Supporting Information
A proton-responsive ligand becomes a dimetal linker for multisubstrate assembly *via* nitrate deoxygenation
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Experimental.

General. All manipulations were carried out under an atmosphere of ultra-high purity nitrogen using standard Schlenk techniques or in a glovebox under N_2 unless otherwise noted. Solvents were purchased from commercial sources, purified using Innovative Technology SPS-400 PureSolv solvent system or by distilling from conventional drying agents and degassed by the freeze-pump-thaw method thrice prior to use. Glassware was oven-dried at 150 °C overnight and flame dried prior to use. NMR spectra were recorded in various deuterated solvents at 25 °C on a Varian Inova-400 or 500 spectrometer (^1H: 400.11 MHz, 500.11 MHz, respectively). Proton chemical shifts are reported in ppm versus solvent protic impurity and referenced to $SiMe_4$. Mass spectrometry analyses were performed in an Agilent 6130 MSD (Agilent Technologies, Santa Clara, CA) quadrupole mass spectrometer equipped with a Multimode (ESI and APCI) source. All starting materials have been obtained from commercial sources and used without further purification.

Synthesis of [(HL)₂Ni(NO₃)]NO₃
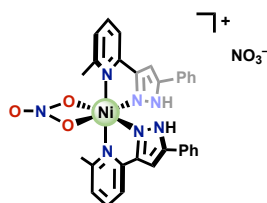
In a 20 mL scintillation vial on the benchtop, 2-methyl-6-(5(3)-phenyl-1H-pyrazol-3(5)-yl)pyridine (**HL**, 0.381 g, 1.62 mmol, in 2 mL DCM) was added to a slurry of nickel (II) nitrate hexahydrate (0.235 g, 0.810 mmol) in DCM (10 mL) and stirred for 4 h, affording a light blue precipitate. The precipitate was collected on a frit, and the resulting powder was gently heated while under vacuum over the course of 12 hours. The product was brought into the glove box and a light blue powder was isolated (0.481 g, 91% yield). Single crystals suitable for X-ray diffraction were grown from a concentrated acetonitrile solution at -35 °C over the course of 2 days.

^1H NMR (Fig S2) (400 MHz, $(CD_3)_2CO$, 298K): δ(ppm) 55.51 (s, 2H), 40.22 (s, 2H), 39.06 (s, 2H), 16.38 (s, 2H), 10.58 (s, 4H), 8.84 (s, 2H), 7.91 (s, 4H), -7.00 (s, 6H, $-CH_3$ groups). The -NH signal is not observed due to line broadening with solvent.
IR (Fig S3): v_{NO} = 1329, 1389, 1476 cm^{-1}
APCI-MS(+): 590.15: $[(HL)_2Ni(NO_3)]^+$, $[M-(NO_3)]^+$

Synthesis of (HL)(L⁻)Ni(NO₃)
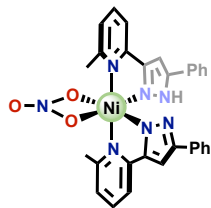
In a glovebox, 1,4-Bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (**TMS₂Pz**, 0.085 g, 0.377 mmol, in 2 mL acetonitrile) was added dropwise to a solution of [(HL)₂Ni(NO₃)]NO₃ (0.246 g, 0.377 mmol) in acetonitrile (5 mL), causing a rapid color change from light blue to deep blue-green. The reaction was stirred for 12 h at room temperature, with no further color changes, upon which is was filtered over a plug of celite, giving rise to a homogeneous deep blue-green solution. All volatiles were removed in vacuo and a blue-green powder was isolated (0.184 g, 83% yield). Single crystals suitable for X-ray diffraction were grown by slow diffusion of pentane vapor into a concentrated THF solution at room temperature.

