Electronic Supplementary Material (ESI) for Chemical Science

Access to Formally Ni(I) States in a Heterobimetallic NiZn System

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Supporting Information

S1. General Procedures and Physical Methods

The synthesis of complexes **5**, 6, **7**, **8**, and **10** were conducted under ambient atmosphere without protection from oxygen or water. All other manipulations were carried out using standard Schlenk or glovebox techniques under an N_2 atmosphere. Unless noted otherwise, reagents were purchased from commercial vendors and used without further purification. [Ni(^{Me}doenH)]ClO_4, [Ni(^{Me}dopnH)]ClO_4,[1] and Me_3TACN[2] were prepared according to previously reported procedures. Dry and degassed solvents were purged with argon and passed through a column of activated alumina (S. G. Waters, Nashua, NH).

Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., degassed, and stored over 3-Å molecular sieves prior to use. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded using Varian 300 MHz and 400 MHz instruments at room temperature and reported in ppm relative to tetramethylsilane, using the residual solvent resonances as an internal reference. Multiplicities are indicated as s (singlet), d (doublet), and t (triplet).

Elemental analyses were performed by Midwest Microlabs, LLC., Indianapolis, IN. IR measurements were performed using a Bruker Alpha spectrometer equipped with a diamond ATR. X-band EPR spectra were obtained on a Bruker EMX spectrometer and simulated using Easyspin. Electrochemical measurements were carried out in a glovebox under an N_2 atmosphere in a single-compartment cell and were recorded with a CH Instruments 630-C Electrochemistry Analyzer using a CHI Version 8.09 software package. UV-Vis measurements were acquired on a Cary 50 UV/Vis Spectrophotometer using a 1-cm two-window quartz cuvette.

Nickel K-edge data were collected through the Molecular Observatory at the Stanford Synchrotron Radiation Lightsource (SSRL) on beamline 12-2, with the ring operating at 3 GeV and 350 mA. A double-crystal monochromator was used for energy selection and data were measured in fluorescence mode. Data collected in 1 eV increments with a 2.0 s exposure time were averaged over four runs and merged with an additional four runs collected at a 0.5 eV offset.

Crystallographic Details. X-ray diffraction studies were carried out at the Beckman Institute Crystallography Facility on a Brüker KAPPA APEX II or Brüker SMART 1000 diffractometer and solved using SHELX v. 6.14. The crystals were mounted on a glass fiber with Paratone-N oil. Data was collected at 100 K using Mo Kα (λ = 0.71073 Å) radiation and solved using SHELXS and refined against *F2* on all data by full-matrix least squares with SHELXL. X-ray quality crystals were grown as described in the experimental procedures.

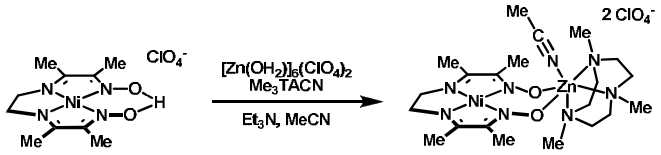
Computational Methods. Geometry optimizations were performed using the Gaussian03 package.[3] The B3LYP exchange-correlation functional was employed with a 6-31G(d) basis set. A full frequency calculation was performed on each structure in order to verify the absence of negative vibrational frequencies. Molecular orbital and spin density isosurfaces are displayed at isovalues of 0.04 and 0.004 respectively.

[1] Uhlig, E.; Friedrich, M. *Anorg. Allg. Chem.* **1966**, *343*, 299–307.

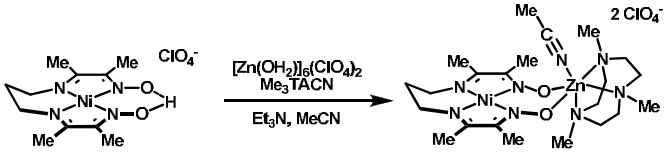
[2] Niibayashi, S.; Hayakawa, H.; Jin, R.-H.; Nagashima, H. *Chem. Commun*., **2007**, 1855–1857.

[3] Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

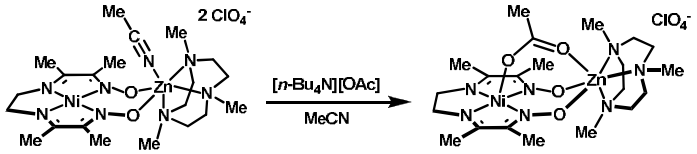
S2. Synthetic Procedures and Characterization Data



[Ni(^{Me}doen)Zn(Me$_3$TACN)(MeCN)](ClO$_4$)$_2$ (5). 376.8 mg of Me$_3$TACN (2.2 mmol, 1.1 eq) was dissolved in 250 mL of MeOH. 819.3 mg of [Zn(H$_2$O)$_6$](ClO$_4$)$_2$ (2.2 mmol, 1.1eq) was added followed by 766.8 mg of [Ni(^{Me}doenH)]ClO$_4$ (2.0 mmol, 1.0 eq). 5 mL of Et$_3$N was added, causing the solution to turn dark red in color, and the heterogeneous reaction mixture was stirred at ambient temperature for 24 h during which time the reaction became homogeneous. The mixture was concentrated under reduced pressure, the residue was redissolved in MeCN, and the solution was reconcentrated to a dark red oil. The residue was taken up in CH$_2$Cl$_2$ and filtered through celite in order to remove a dark brown precipitate. The filtrate was concentrated, and the product was purified by successively redissolving the material in 10 mL of acetonitrile, precipitating the product with 200 mL of Et$_2$O, and decanting the solution away from the precipitated material. 1.380 g of **5** (1.82 mmol, 91% yield) was isolated as a red solid. Single crystals suitable for XRD were obtained by diffusion of Et$_2$O vapor into a concentrated solution in acetonitrile. ^{1}H NMR (400 MHz, CD$_3$CN) δ = 3.85 (s, 4 H), 2.74 (s, 12 H), 2.51 (s, 9 H), 2.15 (s, 12 H). ^{13}C{^{1}H} NMR (101 MHz, CD$_3$CN) δ = 178.7, 159.0, 55.2, 53.9, 47.3, 17.5, 12.6. UV-Vis (MeCN, nm {cm^{-1} M^{-1}}: 258 {22,000}, 309 {8400}, 382 {sh}, 406 {sh}, 422 {3200}, 470 {sh}, 530 {sh}. ESI-MS *m/z*: 616.2, 618.2, 620.1 [Ni(^{Me}doen)Zn(Me$_3$TACN)(ClO$_4$)]$^+$. Anal. Cald for C$_{21}$H$_{40}$Cl$_2$N$_8$NiO$_{10}$Zn: C, 33.20; H, 5.31; N, 14.75; Found: C, 33.37; H, 5.21; N, 14.68.

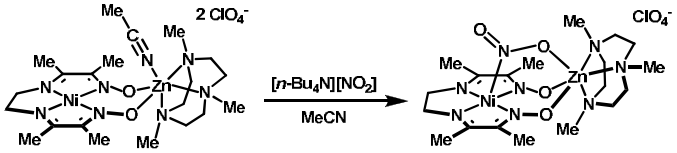


[Ni(^{Me}dopn)Zn(Me$_3$TACN)(MeCN)](ClO$_4$)$_2$ (6). 188.4 mg of Me$_3$TACN (1.1 mmol, 1.1 eq) was dissolved in 100 mL MeOH. 409.6 mg of [Zn(H$_2$O)$_6$](ClO$_4$)$_2$ (1.1 mmol, 1.1 eq) was added followed by 397.4 mg of [Ni(^{Me}dopnH)]ClO$_4$ (1.0 mmol, 1.0 eq). 2 mL of Et$_3$N was added, and the reaction mixture was stirred at reflux for 2 h. The mixture was cooled to room temperature and concentrated to dryness under reduced pressure. The residue was redissolved in a minimal amount of CH$_2$Cl$_2$, and the mixture was filtered through a plug of celite to remove any insoluble dark brown material. The filtrate was concentrated. The residue was redissolved in a minimal quanitity of MeCN, and layering of Et$_2$O yielded 502.1 mg of red-orange crystals (0.65 mmol, 65% yield) suitable for XRD. ^{1}H NMR (400 MHz, CD$_3$CN) δ = 3.22 - 3.11 (m, 4 H), 2.76 (s, 13 H), 2.48 (s, 9 H), 2.17 (s, 6 H), 2.14 (s, 6 H). ^{13}C{^{1}H} NMR (101 MHz, CD$_3$CN) δ = 178.9, 157.0, 53.5, 49.1, 46.8, 28.2, 17.6, 12.9. UV-Vis (MeCN, nm {cm^{-1} M^{-1}}: 252 {17,100}, 320 {6100}, 384 {3300}, 405 {3500}, 460 {sh}, 520 {sh}. ESI-MS *m/z*: 630.0, 632.0, 634.0 [Ni(^{Me}dopn)Zn(Me$_3$TACN)(ClO$_4$)]$^+$. Anal. Cald for C$_{22}$H$_{42}$Cl$_2$N$_8$NiO$_{10}$Zn: C, 34.16; H, 5.47; N, 14.48; Found: C, 33.96; H, 5.54; N, 14.27.

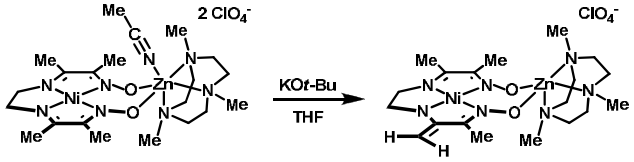


[(μ-OAc)Ni(^{Me}doen)Zn(Me$_3$TACN)]ClO$_4$ (7). 38.0 mg of **5** (0.05 mmol, 1.0 eq) was dissolved in 500 μL of MeCN. 18.1 mg of [*n*-Bu$_4$N][OAc] (0.06 mmol, 1.2 eq) was added as a solution in 500 μL of MeCN. Upon addition, the initially red solution immediately turned dark-brown in color. Diffusion of Et$_2$O vapor into the reaction mixture produced 26.4 mg of 7

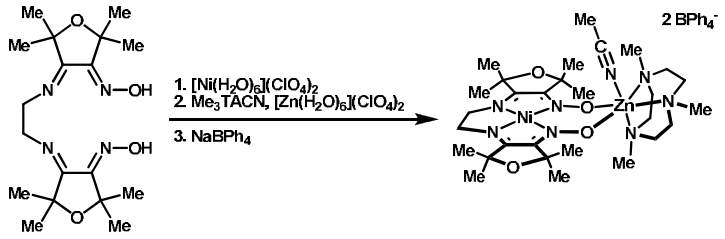
as dark brown crystals (0.39 mmol, 78% yield). ^{1}H NMR (400 MHz, CD_3CN) δ = 3.91 (s, 4 H), 2.89 - 2.60 (m, 12 H), 2.44 (s, 9 H), 2.00 (s, 6 H), 1.92 (s, 3 H), 1.89 (s, 6 H). $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3CN) δ = 178.6, 172.3, 154.2, 55.5, 53.9, 47.3, 26.2, 16.6, 12.0. Anal. Cald for $C_{21}H_{40}ClN_7NiO_8Zn$: C, 37.19; H, 5.95; N, 14.46; Found: C, 37.50; H, 5.94; N, 14.50.



[(μ-NO_2)Ni(^{Me}doen)Zn(Me_3TACN)]ClO_4 (8). 38.0 mg of **5** (0.05 mmol, 1.0 eq) was dissolved in 500 μL of MeCN. 17.3 mg of [*n*-Bu_4N][NO_2] (0.06 mmol, 1.2 eq) was added as a solution in 500 μL of MeCN. Upon addition, the initially red solution immediately turned dark in color. Diffusion of Et_2O vapor into the reaction mixture produced 28.9 mg of **8** as dark brown crystals (0.43 mmol, 87% yield). ^{1}H NMR (400 MHz, CD_3CN) δ = 3.96 (s, 4 H), 2.93 - 2.68 (m, 13 H), 2.45 (s, 9 H), 2.03 (s, 6 H), 1.89 (s, 6 H). $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3CN) δ = 174.4, 154.6, 55.9, 54.0, 47.2, 16.9, 12.0. Anal. Cald for $C_{19}H_{37}ClN_8NiO_8Zn$: C, 34.31; H, 5.61; N, 16.85; Found: C, 35.92; H, 5.81; N, 16.56.[4]



(9). 76.0 mg of **5** (0.1 mmol, 1.0 eq) and 11.2 mg of KO*t*-Bu (0.1 mmol, 1.0 eq) were taken up in 2 mL of MeCN. The dark green mixture was stirred at room temperature, and after 30 min, the mixture was concentrated to dryness under vacuum. The residue was taken up in THF, and filtered through a short plug of celite. Darkly colored crystals form from the filtrate upon standing at room temperature for 24 h. The solution was decanted, and the solid material was washed with two 1-mL portions of THF and two 5-mL portions of Et_2O. After drying under reduced pressure, 26.4 mg of **9** was isolated as a green powder (0.043 mmol, 43% yield). Combustion analysis was consistent with a composition lacking associated solvent molecules. ^{1}H NMR (400 MHz, CD_3CN) δ = 4.01 (s, 1 H), 3.80 (t, *J* = 5.5 Hz, 2 H), 3.75 (s, 1 H), 3.17 (t, *J* = 5.9 Hz, 2 H), 2.79 - 2.62 (m, 14 H), 2.56 (s, 10 H), 2.01 (t, *J* = 1.3 Hz, 3 H), 1.92 (s, 3 H), 1.88 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (101MHz, CD_3CN) δ = 170.1, 160.3, 157.9, 154.9, 82.6, 56.6, 53.9, 53.7, 47.6, 16.3, 12.3, 11.9. UV-Vis (THF, nm {cm^{-1} M^{-1}}: 255 {30,000}, 315 {sh}, 385 {sh}, 355 {5100}, 453 {3700}, 586 {2600}. Anal. Cald for $C_{19}H_{36}ClN_7NiO_6Zn$: C, 36.92; H, 5.87; N, 15.86; Found: C 36.94, H 5.85, N 15.78.

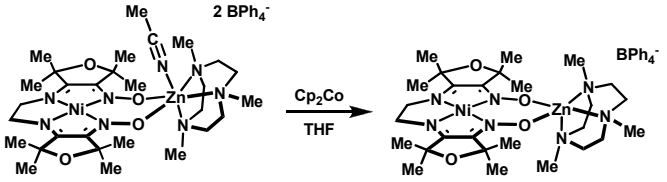


[Ni(^{TMF}doen)Zn(Me_3-tacn)(MeCN)]$(BPh_4)_2$ (10). 439.8 mg of the ^{TMF}doenH_2 ligand[5] (1.2 mmol, 1.2 eq) and 365.7 mg of [$Ni(H_2O)_6$]$(ClO_4)_2$ were stirred in 20 mL of EtOH at room temperature. Over the course of 2 h, a homogeneous red-orange

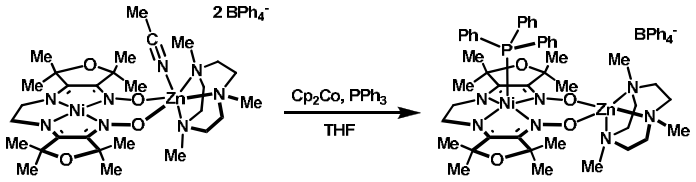
[4] Crystalline samples of **7** retain Et_2O under vacuum. This solvent is observed in the ^{1}H NMR spectrum and can account for deviations in the combustion analysis.

