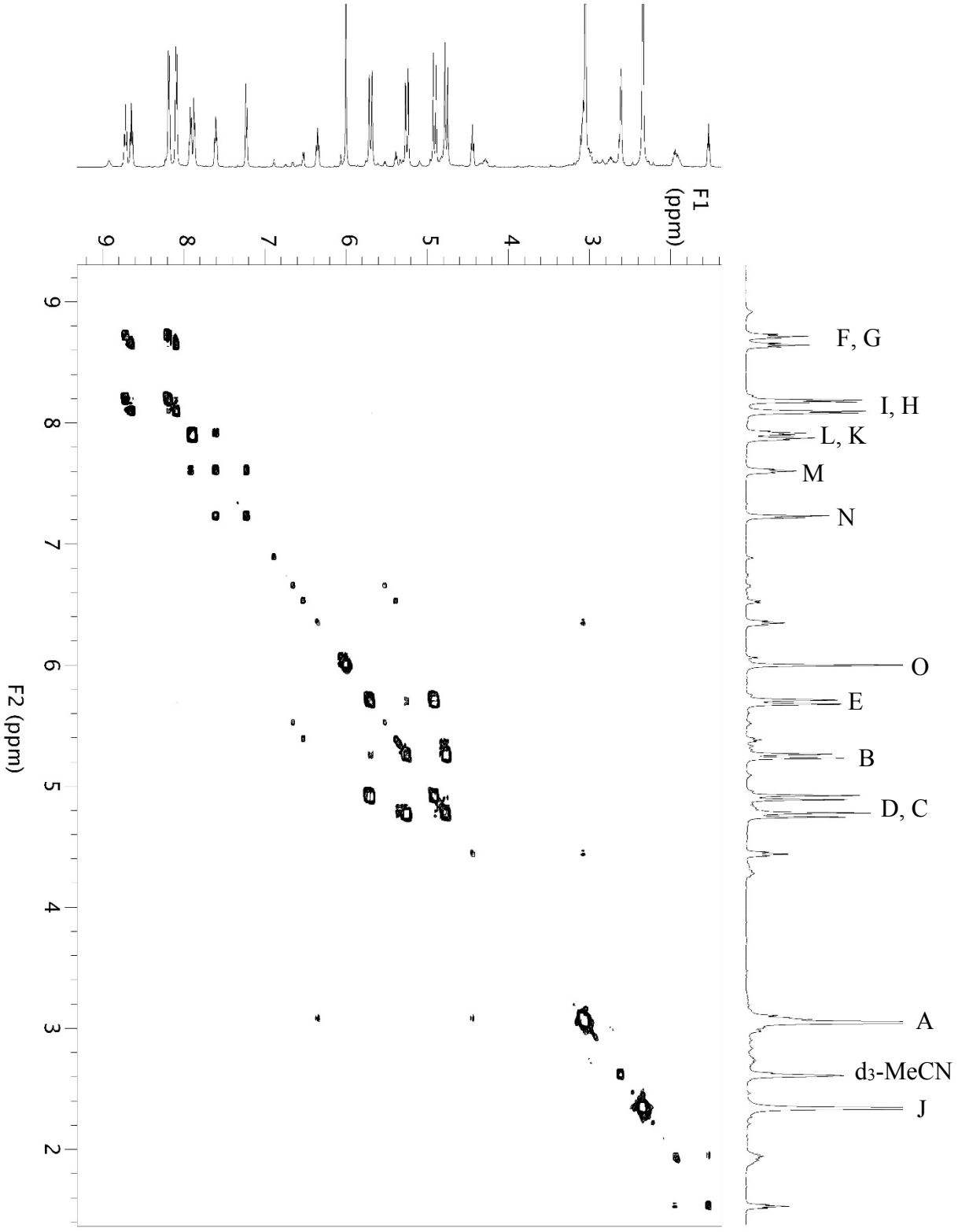


Figure S15. ^{1}H-^{1}H COSY spectrum of [(^{Me}N4)Ni^{IV}(cycloneophyl)](PF$_6$)$_2$ in d$_3$-MeCN at -15°C.

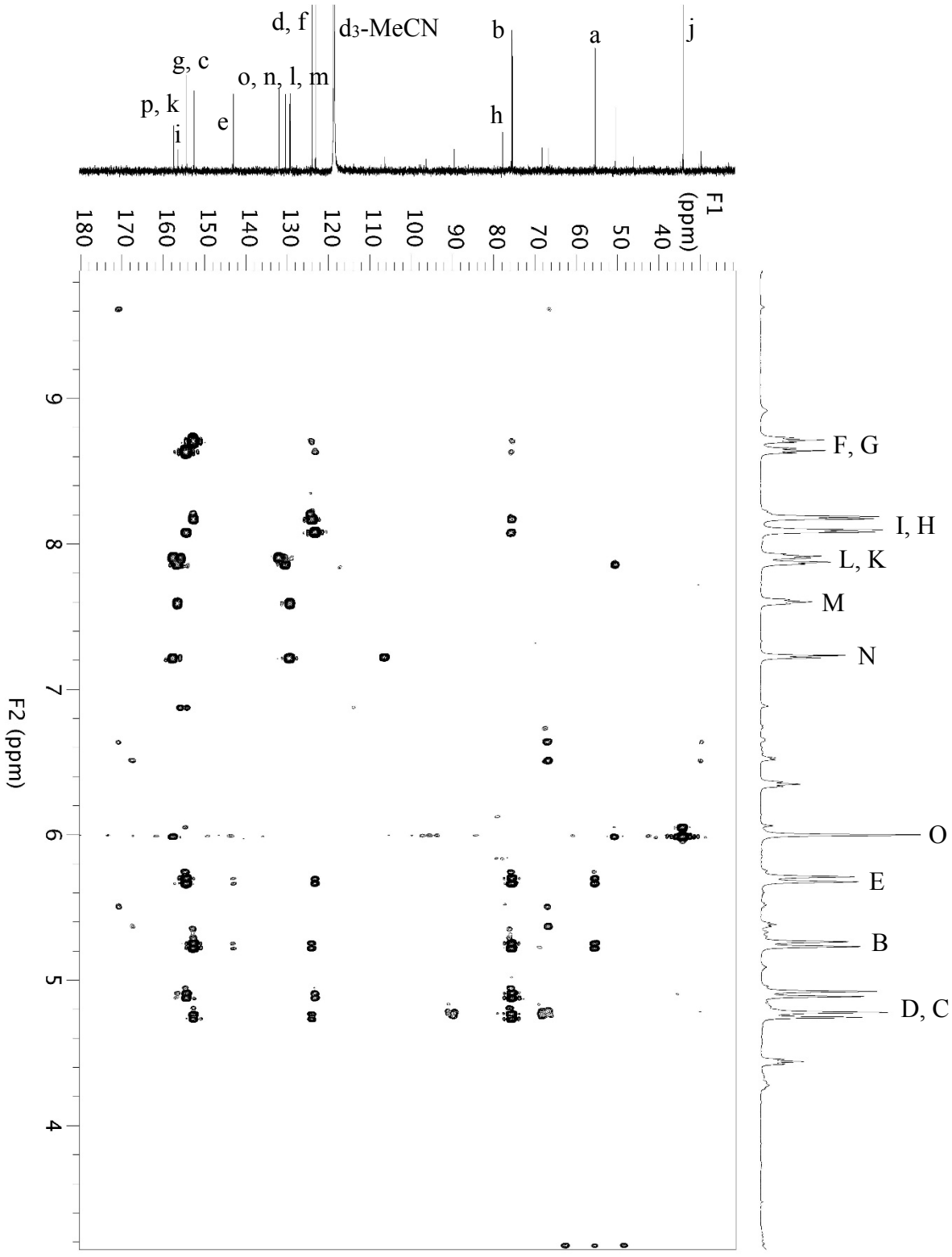


Figure S16. ^{1}H-^{13}C HMBC spectrum of [(^{Me}N4)Ni^{IV}(cycloneophyl)](PF$_6$)$_2$ in d$_3$-MeCN at -15°C.

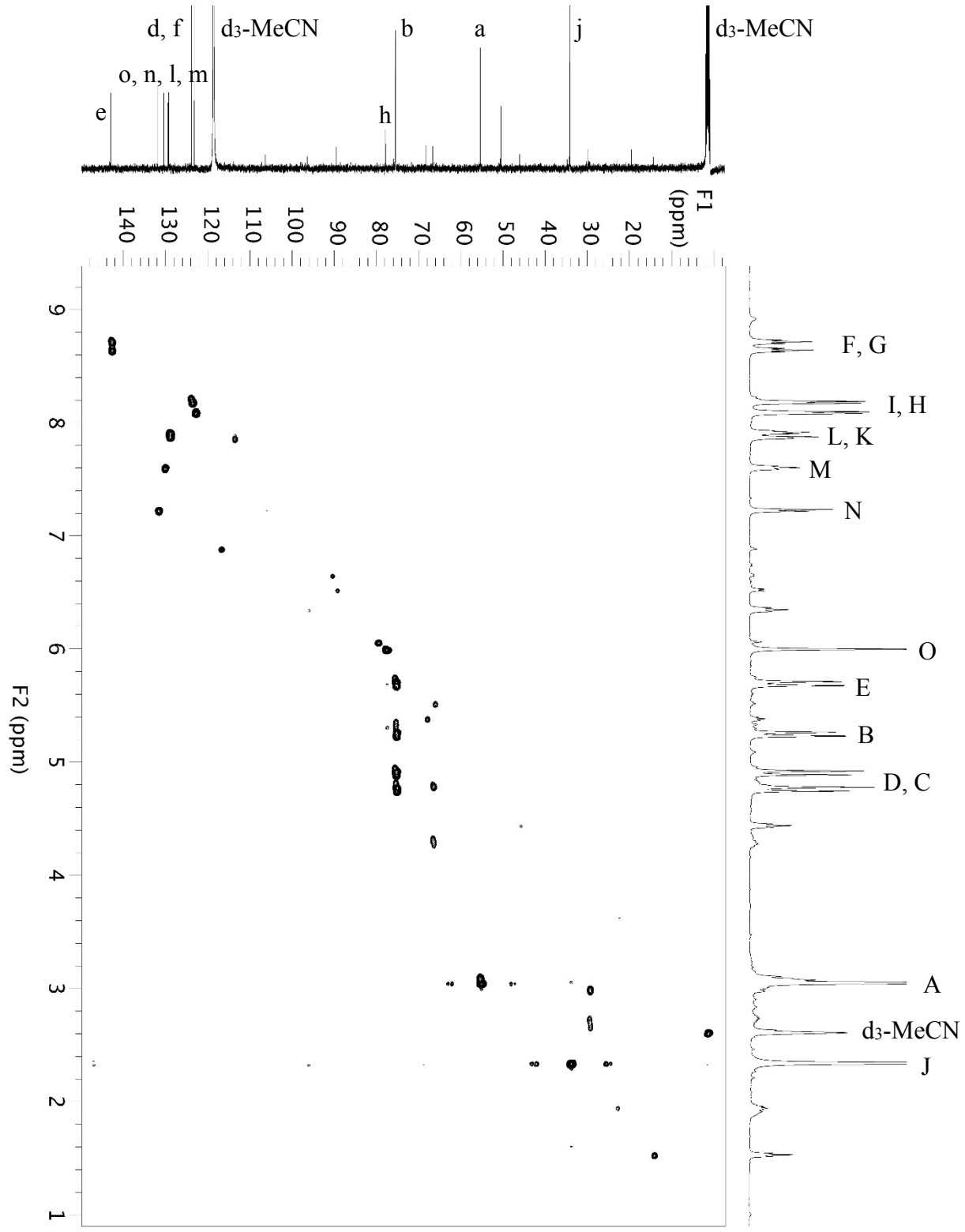


Figure S17. ^{1}H-^{13}C HSQC spectrum of [(^{Me}N4)Ni^{IV}(cycloneophyl)](PF$_6$)$_2$ in d$_3$-MeCN at -15°C.

VII. XPS of Isolated Ni Complexes

Solid samples of [(^{Me}N4)Ni^{III}(cycloneophyl)]PF$_6$ and [(^{Me}N4)Ni^{III}(cycloneophyl)](PF$_6$)$_2$ were prepared and stored on dry ice prior to XPS analysis. Immediately prior to analysis, the two samples were transferred at RT to a piece of tape pre-fixed to the XPS plate. The samples were compressed and quickly loaded into the instrument. XPS spectra were recorded on a PHI 5000 Versa Probe II X-Ray Photoelectron Spectrometer. The XPS experiments was performed in conjunction with the Washington University Institute of Materials Science and Engineering.

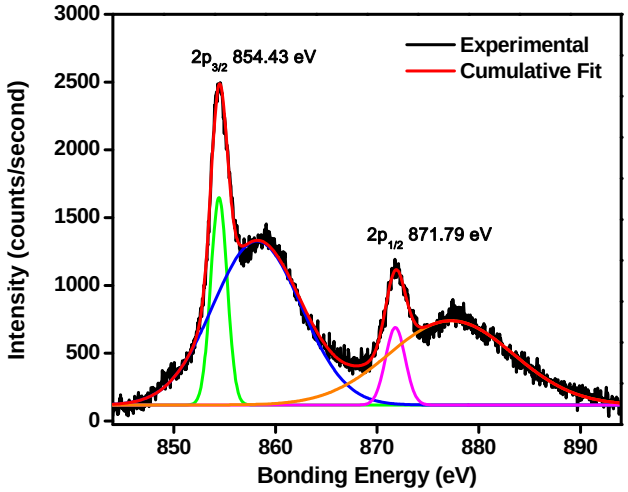


Figure S18. XPS spectrum of [(^{Me}N4)Ni^{III}(cycloneophyl)]PF$_6$, Bonding energies: $2_{p^{3/2}}$, 854.43 eV and $2_{p^{1/2}}$, 871.79 eV.

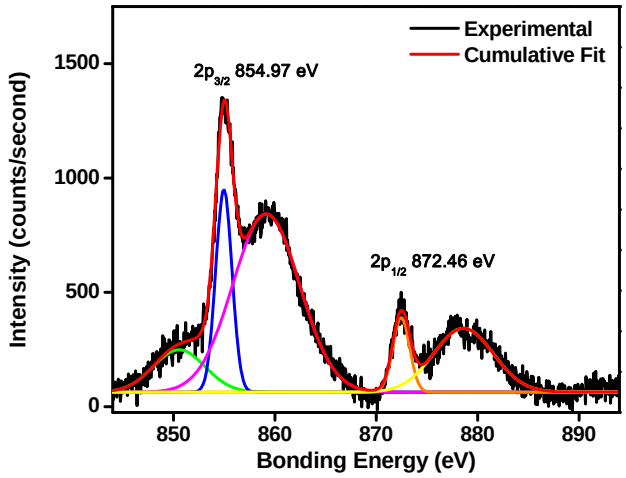


Figure S19. XPS spectrum of [(^{Me}N4)Ni^{IV}(cycloneophyl)](PF$_6$)$_2$, Bonding energies: $2_{p^{3/2}}$, 854.97 eV and $2_{p^{1/2}}$, 872.46 eV.

VIII. Computational Details

The density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations were performed with the program package Gaussian 09.[6] The UB3LYP hybrid functional with the 6-31G* basis set for C, N, H and the modified m6-31G* basis set for Ni were employed. This combination of hybrid functional and basis sets have been previously shown to work well for reproducing experimental parameters of Ni complexes.[7-8] Geometry optimization calculations were performed using the X-ray coordinates as the starting geometry. The ground state wave function was investigated by analyzing the frontier MOs and spin density plot using GaussView 5.0, and the atomic contributions to MOs and spin density plot were calculated using the program Chemissian.[9]

Optimized Geometry Cartesian coordinates for $[(^{Me}N4)Ni^{III}Me_2]^+$:

1	28	0	0.000000	0.000000	0.000000
2	7	0	2.021783	0.000000	0.000000
3	7	0	0.247552	2.005717	0.000000
4	7	0	0.413965	0.365410	-2.235960
5	7	0	0.419656	0.372352	2.241174
6	6	0	-1.956410	0.053589	-0.035459
7	1	0	-2.258512	1.055664	-0.366127
8	1	0	-2.356453	-0.119554	0.969826
9	1	0	-2.393318	-0.686062	-0.713631
10	6	0	-0.201475	-1.944472	0.044929
11	1	0	-0.454668	-2.324964	-0.950937
12	1	0	-0.973494	-2.274171	0.747328
13	1	0	0.760566	-2.375593	0.350811
14	6	0	2.676229	0.180104	1.158779
15	6	0	4.048366	0.433168	1.178537
16	1	0	4.559644	0.577033	2.124988
17	6	0	4.733239	0.512992	-0.033264
18	1	0	5.800032	0.716090	-0.045749
19	6	0	4.033088	0.360188	-1.230792
20	1	0	4.532767	0.447066	-2.190100
21	6	0	2.662779	0.109540	-1.177199
22	6	0	1.813146	-0.096371	-2.410499
23	1	0	2.286108	0.377490	-3.281510
24	1	0	1.774224	-1.173246	-2.610986
25	6	0	0.263782	1.830099	-2.422684
26	1	0	-0.769303	2.012976	-2.738953
27	1	0	0.911701	2.199071	-3.229554
28	6	0	0.498608	2.631796	-1.161196
29	6	0	0.905807	3.966306	-1.185290

30	1	0	1.106378	4.455262	-2.133162
31	6	0	1.061681	4.641538	0.024707
32	1	0	1.382846	5.678954	0.034046
33	6	0	0.829655	3.967515	1.224369
34	1	0	0.970303	4.458019	2.182079
35	6	0	0.427851	2.633527	1.175489
36	6	0	0.129329	1.816944	2.412688
37	1	0	0.660739	2.232452	3.279775
38	1	0	-0.943155	1.906679	2.620101
39	6	0	1.856366	0.045967	2.423202
40	1	0	1.914456	-1.000445	2.742975
41	1	0	2.304417	0.646917	3.226474
42	6	0	-0.462843	-0.344124	-3.189511
43	1	0	-0.380189	-1.421117	-3.028344
44	1	0	-0.193209	-0.122845	-4.233179
45	1	0	-1.498829	-0.041796	-3.022013
46	6	0	-0.387421	-0.411066	3.197862
47	1	0	-1.447138	-0.199663	3.039544
48	1	0	-0.132352	-0.168948	4.240543
49	1	0	-0.213143	-1.476272	3.031335

IX. Reactivity of Ni Complexes

General procedure for the reactivity studies of (^{Me}N4)Ni complexes. In N_2-filled glove box, a solution of 5-7 mg of (^{Me}N4)Ni complex in 2.0 mL of d_3-MeCN was added into a NMR tube containing 1,3,5-trimethoxybenzene as an internal standard. To this solution additional reagents [$FcPF_6$, $^{Ac}FcBF_4$, H_2O_2, O_2, $PhI(Py^{OMe})_2(OTf)_2$, CD_3I, PhMgBr, MeMgCl, or TEMPO] were added in d_3-MeCN. For crossover experiments, equimolar amounts of (^{Me}N4)$NiMe_2$ and (^{Me}N4)$Ni(CD_3)_2$ in d_3-MeCN were added to the NMR tube as separate solutions. For all experiments the NMR tube was filled to the top with additional d_3-MeCN (so that no headspace was left to avoid the escape of volatiles), sealed with a septum, and taken out of the glove box. The reaction mixtures were mixed carefully to form homogeneous solutions, and then kept in the dark and periodically monitored by ^{1}H NMR until no additional changes were observed. The average product yields from at least two independent experiments were determined by NMR integration using 1,3,5-trimethoxybenzene as an internal standard. For the reactivity of (^{Me}N4)Ni^{III} complexes, the amount of [(^{Me}N4)$Ni^{III}Me_2$]$^+$ in solution was determined using EPR spin quantitation.

Ethane. ^{1}H NMR (d_3-MeCN), δ: 0.85 (s). Ethane-d_3. ^{1}H NMR (d_3-MeCN), δ: 0.81 (sept).
Methane. ^{1}H NMR (d_3-MeCN), δ: 0.20 (s). Methane-d_1. ^{1}H NMR (d_3-MeCN), δ: 0.18 (t).
1-Methoxy-2,2,6,6-tetramethylpiperidine (TEMPO-CH_3). ^{1}H NMR (d_3-MeCN), δ: 1.05 (s, 6H), 1.14 (s, 6H), 1.36-1.56 (m, 6H), 3.56 (s, 6H).
1-Methoxy-d_3-2,2,6,6-tetramethylpiperidine (TEMPO-CD_3). ^{1}H NMR (d_3-MeCN), δ: 1.07 (s, 6H), 1.15 (s, 6H), 1.25-1.50 (m, 6H).
1-Hydroxy-2,2,6,6-tetramethylpiperidine (TEMPO-H). ^{1}H NMR (d_3-MeCN), δ: 1.06 (s, 12H), 1.45 (s, 6H).

GC Product Analysis. After no changes were observed by NMR, the reaction mixtures were quenched with 100 μL of 1.0 M HCl and 5 mL H_2O, and extracted with ethyl ether (6 mL). The organic layer was then separated and dried over $MgSO_4$. The yield of product(s) was obtained by GC/FID using 1,3,5-trimethoxybenzene as the internal standard. The identity of the products were confirmed by GC-MS.

Note: Performing the reductive elimination at elevated temperatures does lead to a faster reductive elimination of ethane, yet appreciable amounts of methane were also observed. Thus, all reactivity studies were performed at room temperature to limit the side reactions.

A. Reactivity of (^{Me}N4)Ni(II)Me$_2$.

Table S1. Yields of the products of elimination from (^{Me}N4)NiMe$_2$ in d$_3$-MeCN at RT.

Note: Formation of Ni black was also detected at the end of the reaction, suggesting a different reaction mechanism under these conditions.

Time, h	Me-Me, %	Me-H/D, %
1	3 ± 1	0 ± 1
2	5 ± 2	2 ± 1
4	8 ± 1	3 ± 1
8	11 ± 1	5 ± 1

B. Reactivity of (^{Me}N4)Ni(II)Me$_2$ with 1 equivalent FcPF$_6$.

Table S2. Yields of the products from the reaction of (^{Me}N4)NiMe$_2$ with 1 equivalent of FcPF$_6$ in d$_3$-MeCN at RT.

Time, h	Me-Me, %	Me-H/D, %
1	31 ± 3	5 ± 2
2	36 ± 3	6 ± 2
4	44 ± 4	10 ± 2
8	61 ± 3	24 ± 2

C. Reactivity of (^{Me}N4)Ni(II)Me$_2$ with 1 equivalent ^{Ac}FcPF$_6$.

Table S3. Yields of the products from the reaction of (^{Me}N4)NiMe$_2$ with 1 equivalent of ^{Ac}FcPF$_6$ in d$_3$-MeCN at RT.

Time, h	Me-Me, %	Me-H/D, %
1	35 ± 1	5 ± 1
2	37 ± 2	5 ± 1
4	43 ± 2	11 ± 2
8	62 ± 3	20 ± 2

Table S4. Yields of the products from the reaction of (^{Me}N4)NiMe$_2$ with 1 equivalent of ^{Ac}FcPF$_6$ and 2 equivalents of TEMPO in d$_3$-MeCN at RT.

Time, h	Me-Me, %	Me-H/D, %
1	37 ± 2	4 ± 2
2	42 ± 1	4 ± 2
4	53 ± 3	6 ± 2
8	63 ± 3	11 ± 2

Table S5. Yields of the products from the crossover of (^{Me}N4)NiMe$_2$ and (^{Me}N4)Ni(CD$_3$)$_2$ with 1 equivalent of ^{Ac}FcPF$_6$ in d$_3$-MeCN at RT. The amount of CD$_3$-CD$_3$ was obtained by subtraction from the overall ethane yield for the non-deuteraed (^{Me}N4)NiMe$_2$ complex.

Time, h	Me-Me, %	CD$_3$-CH$_3$, %	[CD$_3$-CD$_3$], %	Me-H/D, %
1	14 ± 1	5 ± 1	16	2 ± 1
2	15 ± 1	6 ± 1	16	2 ± 1
4	17 ± 1	8 ± 2	18	6 ± 2
8	21 ± 2	20 ± 2	21	12 ± 2

D. Reactivity of (^{Me}N4)Ni(II)Me$_2$ with 2 equivalents ^{Ac}FcPF$_6$.

Table S6. Yields of the products from the reaction of (^{Me}N4)NiMe$_2$ with 2 equivalents of ^{Ac}FcPF$_6$ in d$_3$-MeCN at RT.

Time, h	Me-Me, %	Me-H/D, %
0.5	88 ± 1	1 ± 1
8	89 ± 1	1 ± 1

Table S7. Yields of the products from the reaction of (^{Me}N4)NiMe$_2$ with 2 equivalents of ^{Ac}FcPF$_6$ and 2 equivalents of TEMPO in d$_3$-MeCN at RT.

Time, h	Me-Me, %	Me-H/D, %
0.5	86 ± 2	1 ± 1
8	87 ± 2	1 ± 1

Table S8. Yields of the products from the crossover of (^{Me}N4)NiMe$_2$ and (^{Me}N4)Ni(CD$_3$)$_2$ with 2 equivalents of ^{Ac}FcPF$_6$ in d$_3$-MeCN at RT. The amount of CD$_3$-CD$_3$ was obtained by subtraction from the overall ethane yield for the non-deuteraed (^{Me}N4)NiMe$_2$ complex

Time, h	Me-Me, %	CD$_3$-CH$_3$, %	[CD$_3$-CD$_3$], %	Me-H/D, %
0.5	41 ± 2	5 ± 2	42	0
8	41 ± 3	6 ± 2	42	0

E. Reactivity of [(^{Me}N4)Ni^{III}Me$_2$]PF$_6$

Table S9. Yields of the products from the reaction of [(^{Me}N4)Ni^{III}Me$_2$]PF$_6$ in d$_3$-MeCN at RT.

Time, h	Me-Me, %	Me-H/D, %
1	14 ± 2	9 ± 2
2	19 ± 3	10 ± 3
4	31 ± 3	16 ± 3
8	43 ± 3	21 ± 3
24	54 ± 2	30 ± 1

Table S10. Yields of the products from the reaction of [(^{Me}N4)Ni^{III}Me$_2$]PF$_6$ with 1 equivalent of ^{Ac}FcPF$_6$ in d$_3$-MeCN at RT.

Time, h	Me-Me, %	Me-H/D, %
1	25 ± 2	1 ± 1
2	30 ± 3	1 ± 1
4	38 ± 3	1 ± 1
8	59 ± 2	1 ± 1
24	84 ± 2	1 ± 1

F. Reactivity of (^{Me}N4)Ni^{II}Me$_2$ with CD$_3$I.

Table S11. Yields of the products from the reaction of (^{Me}N4)NiMe$_2$ with 1 equivalent of CD$_3$I in d$_3$-MeCN at RT.

Time, h	Me-Me, %	CD$_3$-CH$_3$, %	CH$_3$-H/D, %
1	10	8	2
2	17	10	2
4	32	12	2
8	48	12	2
24	67	20	2

Table S12. Yields of the products from the reaction of (^{Me}N4)NiMe$_2$ with 1 equivalent of CD$_3$I and 2 equivalents of TEMPO in d$_3$-MeCN at RT.

Time, h	Me-Me, %	CD$_3$-CH$_3$, %	CH$_3$-H/D, %	TEMPO-CD$_3$, %	TEMPO-H, %
1	15	8	2	32	0
4	37	10	3	54	2
8	54	11	2	74	3
24	70	8	3	84	7

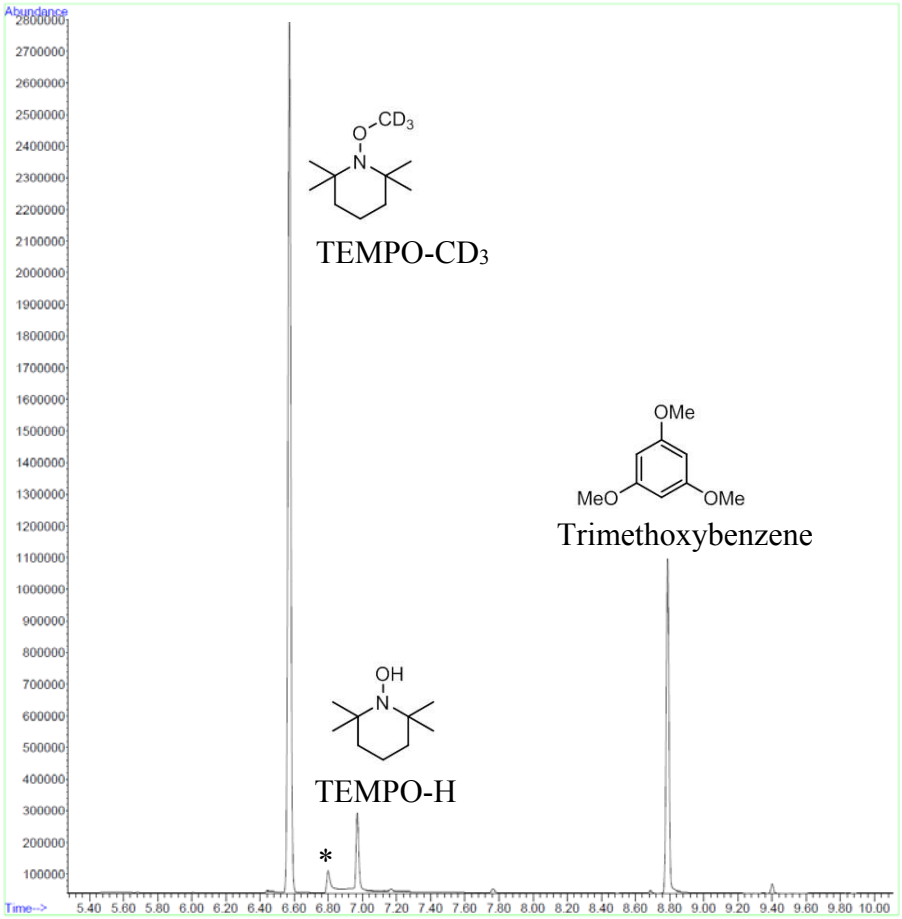


Figure S20. Representative GC chromatogram from the reaction of (^{Me}N4)NiMe$_2$ with 1 equivalents of CD_3I and 2 equivalents of TEMPO in d_3-MeCN at RT. The peak marked with an asterisk corresponds to an unidentified TEMPO adduct. The identity of TEMPO-CD_3 (m/z = 174.18) was confirmed by GC-MS:

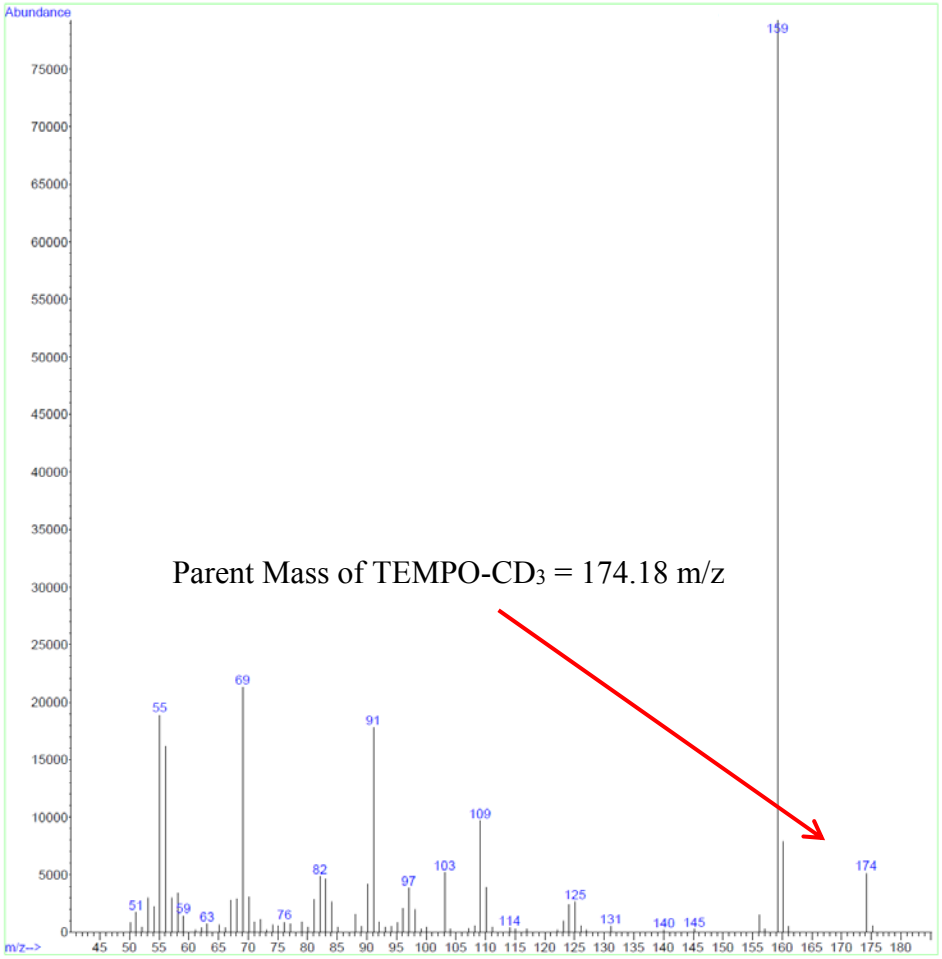


Figure S21. Representative MSD spectrum for the TEMPO-CD_3 peak from the reaction of (^{Me}N4)$NiMe_2$ with 1 equiv CD_3I and 2 equiv TEMPO in d_3-MeCN at RT.

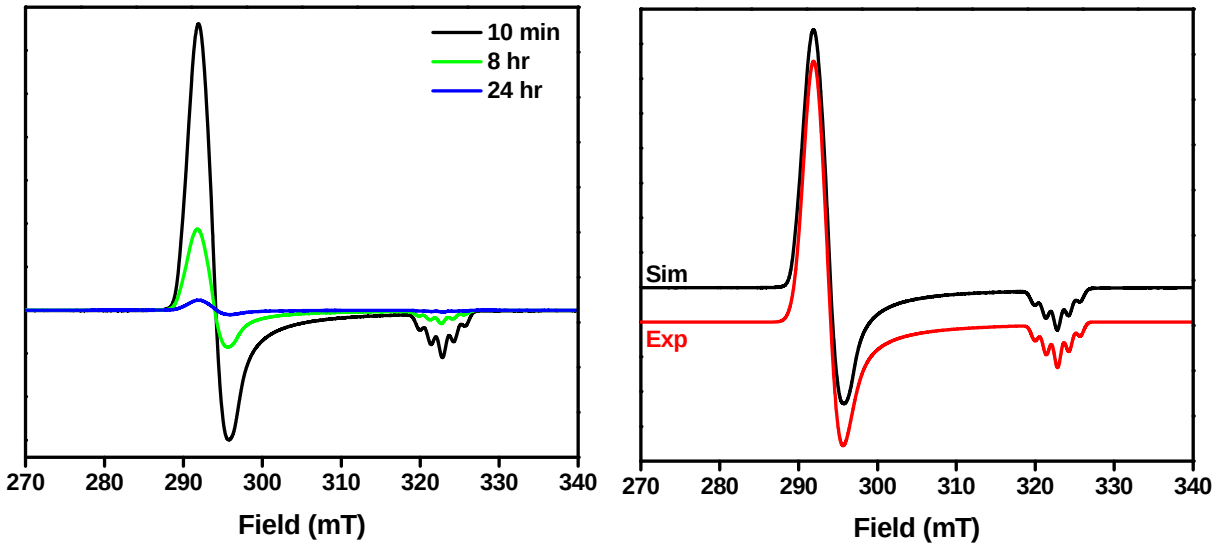


Figure S22. *Left:* EPR monitoring of the reaction of (^{Me}N4)NiMe$_2$ reacting with 1 equiv of CD_3I at RT over 24 hours. *Right:* EPR spectrum and simulation of reaction mixture after 10 min. Simulation used the following parameters: g_x= 2.2283, g_y= 2.2100, g_z= 2.0137 (A_N = 14.30 G).

G. Reactivity of [(^{Me}N4)Ni^{III}(cycloneophyl)]PF$_6$

Table S13. Yields of the products from the reaction of [(^{Me}N4)Ni^{III}(cycloneophyl)]PF$_6$ in MeCN at RT, as determined by GC-MS.

Time, h	1,1-dimethyl-benzocyclobutane, %	tBu-Ph, %
3	9	4
48	10	8

Table S14. Yields of the products from the reaction of [(^{Me}N4)Ni^{III}(cycloneophyl)]PF$_6$ with 1 equiv of NOPF$_6$ in MeCN at RT, as determined by GC-MS.

Time, h	1,1-dimethyl-benzocyclobutane, %	tBu-Ph, %
3	17	0
48	38	0

X. Catalytic Kumada Coupling Reactions

General procedure for the Kumada coupling. Inside a nitrogen filled glove box, a small vial equipped with a magnetic stir bar was charged with the corresponding alkyl halide or aryl halide substrate (0.1 mmol), decane as internal standard and **1** (1.76 mg, 0.05 equiv.) in THF (5.0 mL). To the stirring solution, the Grignard reagent (1.2 equiv) was added slowly over 1 hour via syringe and the resulting solution was allowed to stir at room temperature for 24 hours. A 1 hour, 2 hour, and 24 hour aliquot (500 μL) were taken and the reaction mixture was worked up by quenching with 5 mL of saturated NH_4Cl solution, and extracting the mixture with diethyl ether (3 x 5 mL). The organic layer was separated and dried over $MgSO_4$. The yield of product(s) was obtained by GC/FID using the internal standard for calibration and reported as an average of at least 3 independent runs. The identity of the products was confirmed by GC/MSD. The investigated cross-coupling reactions shown almost complete consumption of the iodide reagent after 1 hour.

Note: No cross coupled products were observed in the absence of **1**.

Kumada Coupling of Iodotoluene and PhMgBr:

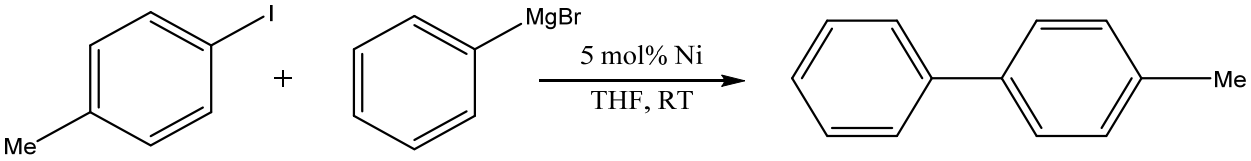
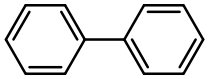
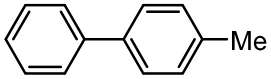
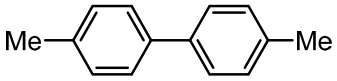


Table S15. Products and yields for the Kumada cross-coupling reaction of iodotoluene and PhMgBr catalyzed by 5 mol % (^{Me}N4)Ni^{II}Me$_2$ (reaction time: 1 hour).