[5] The ligand was prepared using the same procedure reported by Packard with 1,3-diaminoethane in the place of 1,3-diaminopropane: Kiani, S.; Staples, R. J.; Treves, S. T.; Packard, A. B. *Polyhedron*, **2009**, *28*, 775–781. 1.62 g of 4-(hydroxyimino)-2,2,5,5-tetramethyldihydrofuran-3(2H)-one (9.44 mmol, 2.0 eq) and 284 mg of 1,2-diaminoethane (4.72 mmol, 1.0 eq) were stirred in 20 mL of EtOH for 4 days at room temperature. The precipitated material was

solution was formed. This solution was then added to mixture of 239.7 mg of Me_3TACN (1.4 mmol, 1.4 eq) and 521.3 mg of $[Zn(H_2O)_6](ClO_4)_2$ in 50 mL of MeCN. 280 µL of Et_3N (2.0 mmol, 2.0 eq) was added dropwise, and the color of the solution was observed to darken. 1.6427 g of $NaBPh_4$ (4.8 mmol, 4.8 eq) was added, and the reaction mixture was stirred at room temperature for 2 h. The crude mixture was concentrated to a 5-mL total volume under reduced pressure, and 100 mL of Et_2O was added. The cloudy, brown solution was decanted away from the red precipitate, which was then washed with several portions of Et_2O. A minimal amount of CH_2Cl_2 was added to the precipitate in order to dissolve the red material. The mixture was filtered through a medium-porosity glass frit in order to remove the colorless insoluble material, and the filtrate was concentrated to dryness under reduced pressure. The residue was redissolved in 2 mL of MeCN and allowed to stand at room temperature for 12 h, during which time red crystals separated from solution. The solution was then decanted away from the red crystals, and the crystals were washed with three 5-mL portions of 9:1 Et_2O/MeCN followed by one 5-mL portion of Et_2O. Single crystals of the mono-perchlorate mono-tetraphenylborate salt, suitable for XRD, were obtained by slow diffusion of Et_2O vapor into a MeCN solution. The ClO_4^- was exchanged for BPh_4^- by briefly sonication a mixture of the mono-perchlorate mono-tetraphenylborate salt and 344 mg of $NaBPh_4$ in CH_2Cl_2, and filtering the mixture through a short celite plug. 442.3 mg of **10** (0.33 mmol, 33% yield) was obtained as red-orange crystals after by Et_2O vapor diffusion into a concentrated MeCN solution. ^{1}H NMR (400 MHz, CD_3CN) δ = 7.27 (m, 16 H), 6.99 (t, *J* = 7.3 Hz, 16 H), 6.89 - 6.79 (m, 8 H), 3.80 (s, 4 H), 2.81 - 2.62 (m, 12 H), 2.51 (s, 9 H), 1.43 (s, 24 H). ^{13}C{^{1}H} NMR (101 MHz, CD_3CN) d = 186.6, 168.6, 165.3 (q, $^1J_{B\text{-}C}$ = 49.5 Hz), 137.1, 127.1, 127.1, 127.0, 127.0, 123.2, 78.6, 77.8, 54.2, 53.9, 47.6, 26.4, 26.1. UV-Vis (MeCN, nm {cm^{-1} M^{-1}}: 262 {29,000}, 290 {sh}, 329 {8000}, 417 {3000}, 443 {3200}, 510 {sh}, 560 {sh}. Anal. Cald for $C_{77}H_{92}B_2N_8NiO_4Zn$: C, 69.05; H, 6.92; N, 8.37. Found: C, 69.05; H, 6.97; N, 8.42.



[Ni(^TMF doen)Zn(Me$_3$TACN)]BPh$_4$ (11). 107 mg of **10** (1.0 eq, 0.08 mmol) and 21.2 mg of Cp_2Co (1.4 eq, 0.112 mmol) were taken up in 4 mL of THF and stirred at room temperature for 30 min. During this time, the orange-red solid material dissolved, and the solution turned dark green with concomitant formation of a colorless precipitate. 8 mL of pentane was added to precipitate the product, and the mixture was filtered through a short plug of celite. The green solid material was dissolved and eluted through the celite plug with six 1-mL portions of THF. Concentration under reduced pressure yielded 63.6 mg of **11** (0.065 mmol, 81%) as a green-brown plate-like polycrystalline solid. Single crystals suitable for XRD were obtained by diffusion of pentane vapor into a THF solution at room temperature. Single crystals of the THF adduct were obtained by diffusion of pentane vapor into a THF solution at –30 °C. UV-Vis (THF): 380 {sh}, 470 {2800}, 542 {1000}, 623 {1100}. Anal. Cald for $C_{51}H_{69}BN_7NiO_4Zn$: C, 62.57; H, 7.10; N, 10.01. Found: C, 62.25; H, 7.12; N, 9.91.

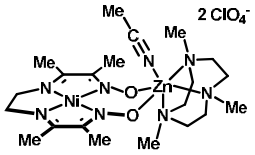


[(PPh$_3$)Ni(^TMF doen)Zn(Me$_3$TACN)]BPh$_4$ (12). 40.2 mg of **10** (0.03 mmol, 1.0 eq), 9.4 mg of PPh_3 (1.4 eq), and 7.9 mg of Cp_2Co (0.036 1.2 eq) were taken up in 2 mL of THF and stirred at room temperature for 30 min. During this time, the orange-red solid material dissolved, and the solution turned dark green-blue with concomitant formation of a colorless precipitate. 8 mL of pentane were added to precipitate the product, and the mixture was filtered through a short plug of

isolated by filtration through a glass-fritted funnel and washed with two 5-mL portions of EtOH and Et_2O. 1.05 g of the $^{TMF}doenH_2$ ligand (2.87 mmol, 61% yield) was isolated as a white solid.

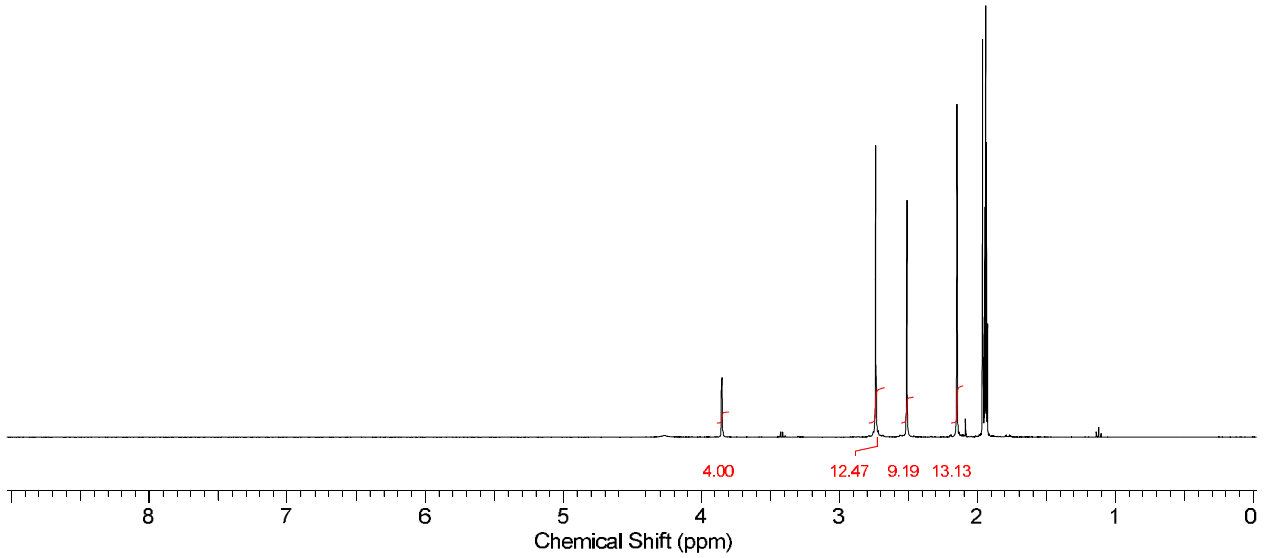
celite. The green solid material was dissolved and eluted through the celite plug with three 1-mL portions of THF. After drying under reduced pressure, 32.1 mg of dark green-blue needles (0.026 mmol, 86% yield) were isolated. Single crystals suitable for XRD were obtained by diffusion of pentane vapor into a THF solution of **12** at –30 °C. UV-Vis: 267 {28,000}, 380 {sh}, 434 {2000}, 634 {1300}. Anal. Cald for $C_{69}H_{84}BN_7NiO_4PZn$: C, 66.76; H, 6.82; N, 7.90. Found: C, 65.91; H, 6.71; N, 8.04.

S3. NMR, IR, and UV-Vis Spectra

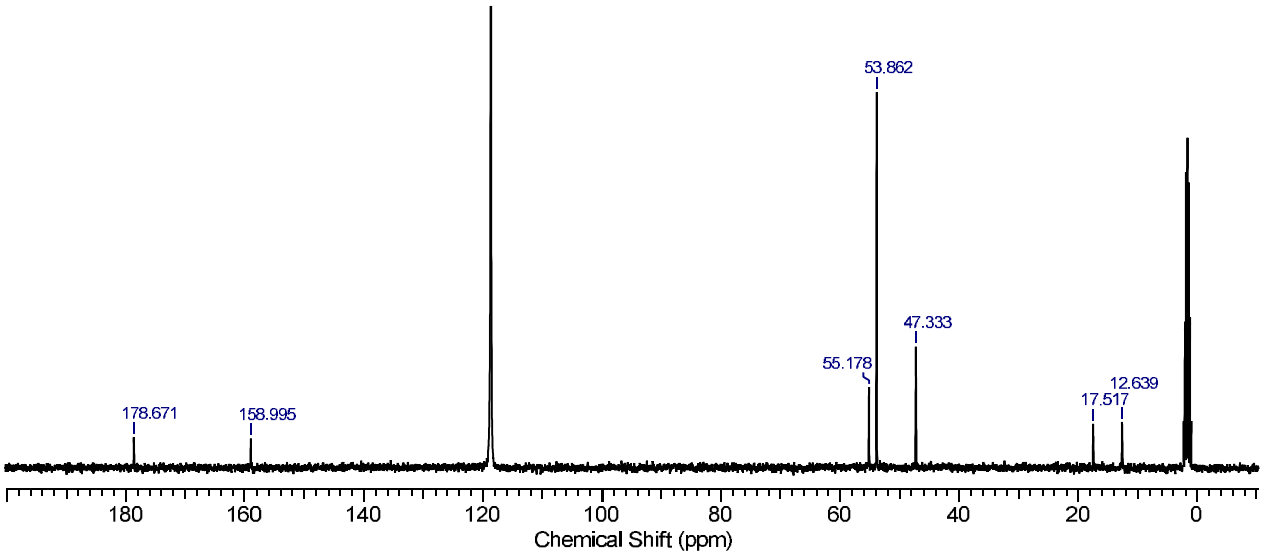


(5)

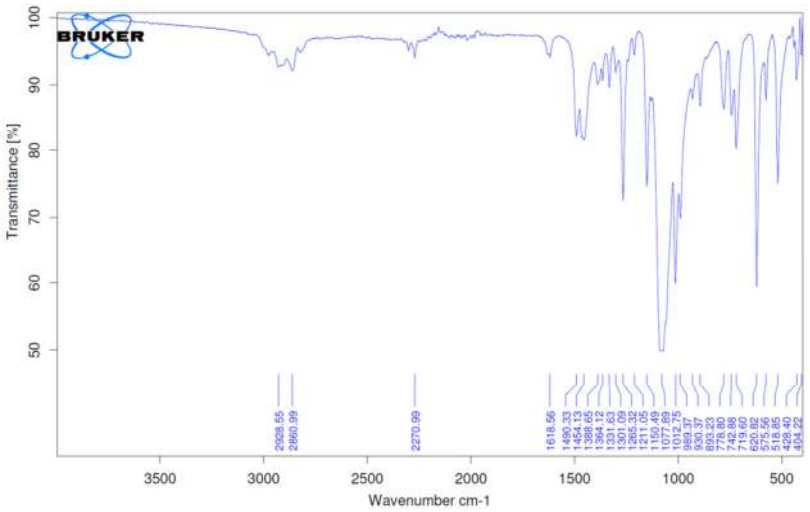
^{1}H NMR (CD_3CN)

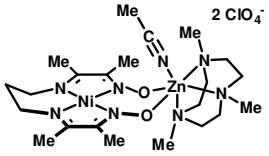


^{13}C{^{1}H} NMR (CD_3CN)



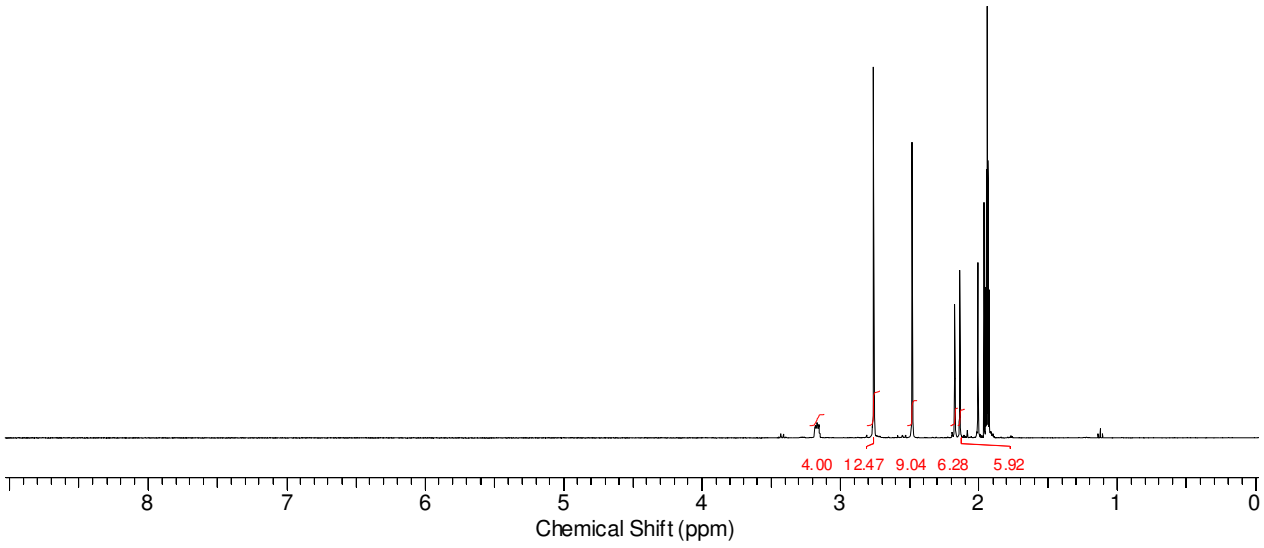
ATR-IR (solid)