Product	**Structure**	**Yield**
Biphenyl		12
4-methyl-1,1'-biphenyl		96
4,4'-dimethylbiphenyl		2

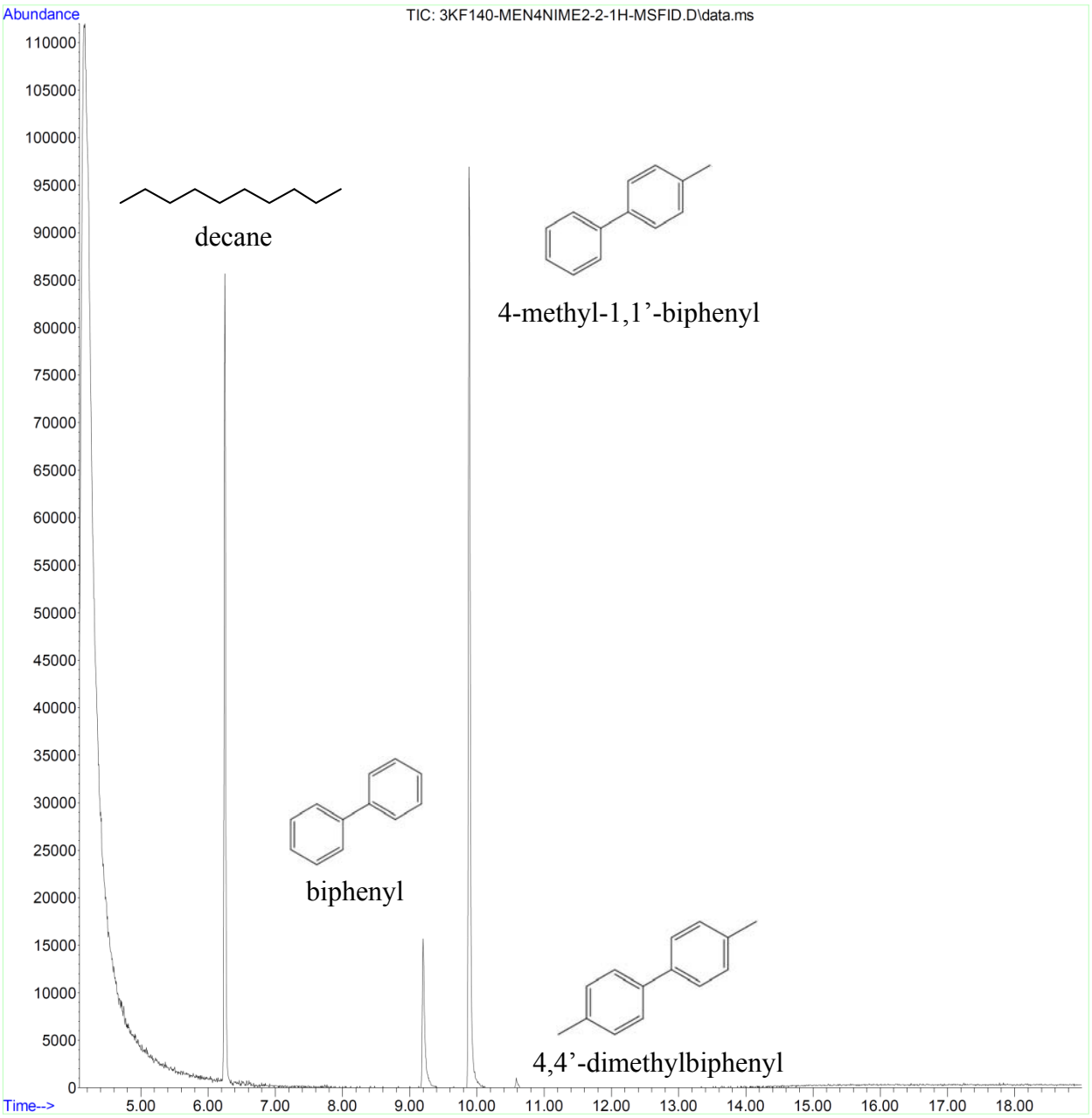


Figure S23. Representative GC chromatogram for the Kumada cross-coupling of Iodotoluene with PhMgBr catalyzed by 5 mol% (^{Me}N4)Ni^{II}Me$_2$.

Kumada Cross-Coupling of Iodotoluene and hexylMgBr:

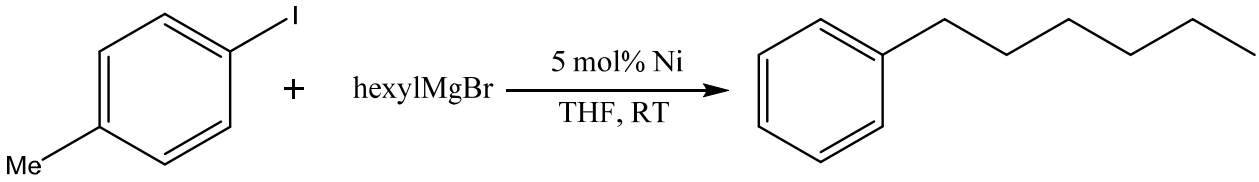
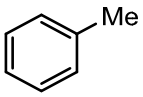
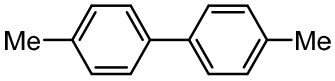
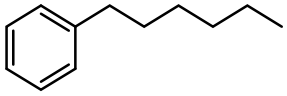


Table S16. Products and yields from the Kumada cross-coupling reactions of Iodotoluene and hexylMgBr catalyzed by 5 mol % (^{Me}N4)Ni^{II}Me$_2$ (reaction time: 1 hour).

Product	**Structure**	**Yield**
Toluene		18
dodecane	$C_{12}H_{26}$	3
4,4'-Dimethylbiphenyl		5
hexylbenzene		60

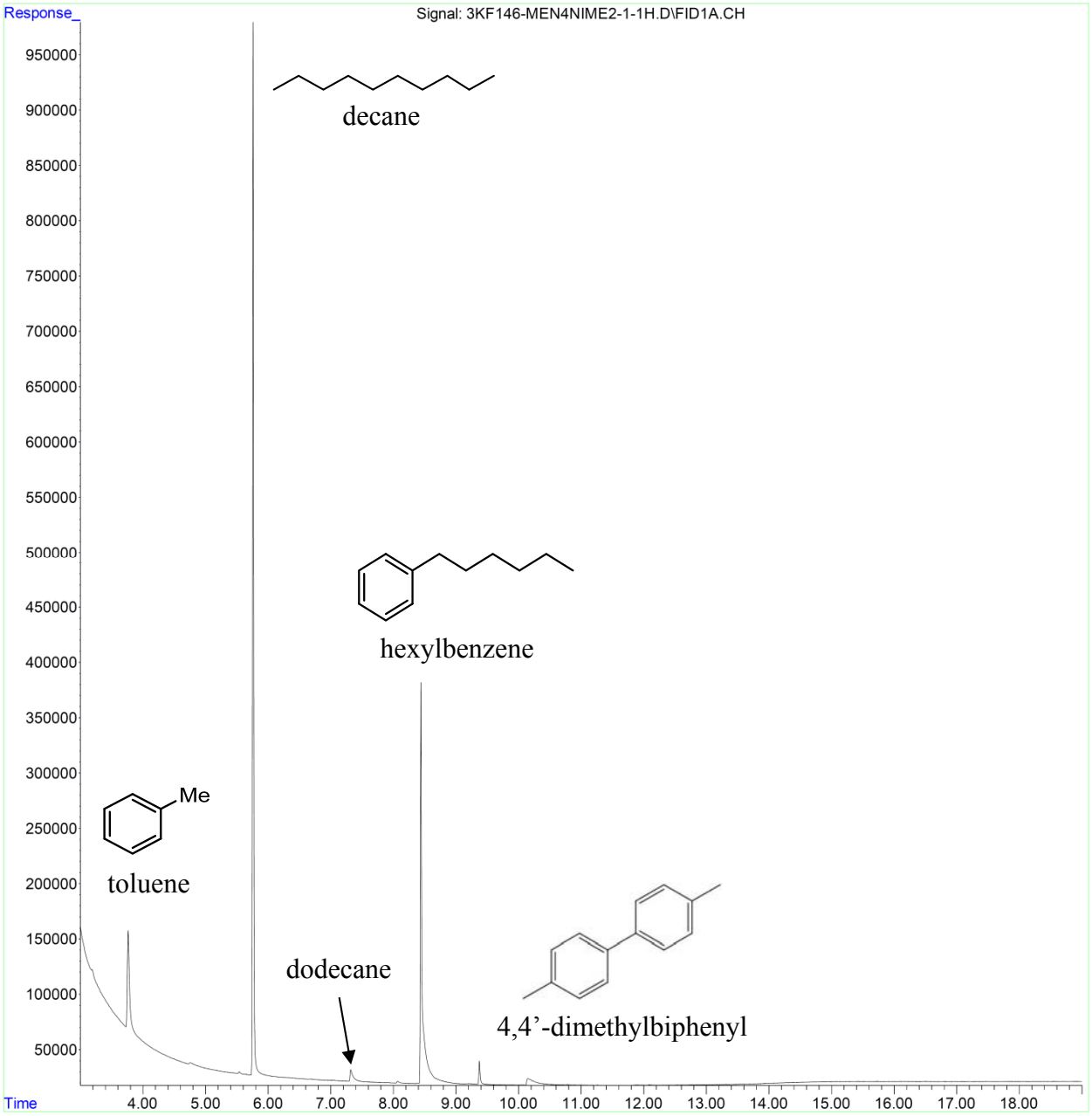


Figure S24. Representative GC chromatogram for the Kumada cross-coupling of Iodotoluene with hexylMgBr catalyzed by 5 mol% (^{Me}N4)Ni^{II}Me$_2$.

Kumada Cross-Coupling of Chlorotoluene and PhMgBr:

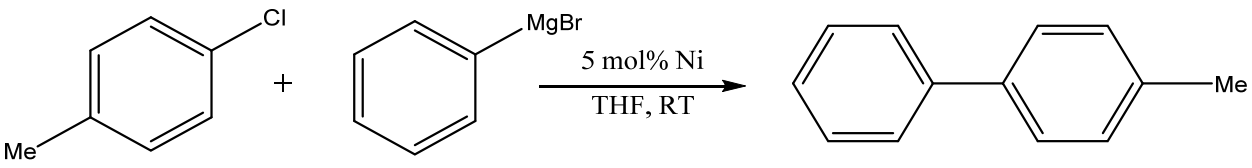
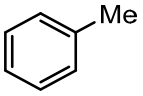
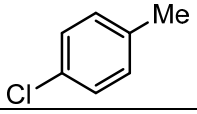
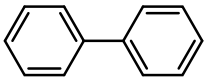
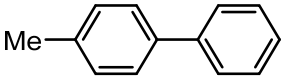
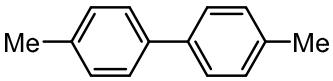


Table S17. Products and yields from the Kumada cross-coupling reactions of Chlorotoluene and PhMgBr catalyzed by 5 mol % (^{Me}N4)Ni^{II}Me$_2$ (reaction time: 1 hour).

Product	Structure	Yield
Toluene		4
Chlorotoluene		21
Biphenyl		38
4-methyl-1,1'-Biphenyl		62
4,4'-Dimethylbiphenyl		11

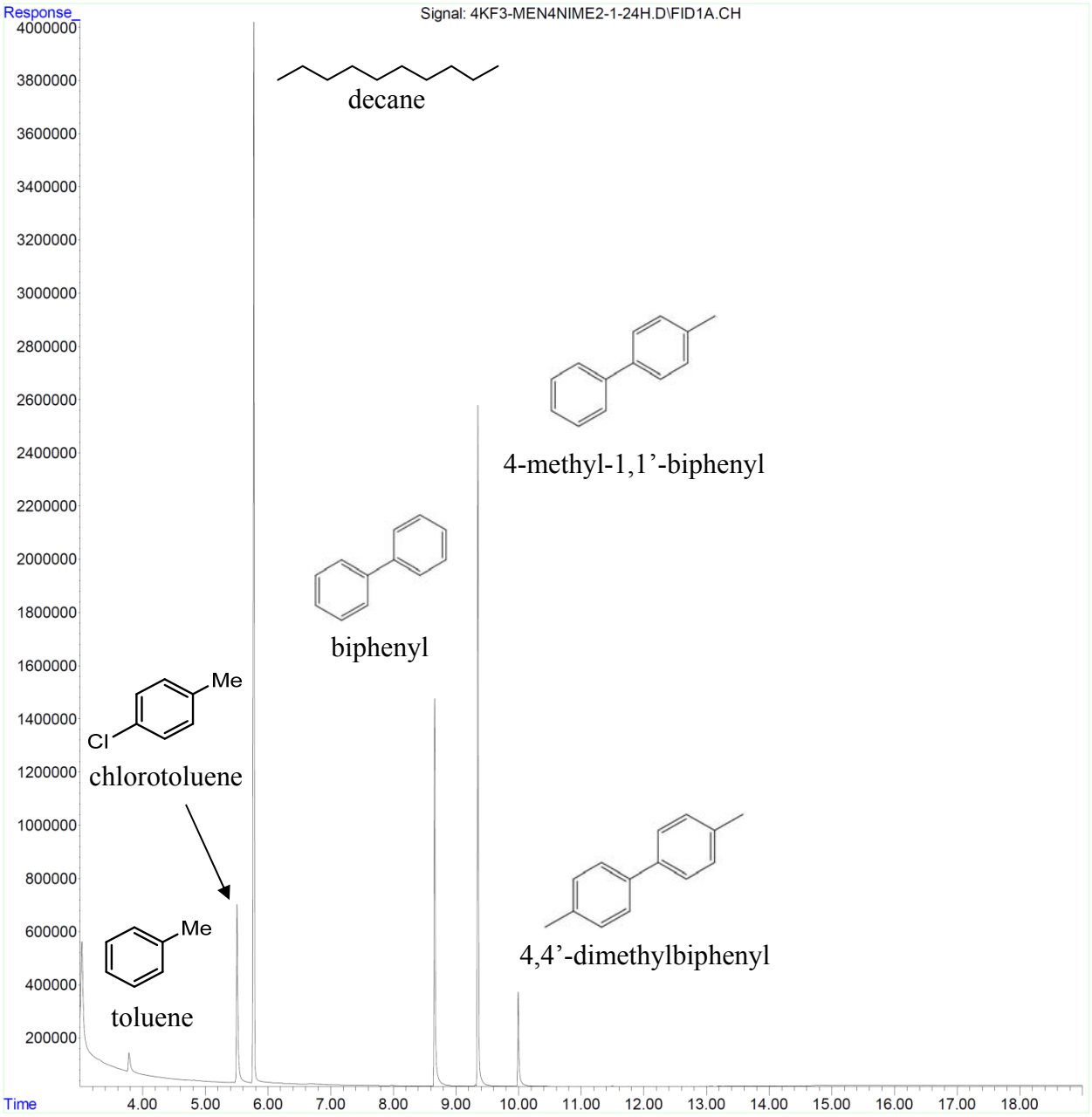


Figure S25. Representative GC chromatogram for the Kumada cross-coupling of chlorotoluene with PhMgBr catalyzed by 5 mol% (^{Me}N4)Ni^{II}Me$_2$.

Kumada Cross-Coupling of Iodooctane and hexylMgBr:

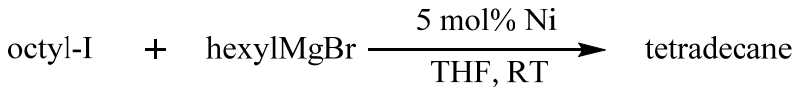
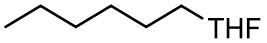


Table S18. Products and yields from the Kumada cross-coupling reactions of iodooctane and hexylMgBr catalyzed by 5 mol % (^{Me}N4)Ni^{II}Me$_2$ (reaction time: 1 hour).

Product	**Structure**	**Yield**
Octane		47
hexyl-THF		8
dodecane	$C_{12}H_{26}$	4
tetradecane	$C_{14}H_{30}$	20

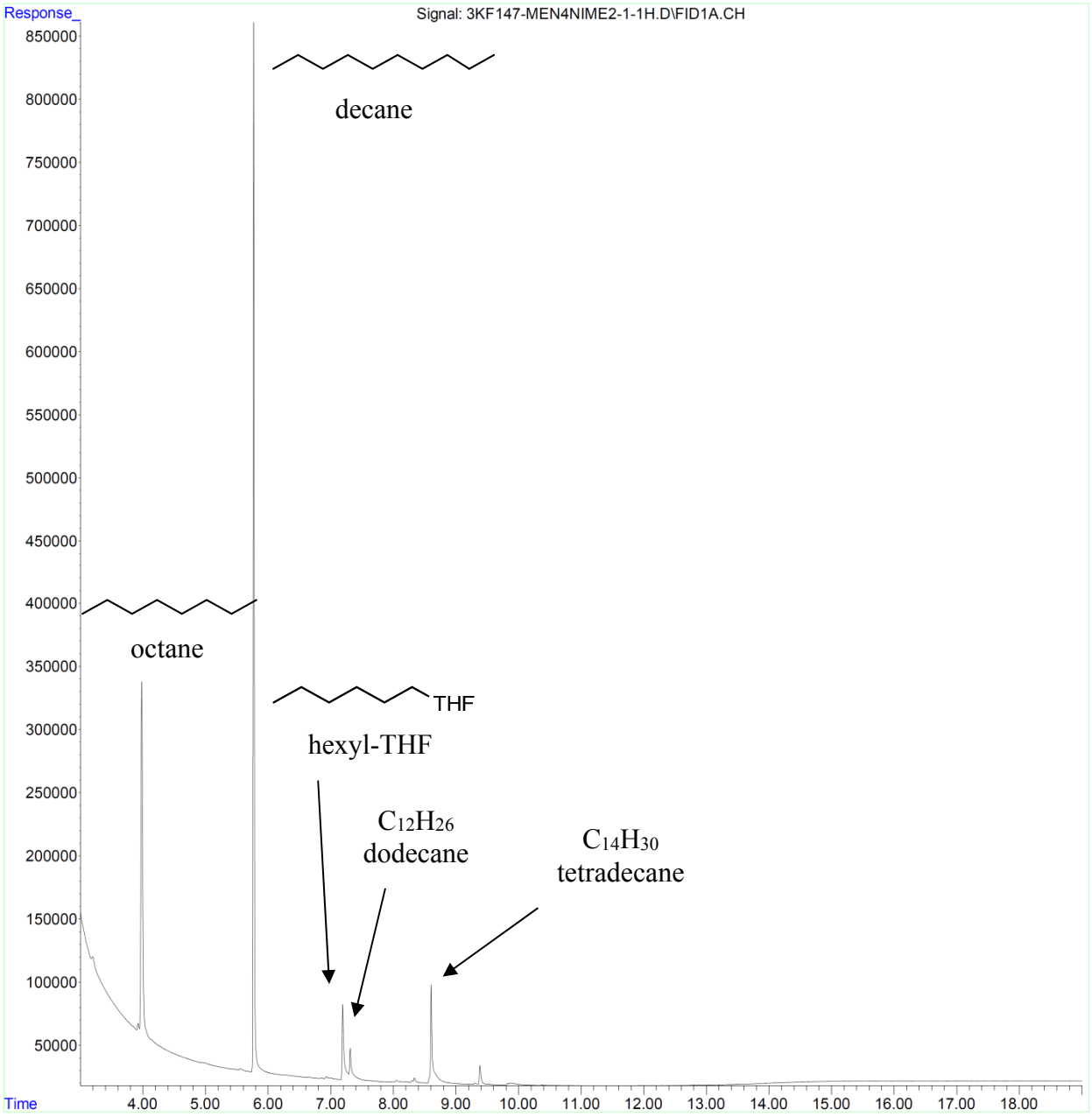


Figure S26. Representative GC chromatogram for the Kumada cross-coupling of iodooctane with hexylMgBr catalyzed by 5 mol% (^{Me}N4)Ni^{II}Me$_2$.

XI. X-ray structure determinations of Ni Complexes

X-ray quality crystals of (^{Me}N4)NiMe$_2$ were obtained by slow pentane diffusion into an ether solution at -35°C. X-ray quality crystals of [(^{Me}N4)NiMe$_2$]BPh$_4$, (^{Me}N4)Ni^{II}(cycloneophyl), and [(^{Me}N4)Ni^{III}(cycloneophyl)]PF$_6$ were obtained by slow pentane vapor diffusion into a tetrahydrofuran solution at -35°C. The [(^{Me}N4)Ni^{II}(MeCN)$_2$](PF$_6$)$_2$ complex was obtained from the reaction mixture of a reductive elimination reactivity of **3** in MeCN, upon slow diethyl ether vapor diffusion at -35 °C. Suitable crystals of appropriate dimensions were mounted on Mitgen loops in random orientations. Preliminary examination and data collection were performed using a Bruker Kappa Apex-II Charge Coupled Device (CCD) Detector system single crystal X-Ray diffractometer equipped with an Oxford Cryostream LT device. Data were collected using graphite monochromated Mo Kα radiation (λ= 0.71073 Å) from a fine focus sealed tube X-Ray source. Preliminary unit cell constants were determined with a set of 36 narrow frame scans. Typical data sets consist of a combination of ω and ϕ scan frames with typical scan width of 0.5° and counting time of 15-30 seconds/frame at a crystal to detector distance of ~4.0 cm. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. Apex II and SAINT software packages (*Bruker Analytical X-Ray, Madison, WI, 2008*) were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by global refinement of reflections from the complete data set. Data were corrected for systematic errors using SADABS (*Bruker Analytical X-Ray, Madison, WI, 2008*) based on the Laue symmetry using equivalent reflections.

Structure solutions and refinement were carried out using the SHELXTL- PLUS software package (*Sheldrick, G. M. (2008), Bruker-SHELXTL, Acta Cryst. A64,112-122*). The structures were refined with full matrix least-squares refinement by minimizing $\Sigma w(F_o^2-F_c^2)^2$. All non-hydrogen atoms were refined anisotropically to convergence. Typically, H atoms are added at the calculated positions in the final refinement cycles.

Acknowledgement: Funding from the National Science Foundation (MRI, CHE-0420497) for the purchase of the ApexII diffractometer is acknowledged.

X-ray structure determination of (^{Me}N4)NiMe$_2$

Table S19. Crystal data and structure refinement for lm13514.

Identification code	l13514/lt/x8/JS-091514-01	
Empirical formula	C18 H26 N4 Ni	
Formula weight	357.14	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal syst em	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 14.2510(7) Å	α = 90°.
	b = 13.1814(5) Å	β = 98.280(3)°.
	c = 9.2333(4) Å	γ = 90°.
Volume	1716.38(13) Å^3	
Z	4	
Density (calculated)	1.382 Mg/m^3	
Absorption coefficient	1.135 mm^{-1}	
F(000)	760	
Crystal size	0.289 x 0.204 x 0.078 mm^3	
Theta range for data collection	2.115 to 28.316°.	
Index ranges	-18≤h≤18, -17≤k≤17, -12≤l≤11	
Reflections collected	10169	
Independent reflections	2135 [R(int) = 0.0360]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8621 and 0.7705	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2135 / 0 / 215	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.0263, wR2 = 0.0544	
R indices (all data)	R1 = 0.0358, wR2 = 0.0591	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.241 and -0.162 e.Å^{-3}	

Table S20. Bond lengths [Å] and angles [°] for lm13514.

Ni(1)-C(1)	1.913(7)	C(1')-H(1'1)	0.9800
Ni(1)-C(1)#1	1.913(7)	C(1')-H(1'2)	0.9800
Ni(1)-N(1)	1.973(6)	C(1')-H(1'3)	0.9800
Ni(1)-N(1)#1	1.973(6)	C(2')-C(3')	1.371(5)
N(1)-C(6)	1.342(6)	C(2')-C(8')	1.519(5)
N(1)-C(2)	1.351(5)	C(3')-C(4')	1.389(6)
N(2)-C(8)#1	1.447(4)	C(3')-H(3')	0.9500
N(2)-C(9)	1.457(4)	C(4')-C(5')	1.348(9)
N(2)-C(7)	1.461(4)	C(4')-H(4')	0.9500
C(1)-H(1A)	0.9800	C(5')-C(6')	1.414(5)
C(1)-H(1B)	0.9800	C(5')-H(5')	0.9500
C(1)-H(1C)	0.9800	C(6')-C(7')	1.509(4)
C(2)-C(3)	1.381(4)	C(7')-H(7'A)	0.9900
C(2)-C(8)	1.520(5)	C(7')-H(7'B)	0.9900
C(3)-C(4)	1.395(4)	C(8')-N(2')#1	1.441(6)
C(3)-H(3)	0.9500	C(8')-H(8'A)	0.9900
C(4)-C(5)	1.402(5)	C(8')-H(8'B)	0.9900
C(4)-H(4)	0.9500	C(9')-H(9'A)	0.9800
C(5)-C(6)	1.389(6)	C(9')-H(9'B)	0.9800
C(5)-H(5)	0.9500	C(9')-H(9'C)	0.9800
C(6)-C(7)	1.493(4)	C(1)-Ni(1)-C(1)#1	91.1(7)
C(7)-H(7A)	0.9900	C(1)-Ni(1)-N(1)	91.6(3)
C(7)-H(7B)	0.9900	C(1)#1-Ni(1)-N(1)	173.5(7)
C(8)-N(2)#1	1.447(4)	C(1)-Ni(1)-N(1)#1	173.5(7)
C(8)-H(8A)	0.9900	C(1)#1-Ni(1)-N(1)#1	91.6(3)
C(8)-H(8B)	0.9900	N(1)-Ni(1)-N(1)#1	86.5(3)
C(9)-H(9A)	0.9800	C(6)-N(1)-C(2)	119.4(4)
C(9)-H(9B)	0.9800	C(6)-N(1)-Ni(1)	120.2(3)
C(9)-H(9C)	0.9800	C(2)-N(1)-Ni(1)	120.5(4)
Ni(1')-C(1')#1	1.915(7)	C(8)#1-N(2)-C(9)	112.8(3)
Ni(1')-C(1')	1.915(7)	C(8)#1-N(2)-C(7)	119.1(3)
Ni(1')-N(1')	1.950(7)	C(9)-N(2)-C(7)	114.4(3)
Ni(1')-N(1')#1	1.950(7)	Ni(1)-C(1)-H(1A)	109.5
N(1')-C(6')	1.341(4)	Ni(1)-C(1)-H(1B)	109.5
N(1')-C(2')	1.353(6)	H(1A)-C(1)-H(1B)	109.5
N(2')-C(8')#1	1.441(6)	Ni(1)-C(1)-H(1C)	109.5
N(2')-C(9')	1.460(5)	H(1A)-C(1)-H(1C)	109.5
N(2')-C(7')	1.470(4)	H(1B)-C(1)-H(1C)	109.5

N(1)-C(2)-C(3)	121.4(4)	C(6')-N(1')-Ni(1')	119.7(4)
N(1)-C(2)-C(8)	118.6(4)	C(2')-N(1')-Ni(1')	121.9(4)
C(3)-C(2)-C(8)	120.0(4)	C(8')#1-N(2')-C(9')	115.1(3)
C(2)-C(3)-C(4)	119.6(3)	C(8')#1-N(2')-C(7')	118.5(3)
C(2)-C(3)-H(3)	120.2	C(9')-N(2')-C(7')	112.1(3)
C(4)-C(3)-H(3)	120.2	Ni(1')-C(1')-H(1'1)	109.5
C(3)-C(4)-C(5)	118.7(4)	Ni(1')-C(1')-H(1'2)	109.5
C(3)-C(4)-H(4)	120.6	H(1'1)-C(1')-H(1'2)	109.5
C(5)-C(4)-H(4)	120.6	Ni(1')-C(1')-H(1'3)	109.5
C(6)-C(5)-C(4)	118.2(5)	H(1'1)-C(1')-H(1'3)	109.5
C(6)-C(5)-H(5)	120.9	H(1'2)-C(1')-H(1'3)	109.5
C(4)-C(5)-H(5)	120.9	N(1')-C(2')-C(3')	122.3(5)
N(1)-C(6)-C(5)	122.6(4)	N(1')-C(2')-C(8')	117.2(4)
N(1)-C(6)-C(7)	118.5(3)	C(3')-C(2')-C(8')	120.5(3)
C(5)-C(6)-C(7)	118.9(4)	C(2')-C(3')-C(4')	118.7(4)
N(2)-C(7)-C(6)	117.7(2)	C(2')-C(3')-H(3')	120.7
N(2)-C(7)-H(7A)	107.9	C(4')-C(3')-H(3')	120.7
C(6)-C(7)-H(7A)	107.9	C(5')-C(4')-C(3')	120.5(5)
N(2)-C(7)-H(7B)	107.9	C(5')-C(4')-H(4')	119.8
C(6)-C(7)-H(7B)	107.9	C(3')-C(4')-H(4')	119.8
H(7A)-C(7)-H(7B)	107.2	C(4')-C(5')-C(6')	118.3(4)
N(2)#1-C(8)-C(2)	118.0(4)	C(4')-C(5')-H(5')	120.9
N(2)#1-C(8)-H(8A)	107.8	C(6')-C(5')-H(5')	120.9
C(2)-C(8)-H(8A)	107.8	N(1')-C(6')-C(5')	121.9(4)
N(2)#1-C(8)-H(8B)	107.8	N(1')-C(6')-C(7')	118.5(4)
C(2)-C(8)-H(8B)	107.8	C(5')-C(6')-C(7')	119.6(4)
H(8A)-C(8)-H(8B)	107.1	N(2')-C(7')-C(6')	117.6(3)
N(2)-C(9)-H(9A)	109.5	N(2')-C(7')-H(7'A)	107.9
N(2)-C(9)-H(9B)	109.5	C(6')-C(7')-H(7'A)	107.9
H(9A)-C(9)-H(9B)	109.5	N(2')-C(7')-H(7'B)	107.9
N(2)-C(9)-H(9C)	109.5	C(6')-C(7')-H(7'B)	107.9
H(9A)-C(9)-H(9C)	109.5	H(7'A)-C(7')-H(7'B)	107.2
H(9B)-C(9)-H(9C)	109.5	N(2')#1-C(8')-C(2')	117.8(3)
C(1')#1-Ni(1')-C(1')	89.2(3)	N(2')#1-C(8')-H(8'A)	107.9
C(1')#1-Ni(1')-N(1')	177.1(3)	C(2')-C(8')-H(8'A)	107.9
C(1')-Ni(1')-N(1')	92.1(2)	N(2')#1-C(8')-H(8'B)	107.9
C(1')#1-Ni(1')-N(1')#1	92.1(2)	C(2')-C(8')-H(8'B)	107.9
C(1')-Ni(1')-N(1')#1	177.1(3)	H(8'A)-C(8')-H(8'B)	107.2
N(1')-Ni(1')-N(1')#1	86.8(3)	N(2')-C(9')-H(9'A)	109.5
C(6')-N(1')-C(2')	118.3(5)	N(2')-C(9')-H(9'B)	109.5

H(9'A)-C(9')-H(9'B)	109.5	H(9'A)-C(9')-H(9'C)	109.5
N(2')-C(9')-H(9'C)	109.5	H(9'B)-C(9')-H(9'C)	109.5

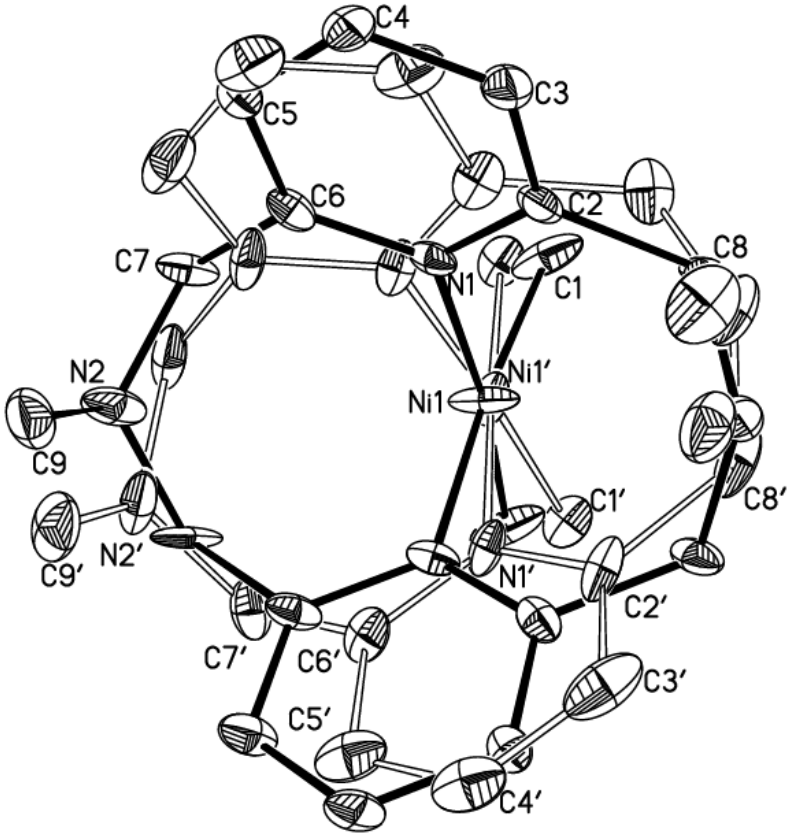


Figure S27. Projection view of lm13514 with 50% thermal ellipsoids.

X-ray structure determination of [(^{Me}N4)NiMe$_2$]BPh$_4$

Table S21. Crystal data and structure refinement for lm8714.

Identification code	l8714_sq/lt/x8/JS-061614-01	
Empirical formula	C_{46} H_{54} B N_4 Ni O	
Formula weight	748.45	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P $\bar{1}$	
Unit cell dimensions	a = 8.9600(7) Å	α = 88.779(4)°.
	b = 14.2611(10) Å	β = 75.985(4)°.
	c = 16.7826(12) Å	γ = 73.867(4)°.
Volume	1996.3(3) Å^3	
Z	2	
Density (calculated)	1.245 Mg/m^3	
Absorption coefficient	0.526 mm^{-1}	
F(000)	798	
Crystal size	0.323 x 0.224 x 0.149 mm^3	
Theta range for data collection	1.252 to 27.608°.	
Index ranges	-11≤h≤11, -18≤k≤18, -21≤l≤21	
Reflections collected	40240	
Independent reflections	9164 [R(int) = 0.0406]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8621 and 0.7941	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9164 / 1 / 487	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.0904	
R indices (all data)	R1 = 0.0518, wR2 = 0.0966	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.532 and -0.437 e.Å^{-3}	

Table S22. Bond lengths [Å] and angles [°] for lm8714.

Ni(1)-C(2)	1.9782(19)	C(9)-H(9A)	0.9900
Ni(1)-N(1)	1.9792(14)	C(9)-H(9B)	0.9900
Ni(1)-C(1)	1.987(2)	C(10)-C(11)	1.381(3)
Ni(1)-C(1')	1.994(9)	C(11)-C(12)	1.384(3)
Ni(1)-N(2)	1.9958(15)	C(11)-H(11)	0.9500
Ni(1)-N(4)	2.2399(14)	C(12)-C(13)	1.388(3)
Ni(1)-N(3)	2.2519(14)	C(12)-H(12)	0.9500
N(1)-C(7)	1.340(2)	C(13)-C(14)	1.378(3)
N(1)-C(3)	1.342(2)	C(13)-H(13)	0.9500
N(2)-C(10)	1.343(2)	C(14)-C(15)	1.506(3)
N(2)-C(14)	1.343(2)	C(15)-H(15A)	0.9900
N(3)-C(17)	1.471(2)	C(15)-H(15B)	0.9900
N(3)-C(8)	1.478(2)	C(16)-H(16A)	0.9900
N(3)-C(9)	1.485(2)	C(16)-H(16B)	0.9900
N(4)-C(18)	1.479(2)	C(17)-H(17A)	0.9800
N(4)-C(15)	1.480(2)	C(17)-H(17B)	0.9800
N(4)-C(16)	1.484(2)	C(17)-H(17C)	0.9800
C(1)-H(1A)	0.9800	C(18)-H(18A)	0.9800
C(1)-H(1B)	0.9800	C(18)-H(18B)	0.9800
C(1)-H(1C)	0.9800	C(18)-H(18C)	0.9800
C(1')-H(1'1)	0.9800	O(1S)-C(1S)	1.417(3)
C(1')-H(1'2)	0.9800	O(1S)-C(4S)	1.432(3)
C(1')-H(1'3)	0.9800	C(1S)-C(2S)	1.497(3)
C(2)-H(2A)	0.9800	C(1S)-H(1SA)	0.9900
C(2)-H(2B)	0.9800	C(1S)-H(1SB)	0.9900
C(2)-H(2C)	0.9800	C(2S)-C(3S)	1.507(3)
C(3)-C(4)	1.381(2)	C(2S)-H(2SA)	0.9900
C(3)-C(16)	1.506(2)	C(2S)-H(2SB)	0.9900
C(4)-C(5)	1.390(3)	C(3S)-C(4S)	1.506(4)
C(4)-H(4)	0.9500	C(3S)-H(3SA)	0.9900
C(5)-C(6)	1.382(3)	C(3S)-H(3SB)	0.9900
C(5)-H(5)	0.9500	C(4S)-H(4SA)	0.9900
C(6)-C(7)	1.383(3)	C(4S)-H(4SB)	0.9900
C(6)-H(6)	0.9500	C(19)-C(24)	1.396(3)
C(7)-C(8)	1.506(2)	C(19)-C(20)	1.402(3)
C(8)-H(8A)	0.9900	C(19)-B(1)	1.645(2)
C(8)-H(8B)	0.9900	C(20)-C(21)	1.394(3)
C(9)-C(10)	1.500(2)	C(20)-H(20)	0.9500

C(21)-C(22)	1.380(3)	C(41)-C(42)	1.391(3)
C(21)-H(21)	0.9500	C(41)-H(41)	0.9500
C(22)-C(23)	1.380(3)	C(42)-H(42)	0.9500
C(22)-H(22)	0.9500	C(2)-Ni(1)-N(1)	93.26(7)
C(23)-C(24)	1.396(3)	C(2)-Ni(1)-C(1)	84.68(17)
C(23)-H(23)	0.9500	N(1)-Ni(1)-C(1)	176.34(10)
C(24)-H(24)	0.9500	C(2)-Ni(1)-C(1')	71.9(8)
C(25)-C(30)	1.400(2)	N(1)-Ni(1)-C(1')	165.1(8)
C(25)-C(26)	1.403(2)	C(2)-Ni(1)-N(2)	176.88(7)
C(25)-B(1)	1.642(2)	N(1)-Ni(1)-N(2)	84.19(6)
C(26)-C(27)	1.389(3)	C(1)-Ni(1)-N(2)	97.96(16)
C(26)-H(26)	0.9500	C(1')-Ni(1)-N(2)	110.7(8)
C(27)-C(28)	1.385(3)	C(2)-Ni(1)-N(4)	97.74(7)
C(27)-H(27)	0.9500	N(1)-Ni(1)-N(4)	80.22(6)
C(28)-C(29)	1.383(3)	C(1)-Ni(1)-N(4)	103.03(9)
C(28)-H(28)	0.9500	C(1')-Ni(1)-N(4)	101.5(6)
C(29)-C(30)	1.387(3)	N(2)-Ni(1)-N(4)	80.07(6)
C(29)-H(29)	0.9500	C(2)-Ni(1)-N(3)	101.88(7)
C(30)-H(30)	0.9500	N(1)-Ni(1)-N(3)	80.42(6)
C(31)-C(36)	1.400(3)	C(1)-Ni(1)-N(3)	97.02(10)
C(31)-C(32)	1.404(3)	C(1')-Ni(1)-N(3)	102.0(6)
C(31)-B(1)	1.644(3)	N(2)-Ni(1)-N(3)	79.51(6)
C(32)-C(33)	1.396(3)	N(4)-Ni(1)-N(3)	153.07(6)
C(32)-H(32)	0.9500	C(7)-N(1)-C(3)	120.86(15)
C(33)-C(34)	1.382(3)	C(7)-N(1)-Ni(1)	119.74(12)
C(33)-H(33)	0.9500	C(3)-N(1)-Ni(1)	118.96(11)
C(34)-C(35)	1.382(3)	C(10)-N(2)-C(14)	120.20(16)
C(34)-H(34)	0.9500	C(10)-N(2)-Ni(1)	119.06(12)
C(35)-C(36)	1.397(3)	C(14)-N(2)-Ni(1)	119.18(12)
C(35)-H(35)	0.9500	C(17)-N(3)-C(8)	109.27(14)
C(36)-H(36)	0.9500	C(17)-N(3)-C(9)	108.37(13)
C(37)-C(42)	1.400(2)	C(8)-N(3)-C(9)	112.00(14)
C(37)-C(38)	1.401(2)	C(17)-N(3)-Ni(1)	116.59(11)
C(37)-B(1)	1.638(2)	C(8)-N(3)-Ni(1)	106.15(10)
C(38)-C(39)	1.390(3)	C(9)-N(3)-Ni(1)	104.45(10)
C(38)-H(38)	0.9500	C(18)-N(4)-C(15)	108.70(14)
C(39)-C(40)	1.385(3)	C(18)-N(4)-C(16)	108.27(14)
C(39)-H(39)	0.9500	C(15)-N(4)-C(16)	112.40(14)
C(40)-C(41)	1.385(3)	C(18)-N(4)-Ni(1)	116.36(11)
C(40)-H(40)	0.9500	C(15)-N(4)-Ni(1)	106.94(10)