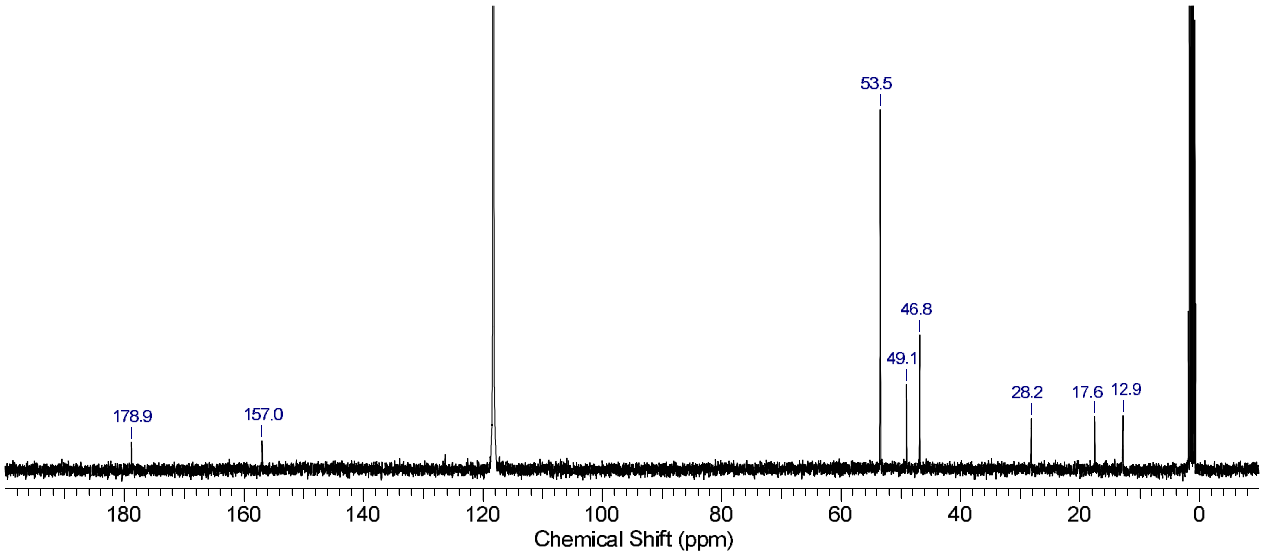


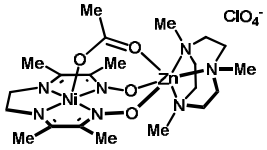
(6)

^{1}H NMR (CD_3CN)



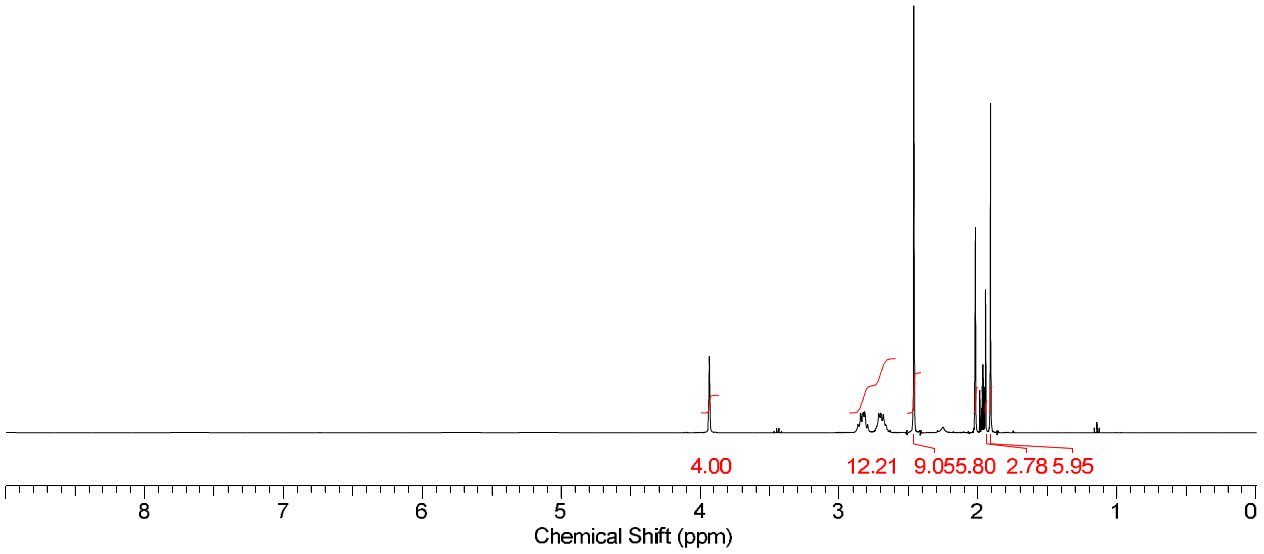
$^{13}C\{^{1}H\}$ NMR (CD_3CN)



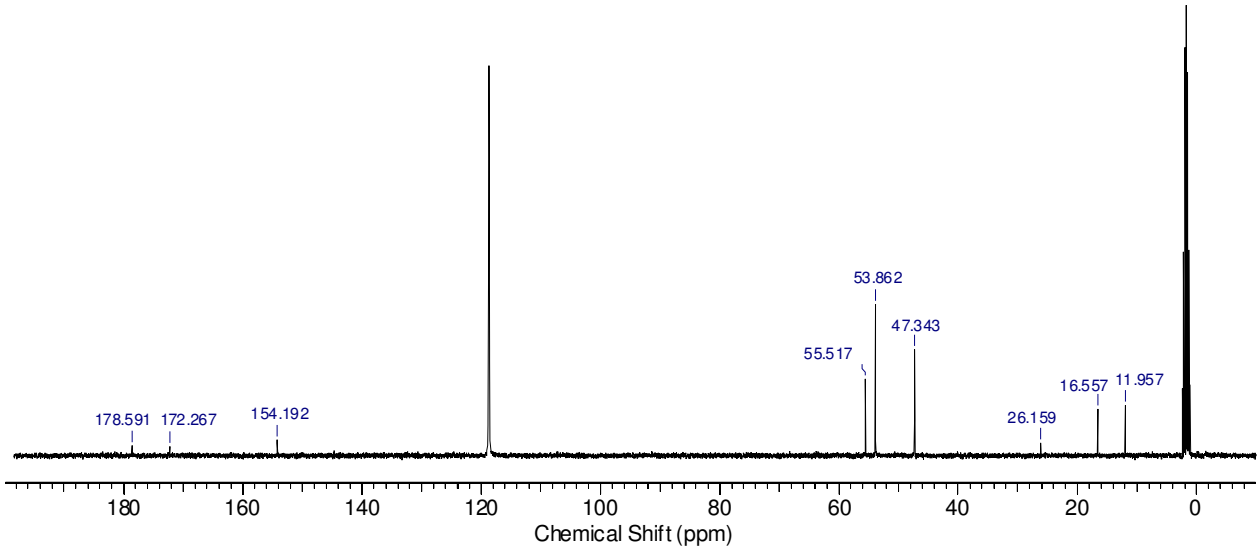


(7)

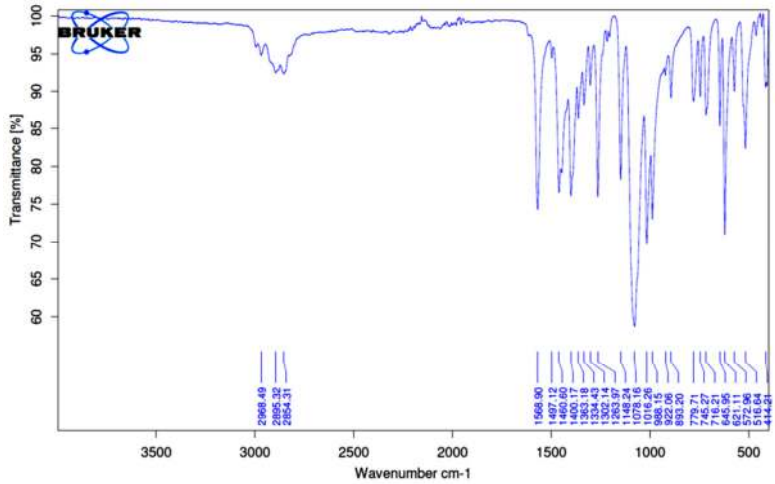
^{1}H NMR (CD_3CN)

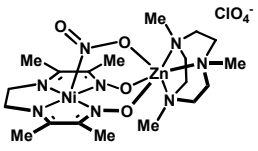


$^{13}C\{^{1}H\}$ NMR (CD_3CN)



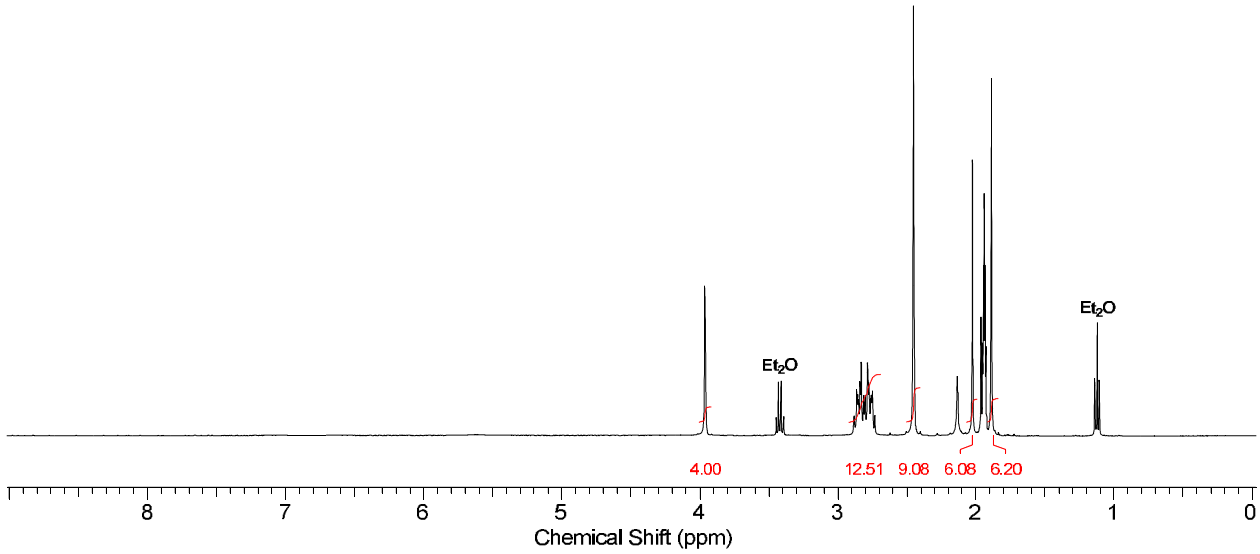
ATR-IR (solid)



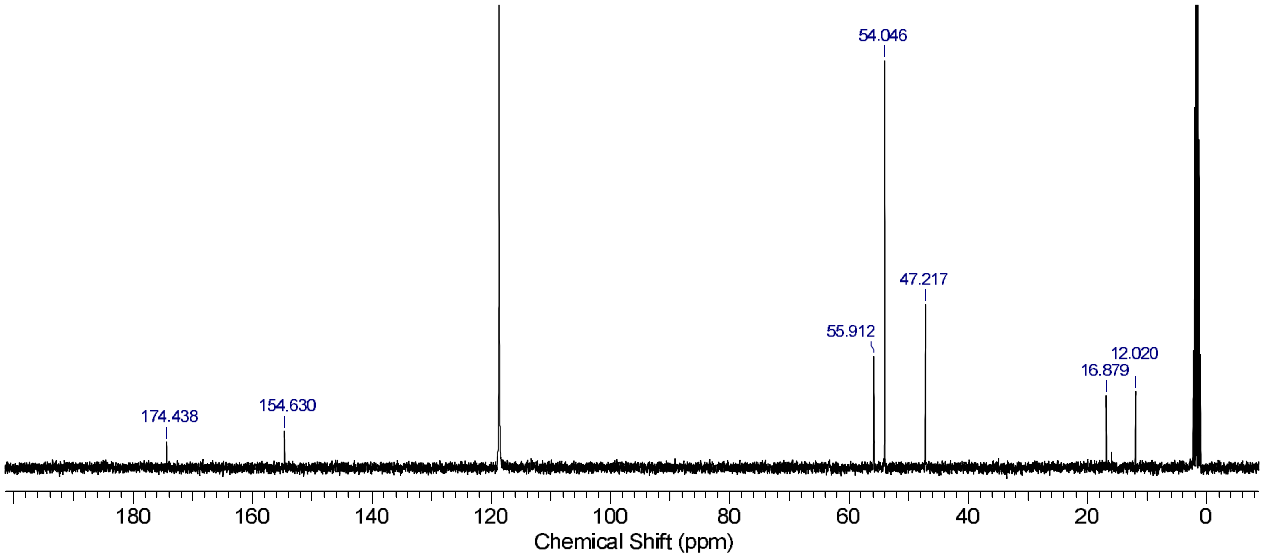


(8)

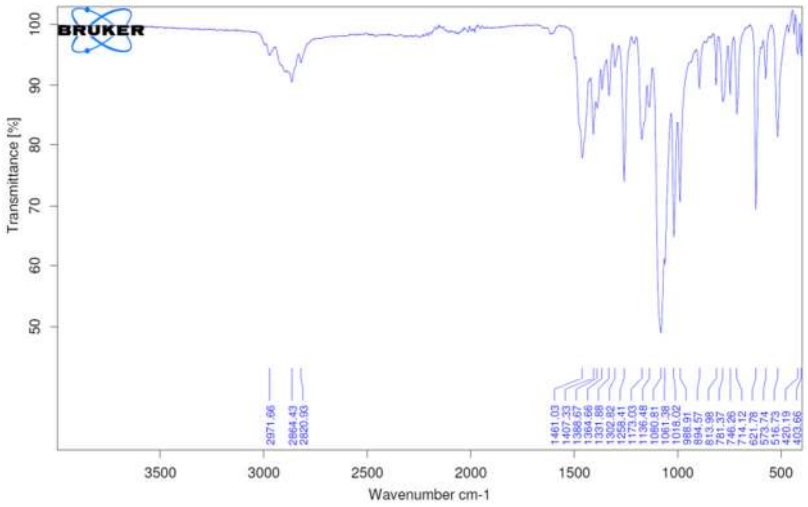
^{1}H NMR (CD_3CN)