C(16)-N(4)-Ni(1)	104.21(10)	N(3)-C(9)-C(10)	111.81(14)
Ni(1)-C(1)-H(1A)	109.5	N(3)-C(9)-H(9A)	109.3
Ni(1)-C(1)-H(1B)	109.5	C(10)-C(9)-H(9A)	109.3
H(1A)-C(1)-H(1B)	109.5	N(3)-C(9)-H(9B)	109.3
Ni(1)-C(1)-H(1C)	109.5	C(10)-C(9)-H(9B)	109.3
H(1A)-C(1)-H(1C)	109.5	H(9A)-C(9)-H(9B)	107.9
H(1B)-C(1)-H(1C)	109.5	N(2)-C(10)-C(11)	121.49(17)
Ni(1)-C(1')-H(1'1)	109.5	N(2)-C(10)-C(9)	114.91(15)
Ni(1)-C(1')-H(1'2)	109.5	C(11)-C(10)-C(9)	123.56(16)
H(1'1)-C(1')-H(1'2)	109.5	C(10)-C(11)-C(12)	118.48(18)
Ni(1)-C(1')-H(1'3)	109.5	C(10)-C(11)-H(11)	120.8
H(1'1)-C(1')-H(1'3)	109.5	C(12)-C(11)-H(11)	120.8
H(1'2)-C(1')-H(1'3)	109.5	C(11)-C(12)-C(13)	119.78(19)
Ni(1)-C(2)-H(2A)	109.5	C(11)-C(12)-H(12)	120.1
Ni(1)-C(2)-H(2B)	109.5	C(13)-C(12)-H(12)	120.1
H(2A)-C(2)-H(2B)	109.5	C(14)-C(13)-C(12)	118.82(18)
Ni(1)-C(2)-H(2C)	109.5	C(14)-C(13)-H(13)	120.6
H(2A)-C(2)-H(2C)	109.5	C(12)-C(13)-H(13)	120.6
H(2B)-C(2)-H(2C)	109.5	N(2)-C(14)-C(13)	121.15(17)
N(1)-C(3)-C(4)	120.85(16)	N(2)-C(14)-C(15)	115.85(16)
N(1)-C(3)-C(16)	115.40(15)	C(13)-C(14)-C(15)	122.91(17)
C(4)-C(3)-C(16)	123.69(15)	N(4)-C(15)-C(14)	112.96(14)
C(3)-C(4)-C(5)	118.80(16)	N(4)-C(15)-H(15A)	109.0
C(3)-C(4)-H(4)	120.6	C(14)-C(15)-H(15A)	109.0
C(5)-C(4)-H(4)	120.6	N(4)-C(15)-H(15B)	109.0
C(6)-C(5)-C(4)	119.61(17)	C(14)-C(15)-H(15B)	109.0
C(6)-C(5)-H(5)	120.2	H(15A)-C(15)-H(15B)	107.8
C(4)-C(5)-H(5)	120.2	N(4)-C(16)-C(3)	112.52(14)
C(5)-C(6)-C(7)	118.94(16)	N(4)-C(16)-H(16A)	109.1
C(5)-C(6)-H(6)	120.5	C(3)-C(16)-H(16A)	109.1
C(7)-C(6)-H(6)	120.5	N(4)-C(16)-H(16B)	109.1
N(1)-C(7)-C(6)	120.86(16)	C(3)-C(16)-H(16B)	109.1
N(1)-C(7)-C(8)	116.22(15)	H(16A)-C(16)-H(16B)	107.8
C(6)-C(7)-C(8)	122.84(16)	N(3)-C(17)-H(17A)	109.5
N(3)-C(8)-C(7)	114.13(14)	N(3)-C(17)-H(17B)	109.5
N(3)-C(8)-H(8A)	108.7	H(17A)-C(17)-H(17B)	109.5
C(7)-C(8)-H(8A)	108.7	N(3)-C(17)-H(17C)	109.5
N(3)-C(8)-H(8B)	108.7	H(17A)-C(17)-H(17C)	109.5
C(7)-C(8)-H(8B)	108.7	H(17B)-C(17)-H(17C)	109.5
H(8A)-C(8)-H(8B)	107.6	N(4)-C(18)-H(18A)	109.5

N(4)-C(18)-H(18B)	109.5	C(21)-C(22)-H(22)	120.4
H(18A)-C(18)-H(18B)	109.5	C(23)-C(22)-H(22)	120.4
N(4)-C(18)-H(18C)	109.5	C(22)-C(23)-C(24)	120.03(19)
H(18A)-C(18)-H(18C)	109.5	C(22)-C(23)-H(23)	120.0
H(18B)-C(18)-H(18C)	109.5	C(24)-C(23)-H(23)	120.0
C(1S)-O(1S)-C(4S)	108.59(17)	C(23)-C(24)-C(19)	122.72(19)
O(1S)-C(1S)-C(2S)	107.74(19)	C(23)-C(24)-H(24)	118.6
O(1S)-C(1S)-H(1SA)	110.2	C(19)-C(24)-H(24)	118.6
C(2S)-C(1S)-H(1SA)	110.2	C(30)-C(25)-C(26)	115.08(16)
O(1S)-C(1S)-H(1SB)	110.2	C(30)-C(25)-B(1)	121.90(15)
C(2S)-C(1S)-H(1SB)	110.2	C(26)-C(25)-B(1)	122.61(15)
H(1SA)-C(1S)-H(1SB)	108.5	C(27)-C(26)-C(25)	122.76(17)
C(1S)-C(2S)-C(3S)	101.1(2)	C(27)-C(26)-H(26)	118.6
C(1S)-C(2S)-H(2SA)	111.6	C(25)-C(26)-H(26)	118.6
C(3S)-C(2S)-H(2SA)	111.6	C(28)-C(27)-C(26)	120.27(17)
C(1S)-C(2S)-H(2SB)	111.6	C(28)-C(27)-H(27)	119.9
C(3S)-C(2S)-H(2SB)	111.6	C(26)-C(27)-H(27)	119.9
H(2SA)-C(2S)-H(2SB)	109.4	C(29)-C(28)-C(27)	118.67(17)
C(4S)-C(3S)-C(2S)	102.12(19)	C(29)-C(28)-H(28)	120.7
C(4S)-C(3S)-H(3SA)	111.3	C(27)-C(28)-H(28)	120.7
C(2S)-C(3S)-H(3SA)	111.3	C(28)-C(29)-C(30)	120.36(17)
C(4S)-C(3S)-H(3SB)	111.3	C(28)-C(29)-H(29)	119.8
C(2S)-C(3S)-H(3SB)	111.3	C(30)-C(29)-H(29)	119.8
H(3SA)-C(3S)-H(3SB)	109.2	C(29)-C(30)-C(25)	122.85(17)
O(1S)-C(4S)-C(3S)	105.58(19)	C(29)-C(30)-H(30)	118.6
O(1S)-C(4S)-H(4SA)	110.6	C(25)-C(30)-H(30)	118.6
C(3S)-C(4S)-H(4SA)	110.6	C(36)-C(31)-C(32)	115.30(16)
O(1S)-C(4S)-H(4SB)	110.6	C(36)-C(31)-B(1)	122.82(16)
C(3S)-C(4S)-H(4SB)	110.6	C(32)-C(31)-B(1)	121.59(16)
H(4SA)-C(4S)-H(4SB)	108.8	C(33)-C(32)-C(31)	122.94(18)
C(24)-C(19)-C(20)	115.28(16)	C(33)-C(32)-H(32)	118.5
C(24)-C(19)-B(1)	123.96(16)	C(31)-C(32)-H(32)	118.5
C(20)-C(19)-B(1)	120.40(16)	C(34)-C(33)-C(32)	119.62(18)
C(21)-C(20)-C(19)	122.63(19)	C(34)-C(33)-H(33)	120.2
C(21)-C(20)-H(20)	118.7	C(32)-C(33)-H(33)	120.2
C(19)-C(20)-H(20)	118.7	C(35)-C(34)-C(33)	119.47(18)
C(22)-C(21)-C(20)	120.08(19)	C(35)-C(34)-H(34)	120.3
C(22)-C(21)-H(21)	120.0	C(33)-C(34)-H(34)	120.3
C(20)-C(21)-H(21)	120.0	C(34)-C(35)-C(36)	120.13(19)
C(21)-C(22)-C(23)	119.20(17)	C(34)-C(35)-H(35)	119.9

C(36)-C(35)-H(35)	119.9	C(41)-C(40)-H(40)	120.4
C(35)-C(36)-C(31)	122.46(18)	C(39)-C(40)-H(40)	120.4
C(35)-C(36)-H(36)	118.8	C(40)-C(41)-C(42)	119.88(18)
C(31)-C(36)-H(36)	118.8	C(40)-C(41)-H(41)	120.1
C(42)-C(37)-C(38)	115.69(16)	C(42)-C(41)-H(41)	120.1
C(42)-C(37)-B(1)	122.14(15)	C(41)-C(42)-C(37)	122.67(18)
C(38)-C(37)-B(1)	121.88(16)	C(41)-C(42)-H(42)	118.7
C(39)-C(38)-C(37)	122.36(18)	C(37)-C(42)-H(42)	118.7
C(39)-C(38)-H(38)	118.8	C(37)-B(1)-C(25)	112.17(14)
C(37)-C(38)-H(38)	118.8	C(37)-B(1)-C(31)	104.59(13)
C(40)-C(39)-C(38)	120.19(18)	C(25)-B(1)-C(31)	112.04(14)
C(40)-C(39)-H(39)	119.9	C(37)-B(1)-C(19)	111.37(14)
C(38)-C(39)-H(39)	119.9	C(25)-B(1)-C(19)	103.18(13)
C(41)-C(40)-C(39)	119.19(17)	C(31)-B(1)-C(19)	113.74(14)

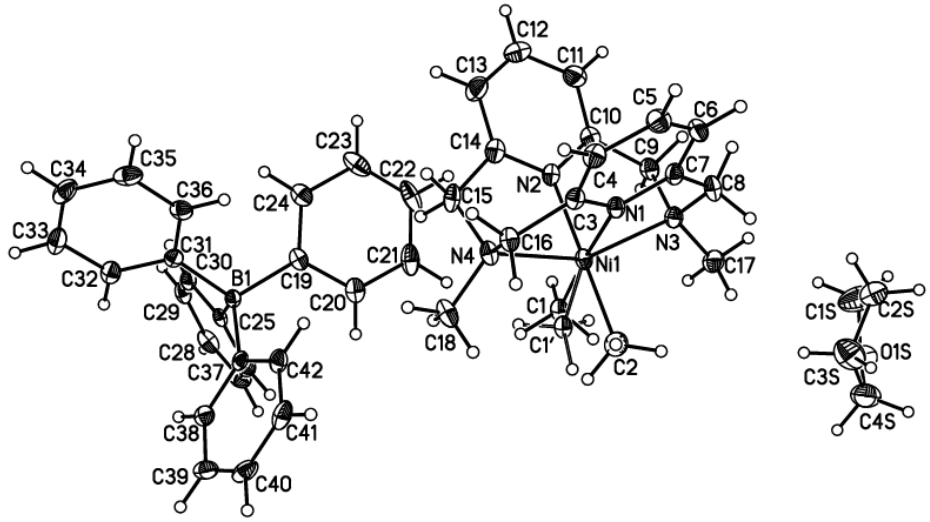


Figure S28. Projection view of lm8714 with 50% thermal ellipsoids.

X-ray structure determination of (^{Me}N4)Ni^{II}(cycloneophyl)

Table S23. Crystal data and structure refinement for lm19415t5.

Identification code	l19415t5/lt/JS-092815-01	
Empirical formula	C_{30} H_{40} N_4 Ni O	
Formula weight	531.37	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Pn	
Unit cell dimensions	a = 11.5021(9) Å	α = 90°.
	b = 17.8327(13) Å	β = 90.026(5)°.
	c = 12.9451(11) Å	γ = 90°.
Volume	2655.2(4) Å^3	
Z	4	
Density (calculated)	1.329 Mg/m^3	
Absorption coefficient	0.761 mm^{-1}	
F(000)	1136	
Crystal size	0.589 x 0.566 x 0.232 mm^3	
Theta range for data collection	1.142 to 30.624°.	
Index ranges	-16≤h≤16, -25≤k≤25, -18≤l≤18	
Reflections collected	29108	
Independent reflections	29108 [R(int) = 0.042]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.746070 and 0.621766	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	29108 / 2 / 658	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0508, wR2 = 0.1253	
R indices (all data)	R1 = 0.0587, wR2 = 0.1316	
Absolute structure parameter	-0.010(16)	
Largest diff. peak and hole	1.273 and -1.586 e.Å^{-3}	

Table S24. Bond lengths [Å] and angles [°] for l19415t5.

Ni(1)-C(1)	1.879(9)	C(10)-H(10A)	0.9800
Ni(1)-N(1)	1.936(7)	C(10)-H(10B)	0.9800
Ni(1)-C(8)	1.954(9)	C(10)-H(10C)	0.9800
Ni(1)-N(2)	1.997(7)	C(11)-C(12)	1.366(13)
N(1)-C(15)	1.339(10)	C(11)-C(24)	1.479(12)
N(1)-C(11)	1.371(11)	C(12)-C(13)	1.373(13)
N(2)-C(18)	1.343(11)	C(12)-H(12)	0.9500
N(2)-C(22)	1.367(12)	C(13)-C(14)	1.383(14)
N(3)-C(17)	1.442(12)	C(13)-H(13)	0.9500
N(3)-C(25)	1.454(11)	C(14)-C(15)	1.374(12)
N(3)-C(16)	1.473(11)	C(14)-H(14)	0.9500
N(4)-C(23)	1.448(12)	C(15)-C(16)	1.511(13)
N(4)-C(26)	1.462(12)	C(16)-H(16A)	0.9900
N(4)-C(24)	1.476(11)	C(16)-H(16B)	0.9900
C(1)-C(6)	1.411(12)	C(17)-C(18)	1.524(12)
C(1)-C(2)	1.421(12)	C(17)-H(17A)	0.9900
C(2)-C(3)	1.379(12)	C(17)-H(17B)	0.9900
C(2)-H(2)	0.9500	C(18)-C(19)	1.393(12)
C(3)-C(4)	1.391(13)	C(19)-C(20)	1.395(13)
C(3)-H(3)	0.9500	C(19)-H(19)	0.9500
C(4)-C(5)	1.391(13)	C(20)-C(21)	1.389(13)
C(4)-H(4A)	0.9500	C(20)-H(20)	0.9500
C(5)-C(6)	1.375(12)	C(21)-C(22)	1.389(13)
C(5)-H(5)	0.9500	C(21)-H(21)	0.9500
C(6)-C(7)	1.521(13)	C(22)-C(23)	1.515(13)
C(7)-C(8)	1.506(12)	C(23)-H(23A)	0.9900
C(7)-C(9)	1.537(12)	C(23)-H(23B)	0.9900
C(7)-C(10)	1.546(13)	C(24)-H(24A)	0.9900
C(8)-H(8A)	0.9900	C(24)-H(24B)	0.9900
C(8)-H(8B)	0.9900	C(25)-H(25A)	0.9800
C(9)-H(9A)	0.9800	C(25)-H(25B)	0.9800
C(9)-H(9B)	0.9800	C(25)-H(25C)	0.9800
C(9)-H(9C)	0.9800	C(26)-H(26A)	0.9800

C(26)-H(26B)	0.9800	C(10A)-H(10E)	0.9800
C(26)-H(26C)	0.9800	C(10A)-H(10F)	0.9800
Ni(1A)-C(8A)	1.903(8)	C(11A)-C(12A)	1.405(13)
Ni(1A)-C(1A)	1.905(9)	C(11A)-C(24A)	1.529(12)
Ni(1A)-N(2A)	1.944(7)	C(12A)-C(13A)	1.386(13)
Ni(1A)-N(1A)	1.973(7)	C(12A)-H(12A)	0.9500
N(1A)-C(15A)	1.350(11)	C(13A)-C(14A)	1.396(14)
N(1A)-C(11A)	1.362(12)	C(13A)-H(13A)	0.9500
N(2A)-C(22A)	1.343(12)	C(14A)-C(15A)	1.401(13)
N(2A)-C(18A)	1.350(11)	C(14A)-H(14A)	0.9500
N(3A)-C(16A)	1.453(10)	C(15A)-C(16A)	1.519(13)
N(3A)-C(25A)	1.454(11)	C(16A)-H(16C)	0.9900
N(3A)-C(17A)	1.465(11)	C(16A)-H(16D)	0.9900
N(4A)-C(24A)	1.431(12)	C(17A)-C(18A)	1.515(13)
N(4A)-C(26A)	1.451(11)	C(17A)-H(17C)	0.9900
N(4A)-C(23A)	1.465(11)	C(17A)-H(17D)	0.9900
C(1A)-C(2A)	1.383(12)	C(18A)-C(19A)	1.370(11)
C(1A)-C(6A)	1.409(11)	C(19A)-C(20A)	1.387(13)
C(2A)-C(3A)	1.400(12)	C(19A)-H(19A)	0.9500
C(2A)-H(2A)	0.9500	C(20A)-C(21A)	1.374(13)
C(3A)-C(4A)	1.377(13)	C(20A)-H(20A)	0.9500
C(3A)-H(3AA)	0.9500	C(21A)-C(22A)	1.369(12)
C(4A)-C(5A)	1.378(13)	C(21A)-H(21A)	0.9500
C(4A)-H(4AA)	0.9500	C(22A)-C(23A)	1.533(13)
C(5A)-C(6A)	1.402(12)	C(23A)-H(23C)	0.9900
C(5A)-H(5A)	0.9500	C(23A)-H(23D)	0.9900
C(6A)-C(7A)	1.490(12)	C(24A)-H(24C)	0.9900
C(7A)-C(9A)	1.508(12)	C(24A)-H(24D)	0.9900
C(7A)-C(8A)	1.554(13)	C(25A)-H(25D)	0.9800
C(7A)-C(10A)	1.569(14)	C(25A)-H(25E)	0.9800
C(8A)-H(8AA)	0.9900	C(25A)-H(25F)	0.9800
C(8A)-H(8AB)	0.9900	C(26A)-H(26D)	0.9800
C(9A)-H(9AA)	0.9800	C(26A)-H(26E)	0.9800
C(9A)-H(9AB)	0.9800	C(26A)-H(26F)	0.9800
C(9A)-H(9AC)	0.9800	O(1S)-C(1S)	1.409(13)
C(10A)-H(10D)	0.9800	O(1S)-C(4S)	1.450(12)

C(1S)-C(2S)	1.517(14)	C(17)-N(3)-C(25)	113.4(7)
C(1S)-H(1SA)	0.9900	C(17)-N(3)-C(16)	118.1(6)
C(1S)-H(1SB)	0.9900	C(25)-N(3)-C(16)	115.0(7)
C(2S)-C(3S)	1.500(16)	C(23)-N(4)-C(26)	113.8(9)
C(2S)-H(2SA)	0.9900	C(23)-N(4)-C(24)	117.7(7)
C(2S)-H(2SB)	0.9900	C(26)-N(4)-C(24)	113.3(8)
C(3S)-C(4S)	1.516(16)	C(6)-C(1)-C(2)	117.8(8)
C(3S)-H(3SA)	0.9900	C(6)-C(1)-Ni(1)	116.6(7)
C(3S)-H(3SB)	0.9900	C(2)-C(1)-Ni(1)	125.6(6)
C(4S)-H(4SA)	0.9900	C(3)-C(2)-C(1)	120.8(9)
C(4S)-H(4SB)	0.9900	C(3)-C(2)-H(2)	119.6
O(2S)-C(8S)	1.403(12)	C(1)-C(2)-H(2)	119.6
O(2S)-C(5S)	1.426(14)	C(2)-C(3)-C(4)	120.0(9)
C(5S)-C(6S)	1.490(17)	C(2)-C(3)-H(3)	120.0
C(5S)-H(5SA)	0.9900	C(4)-C(3)-H(3)	120.0
C(5S)-H(5SB)	0.9900	C(3)-C(4)-C(5)	120.1(9)
C(6S)-C(7S)	1.514(19)	C(3)-C(4)-H(4A)	120.0
C(6S)-H(6SA)	0.9900	C(5)-C(4)-H(4A)	120.0
C(6S)-H(6SB)	0.9900	C(6)-C(5)-C(4)	120.5(9)
C(7S)-C(8S)	1.493(17)	C(6)-C(5)-H(5)	119.7
C(7S)-H(7SA)	0.9900	C(4)-C(5)-H(5)	119.7
C(7S)-H(7SB)	0.9900	C(5)-C(6)-C(1)	120.7(8)
C(8S)-H(8S1)	0.9900	C(5)-C(6)-C(7)	124.2(8)
C(8S)-H(8S2)	0.9900	C(1)-C(6)-C(7)	114.9(8)
C(1)-Ni(1)-N(1)	176.0(3)	C(8)-C(7)-C(6)	105.3(7)
C(1)-Ni(1)-C(8)	83.5(3)	C(8)-C(7)-C(9)	109.6(8)
N(1)-Ni(1)-C(8)	93.6(3)	C(6)-C(7)-C(9)	109.5(7)
C(1)-Ni(1)-N(2)	98.7(3)	C(8)-C(7)-C(10)	111.4(8)
N(1)-Ni(1)-N(2)	84.4(3)	C(6)-C(7)-C(10)	112.5(8)
C(8)-Ni(1)-N(2)	175.3(4)	C(9)-C(7)-C(10)	108.4(8)
C(15)-N(1)-C(11)	118.5(7)	C(7)-C(8)-Ni(1)	113.8(6)
C(15)-N(1)-Ni(1)	120.2(6)	C(7)-C(8)-H(8A)	108.8
C(11)-N(1)-Ni(1)	120.8(6)	Ni(1)-C(8)-H(8A)	108.8
C(18)-N(2)-C(22)	117.0(8)	C(7)-C(8)-H(8B)	108.8
C(18)-N(2)-Ni(1)	121.9(6)	Ni(1)-C(8)-H(8B)	108.8
C(22)-N(2)-Ni(1)	120.1(6)	H(8A)-C(8)-H(8B)	107.7

C(7)-C(9)-H(9A)	109.5	N(3)-C(17)-H(17B)	107.8
C(7)-C(9)-H(9B)	109.5	C(18)-C(17)-H(17B)	107.8
H(9A)-C(9)-H(9B)	109.5	H(17A)-C(17)-H(17B)	107.2
C(7)-C(9)-H(9C)	109.5	N(2)-C(18)-C(19)	123.4(8)
H(9A)-C(9)-H(9C)	109.5	N(2)-C(18)-C(17)	114.6(8)
H(9B)-C(9)-H(9C)	109.5	C(19)-C(18)-C(17)	121.9(8)
C(7)-C(10)-H(10A)	109.5	C(18)-C(19)-C(20)	119.6(8)
C(7)-C(10)-H(10B)	109.5	C(18)-C(19)-H(19)	120.2
H(10A)-C(10)-H(10B)	109.5	C(20)-C(19)-H(19)	120.2
C(7)-C(10)-H(10C)	109.5	C(21)-C(20)-C(19)	117.3(8)
H(10A)-C(10)-H(10C)	109.5	C(21)-C(20)-H(20)	121.3
H(10B)-C(10)-H(10C)	109.5	C(19)-C(20)-H(20)	121.3
C(12)-C(11)-N(1)	121.8(8)	C(22)-C(21)-C(20)	120.3(9)
C(12)-C(11)-C(24)	120.8(9)	C(22)-C(21)-H(21)	119.8
N(1)-C(11)-C(24)	117.3(8)	C(20)-C(21)-H(21)	119.8
C(11)-C(12)-C(13)	119.6(9)	N(2)-C(22)-C(21)	122.4(8)
C(11)-C(12)-H(12)	120.2	N(2)-C(22)-C(23)	116.5(8)
C(13)-C(12)-H(12)	120.2	C(21)-C(22)-C(23)	121.1(8)
C(12)-C(13)-C(14)	118.5(9)	N(4)-C(23)-C(22)	119.8(8)
C(12)-C(13)-H(13)	120.8	N(4)-C(23)-H(23A)	107.4
C(14)-C(13)-H(13)	120.8	C(22)-C(23)-H(23A)	107.4
C(15)-C(14)-C(13)	120.3(9)	N(4)-C(23)-H(23B)	107.4
C(15)-C(14)-H(14)	119.9	C(22)-C(23)-H(23B)	107.4
C(13)-C(14)-H(14)	119.9	H(23A)-C(23)-H(23B)	106.9
N(1)-C(15)-C(14)	121.3(9)	N(4)-C(24)-C(11)	117.9(7)
N(1)-C(15)-C(16)	116.2(7)	N(4)-C(24)-H(24A)	107.8
C(14)-C(15)-C(16)	122.5(8)	C(11)-C(24)-H(24A)	107.8
N(3)-C(16)-C(15)	117.9(7)	N(4)-C(24)-H(24B)	107.8
N(3)-C(16)-H(16A)	107.8	C(11)-C(24)-H(24B)	107.8
C(15)-C(16)-H(16A)	107.8	H(24A)-C(24)-H(24B)	107.2
N(3)-C(16)-H(16B)	107.8	N(3)-C(25)-H(25A)	109.5
C(15)-C(16)-H(16B)	107.8	N(3)-C(25)-H(25B)	109.5
H(16A)-C(16)-H(16B)	107.2	H(25A)-C(25)-H(25B)	109.5
N(3)-C(17)-C(18)	117.9(7)	N(3)-C(25)-H(25C)	109.5
N(3)-C(17)-H(17A)	107.8	H(25A)-C(25)-H(25C)	109.5
C(18)-C(17)-H(17A)	107.8	H(25B)-C(25)-H(25C)	109.5

N(4)-C(26)-H(26A)	109.5	C(4A)-C(5A)-C(6A)	120.8(8)
N(4)-C(26)-H(26B)	109.5	C(4A)-C(5A)-H(5A)	119.6
H(26A)-C(26)-H(26B)	109.5	C(6A)-C(5A)-H(5A)	119.6
N(4)-C(26)-H(26C)	109.5	C(5A)-C(6A)-C(1A)	121.9(8)
H(26A)-C(26)-H(26C)	109.5	C(5A)-C(6A)-C(7A)	123.7(8)
H(26B)-C(26)-H(26C)	109.5	C(1A)-C(6A)-C(7A)	114.3(8)
C(8A)-Ni(1A)-C(1A)	83.9(4)	C(6A)-C(7A)-C(9A)	112.4(8)
C(8A)-Ni(1A)-N(2A)	175.8(4)	C(6A)-C(7A)-C(8A)	106.4(7)
C(1A)-Ni(1A)-N(2A)	98.3(3)	C(9A)-C(7A)-C(8A)	112.6(8)
C(8A)-Ni(1A)-N(1A)	94.3(3)	C(6A)-C(7A)-C(10A)	108.0(7)
C(1A)-Ni(1A)-N(1A)	176.1(3)	C(9A)-C(7A)-C(10A)	109.3(8)
N(2A)-Ni(1A)-N(1A)	83.7(3)	C(8A)-C(7A)-C(10A)	107.9(8)
C(15A)-N(1A)-C(11A)	119.7(8)	C(7A)-C(8A)-Ni(1A)	113.7(6)
C(15A)-N(1A)-Ni(1A)	118.9(6)	C(7A)-C(8A)-H(8AA)	108.8
C(11A)-N(1A)-Ni(1A)	120.8(6)	Ni(1A)-C(8A)-H(8AA)	108.8
C(22A)-N(2A)-C(18A)	119.2(7)	C(7A)-C(8A)-H(8AB)	108.8
C(22A)-N(2A)-Ni(1A)	118.8(6)	Ni(1A)-C(8A)-H(8AB)	108.8
C(18A)-N(2A)-Ni(1A)	121.3(6)	H(8AA)-C(8A)-H(8AB)	107.7
C(16A)-N(3A)-C(25A)	113.5(7)	C(7A)-C(9A)-H(9AA)	109.5
C(16A)-N(3A)-C(17A)	116.8(7)	C(7A)-C(9A)-H(9AB)	109.5
C(25A)-N(3A)-C(17A)	115.6(7)	H(9AA)-C(9A)-H(9AB)	109.5
C(24A)-N(4A)-C(26A)	113.2(7)	C(7A)-C(9A)-H(9AC)	109.5
C(24A)-N(4A)-C(23A)	118.3(7)	H(9AA)-C(9A)-H(9AC)	109.5
C(26A)-N(4A)-C(23A)	115.0(8)	H(9AB)-C(9A)-H(9AC)	109.5
C(2A)-C(1A)-C(6A)	115.6(8)	C(7A)-C(10A)-H(10D)	109.5
C(2A)-C(1A)-Ni(1A)	127.6(6)	C(7A)-C(10A)-H(10E)	109.5
C(6A)-C(1A)-Ni(1A)	116.7(6)	H(10D)-C(10A)-H(10E)	109.5
C(1A)-C(2A)-C(3A)	122.5(8)	C(7A)-C(10A)-H(10F)	109.5
C(1A)-C(2A)-H(2A)	118.7	H(10D)-C(10A)-H(10F)	109.5
C(3A)-C(2A)-H(2A)	118.7	H(10E)-C(10A)-H(10F)	109.5
C(4A)-C(3A)-C(2A)	120.9(8)	N(1A)-C(11A)-C(12A)	119.9(8)
C(4A)-C(3A)-H(3AA)	119.5	N(1A)-C(11A)-C(24A)	117.6(8)
C(2A)-C(3A)-H(3AA)	119.5	C(12A)-C(11A)-C(24A)	122.5(8)
C(3A)-C(4A)-C(5A)	118.2(9)	C(13A)-C(12A)-C(11A)	121.4(9)
C(3A)-C(4A)-H(4AA)	120.9	C(13A)-C(12A)-H(12A)	119.3
C(5A)-C(4A)-H(4AA)	120.9	C(11A)-C(12A)-H(12A)	119.3

C(12A)-C(13A)-C(14A)	117.5(8)	N(4A)-C(23A)-C(22A)	117.2(8)
C(12A)-C(13A)-H(13A)	121.3	N(4A)-C(23A)-H(23C)	108.0
C(14A)-C(13A)-H(13A)	121.3	C(22A)-C(23A)-H(23C)	108.0
C(13A)-C(14A)-C(15A)	119.8(8)	N(4A)-C(23A)-H(23D)	108.0
C(13A)-C(14A)-H(14A)	120.1	C(22A)-C(23A)-H(23D)	108.0
C(15A)-C(14A)-H(14A)	120.1	H(23C)-C(23A)-H(23D)	107.2
N(1A)-C(15A)-C(14A)	121.7(9)	N(4A)-C(24A)-C(11A)	118.4(7)
N(1A)-C(15A)-C(16A)	118.1(8)	N(4A)-C(24A)-H(24C)	107.7
C(14A)-C(15A)-C(16A)	120.2(8)	C(11A)-C(24A)-H(24C)	107.7
N(3A)-C(16A)-C(15A)	118.5(7)	N(4A)-C(24A)-H(24D)	107.7
N(3A)-C(16A)-H(16C)	107.7	C(11A)-C(24A)-H(24D)	107.7
C(15A)-C(16A)-H(16C)	107.7	H(24C)-C(24A)-H(24D)	107.1
N(3A)-C(16A)-H(16D)	107.7	N(3A)-C(25A)-H(25D)	109.5
C(15A)-C(16A)-H(16D)	107.7	N(3A)-C(25A)-H(25E)	109.5
H(16C)-C(16A)-H(16D)	107.1	H(25D)-C(25A)-H(25E)	109.5
N(3A)-C(17A)-C(18A)	117.7(8)	N(3A)-C(25A)-H(25F)	109.5
N(3A)-C(17A)-H(17C)	107.9	H(25D)-C(25A)-H(25F)	109.5
C(18A)-C(17A)-H(17C)	107.9	H(25E)-C(25A)-H(25F)	109.5
N(3A)-C(17A)-H(17D)	107.9	N(4A)-C(26A)-H(26D)	109.5
C(18A)-C(17A)-H(17D)	107.9	N(4A)-C(26A)-H(26E)	109.5
H(17C)-C(17A)-H(17D)	107.2	H(26D)-C(26A)-H(26E)	109.5
N(2A)-C(18A)-C(19A)	121.9(8)	N(4A)-C(26A)-H(26F)	109.5
N(2A)-C(18A)-C(17A)	117.2(7)	H(26D)-C(26A)-H(26F)	109.5
C(19A)-C(18A)-C(17A)	120.8(8)	H(26E)-C(26A)-H(26F)	109.5
C(18A)-C(19A)-C(20A)	118.6(8)	C(1S)-O(1S)-C(4S)	108.4(9)
C(18A)-C(19A)-H(19A)	120.7	O(1S)-C(1S)-C(2S)	108.0(8)
C(20A)-C(19A)-H(19A)	120.7	O(1S)-C(1S)-H(1SA)	110.1
C(21A)-C(20A)-C(19A)	119.1(8)	C(2S)-C(1S)-H(1SA)	110.1
C(21A)-C(20A)-H(20A)	120.5	O(1S)-C(1S)-H(1SB)	110.1
C(19A)-C(20A)-H(20A)	120.5	C(2S)-C(1S)-H(1SB)	110.1
C(22A)-C(21A)-C(20A)	119.8(9)	H(1SA)-C(1S)-H(1SB)	108.4
C(22A)-C(21A)-H(21A)	120.1	C(3S)-C(2S)-C(1S)	102.6(9)
C(20A)-C(21A)-H(21A)	120.1	C(3S)-C(2S)-H(2SA)	111.3
N(2A)-C(22A)-C(21A)	121.2(9)	C(1S)-C(2S)-H(2SA)	111.3
N(2A)-C(22A)-C(23A)	118.0(8)	C(3S)-C(2S)-H(2SB)	111.3
C(21A)-C(22A)-C(23A)	120.6(8)	C(1S)-C(2S)-H(2SB)	111.3

H(2SA)-C(2S)-H(2SB)	109.2	H(5SA)-C(5S)-H(5SB)	108.4
C(2S)-C(3S)-C(4S)	102.0(9)	C(5S)-C(6S)-C(7S)	103.9(10)
C(2S)-C(3S)-H(3SA)	111.4	C(5S)-C(6S)-H(6SA)	111.0
C(4S)-C(3S)-H(3SA)	111.4	C(7S)-C(6S)-H(6SA)	111.0
C(2S)-C(3S)-H(3SB)	111.4	C(5S)-C(6S)-H(6SB)	111.0
C(4S)-C(3S)-H(3SB)	111.4	C(7S)-C(6S)-H(6SB)	111.0
H(3SA)-C(3S)-H(3SB)	109.2	H(6SA)-C(6S)-H(6SB)	109.0
O(1S)-C(4S)-C(3S)	106.4(9)	C(8S)-C(7S)-C(6S)	102.8(10)
O(1S)-C(4S)-H(4SA)	110.4	C(8S)-C(7S)-H(7SA)	111.2
C(3S)-C(4S)-H(4SA)	110.4	C(6S)-C(7S)-H(7SA)	111.2
O(1S)-C(4S)-H(4SB)	110.4	C(8S)-C(7S)-H(7SB)	111.2
C(3S)-C(4S)-H(4SB)	110.4	C(6S)-C(7S)-H(7SB)	111.2
H(4SA)-C(4S)-H(4SB)	108.6	H(7SA)-C(7S)-H(7SB)	109.1
C(8S)-O(2S)-C(5S)	108.0(8)	O(2S)-C(8S)-C(7S)	105.1(10)
O(2S)-C(5S)-C(6S)	107.9(9)	O(2S)-C(8S)-H(8S1)	110.7
O(2S)-C(5S)-H(5SA)	110.1	C(7S)-C(8S)-H(8S1)	110.7
C(6S)-C(5S)-H(5SA)	110.1	O(2S)-C(8S)-H(8S2)	110.7
O(2S)-C(5S)-H(5SB)	110.1	C(7S)-C(8S)-H(8S2)	110.7
C(6S)-C(5S)-H(5SB)	110.1	H(8S1)-C(8S)-H(8S2)	108.8

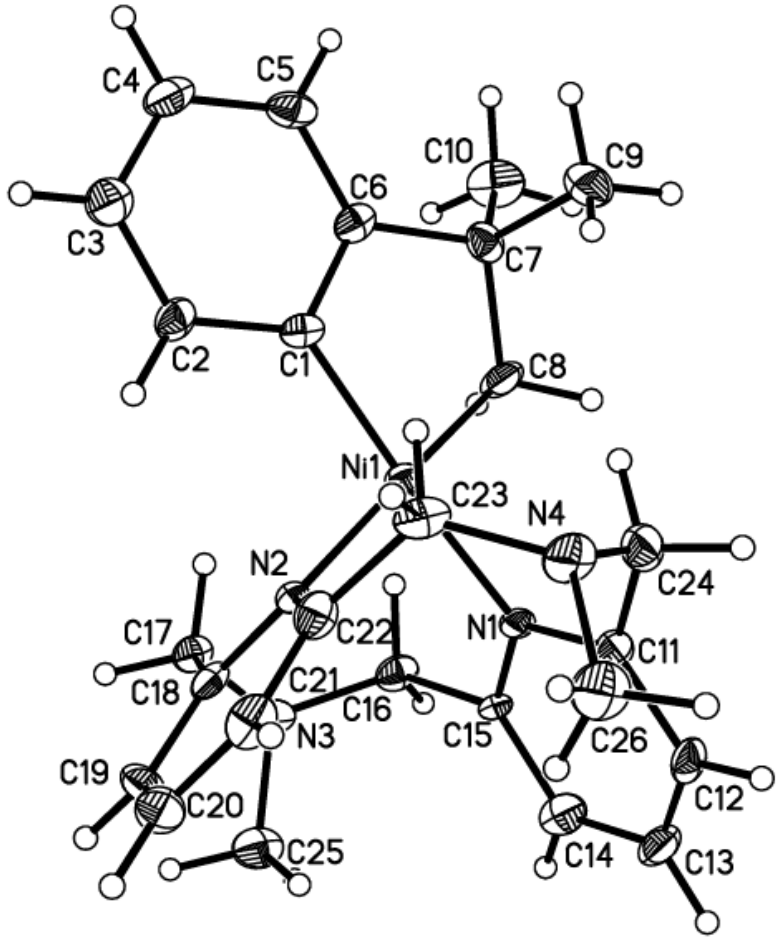


Figure S29. Projection view of l19415t5 with 50% thermal ellipsoids.

X-ray structure determination of [(^{Me}N4)Ni^{III}(cycloneophyl)]BPh$_4$

Table S25. Crystal data and structure refinement for lm9315.