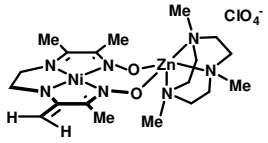


^{13}C{^{1}H } NMR (CD_3CN)



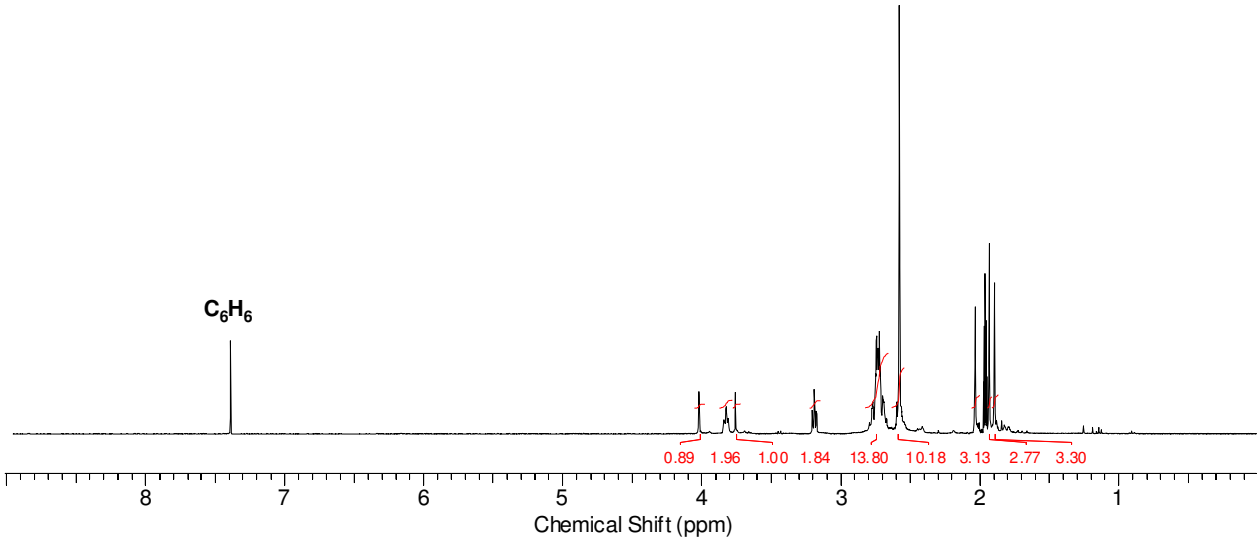
ATR-IR (solid)



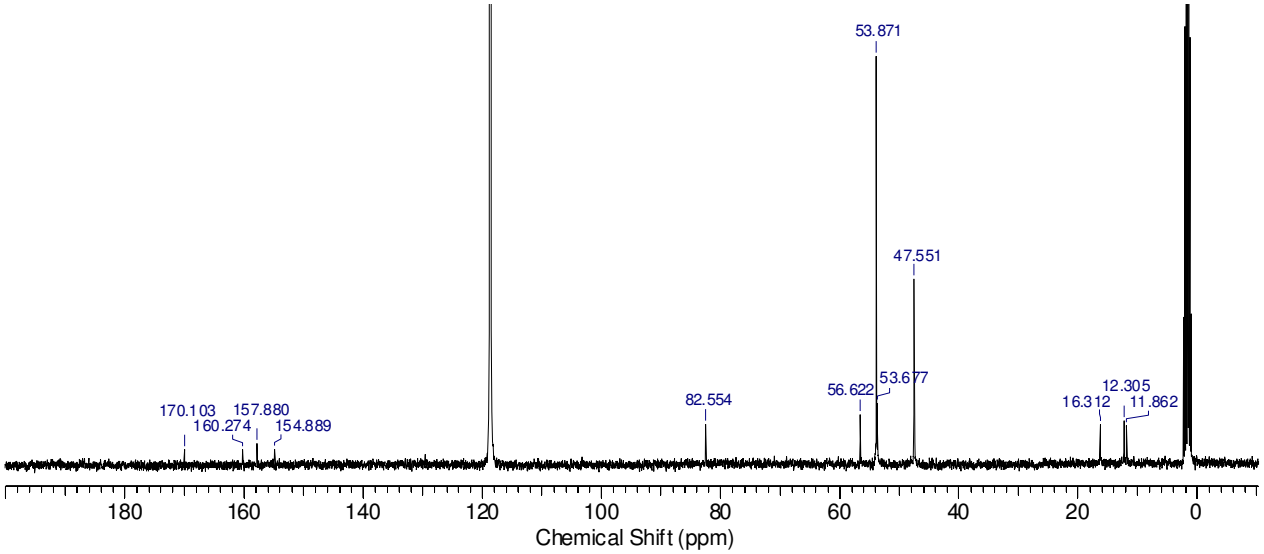


(9)

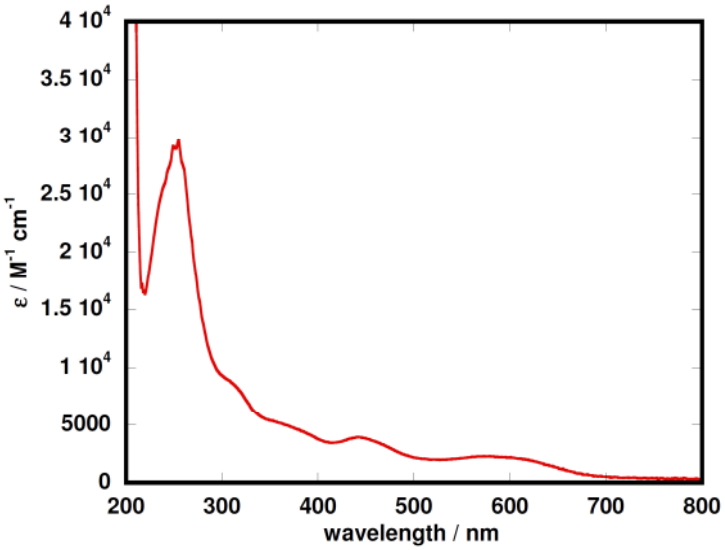
^{1}H NMR (CD_3CN)



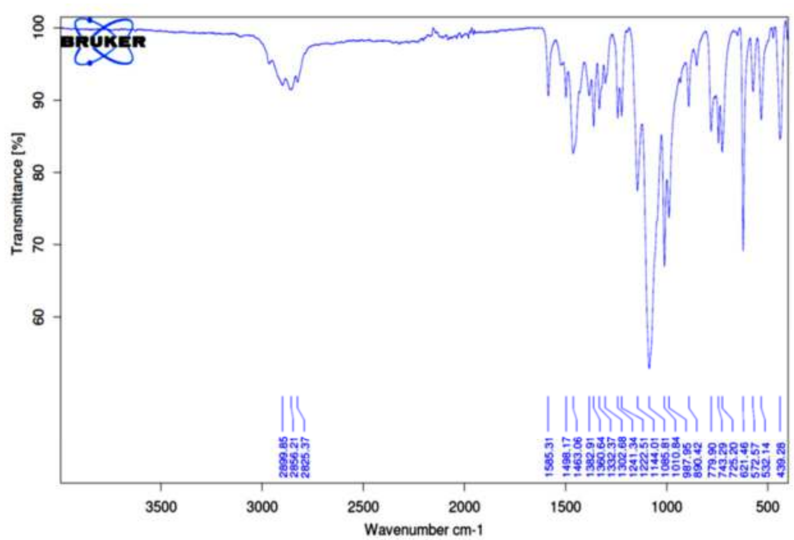
$^{13}C\{^{1}H\}$ NMR (CD_3CN)

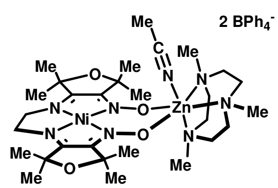


UV-Vis (MeCN)



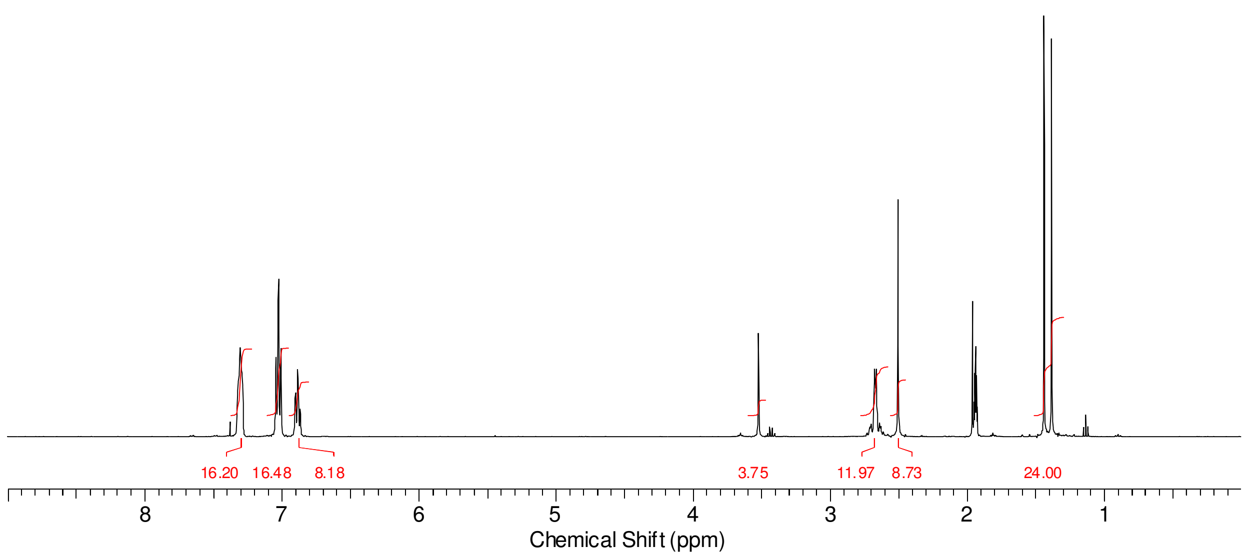
ATR-IR (solid)



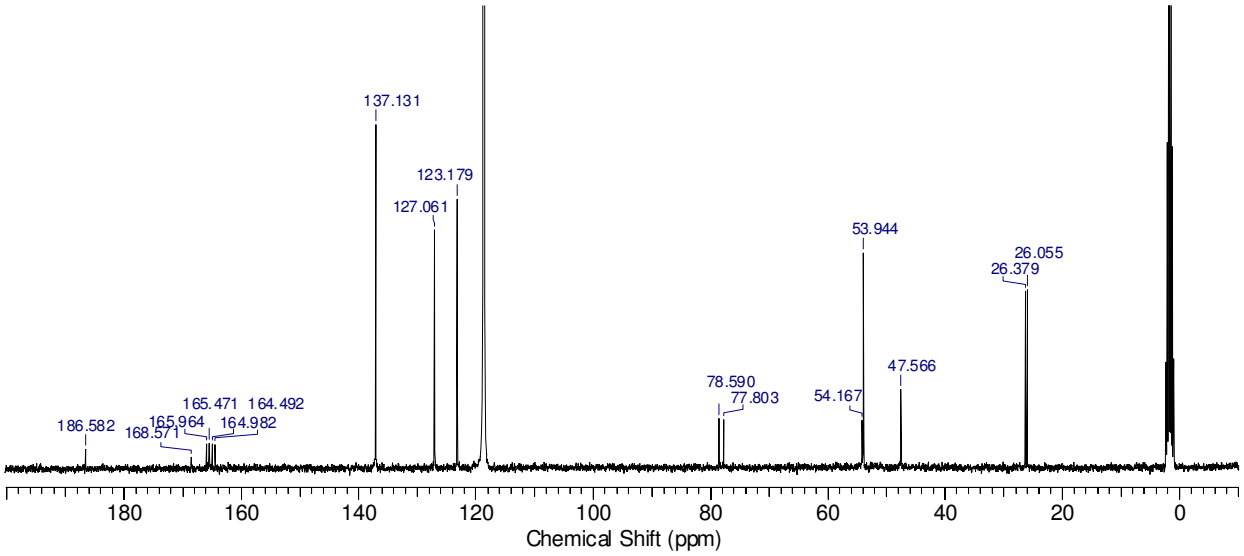


(10)

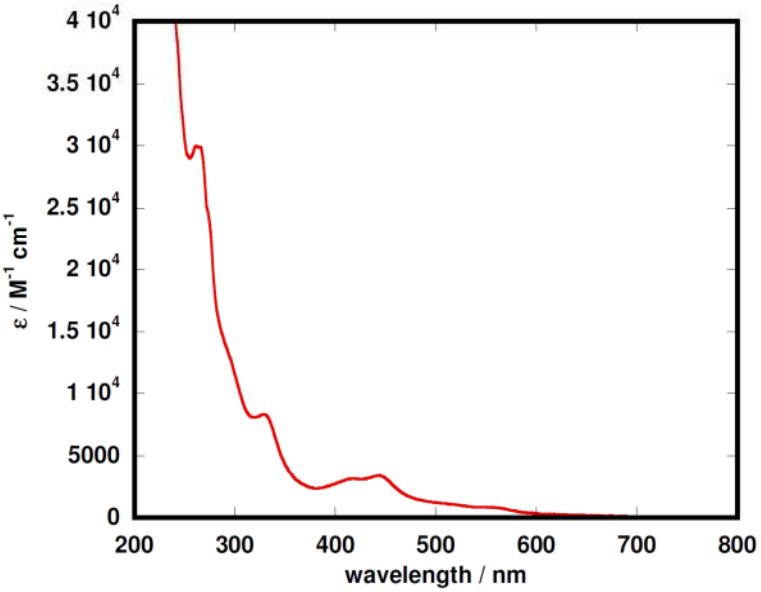
^{1}H-NMR (CD_3CN)



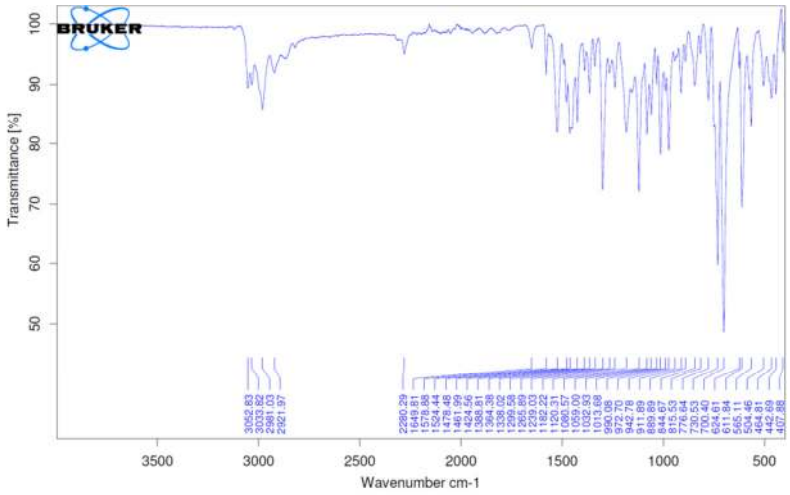
$^{13}C\{^{1}H\}$-NMR (CD_3CN)

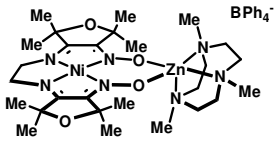


UV-Vis (MeCN)



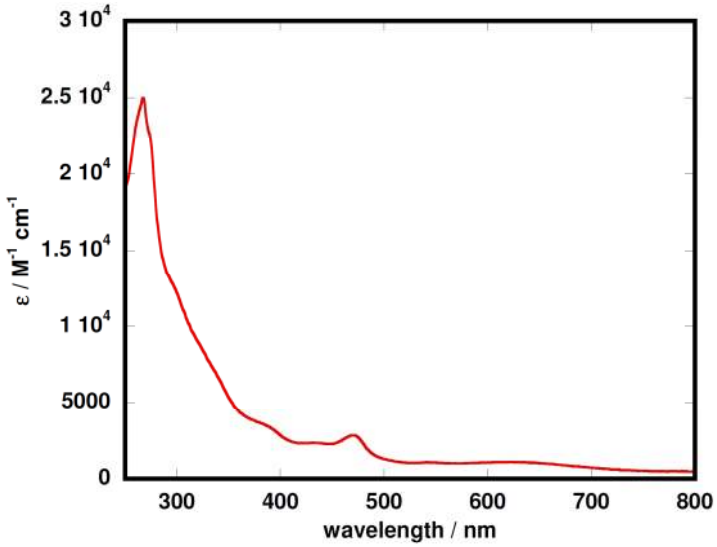
ATR-IR (solid)



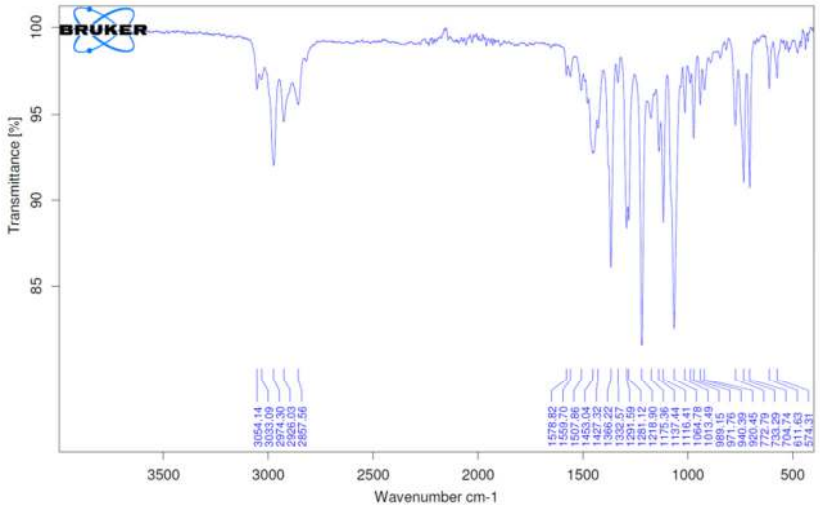


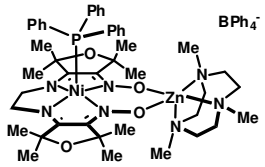
(11)

UV-Vis (THF)



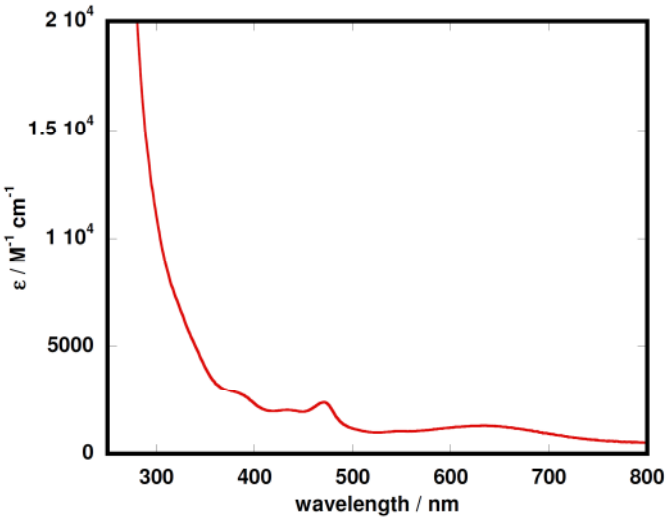
ATR-IR (solid)



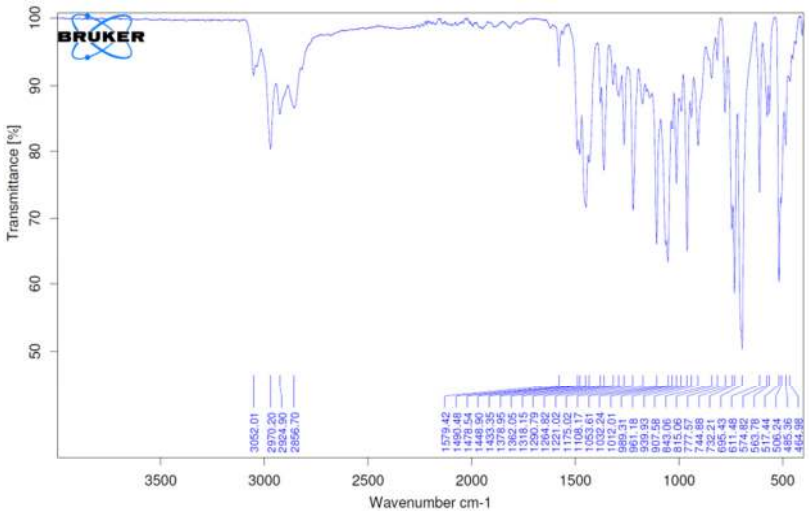


(12)

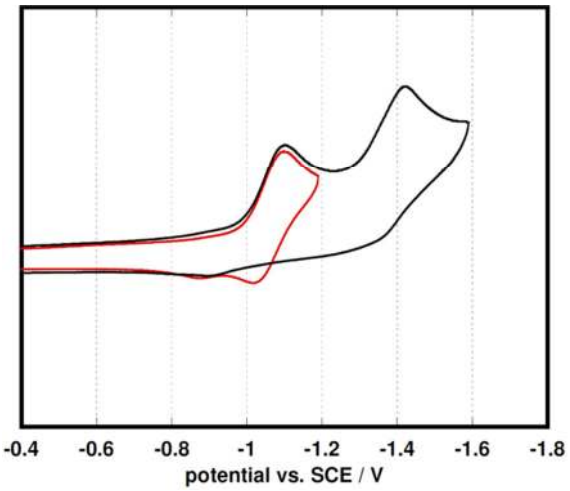
UV-Vis (THF)



ATR-IR (solid)

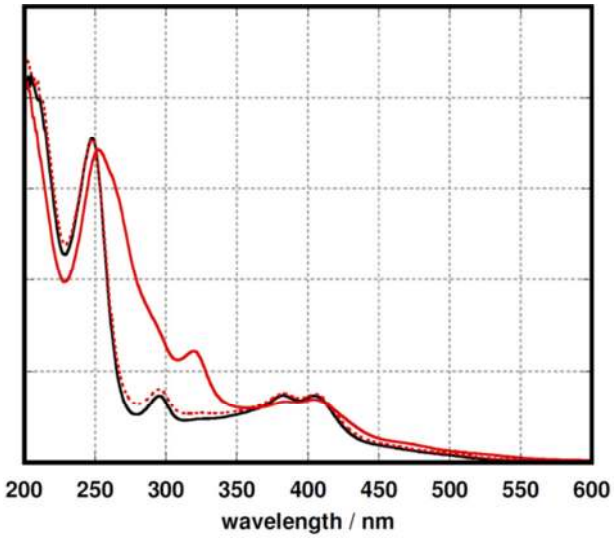

BRUKER
Transmittance [%]
100
90
80
70
60
50
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3052.01
2970.20
2924.90
2856.70
1579.42
1493.48
1478.54
1448.90
1433.35
1378.95
1362.05
1316.15
1290.79
1264.62
1221.02
1175.02
1106.17
1053.61
1029.24
1012.01
989.31
961.18
909.93
880.58
843.06
815.06
777.57
748.88
732.21
695.43
611.48
574.82
557.78
517.44
506.24
485.36
464.98

S4. Cyclic Voltammogram for [Ni(^{Me}dopn)Zn(Me_3TACN)(MeCN)](ClO_4)$_2$

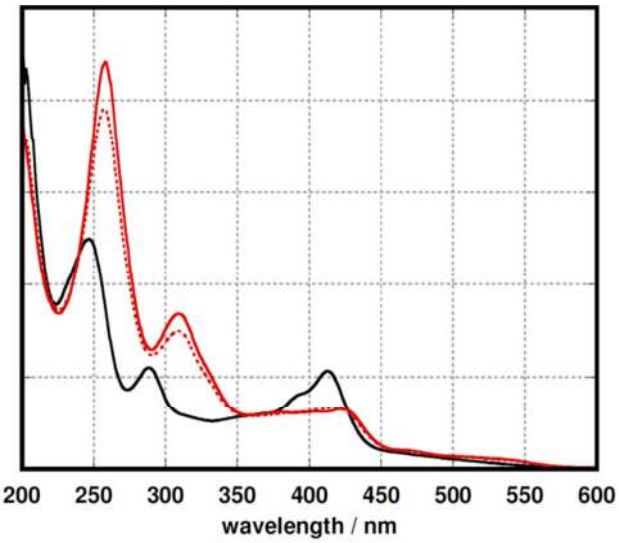


0.5 mM [Ni(^{Me}dopn)Zn(Me_3TACN)(MeCN)](ClO_4)$_2$ (**6**) in MeCN; 0.1 M [*n*-Bu_4N][ClO_4] supporting electrolyte; 100 mV/s scan rate; glassy carbon working electrode; internally referenced to the Fc/Fc^+ redox couple at + 0.38 V vs. SCE.

S5. UV-Vis Stability Studies of Complexes 5 and 6 Toward Protonolysis

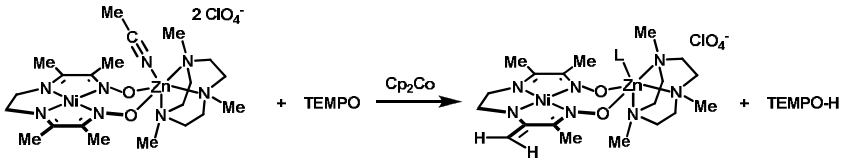


(black, solid) [Ni(^{Me}dopnH)]ClO_4
(red, solid) [Ni(^{Me}dopn)Zn(Me_3TACN)(MeCN)]$(ClO_4)_2$
(red, dotted) [Ni(^{Me}dopn)Zn(Me_3TACN)(MeCN)]$(ClO_4)_2$ + 10 eq AcOH



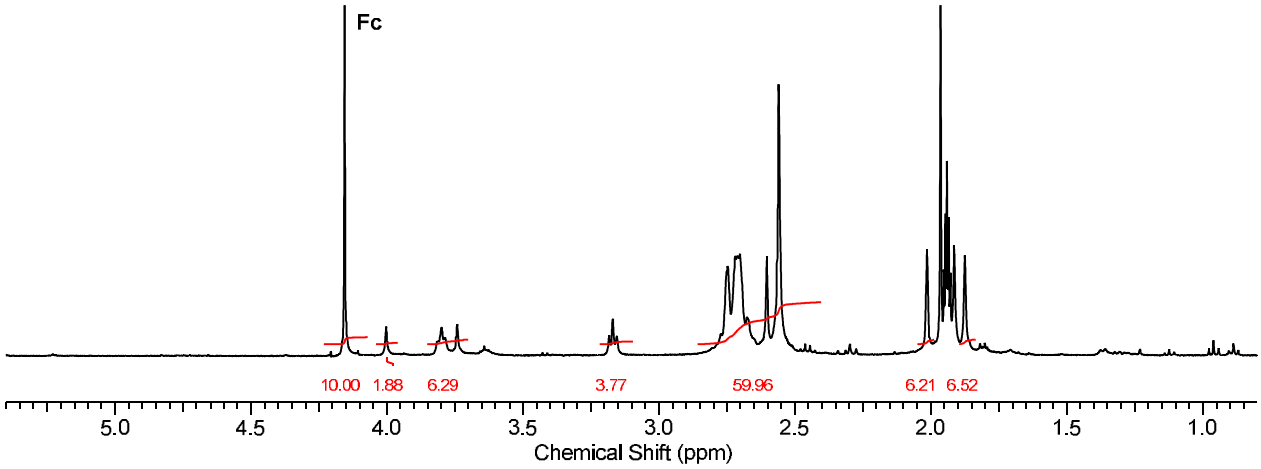
(black, solid) [Ni(^{Me}doenH)]ClO_4
(red, solid) [Ni(^{Me}doen)Zn(Me_3TACN)(MeCN)]$(ClO_4)_2$
(red, dotted) [Ni(^{Me}doen)Zn(Me_3TACN)(MeCN)]$(ClO_4)_2$ + 10 eq AcOH

S6. NMR Studies of Reactions with TEMPO



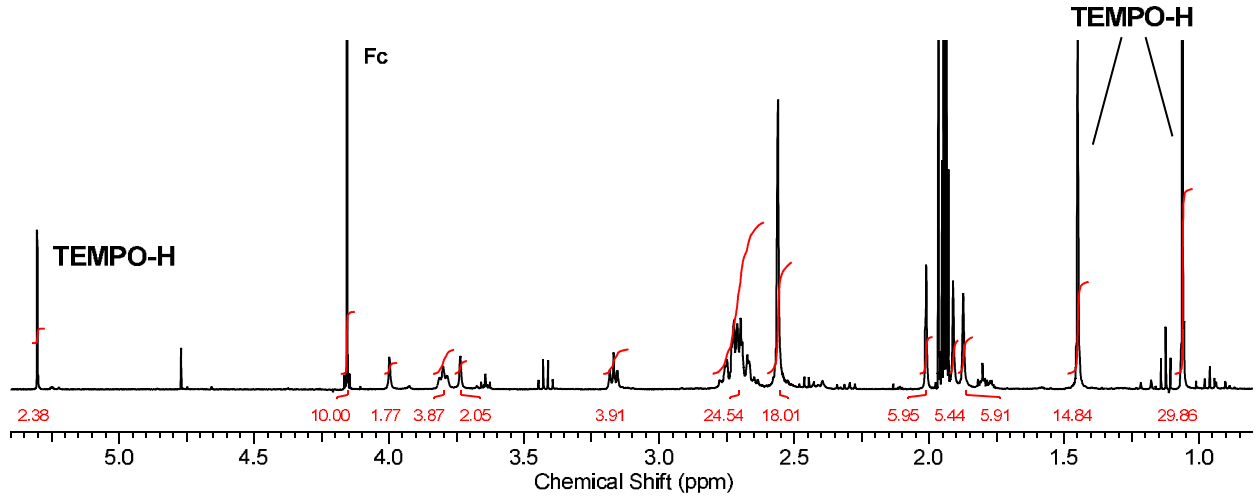
15.1 mg of complex **5** (0.02 mmol, 1.0 eq), 4.5 mg of Cp_2Co (0.024 mmol, 1.2 eq), and 1.4 mg of ferrocene (0.0075 mmol, 0.376 eq) were taken up in 1 mL of CD_3CN and mixed for 5 min, producing a homogeneous dark green solution. The yield of the diamagnetic enamide product was determined to be 71% by integration against the ferrocene standard.