Identification code	l9315/lt/smart/JS-050415-01	
Empirical formula	C_{62} H_{76} B N_4 Ni O_3	
Formula weight	994.78	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 18.0244(6) Å	α = 90°.
	b = 12.6029(4) Å	β = 98.4100(16)°.
	c = 23.9084(8) Å	γ = 90°.
Volume	5372.6(3) Å^3	
Z	4	
Density (calculated)	1.230 Mg/m^3	
Absorption coefficient	0.410 mm^{-1}	
F(000)	2132	
Crystal size	0.572 x 0.194 x 0.072 mm^3	
Theta range for data collection	1.722 to 27.512°.	
Index ranges	-23≤h≤23, -8≤k≤16, -31≤l≤30	
Reflections collected	84276	
Independent reflections	12338 [R(int) = 0.0678]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8621 and 0.7578	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12338 / 114 / 645	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0613, wR2 = 0.1446	
R indices (all data)	R1 = 0.0970, wR2 = 0.1660	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.858 and -0.570 e.Å^{-3}	

Table S26. Bond lengths [Å] and angles [°] for lm9315.

Ni(1)-C(18)	1.920(3)	C(11)-C(12)	1.398(4)
Ni(1)-C(17)	1.973(3)	C(11)-H(11)	0.9500
Ni(1)-N(2)	1.997(2)	C(12)-C(13)	1.489(5)
Ni(1)-N(1)	2.001(2)	C(13)-H(13A)	0.9900
Ni(1)-N(3)	2.241(2)	C(13)-H(13B)	0.9900
Ni(1)-N(4)	2.266(3)	C(14)-H(14A)	0.9900
N(1)-C(5)	1.340(3)	C(14)-H(14B)	0.9900
N(1)-C(1)	1.345(4)	C(15)-H(15A)	0.9800
N(2)-C(8)	1.338(4)	C(15)-H(15B)	0.9800
N(2)-C(12)	1.346(4)	C(15)-H(15C)	0.9800
N(3)-C(15)	1.478(3)	C(16)-H(16A)	0.9800
N(3)-C(7)	1.484(4)	C(16)-H(16B)	0.9800
N(3)-C(6)	1.485(4)	C(16)-H(16C)	0.9800
N(4)-C(16)	1.474(4)	C(17)-C(24)	1.551(4)
N(4)-C(13)	1.488(4)	C(17)-H(17A)	0.9900
N(4)-C(14)	1.490(4)	C(17)-H(17B)	0.9900
C(1)-C(2)	1.386(4)	C(18)-C(19)	1.393(4)
C(1)-C(14)	1.507(4)	C(18)-C(23)	1.403(4)
C(2)-C(3)	1.380(4)	C(19)-C(20)	1.393(5)
C(2)-H(2)	0.9500	C(19)-H(19)	0.9500
C(3)-C(4)	1.388(4)	C(20)-C(21)	1.381(5)
C(3)-H(3)	0.9500	C(20)-H(20)	0.9500
C(4)-C(5)	1.383(4)	C(21)-C(22)	1.384(5)
C(4)-H(4)	0.9500	C(21)-H(21)	0.9500
C(5)-C(6)	1.502(4)	C(22)-C(23)	1.401(4)
C(6)-H(6A)	0.9900	C(22)-H(22)	0.9500
C(6)-H(6B)	0.9900	C(23)-C(24)	1.509(4)
C(7)-C(8)	1.494(4)	C(24)-C(25)	1.539(4)
C(7)-H(7A)	0.9900	C(24)-C(26)	1.539(4)
C(7)-H(7B)	0.9900	C(25)-H(25A)	0.9800
C(8)-C(9)	1.395(4)	C(25)-H(25B)	0.9800
C(9)-C(10)	1.369(5)	C(25)-H(25C)	0.9800
C(9)-H(9)	0.9500	C(26)-H(26A)	0.9800
C(10)-C(11)	1.374(5)	C(26)-H(26B)	0.9800
C(10)-H(10)	0.9500	C(26)-H(26C)	0.9800

C(27)-C(32)	1.405(4)	C(45)-C(50)	1.399(4)
C(27)-C(28)	1.408(4)	C(45)-C(46)	1.406(4)
C(27)-B(1)	1.648(4)	C(45)-B(1)	1.655(4)
C(28)-C(29)	1.388(4)	C(46)-C(47)	1.391(4)
C(28)-H(28)	0.9500	C(46)-H(46)	0.9500
C(29)-C(30)	1.386(4)	C(47)-C(48)	1.382(5)
C(29)-H(29)	0.9500	C(47)-H(47)	0.9500
C(30)-C(31)	1.383(4)	C(48)-C(49)	1.391(5)
C(30)-H(30)	0.9500	C(48)-H(48)	0.9500
C(31)-C(32)	1.394(4)	C(49)-C(50)	1.395(4)
C(31)-H(31)	0.9500	C(49)-H(49)	0.9500
C(32)-H(32)	0.9500	C(50)-H(50)	0.9500
C(33)-C(38)	1.401(4)	O(1S)-C(1S)	1.388(7)
C(33)-C(34)	1.412(4)	O(1S)-C(4S)	1.495(8)
C(33)-B(1)	1.654(4)	C(1S)-O(1S')	1.429(16)
C(34)-C(35)	1.396(4)	C(1S)-C(2S)	1.472(7)
C(34)-H(34)	0.9500	C(1S)-H(1SA)	0.9900
C(35)-C(36)	1.383(5)	C(1S)-H(1SB)	0.9900
C(35)-H(35)	0.9500	C(2S)-C(3S)	1.510(7)
C(36)-C(37)	1.381(5)	C(2S)-H(2SA)	0.9900
C(36)-H(36)	0.9500	C(2S)-H(2SB)	0.9900
C(37)-C(38)	1.386(4)	C(3S)-C(4S)	1.414(7)
C(37)-H(37)	0.9500	C(3S)-H(3SA)	0.9900
C(38)-H(38)	0.9500	C(3S)-H(3SB)	0.9900
C(39)-C(44)	1.400(4)	C(4S)-O(1S')	1.233(15)
C(39)-C(40)	1.406(4)	C(4S)-H(4SA)	0.9900
C(39)-B(1)	1.638(4)	C(4S)-H(4SB)	0.9900
C(40)-C(41)	1.392(4)	O(2S)-C(8S)	1.378(7)
C(40)-H(40)	0.9500	O(2S)-C(5S)	1.468(8)
C(41)-C(42)	1.382(5)	C(5S)-C(6S)	1.416(10)
C(41)-H(41)	0.9500	C(5S)-O(2S')	1.501(15)
C(42)-C(43)	1.381(5)	C(5S)-H(5S1)	0.9900
C(42)-H(42)	0.9500	C(5S)-H(5S2)	0.9900
C(43)-C(44)	1.396(4)	C(6S)-C(7S)	1.468(9)
C(43)-H(43)	0.9500	C(6S)-H(6SA)	0.9900
C(44)-H(44)	0.9500	C(6S)-H(6SB)	0.9900

C(7S)-C(8S)	1.502(8)	C(1)-N(1)-Ni(1)	119.31(19)
C(7S)-H(7SA)	0.9900	C(8)-N(2)-C(12)	119.9(3)
C(7S)-H(7SB)	0.9900	C(8)-N(2)-Ni(1)	119.0(2)
C(8S)-O(2S')	1.666(16)	C(12)-N(2)-Ni(1)	118.8(2)
C(8S)-H(8S1)	0.9900	C(15)-N(3)-C(7)	109.8(2)
C(8S)-H(8S2)	0.9900	C(15)-N(3)-C(6)	108.6(2)
O(3S)-C(12S)	1.395(6)	C(7)-N(3)-C(6)	111.3(2)
O(3S)-C(9S)	1.399(6)	C(15)-N(3)-Ni(1)	116.63(17)
C(9S)-C(10S)	1.490(6)	C(7)-N(3)-Ni(1)	107.22(17)
C(9S)-H(9SA)	0.9900	C(6)-N(3)-Ni(1)	103.21(16)
C(9S)-H(9SB)	0.9900	C(16)-N(4)-C(13)	109.7(3)
C(10S)-C(11S)	1.504(6)	C(16)-N(4)-C(14)	108.9(3)
C(10S)-H(10A)	0.9900	C(13)-N(4)-C(14)	112.2(3)
C(10S)-H(10B)	0.9900	C(16)-N(4)-Ni(1)	116.6(2)
C(11S)-C(12S)	1.489(7)	C(13)-N(4)-Ni(1)	103.31(18)
C(11S)-H(11A)	0.9900	C(14)-N(4)-Ni(1)	106.08(18)
C(11S)-H(11B)	0.9900	N(1)-C(1)-C(2)	121.0(3)
C(12S)-H(12A)	0.9900	N(1)-C(1)-C(14)	115.2(3)
C(12S)-H(12B)	0.9900	C(2)-C(1)-C(14)	123.7(3)
C(18)-Ni(1)-C(17)	82.88(12)	C(3)-C(2)-C(1)	119.0(3)
C(18)-Ni(1)-N(2)	177.67(11)	C(3)-C(2)-H(2)	120.5
C(17)-Ni(1)-N(2)	95.35(10)	C(1)-C(2)-H(2)	120.5
C(18)-Ni(1)-N(1)	99.00(11)	C(2)-C(3)-C(4)	119.8(3)
C(17)-Ni(1)-N(1)	178.08(11)	C(2)-C(3)-H(3)	120.1
N(2)-Ni(1)-N(1)	82.78(9)	C(4)-C(3)-H(3)	120.1
C(18)-Ni(1)-N(3)	102.09(11)	C(5)-C(4)-C(3)	118.4(3)
C(17)-Ni(1)-N(3)	99.39(10)	C(5)-C(4)-H(4)	120.8
N(2)-Ni(1)-N(3)	79.68(9)	C(3)-C(4)-H(4)	120.8
N(1)-Ni(1)-N(3)	79.84(9)	N(1)-C(5)-C(4)	121.8(3)
C(18)-Ni(1)-N(4)	99.36(11)	N(1)-C(5)-C(6)	114.3(2)
C(17)-Ni(1)-N(4)	100.34(11)	C(4)-C(5)-C(6)	124.0(3)
N(2)-Ni(1)-N(4)	79.42(10)	N(3)-C(6)-C(5)	111.1(2)
N(1)-Ni(1)-N(4)	79.82(9)	N(3)-C(6)-H(6A)	109.4
N(3)-Ni(1)-N(4)	152.39(9)	C(5)-C(6)-H(6A)	109.4
C(5)-N(1)-C(1)	120.0(2)	N(3)-C(6)-H(6B)	109.4
C(5)-N(1)-Ni(1)	118.05(18)	C(5)-C(6)-H(6B)	109.4

H(6A)-C(6)-H(6B)	108.0	H(15A)-C(15)-H(15B)	109.5
N(3)-C(7)-C(8)	112.5(2)	N(3)-C(15)-H(15C)	109.5
N(3)-C(7)-H(7A)	109.1	H(15A)-C(15)-H(15C)	109.5
C(8)-C(7)-H(7A)	109.1	H(15B)-C(15)-H(15C)	109.5
N(3)-C(7)-H(7B)	109.1	N(4)-C(16)-H(16A)	109.5
C(8)-C(7)-H(7B)	109.1	N(4)-C(16)-H(16B)	109.5
H(7A)-C(7)-H(7B)	107.8	H(16A)-C(16)-H(16B)	109.5
N(2)-C(8)-C(9)	121.6(3)	N(4)-C(16)-H(16C)	109.5
N(2)-C(8)-C(7)	116.0(3)	H(16A)-C(16)-H(16C)	109.5
C(9)-C(8)-C(7)	122.3(3)	H(16B)-C(16)-H(16C)	109.5
C(10)-C(9)-C(8)	118.6(3)	C(24)-C(17)-Ni(1)	116.21(19)
C(10)-C(9)-H(9)	120.7	C(24)-C(17)-H(17A)	108.2
C(8)-C(9)-H(9)	120.7	Ni(1)-C(17)-H(17A)	108.2
C(9)-C(10)-C(11)	120.1(3)	C(24)-C(17)-H(17B)	108.2
C(9)-C(10)-H(10)	119.9	Ni(1)-C(17)-H(17B)	108.2
C(11)-C(10)-H(10)	119.9	H(17A)-C(17)-H(17B)	107.4
C(10)-C(11)-C(12)	119.0(3)	C(19)-C(18)-C(23)	118.5(3)
C(10)-C(11)-H(11)	120.5	C(19)-C(18)-Ni(1)	123.2(2)
C(12)-C(11)-H(11)	120.5	C(23)-C(18)-Ni(1)	118.2(2)
N(2)-C(12)-C(11)	120.7(3)	C(20)-C(19)-C(18)	121.3(3)
N(2)-C(12)-C(13)	114.8(3)	C(20)-C(19)-H(19)	119.4
C(11)-C(12)-C(13)	124.5(3)	C(18)-C(19)-H(19)	119.4
N(4)-C(13)-C(12)	112.0(3)	C(21)-C(20)-C(19)	119.8(3)
N(4)-C(13)-H(13A)	109.2	C(21)-C(20)-H(20)	120.1
C(12)-C(13)-H(13A)	109.2	C(19)-C(20)-H(20)	120.1
N(4)-C(13)-H(13B)	109.2	C(20)-C(21)-C(22)	120.0(3)
C(12)-C(13)-H(13B)	109.2	C(20)-C(21)-H(21)	120.0
H(13A)-C(13)-H(13B)	107.9	C(22)-C(21)-H(21)	120.0
N(4)-C(14)-C(1)	112.9(2)	C(21)-C(22)-C(23)	120.5(3)
N(4)-C(14)-H(14A)	109.0	C(21)-C(22)-H(22)	119.7
C(1)-C(14)-H(14A)	109.0	C(23)-C(22)-H(22)	119.7
N(4)-C(14)-H(14B)	109.0	C(22)-C(23)-C(18)	119.8(3)
C(1)-C(14)-H(14B)	109.0	C(22)-C(23)-C(24)	123.7(3)
H(14A)-C(14)-H(14B)	107.8	C(18)-C(23)-C(24)	116.4(3)
N(3)-C(15)-H(15A)	109.5	C(23)-C(24)-C(25)	110.3(2)
N(3)-C(15)-H(15B)	109.5	C(23)-C(24)-C(26)	111.1(3)

C(25)-C(24)-C(26)	107.9(2)	C(34)-C(33)-B(1)	121.3(3)
C(23)-C(24)-C(17)	106.2(2)	C(35)-C(34)-C(33)	122.7(3)
C(25)-C(24)-C(17)	110.2(2)	C(35)-C(34)-H(34)	118.6
C(26)-C(24)-C(17)	111.2(2)	C(33)-C(34)-H(34)	118.6
C(24)-C(25)-H(25A)	109.5	C(36)-C(35)-C(34)	120.1(3)
C(24)-C(25)-H(25B)	109.5	C(36)-C(35)-H(35)	120.0
H(25A)-C(25)-H(25B)	109.5	C(34)-C(35)-H(35)	120.0
C(24)-C(25)-H(25C)	109.5	C(37)-C(36)-C(35)	118.9(3)
H(25A)-C(25)-H(25C)	109.5	C(37)-C(36)-H(36)	120.5
H(25B)-C(25)-H(25C)	109.5	C(35)-C(36)-H(36)	120.5
C(24)-C(26)-H(26A)	109.5	C(36)-C(37)-C(38)	120.4(3)
C(24)-C(26)-H(26B)	109.5	C(36)-C(37)-H(37)	119.8
H(26A)-C(26)-H(26B)	109.5	C(38)-C(37)-H(37)	119.8
C(24)-C(26)-H(26C)	109.5	C(37)-C(38)-C(33)	123.2(3)
H(26A)-C(26)-H(26C)	109.5	C(37)-C(38)-H(38)	118.4
H(26B)-C(26)-H(26C)	109.5	C(33)-C(38)-H(38)	118.4
C(32)-C(27)-C(28)	114.8(3)	C(44)-C(39)-C(40)	115.0(3)
C(32)-C(27)-B(1)	124.7(2)	C(44)-C(39)-B(1)	123.6(3)
C(28)-C(27)-B(1)	120.3(2)	C(40)-C(39)-B(1)	121.4(3)
C(29)-C(28)-C(27)	122.9(3)	C(41)-C(40)-C(39)	122.6(3)
C(29)-C(28)-H(28)	118.6	C(41)-C(40)-H(40)	118.7
C(27)-C(28)-H(28)	118.6	C(39)-C(40)-H(40)	118.7
C(30)-C(29)-C(28)	120.2(3)	C(42)-C(41)-C(40)	120.1(3)
C(30)-C(29)-H(29)	119.9	C(42)-C(41)-H(41)	120.0
C(28)-C(29)-H(29)	119.9	C(40)-C(41)-H(41)	120.0
C(31)-C(30)-C(29)	118.9(3)	C(43)-C(42)-C(41)	119.5(3)
C(31)-C(30)-H(30)	120.5	C(43)-C(42)-H(42)	120.2
C(29)-C(30)-H(30)	120.5	C(41)-C(42)-H(42)	120.2
C(30)-C(31)-C(32)	120.2(3)	C(42)-C(43)-C(44)	119.5(3)
C(30)-C(31)-H(31)	119.9	C(42)-C(43)-H(43)	120.2
C(32)-C(31)-H(31)	119.9	C(44)-C(43)-H(43)	120.2
C(31)-C(32)-C(27)	122.8(3)	C(43)-C(44)-C(39)	123.2(3)
C(31)-C(32)-H(32)	118.6	C(43)-C(44)-H(44)	118.4
C(27)-C(32)-H(32)	118.6	C(39)-C(44)-H(44)	118.4
C(38)-C(33)-C(34)	114.6(3)	C(50)-C(45)-C(46)	114.8(3)
C(38)-C(33)-B(1)	124.1(3)	C(50)-C(45)-B(1)	123.5(2)

C(46)-C(45)-B(1)	121.5(3)	C(4S)-C(3S)-C(2S)	103.1(4)
C(47)-C(46)-C(45)	123.2(3)	C(4S)-C(3S)-H(3SA)	111.2
C(47)-C(46)-H(46)	118.4	C(2S)-C(3S)-H(3SA)	111.2
C(45)-C(46)-H(46)	118.4	C(4S)-C(3S)-H(3SB)	111.2
C(48)-C(47)-C(46)	120.1(3)	C(2S)-C(3S)-H(3SB)	111.2
C(48)-C(47)-H(47)	119.9	H(3SA)-C(3S)-H(3SB)	109.1
C(46)-C(47)-H(47)	119.9	O(1S')-C(4S)-C(3S)	103.8(8)
C(47)-C(48)-C(49)	118.8(3)	C(3S)-C(4S)-O(1S)	110.8(4)
C(47)-C(48)-H(48)	120.6	C(3S)-C(4S)-H(4SA)	109.5
C(49)-C(48)-H(48)	120.6	O(1S)-C(4S)-H(4SA)	109.5
C(48)-C(49)-C(50)	120.0(3)	C(3S)-C(4S)-H(4SB)	109.5
C(48)-C(49)-H(49)	120.0	O(1S)-C(4S)-H(4SB)	109.5
C(50)-C(49)-H(49)	120.0	H(4SA)-C(4S)-H(4SB)	108.1
C(49)-C(50)-C(45)	123.1(3)	C(8S)-O(2S)-C(5S)	102.3(5)
C(49)-C(50)-H(50)	118.5	C(6S)-C(5S)-O(2S)	105.4(7)
C(45)-C(50)-H(50)	118.5	C(6S)-C(5S)-O(2S')	113.4(8)
C(39)-B(1)-C(27)	109.7(2)	C(6S)-C(5S)-H(5S1)	110.7
C(39)-B(1)-C(33)	110.6(2)	O(2S)-C(5S)-H(5S1)	110.7
C(27)-B(1)-C(33)	108.9(2)	C(6S)-C(5S)-H(5S2)	110.7
C(39)-B(1)-C(45)	107.9(2)	O(2S)-C(5S)-H(5S2)	110.7
C(27)-B(1)-C(45)	109.5(2)	H(5S1)-C(5S)-H(5S2)	108.8
C(33)-B(1)-C(45)	110.2(2)	C(5S)-C(6S)-C(7S)	105.1(6)
C(1S)-O(1S)-C(4S)	101.6(4)	C(5S)-C(6S)-H(6SA)	110.7
O(1S)-C(1S)-C(2S)	106.4(4)	C(7S)-C(6S)-H(6SA)	110.7
O(1S')-C(1S)-C(2S)	101.6(7)	C(5S)-C(6S)-H(6SB)	110.7
O(1S)-C(1S)-H(1SA)	110.5	C(7S)-C(6S)-H(6SB)	110.7
C(2S)-C(1S)-H(1SA)	110.5	H(6SA)-C(6S)-H(6SB)	108.8
O(1S)-C(1S)-H(1SB)	110.5	C(6S)-C(7S)-C(8S)	104.6(5)
C(2S)-C(1S)-H(1SB)	110.5	C(6S)-C(7S)-H(7SA)	110.8
H(1SA)-C(1S)-H(1SB)	108.6	C(8S)-C(7S)-H(7SA)	110.8
C(1S)-C(2S)-C(3S)	102.2(4)	C(6S)-C(7S)-H(7SB)	110.8
C(1S)-C(2S)-H(2SA)	111.3	C(8S)-C(7S)-H(7SB)	110.8
C(3S)-C(2S)-H(2SA)	111.3	H(7SA)-C(7S)-H(7SB)	108.9
C(1S)-C(2S)-H(2SB)	111.3	O(2S)-C(8S)-C(7S)	103.5(5)
C(3S)-C(2S)-H(2SB)	111.3	C(7S)-C(8S)-O(2S')	106.1(6)
H(2SA)-C(2S)-H(2SB)	109.2	O(2S)-C(8S)-H(8S1)	111.1

C(7S)-C(8S)-H(8S1)	111.1	H(10A)-C(10S)-H(10B)	109.2
O(2S)-C(8S)-H(8S2)	111.1	C(12S)-C(11S)-C(10S)	100.7(4)
C(7S)-C(8S)-H(8S2)	111.1	C(12S)-C(11S)-H(11A)	111.6
H(8S1)-C(8S)-H(8S2)	109.0	C(10S)-C(11S)-H(11A)	111.6
C(12S)-O(3S)-C(9S)	109.2(4)	C(12S)-C(11S)-H(11B)	111.6
O(3S)-C(9S)-C(10S)	107.2(4)	C(10S)-C(11S)-H(11B)	111.6
O(3S)-C(9S)-H(9SA)	110.3	H(11A)-C(11S)-H(11B)	109.4
C(10S)-C(9S)-H(9SA)	110.3	O(3S)-C(12S)-C(11S)	106.8(4)
O(3S)-C(9S)-H(9SB)	110.3	O(3S)-C(12S)-H(12A)	110.4
C(10S)-C(9S)-H(9SB)	110.3	C(11S)-C(12S)-H(12A)	110.4
H(9SA)-C(9S)-H(9SB)	108.5	O(3S)-C(12S)-H(12B)	110.4
C(9S)-C(10S)-C(11S)	102.0(4)	C(11S)-C(12S)-H(12B)	110.4
C(9S)-C(10S)-H(10A)	111.4	H(12A)-C(12S)-H(12B)	108.6
C(11S)-C(10S)-H(10A)	111.4	C(4S)-O(1S')-C(1S)	114.1(12)
C(9S)-C(10S)-H(10B)	111.4	C(5S)-O(2S')-C(8S)	88.7(9)
C(11S)-C(10S)-H(10B)	111.4		

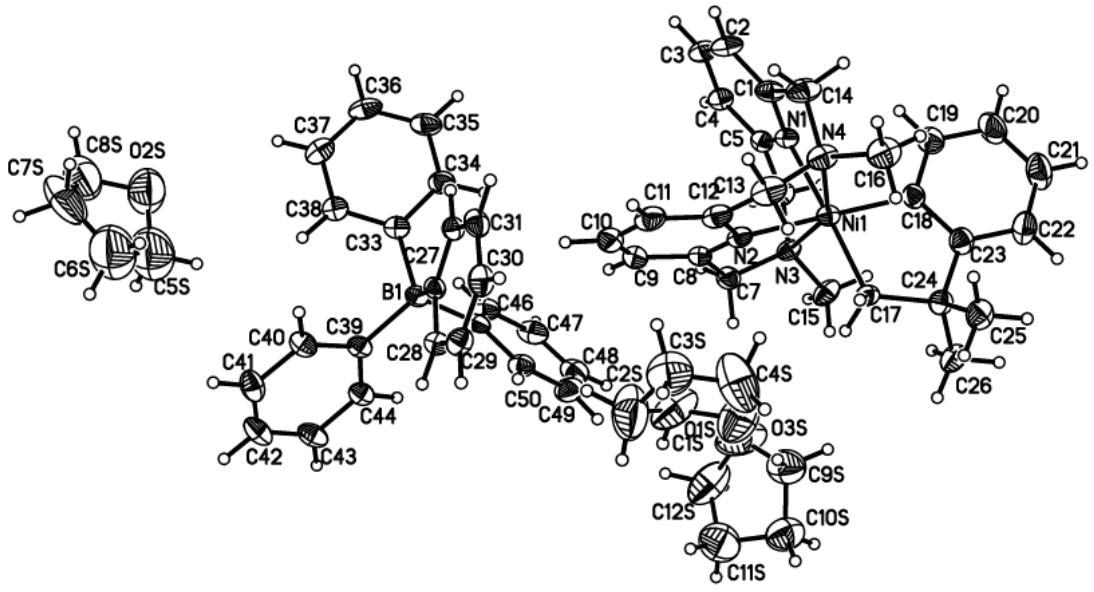


Figure S30. Projection view of lm9315 with 50% thermal ellipsoids.

X-ray structure determination of $[(^{Me}N4)Ni^{II}(MeCN)_2](PF_6)_2$

Table S27. Crystal data and structure refinement for lm10215.

Identification code	l10215/lt/x8/JS-051915-O2	
Empirical formula	$C_{20}\ H_{26}\ F_{12}\ N_6\ Ni\ P_2$	
Formula weight	699.12	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 9.2668(5) Å	α= 90°.
	b = 16.5937(10) Å	β= 92.739(3)°.
	c = 18.2485(11) Å	γ = 90°.
Volume	2802.9(3) $Å^3$	
Z	4	
Density (calculated)	1.657 Mg/m^3	
Absorption coefficient	0.909 mm^{-1}	
F(000)	1416	
Crystal size	0.374 x 0.303 x 0.257 mm^3	
Theta range for data collection	1.660 to 27.534°.	
Index ranges	$-12\leq h\leq 10$, $-18\leq k\leq 21$, $-22\leq l\leq 23$	
Reflections collected	23715	
Independent reflections	6328 [R(int) = 0.0378]	
Completeness to theta = 25.000°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8621 and 0.7835	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6328 / 0 / 374	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0663, wR2 = 0.1834	
R indices (all data)	R1 = 0.0919, wR2 = 0.2007	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.383 and -1.130 $e.Å^{-3}$	

Table S28. Bond lengths [Å] and angles [°] for lm10215.

Ni(1)-N(2)	2.011(4)	C(10)-C(11)	1.377(7)
Ni(1)-N(1)	2.014(4)	C(10)-H(10)	0.9500
Ni(1)-N(5)	2.051(4)	C(11)-C(12)	1.389(7)
Ni(1)-N(6)	2.058(4)	C(11)-H(11)	0.9500
Ni(1)-N(4)	2.179(4)	C(12)-C(13)	1.496(7)
Ni(1)-N(3)	2.186(4)	C(13)-H(13A)	0.9900
N(1)-C(1)	1.329(6)	C(13)-H(13B)	0.9900
N(1)-C(5)	1.347(6)	C(14)-H(14A)	0.9900
N(2)-C(8)	1.326(6)	C(14)-H(14B)	0.9900
N(2)-C(12)	1.332(6)	C(15)-H(15A)	0.9800
N(3)-C(15)	1.478(6)	C(15)-H(15B)	0.9800
N(3)-C(7)	1.492(6)	C(15)-H(15C)	0.9800
N(3)-C(6)	1.496(6)	C(16)-H(16A)	0.9800
N(4)-C(16)	1.485(6)	C(16)-H(16B)	0.9800
N(4)-C(14)	1.489(6)	C(16)-H(16C)	0.9800
N(4)-C(13)	1.494(6)	C(17)-C(18)	1.472(7)
N(5)-C(17)	1.116(6)	C(18)-H(18A)	0.9800
N(6)-C(19)	1.130(6)	C(18)-H(18B)	0.9800
C(1)-C(2)	1.383(7)	C(18)-H(18C)	0.9800
C(1)-C(14)	1.497(7)	C(19)-C(20)	1.464(7)
C(2)-C(3)	1.397(7)	C(20)-H(20A)	0.9800
C(2)-H(2)	0.9500	C(20)-H(20B)	0.9800
C(3)-C(4)	1.386(7)	C(20)-H(20C)	0.9800
C(3)-H(3)	0.9500	P(1)-F(6)	1.575(3)
C(4)-C(5)	1.377(7)	P(1)-F(2)	1.579(3)
C(4)-H(4)	0.9500	P(1)-F(1)	1.590(3)
C(5)-C(6)	1.501(6)	P(1)-F(5)	1.592(3)
C(6)-H(6A)	0.9900	P(1)-F(4)	1.595(3)
C(6)-H(6B)	0.9900	P(1)-F(3)	1.598(3)
C(7)-C(8)	1.515(6)	P(2)-F(11)	1.531(5)
C(7)-H(7A)	0.9900	P(2)-F(7)	1.554(3)
C(7)-H(7B)	0.9900	P(2)-F(12)	1.577(5)
C(8)-C(9)	1.374(7)	P(2)-F(9)	1.584(5)
C(9)-C(10)	1.379(7)	P(2)-F(8)	1.584(4)
C(9)-H(9)	0.9500	P(2)-F(10)	1.596(4)

N(2)-Ni(1)-N(1)	83.14(15)	N(1)-C(1)-C(14)	114.0(4)
N(2)-Ni(1)-N(5)	176.48(16)	C(2)-C(1)-C(14)	124.8(5)
N(1)-Ni(1)-N(5)	93.63(15)	C(1)-C(2)-C(3)	118.0(5)
N(2)-Ni(1)-N(6)	91.07(15)	C(1)-C(2)-H(2)	121.0
N(1)-Ni(1)-N(6)	174.05(15)	C(3)-C(2)-H(2)	121.0
N(5)-Ni(1)-N(6)	92.12(16)	C(4)-C(3)-C(2)	120.2(5)
N(2)-Ni(1)-N(4)	81.22(15)	C(4)-C(3)-H(3)	119.9
N(1)-Ni(1)-N(4)	80.42(15)	C(2)-C(3)-H(3)	119.9
N(5)-Ni(1)-N(4)	96.89(15)	C(5)-C(4)-C(3)	118.4(4)
N(6)-Ni(1)-N(4)	97.39(15)	C(5)-C(4)-H(4)	120.8
N(2)-Ni(1)-N(3)	80.46(15)	C(3)-C(4)-H(4)	120.8
N(1)-Ni(1)-N(3)	80.97(15)	N(1)-C(5)-C(4)	121.0(4)
N(5)-Ni(1)-N(3)	100.47(15)	N(1)-C(5)-C(6)	113.9(4)
N(6)-Ni(1)-N(3)	99.47(15)	C(4)-C(5)-C(6)	125.1(4)
N(4)-Ni(1)-N(3)	155.24(14)	N(3)-C(6)-C(5)	112.5(4)
C(1)-N(1)-C(5)	121.1(4)	N(3)-C(6)-H(6A)	109.1
C(1)-N(1)-Ni(1)	117.6(3)	C(5)-C(6)-H(6A)	109.1
C(5)-N(1)-Ni(1)	117.6(3)	N(3)-C(6)-H(6B)	109.1
C(8)-N(2)-C(12)	122.1(4)	C(5)-C(6)-H(6B)	109.1
C(8)-N(2)-Ni(1)	117.9(3)	H(6A)-C(6)-H(6B)	107.8
C(12)-N(2)-Ni(1)	116.7(3)	N(3)-C(7)-C(8)	110.7(4)
C(15)-N(3)-C(7)	108.6(4)	N(3)-C(7)-H(7A)	109.5
C(15)-N(3)-C(6)	108.8(3)	C(8)-C(7)-H(7A)	109.5
C(7)-N(3)-C(6)	111.3(4)	N(3)-C(7)-H(7B)	109.5
C(15)-N(3)-Ni(1)	116.7(3)	C(8)-C(7)-H(7B)	109.5
C(7)-N(3)-Ni(1)	105.3(3)	H(7A)-C(7)-H(7B)	108.1
C(6)-N(3)-Ni(1)	106.1(3)	N(2)-C(8)-C(9)	120.8(4)
C(16)-N(4)-C(14)	109.5(4)	N(2)-C(8)-C(7)	113.7(4)
C(16)-N(4)-C(13)	108.6(4)	C(9)-C(8)-C(7)	125.5(4)
C(14)-N(4)-C(13)	111.2(4)	C(8)-C(9)-C(10)	118.0(5)
C(16)-N(4)-Ni(1)	116.4(3)	C(8)-C(9)-H(9)	121.0
C(14)-N(4)-Ni(1)	105.8(3)	C(10)-C(9)-H(9)	121.0
C(13)-N(4)-Ni(1)	105.2(3)	C(11)-C(10)-C(9)	121.1(5)
C(17)-N(5)-Ni(1)	173.1(4)	C(11)-C(10)-H(10)	119.4
C(19)-N(6)-Ni(1)	169.6(4)	C(9)-C(10)-H(10)	119.4
N(1)-C(1)-C(2)	121.2(4)	C(10)-C(11)-C(12)	117.8(5)

C(10)-C(11)-H(11)	121.1	N(6)-C(19)-C(20)	178.9(6)
C(12)-C(11)-H(11)	121.1	C(19)-C(20)-H(20A)	109.5
N(2)-C(12)-C(11)	120.1(4)	C(19)-C(20)-H(20B)	109.5
N(2)-C(12)-C(13)	114.2(4)	H(20A)-C(20)-H(20B)	109.5
C(11)-C(12)-C(13)	125.6(4)	C(19)-C(20)-H(20C)	109.5
N(4)-C(13)-C(12)	111.7(4)	H(20A)-C(20)-H(20C)	109.5
N(4)-C(13)-H(13A)	109.3	H(20B)-C(20)-H(20C)	109.5
C(12)-C(13)-H(13A)	109.3	F(6)-P(1)-F(2)	91.5(2)
N(4)-C(13)-H(13B)	109.3	F(6)-P(1)-F(1)	90.10(19)
C(12)-C(13)-H(13B)	109.3	F(2)-P(1)-F(1)	91.6(2)
H(13A)-C(13)-H(13B)	107.9	F(6)-P(1)-F(5)	179.3(2)
N(4)-C(14)-C(1)	111.4(4)	F(2)-P(1)-F(5)	88.8(2)
N(4)-C(14)-H(14A)	109.3	F(1)-P(1)-F(5)	89.23(18)
C(1)-C(14)-H(14A)	109.3	F(6)-P(1)-F(4)	90.43(19)
N(4)-C(14)-H(14B)	109.3	F(2)-P(1)-F(4)	177.6(2)
C(1)-C(14)-H(14B)	109.3	F(1)-P(1)-F(4)	89.82(19)
H(14A)-C(14)-H(14B)	108.0	F(5)-P(1)-F(4)	89.30(19)
N(3)-C(15)-H(15A)	109.5	F(6)-P(1)-F(3)	90.13(18)
N(3)-C(15)-H(15B)	109.5	F(2)-P(1)-F(3)	89.2(2)
H(15A)-C(15)-H(15B)	109.5	F(1)-P(1)-F(3)	179.2(2)
N(3)-C(15)-H(15C)	109.5	F(5)-P(1)-F(3)	90.53(18)
H(15A)-C(15)-H(15C)	109.5	F(4)-P(1)-F(3)	89.36(19)
H(15B)-C(15)-H(15C)	109.5	F(11)-P(2)-F(7)	92.7(3)
N(4)-C(16)-H(16A)	109.5	F(11)-P(2)-F(12)	174.6(3)
N(4)-C(16)-H(16B)	109.5	F(7)-P(2)-F(12)	91.9(2)
H(16A)-C(16)-H(16B)	109.5	F(11)-P(2)-F(9)	86.1(3)
N(4)-C(16)-H(16C)	109.5	F(7)-P(2)-F(9)	178.2(3)
H(16A)-C(16)-H(16C)	109.5	F(12)-P(2)-F(9)	89.4(3)
H(16B)-C(16)-H(16C)	109.5	F(11)-P(2)-F(8)	94.3(3)
N(5)-C(17)-C(18)	179.1(6)	F(7)-P(2)-F(8)	91.4(2)
C(17)-C(18)-H(18A)	109.5	F(12)-P(2)-F(8)	88.6(3)
C(17)-C(18)-H(18B)	109.5	F(9)-P(2)-F(8)	87.4(2)
H(18A)-C(18)-H(18B)	109.5	F(11)-P(2)-F(10)	89.7(3)
C(17)-C(18)-H(18C)	109.5	F(7)-P(2)-F(10)	91.4(2)
H(18A)-C(18)-H(18C)	109.5	F(12)-P(2)-F(10)	87.2(3)
H(18B)-C(18)-H(18C)	109.5	F(9)-P(2)-F(10)	90.0(2)

F(8)-P(2)-F(10)	175.1(3)

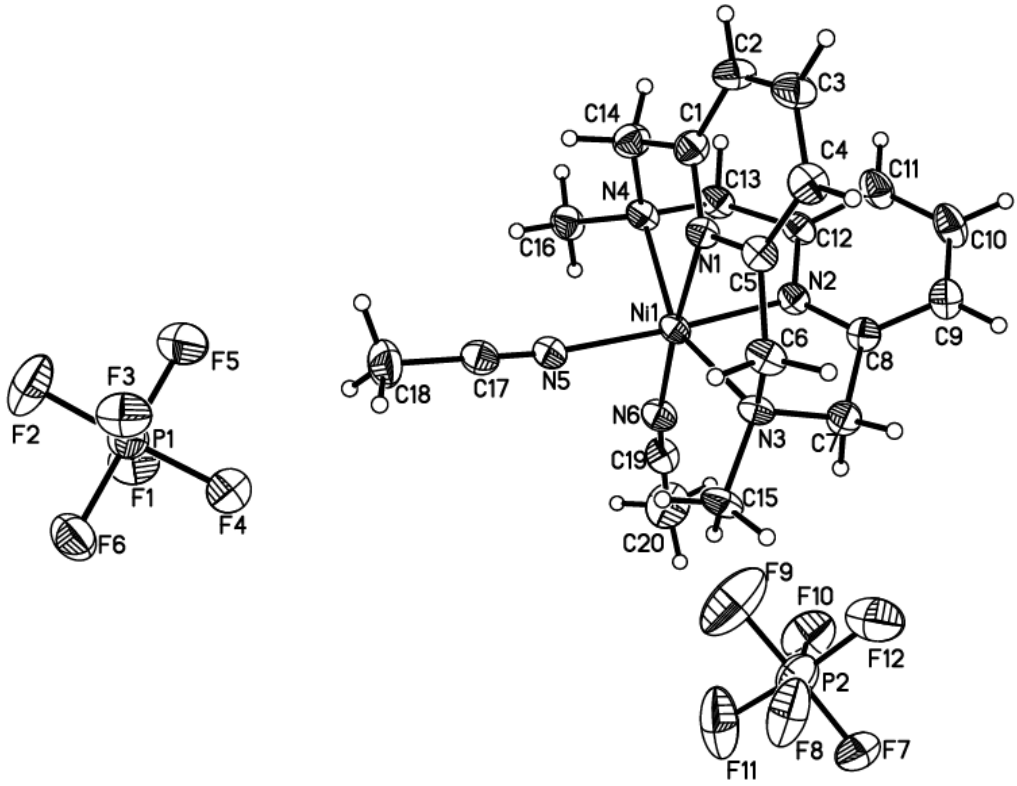


Figure S31. Projection view of lm10215 with 50% thermal ellipsoids.

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