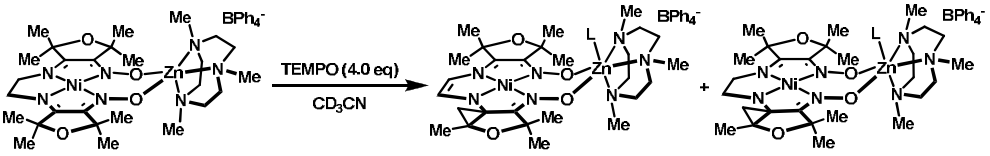
^{1}H NMR Spectrum (crude reaction mixture, CD_3CN)



15.1 mg of complex **5** (0.02 mmol, 1.0 eq), 4.5 mg of Cp_2Co (0.024 mmol, 1.2 eq), 3.1 mg of TEMPO (0.02 mmol, 1.0 eq) and 1.8 mg of ferrocene (0.010 mmol, 0.484 eq) were taken up in 1 mL of CD_3CN and mixed for 5 min, producing a homogeneous dark green solution. The yield of the diamagnetic enamide product was determined to be 95% by integration against the ferrocene standard.

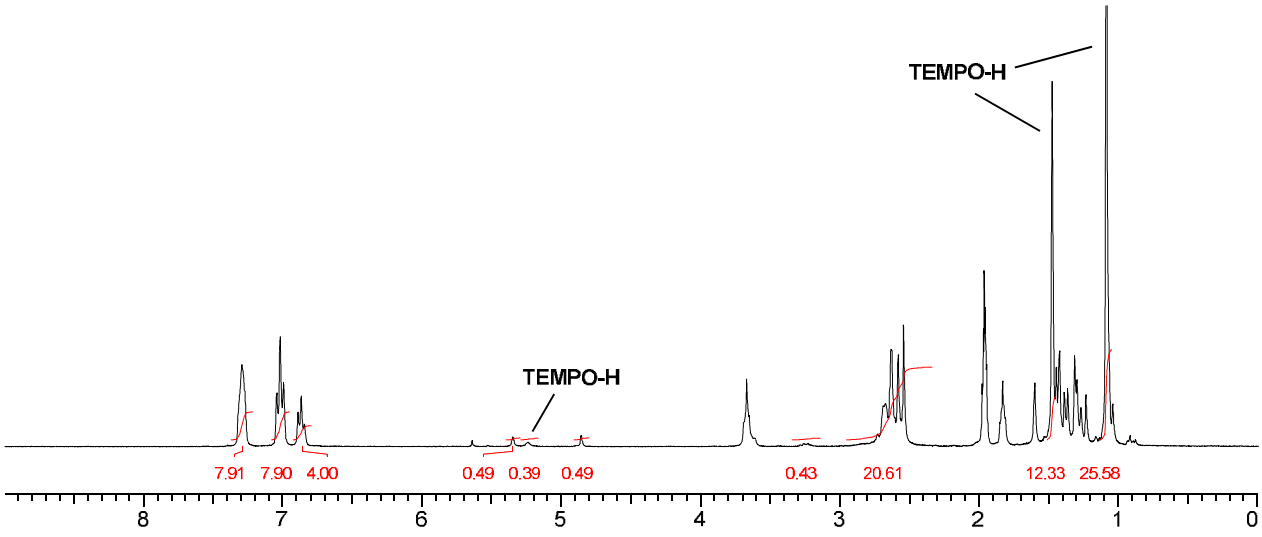
^{1}H NMR Spectrum (crude reaction mixture, TEMPO, CD_3CN)



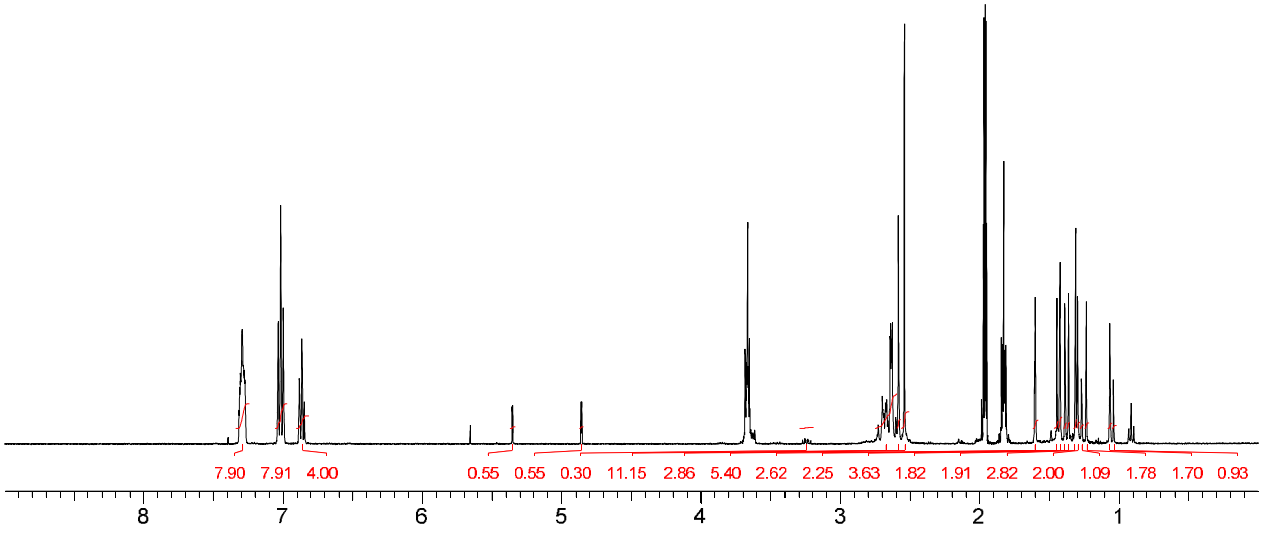


19.6 mg of complex **10** (0.02 mmol, 1.0 eq) and 12.5 mg of TEMPO (0.08 mmol, 4.0 eq) were mixed in 1 mL of CD_3CN for 1 h during which time a modest color change to a lighter shade of green was observed. The crude reaction mixture was analyzed by ^1H NMR. After concentrating the reaction mixture to dryness under reduced pressure, the residue was washed with several portions of Et_2O in order to remove TEMPO-H and unreacted TEMPO. The product mixture was analyzed by ^1H NMR, and the yields of the cyclopropane-containing products were determined by integration against the tetraphenylborate anion resonances.

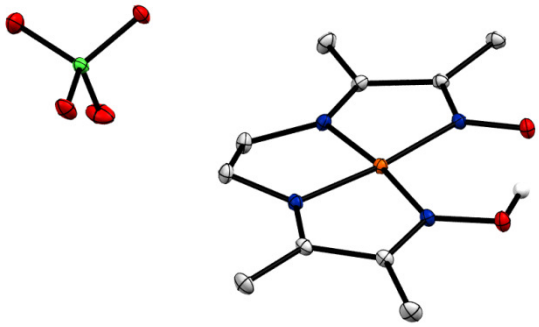
^1H NMR Spectrum (crude reaction mixture, CD_3CN)



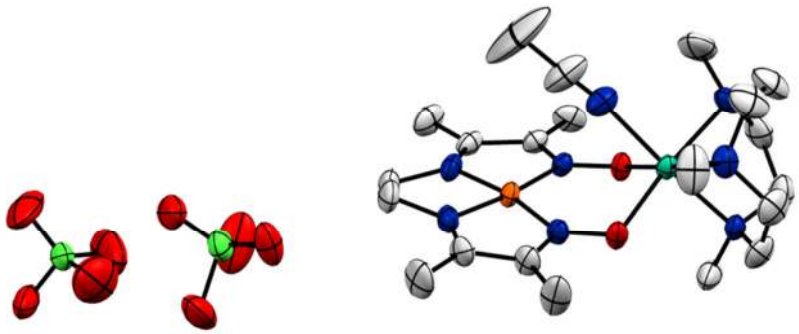
^1H NMR Spectrum (purified product, CD_3CN)



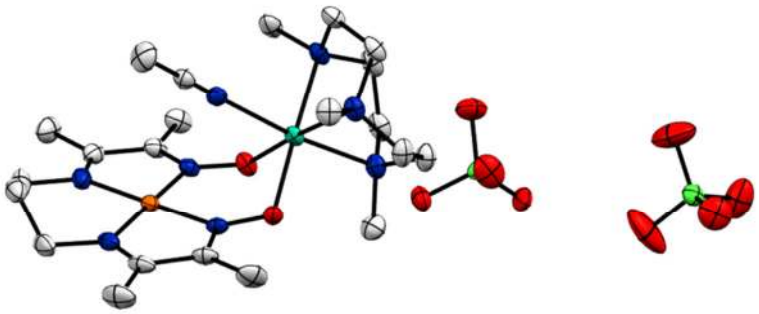
S7. Crystallographic Details



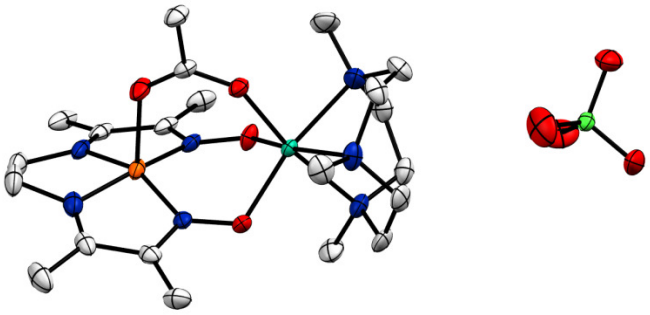
Identification code	[Ni(^{Me}doenH)]ClO_4
Empirical formula	$C_{10}H_{17}ClN_4NiO_6$
Formula weight	383.44
Temperature/K	100(2)
Crystal system	monoclinic
Space group	P21/n
a/Å	7.3309(2)
b/Å	16.9368(5)
c/Å	12.1796(4)
α/°	90.00
β/°	95.4410(10)
γ/°	90.00
Volume/Å3	1505.43(8)
Z	4
ρcalcmg/mm3	1.692
m/mm‑1	1.500
F(000)	792.0
Crystal size/mm3	0.29 × 0.22 × 0.20
2Θ range for data collection	4.14 to 90.76°
Index ranges	-14 ≤ h ≤ 14, -33 ≤ k ≤ 33, -24 ≤ l ≤ 24
Reflections collected	77236
Independent reflections	12451[R(int) = 0.0497]
Data/restraints/parameters	12451/0/207
Goodness-of-fit on F2	1.056
Final R indexes [I>=2σ (I)]	R1 = 0.0386, wR2 = 0.0808
Final R indexes [all data]	R1 = 0.0632, wR2 = 0.0907
Largest diff. peak/hole / e Å-3	0.89/-0.55



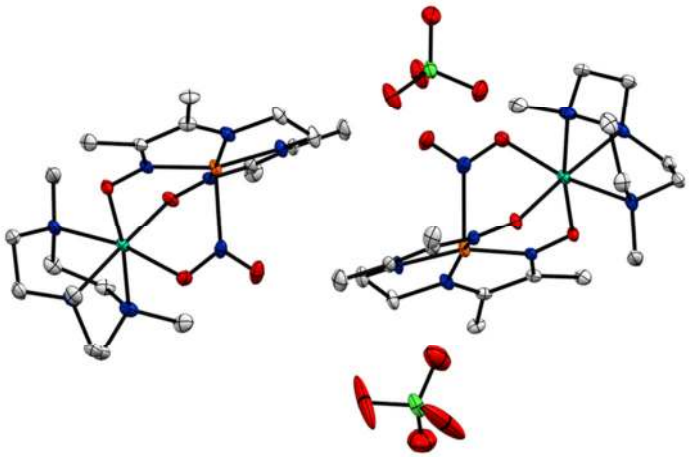
Identification code	[Ni(^{Me}doen)Zn(Me_3TACN)(MeCN)](ClO_4)$_2$ · 1/2 MeCN
Empirical formula	$C_{22}H_{40}Cl_2N_{8.5}NiO_{10}Zn$
Formula weight	778.61
Temperature/K	100(2)
Crystal system	monoclinic
Space group	P21/n
a/Å	11.5005(4)
b/Å	20.8961(7)
c/Å	14.2514(4)
α/°	90.00
β/°	109.6370(10)
γ/°	90.00
Volume/Å3	3225.65(18)
Z	4
ρcalcmg/mm3	1.603
m/mm‑1	1.557
F(000)	1614.0
Crystal size/mm3	0.36 × 0.34 × 0.29
2Θ range for data collection	3.6 to 74.96°
Index ranges	-19 ≤ h ≤ 19, -35 ≤ k ≤ 35, -23 ≤ l ≤ 24
Reflections collected	138960
Independent reflections	16269[R(int) = 0.0509]
Data/restraints/parameters	16269/0/507
Goodness-of-fit on F2	1.020
Final R indexes [I>=2σ (I)]	R1 = 0.0564, wR2 = 0.1403
Final R indexes [all data]	R1 = 0.0955, wR2 = 0.1662
Largest diff. peak/hole / e Å-3	1.48/-0.69



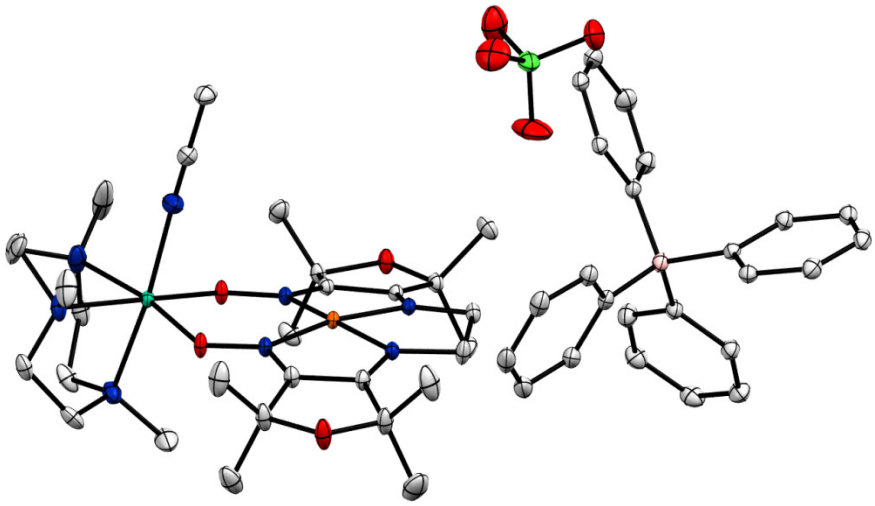
Identification code	[Ni(^{Me}dopn)Zn(Me_3TACN)(MeCN)](ClO_4)$_2$
Empirical formula	$C_{22}H_{42}Cl_2N_8NiO_{10}Zn$
Formula weight	773.62
Temperature/K	100(2)
Crystal system	monoclinic
Space group	P21/n
a/Å	11.5533(5)
b/Å	22.0368(8)
c/Å	12.9726(5)
α/°	90.00
β/°	104.810(2)
γ/°	90.00
Volume/Å3	3193.1(2)
Z	4
ρcalcmg/mm3	1.609
m/mm‑1	1.572
F(000)	1608.0
Crystal size/mm3	0.36 × 0.26 × 0.25
2Θ range for data collection	3.74 to 78.42°
Index ranges	-20 ≤ h ≤ 19, -38 ≤ k ≤ 38, -22 ≤ l ≤ 22
Reflections collected	126335
Independent reflections	18185[R(int) = 0.0350]
Data/restraints/parameters	18185/0/442
Goodness-of-fit on F2	1.131
Final R indexes [I>=2σ (I)]	R1 = 0.0686, wR2 = 0.1802
Final R indexes [all data]	R1 = 0.0900, wR2 = 0.1924
Largest diff. peak/hole / e Å-3	3.03/-1.10



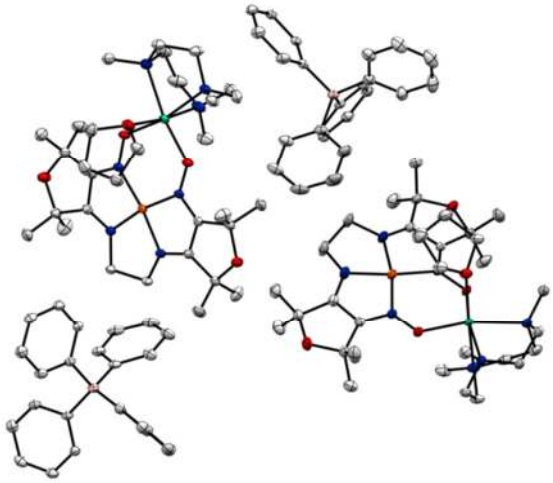
Identification code	[(μ-OAc)Ni(^{Me}doen)Zn(Me_3TACN)]ClO_4
Empirical formula	$C_{21}H_{40}ClN_7NiO_8Zn$
Formula weight	678.13
Temperature/K	100(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	18.853(4)
b/Å	18.337(4)
c/Å	16.409(3)
α/°	90.00
β/°	90.05(3)
γ/°	90.00
Volume/Å3	5673(2)
Z	8
ρcalcmg/mm3	1.588
m/mm‑1	1.660
F(000)	2832.0
Crystal size/mm3	0.44 × 0.35 × 0.05
2Θ range for data collection	3.1 to 58.26°
Index ranges	-24 ≤ h ≤ 25, -24 ≤ k ≤ 24, -22 ≤ l ≤ 22
Reflections collected	51719
Independent reflections	7185[R(int) = 0.0440]
Data/restraints/parameters	7185/0/454
Goodness-of-fit on F2	1.038
Final R indexes [I>=2σ (I)]	R1 = 0.0474, wR2 = 0.0998
Final R indexes [all data]	R1 = 0.0711, wR2 = 0.1142
Largest diff. peak/hole / e Å-3	2.05/-1.45

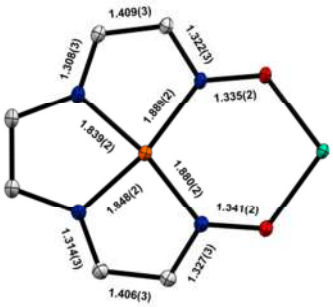


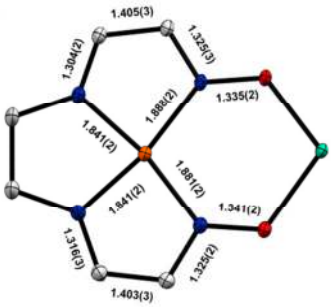
Identification code	2 [(μ-NO_2)Ni(^{Me}doen)Zn(Me_3TACN)]ClO_4
Empirical formula	$C_{19}H_{37}ClN_8NiO_8Zn$
Formula weight	665.10
Temperature/K	100(2)
Crystal system	triclinic
Space group	P1
a/Å	8.5274(4)
b/Å	12.4106(5)
c/Å	13.0776(5)
α/°	98.7540(10)
β/°	96.0040(10)
γ/°	90.074(2)
Volume/Å3	1360.17(10)
Z	2
ρcalcmg/mm3	1.624
m/mm‑1	1.730
F(000)	692.0
Crystal size/mm3	0.44 × 0.22 × 0.14
2Θ range for data collection	3.16 to 66.38°
Index ranges	-12 ≤ h ≤ 13, -19 ≤ k ≤ 19, -20 ≤ l ≤ 20
Reflections collected	42058
Independent reflections	19253[R(int) = 0.0380]
Data/restraints/parameters	19253/3/699
Goodness-of-fit on F2	1.063
Final R indexes [I>=2σ (I)]	R1 = 0.0493, wR2 = 0.1084
Final R indexes [all data]	R1 = 0.0687, wR2 = 0.1169
Largest diff. peak/hole / e Å-3	1.12/-0.51
Flack parameter	0.467(9)



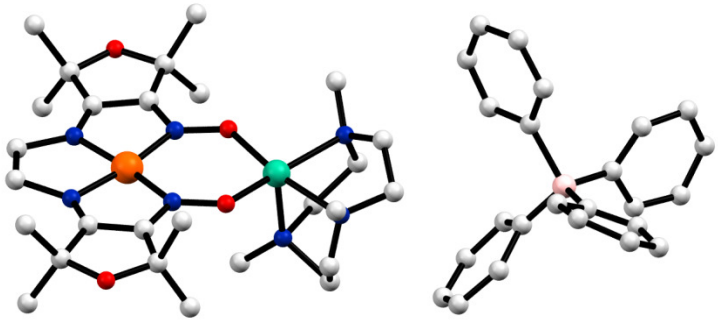
Identification code	[Ni(^{TMF}doen)Zn(Me$_3$TACN)(MeCN)](BPh$_4$)(ClO$_4$) · MeCN
Empirical formula	$C_{110}H_{150}B_2Cl_2N_{18}Ni_2O_{16}Zn_2$
Formula weight	2321.16
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	11.7327(7)
b/Å	15.5512(9)
c/Å	17.9328(10)
α/°	67.784(3)
β/°	71.146(3)
γ/°	77.960(3)
Volume/Å3	2852.6(3)
Z	1
ρcalcmg/mm3	1.351
m/mm‑1	0.857
F(000)	1224.0
Crystal size/mm3	0.38 × 0.34 × 0.11
2Θ range for data collection	3.68 to 91.72°
Index ranges	-23 ≤ h ≤ 23, -30 ≤ k ≤ 31, -36 ≤ l ≤ 35
Reflections collected	342149
Independent reflections	48552[R(int) = 0.0679]
Data/restraints/parameters	48552/0/753
Goodness-of-fit on F2	0.908
Final R indexes [I>=2σ (I)]	R1 = 0.0326, wR2 = 0.0782
Final R indexes [all data]	R1 = 0.0645, wR2 = 0.0830
Largest diff. peak/hole / e Å-3	0.84/-0.79



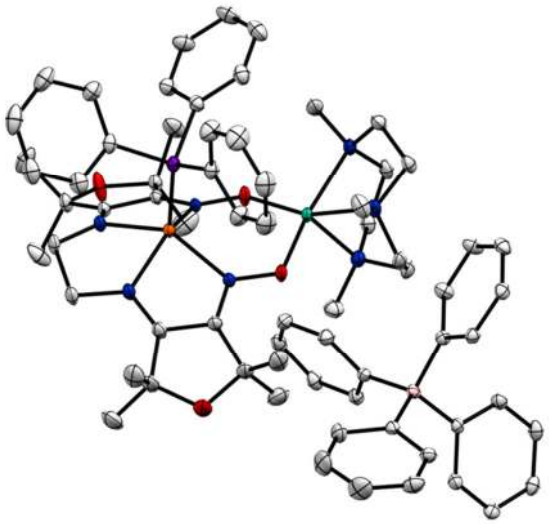




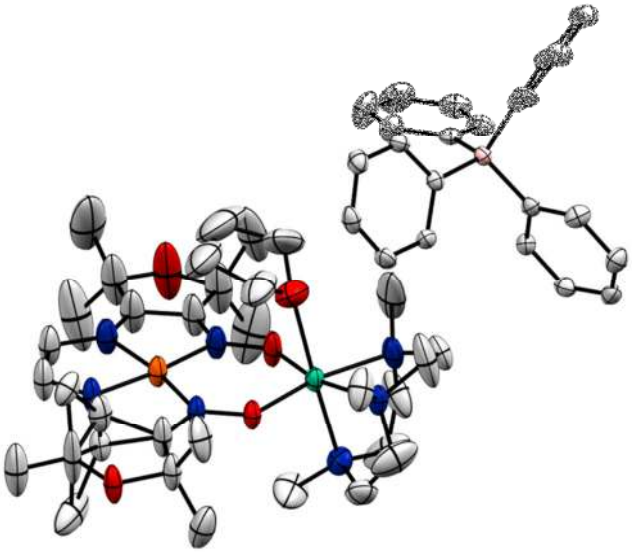
Identification code	2 [Ni(^{TMF}doen)Zn(Me_3TACN)(THF)]BPh_4 · 3 THF
Empirical formula	$C_{122}H_{178}B_2N_{14}Ni_2O_{13}Zn_2$
Formula weight	2318.56
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	11.9784(8)
b/Å	19.7901(14)
c/Å	26.2940(18)
α/°	104.912(4)
β/°	91.396(4)
γ/°	98.300(4)
Volume/Å3	5947.7(7)
Z	2
ρcalcmg/mm3	1.295
m/mm-1	0.776
F(000)	2476.0
Crystal size/mm3	0.42 × 0.19 × 0.08
2Θ range for data collection	3 to 71.5°
Index ranges	-19 ≤ h ≤ 19, -32 ≤ k ≤ 32, -41 ≤ l ≤ 42
Reflections collected	288123
Independent reflections	51564[R(int) = 0.0882]
Data/restraints/parameters	51564/0/1446
Goodness-of-fit on F2	1.013
Final R indexes [I>=2σ (I)]	R1 = 0.0552, wR2 = 0.1179
Final R indexes [all data]	R1 = 0.1235, wR2 = 0.1432
Largest diff. peak/hole / e Å-3	1.30/-0.89



Identification code	[Ni(^{TMF}doen)Zn(Me_3TACN)]BPh_4
Empirical formula	$C_{51}H_{69}BN_7NiO_4Zn$
Formula weight	979.02
Temperature/K	100(2)
Crystal system	monoclinic
Space group	P21
a/Å	11.4468(10)
b/Å	10.8318(10)
c/Å	20.204(2)
α/°	90.00
β/°	92.300(7)
γ/°	90.00
Volume/Å3	2503.0(4)
Z	2
ρcalcmg/mm3	1.299
m/mm‑1	0.906
F(000)	1038.0
Crystal size/mm3	0.38 × 0.29 × 0.02
2Θ range for data collection	3.56 to 70.62°
Index ranges	-17 ≤ h ≤ 17, -17 ≤ k ≤ 17, -32 ≤ l ≤ 32
Reflections collected	118113
Independent reflections	20278[R(int) = 0.2000]
Data/restraints/parameters	20278/1/597
Goodness-of-fit on F2	1.106
Final R indexes [I>=2σ (I)]	R1 = 0.1911, wR2 = 0.4169
Final R indexes [all data]	R1 = 0.2215, wR2 = 0.4336
Largest diff. peak/hole / e Å-3	2.34/-5.91



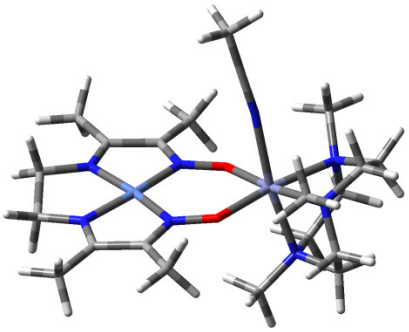
Identification code	$[(PPh_3)Ni(^{TMF}doen)Zn(Me_3TACN)]BPh_4 \cdot 2\ THF$
Empirical formula	$C_{77}H_{100}BN_7NiO_6PZn$
Formula weight	1385.55
Temperature/K	100(2)
Crystal system	monoclinic
Space group	P21/c
a/Å	21.7065(12)
b/Å	13.6234(7)
c/Å	24.0450(12)
α/°	90.00
β/°	90.533(3)
γ/°	90.00
Volume/Å3	7110.2(6)
Z	4
ρcalcmg/mm3	1.264
m/mm‑1	0.679
F(000)	2884.0
Crystal size/mm3	0.47 × 0.40 × 0.04
2Θ range for data collection	3.44 to 75.16°
Index ranges	$-36 \le h \le 34, -22 \le k \le 21, -39 \le l \le 36$
Reflections collected	217603
Independent reflections	34190[R(int) = 0.0986]
Data/restraints/parameters	34190/0/858
Goodness-of-fit on F2	1.020
Final R indexes [I>=2σ (I)]	R1 = 0.0568, wR2 = 0.1198
Final R indexes [all data]	R1 = 0.1249, wR2 = 0.1422
Largest diff. peak/hole / e Å-3	1.92/-1.12



Identification code	Complex **13**
Empirical formula	$C_{55}H_{47}BN_7NiO_5Zn$
Formula weight	1048.10
Temperature/K	100(2)
Crystal system	monoclinic
Space group	P21/c
a/Å	17.2117(13)
b/Å	12.9449(10)
c/Å	24.7109(17)
α/°	90.00
β/°	101.430(3)
γ/°	90.00
Volume/Å3	5396.5(7)
Z	4
ρcalcmg/mm3	1.290
m/mm‑1	0.846
F(000)	2224.0
Crystal size/mm3	0.48 × 0.20 × 0.05
2Θ range for data collection	3.56 to 61.14°
Index ranges	$-24 \le h \le 24$, $-17 \le k \le 11$, $-34 \le l \le 33$
Reflections collected	72415
Independent reflections	14374[R(int) = 0.0708]
Data/restraints/parameters	14374/0/660
Goodness-of-fit on F2	1.026
Final R indexes [I>=2σ (I)]	R1 = 0.0728, wR2 = 0.1625
Final R indexes [all data]	R1 = 0.1547, wR2 = 0.1969
Largest diff. peak/hole / e Å-3	1.01/-0.72

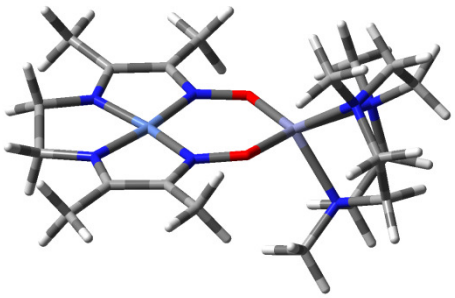
XRD data for complex **13** are of relatively poor quality presumably due to the small size and polycrystalline leaf-like morphology of the crystals that were obtained despite several crystallization attempts. Nevertheless, the data was sufficient to establish the cyclopropane structure described, which is clearly distinguishable from the other methyl substituents on the macrocycle ligand by examination of the density map.

S8. Calculated Geometries



[Ni(^{Me}doen)Zn(Me$_3$TACN)(MeCN)]$^{2+}$
B3LYP/6-31G(d)
Z = +2, M = 1
E = -4699.68146159

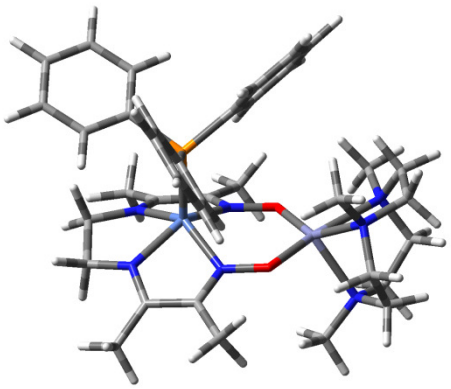
N	3.57028300	-1.27853900	-0.10777500
C	3.17199100	-2.51063900	-0.21880700
N	1.08545400	-1.48014200	-0.23576800
C	1.71121900	-2.63981300	-0.33418000
N	1.14031300	1.52935800	0.03145800
C	1.80420500	2.67248800	0.06127300
N	3.61404800	1.23965600	-0.11979600
C	3.25583500	2.48899800	-0.07194000
C	4.95338000	0.68888700	-0.36549800
H	5.73627400	1.25184600	0.15121100
H	5.15645200	0.73231000	-1.44283300
C	4.93227800	-0.77532400	0.11204700
H	5.15133600	-0.82568000	1.18597400
H	5.68617000	-1.36536000	-0.41698400
C	1.10611300	3.98583200	0.20531900
H	1.80117400	4.82482600	0.15255800
C	4.18639700	3.65800300	-0.16265300
H	3.93025100	4.27839600	-1.03004700
C	0.97066600	-3.92138600	-0.53972900
H	1.64533700	-4.77567500	-0.60862900
C	4.06419800	-3.71275100	-0.21875100
H	3.78805000	-4.38939600	0.59866600
O	-0.21324700	-1.47838700	-0.34316800
O	-0.15457300	1.57084000	0.13805100
Zn	-1.53824800	0.03842200	0.04268500
N	-3.25769200	-1.43798700	-0.15085400
N	-2.14212100	0.34471500	-2.03675000
N	-3.13037200	1.41756600	0.49941800
C	-3.30904900	-1.85387500	-1.58786800
H	-3.01335600	-2.90328700	-1.66504800
H	-4.34248800	-1.80708700	-1.94567900
C	-2.37091700	-1.04051200	-2.50765100
H	-2.76962600	-1.05188500	-3.53258100
H	-1.38808200	-1.51589600	-2.52850600
C	-3.46020900	2.07932600	-0.79441800
H	-2.73177800	2.88614300	-0.91261000
H	-4.45433600	2.54698900	-0.74890200
C	-3.38140400	1.16856400	-2.02943300
H	-3.42451300	1.80249000	-2.92403300
H	-4.24720800	0.51191900	-2.09224100
C	-4.21004300	0.56585400	1.06072200
H	-3.88356400	0.28880000	2.06701400
H	-5.14222400	1.13988200	1.16908800
C	-4.49782600	-0.70388200	0.25754700
H	-5.13283100	-1.35487500	0.87070900
H	-5.08928300	-0.46594700	-0.62593900
C	-1.09143800	0.98875600	-2.85352000
H	-0.16506200	0.41403600	-2.77390200
H	-1.38401900	1.04486500	-3.91103800
H	-0.90443200	1.99704600	-2.47913900
C	-3.06292600	-2.62066200	0.72310200
H	-3.04868400	-2.30183500	1.76735800
H	-3.86703000	-3.35689600	0.58891300
H	-2.10175600	-3.08203200	0.49154100
C	-2.80422200	2.47113200	1.49388200
H	-1.95457700	3.05259600	1.13640600
H	-3.66182600	3.13668300	1.66154500
H	-2.52995100	2.00373200	2.44098400
Ni	2.24877900	0.00434500	-0.09040000
H	0.57629000	4.03667700	1.16417500
H	5.22927300	3.35436000	-0.25706400
H	4.08814400	4.29395000	0.72482000
H	5.11628100	-3.45088900	-0.10434000
H	3.94554400	-4.27493600	-1.15252900
H	0.37417800	-3.87592000	-1.45829300
H	0.27052000	-4.09808400	0.28516900
H	0.35252600	4.10845900	-0.58097200
N	-1.22855300	-0.37409700	2.30728700
C	-0.94417300	-0.55273800	3.41649600
C	-0.60520200	-0.77699400	4.81757500
H	-1.51527400	-0.77880800	5.42596200
H	-0.10174400	-1.74180000	4.93328900
H	0.05729000	0.01702300	5.17588300



[Ni(^{Me}doen)Zn(Me$_3$TACN)]$^{1+}$
UB3LYP/6-31G(d)
Z = +1, M = 2
E = -4567.16654270

N	3.40917500	1.39059400	0.00269600
C	2.97038200	2.63955800	-0.09339300
N	0.95116800	1.51524500	-0.09774100
C	1.53542900	2.71915800	-0.10095700
N	1.12224800	-1.46676400	-0.12437100
C	1.82902600	-2.60360000	-0.11265500

N	3.54003700	-1.08149300	0.08005200
C	3.23682300	-2.37235000	0.06367500
C	4.85298200	-0.50624400	0.35604800
H	5.65461500	-1.05046300	-0.15852500
H	5.06314500	-0.55203500	1.43399300
C	4.80028600	0.96160200	-0.10942400
H	5.13294900	1.03555800	-1.15450800
H	5.47082200	1.58709800	0.49338900
C	1.15755700	-3.92885100	-0.29670900
H	1.87121800	-4.75354900	-0.26190100
C	4.27753700	-3.44251800	0.22826800
H	3.83857800	-4.43955300	0.27863800
C	0.71678000	3.97201500	-0.09859200
H	1.33961100	4.86480300	-0.17067700
C	3.90745400	3.80802100	-0.20016600
H	3.37800300	4.75684500	-0.29129100
O	-0.39617600	1.52997800	-0.05918900
O	-0.19192900	-1.58294400	-0.32876100
Zn	-1.43566200	-0.06549300	-0.10466000
N	-3.41961400	1.49318400	0.14304700
N	-2.54071100	-0.83696100	1.52736100
N	-2.84855200	-0.91574400	-1.41012400
C	-3.81316500	1.35570100	1.56383700
H	-3.71357200	2.32005700	2.07275900
H	-4.87396000	1.09056300	1.64032600
C	-2.94958800	0.33931600	2.33585800
H	-3.48755700	0.02413500	3.24285800
H	-2.01957700	0.81822500	2.65932000
C	-3.42161300	-1.98743600	-0.54332300
H	-2.68585700	-2.79547300	-0.54955600
H	-4.35068800	-2.38450200	-0.97839300
C	-3.68282000	-1.58419100	0.92360100
H	-3.87379700	-2.50274200	1.49200800
H	-4.58758900	-0.98677200	1.01106100
C	-3.82160700	0.09522900	-1.89546300
H	-3.27129300	0.73034200	-2.59726200
H	-4.62808900	-0.39237700	-2.46474500
C	-4.43408400	0.97064400	-0.80049200
H	-4.96847900	1.79556400	-1.29278100
H	-5.19839700	0.41203600	-0.25684700
C	-1.69064800	-1.73368800	2.34431700
H	-0.81717300	-1.18123500	2.70036700
H	-2.24605000	-2.12278400	3.20879400
H	-1.33522800	-2.55770600	1.72555600
C	-3.05544200	2.88208500	-0.19710400
H	-2.71331600	2.92641600	-1.23410700
H	-3.90836600	3.56821400	-0.07478800
H	-2.22583700	3.20360000	0.43138800
C	-2.19988300	-1.54379000	-2.59239800
H	-1.40282600	-2.20407200	-2.25277000
H	-2.93062100	-2.10354700	-3.19213500
H	-1.75778000	-0.76195000	-3.21501100
Ni	2.14637000	0.08226100	-0.02654800
H	0.63889100	-3.96933300	-1.26215700
H	4.85507200	-3.28522200	1.14768700
H	4.99076600	-3.43306900	-0.60624500
H	4.56032300	3.70474200	-1.07656800
H	4.55931100	3.87268400	0.68052400
H	0.12295600	4.04660700	0.82103900
H	0.00898800	3.97359500	-0.93476100
H	0.39845900	-4.09986800	0.47606800



[(PPh_3)Ni(^{Me}doen)Zn(Me_3TACN)]$^{1+}$
UB3LYP/6-31G(d)
Z = +1, M = 2
E = -5603.47845668

Zn	2.47102900	-0.19119000	0.02877000
Ni	-1.03165600	-1.21226500	0.08321700
P	-1.94749400	0.87803000	-0.06227800
C	-0.07366900	-2.16077400	-2.42584600
C	5.33086000	-0.14569400	-1.31720800
C	-0.18563600	-1.74304600	2.72183800
C	-1.39910500	-2.77285900	-2.25810000
C	-1.01287800	2.14637200	-1.04086900
C	3.97746900	0.89164300	2.12971800
C	-1.40475300	-2.52966300	2.55478000
C	5.08299900	-1.41693100	-0.49732700
C	-3.60712000	0.84720800	-0.88090400
C	-3.03356800	-3.26039700	0.89142200
C	4.30535200	2.31458700	0.13362400
C	-0.40211300	1.74762500	-2.24222800
C	-3.24008900	-2.96872200	-0.62076900
C	-2.30646300	1.76993600	1.51951800
C	-0.90096400	3.48944600	-0.64612900
C	4.12248700	2.01046400	-1.35389800
C	2.26408300	2.48819200	1.45850400
C	3.87122900	-2.45951100	1.33729300
C	3.67008100	0.32697000	-3.02667400
C	-4.68106800	0.26662900	-0.18125000
C	4.89823100	-0.26112800	1.69509000
C	-3.83068300	1.31683500	-2.18225800
C	0.27876300	2.67182400	-3.03804800
C	-0.20149800	4.40803100	-1.43257300
C	-3.39398800	2.64806400	1.66552200
C	-5.94412100	0.17097900	-0.76458500
C	-1.43019000	1.60020000	2.60326900
C	-2.72571200	3.14927000	3.93752000
C	-1.63819700	2.28583500	3.80173400
C	-3.60183000	3.32957100	2.86544100
C	-6.15412500	0.63945200	-2.06408900
C	-5.09454600	1.20953700	-2.76878800
C	0.38572600	4.00467600	-2.63350100
H	6.01435300	0.52243800	-0.78696700
H	5.85358600	-0.42841600	-2.24008700
H	4.55727700	1.60503000	2.73533100
H	3.16810700	0.49549200	2.74598300

H	6.04745100	-1.87158800	-0.22269500
H	4.54019500	-2.14289300	-1.11150400
H	-3.98617400	-3.14149700	1.42613300
H	-2.71969400	-4.30585100	1.01388900
H	4.20035300	3.39427000	0.29184000
H	5.31981500	2.06403700	0.45401600
H	-0.46175700	0.71093500	-2.55574600
H	-4.00783600	-2.19644700	-0.74849200
H	-3.59702600	-3.87565100	-1.12287100
H	-1.36608300	3.82524200	0.27451400
H	3.17297800	2.43531800	-1.69855100
H	4.92611900	2.50808300	-1.92313700
H	2.67331600	3.25695500	2.13006300
H	1.50631500	1.90558600	1.98080100
H	1.79544600	2.97931500	0.60198800
H	4.75502800	-3.00854100	1.69180000
H	3.19858300	-2.25595000	2.17107700
H	3.33578400	-3.07707300	0.61090300
H	2.68170900	0.75327800	-3.19850300
H	4.39382700	0.77234900	-3.72847700
H	3.60253300	-0.74599000	-3.20973300
H	-4.53249200	-0.09249200	0.83407100
H	5.18821200	-0.82406000	2.58948100
H	5.82759300	0.12504000	1.26974700
H	-3.02441300	1.77888900	-2.74224500
H	0.71912800	2.35059900	-3.97856700
H	-0.13151700	5.44432400	-1.11267600
H	-4.08404200	2.79985400	0.84190400
H	-6.76504400	-0.26667100	-0.20281600
H	-0.58428300	0.92918300	2.50843500
H	-2.89108800	3.67808700	4.87207000
H	-0.95256700	2.13970500	4.63237700
H	-4.44955300	4.00251100	2.96098200
H	-7.13738600	0.56476400	-2.51969700
H	-5.24974700	1.58353500	-3.77716300
H	0.91253700	4.72472900	-3.25382800
N	0.31955800	-1.43319500	-1.40034300
N	-1.99254600	-2.45018800	-1.14853600
N	-2.00070300	-2.36536400	1.40568600
N	0.25247200	-1.19976600	1.60007000
N	3.32798700	1.57547200	0.97916000
N	4.06738600	0.56345200	-1.62687800
N	4.24898700	-1.17494800	0.70564500
O	1.55494500	-0.90045400	-1.50923000
O	1.39877500	-0.49425700	1.68512300
C	-1.94021400	-3.70937900	-3.31035600
H	-2.07681200	-3.18496100	-4.26397200
H	-1.24973500	-4.54032900	-3.49600000
H	-2.90620800	-4.12873600	-3.02546600
C	0.80596400	-2.37837300	-3.62250900
H	0.30903900	-2.96653200	-4.39572900
H	1.10958000	-1.41987100	-4.05817000
H	1.73027900	-2.89600900	-3.33615700
C	0.55534800	-1.60654100	4.02009400
H	-0.03722600	-1.96665900	4.86370900
H	1.50103700	-2.16488900	4.00953600
H	0.81569000	-0.55795600	4.20169700
C	-1.84385100	-3.49084700	3.63196800
H	-1.00265700	-4.07787300	4.01647600
H	-2.27357900	-2.94737700	4.48386000
H	-2.60603100	-4.18400700	3.27021200