^{1}H NMR (Fig S4) (400 MHz, CD$_3$CN, 298K): δ(ppm) 16.70 (s, 2H), 16.31 (s, 2H), 10.22 (s, 2H), 9.55 (s, 4H), 8.72 (s, 2H), 8.46 (s, 2H), 7.85 (s, 4H), 7.58 (s, 6H, -CH$_3$ groups).
IR (Fig S5): ν_{NO} = 1456 cm^{-1}
APCI-MS(+): 527.15: [(HL)(L$^-$)Ni]$^+$, [M-(NO$_3$)]$^+$, 590.15: [(HL)$_2$Ni(NO$_3$)]$^+$, [M+H]$^+$

Synthesis of [(L$^-$)Ni(NO)]$_2$
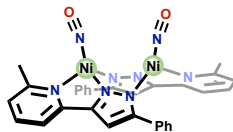
In a glovebox, TMS$_2$Pz (0.0757 g, 0.334 mmol) was added dropwise to a solution of (HL)(L$^-$)Ni(NO$_3$) (0.0941 g, 0.159 mmol) in THF (7 mL), causing a rapid color change from blue-green to dark blue. The reaction was stirred for 6 h at room temperature, with no further color changes. All volatiles were removed in vacuo and a dark blue powder was isolated (0.044 g, 86% yield). Single crystals suitable for X-ray diffraction were grown by slow diffusion of pentane vapor into a concentrated THF solution at room temperature.

^{1}H NMR (Fig S6) (400 MHz, CD$_2$Cl$_2$, 298K): δ(ppm) 7.90 (d, $J_{H,H}$ = 7.4 Hz, 4H), 7.66 (t, $J_{H,H}$ = 7.7 Hz, 2H), 7.55 (d, $J_{H,H}$ = 7.5 Hz, 2H), 7.43 (t, $J_{H,H}$ = 7.5 Hz, 4H), 7.35 (t, $J_{H,H}$ = 7.3 Hz, 2H), 7.11 (d, $J_{H,H}$ = 7.6 Hz, 2H), 7.07 (s, 2H), 2.57 (s, 6H, -CH$_3$ groups).
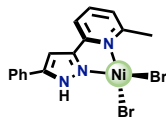**^{13}C NMR (Fig S7)** (126 MHz, CD$_2$Cl$_2$, 298K): δ(ppm) 158.51 (s), 147.61 (s), 137.15 (s), 133.02 (s), 128.62 (s), 127.79 (s), 125.49 (s), 122.53 (s), 116.95 (s), 99.89 (s), 24.08 (s).
IR (Fig S9): ν_{NO} = 1779 cm^{-1}
ESI-MS(-): 679.04: [(L$^-$)$_2$Ni$_2$(NO)$_2$Cl]$^-$, [M+Cl]$^-$

Synthesis of (HL)NiBr$_2$

In a 50 mL round bottom flask, HL (0.550 g, 2.35 mmol, in 10 mL THF) was added to a solution of nickel (II) bromide dimethoxyethane complex (0.725 g, 2.35 mmol) in THF (10 mL) and stirred for 12 h, affording a homogenous pink solution. All volatile material was removed in vacuo, which caused a color change to orange, and an orange powder was isolated (0.957 g, 90% yield). This color change is reversible; the product is pink in solution and orange in the solid state (see below). The material was characterized by ^{1}H NMR and IR spectroscopy and mass spectrometry. Single crystals were grown by vapor diffusion of either ether or pentane vapors into a concentrated THF solution at room temperature over the course of 12 hours. Both orange crystals (>95% crystalline yield) and pink crystals (<5% crystalline yield) cocrystallized and were both analyzed.

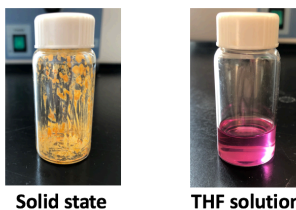**Solid state**   **THF solution**

Figure S1. Color changes of (HL)NiBr$_2$ in solid state vs. solution phase

^{1}H NMR (Fig S10) (400 MHz, d$_8$-THF, 298K): δ(ppm) 78.30 (s, 1H), 62.27 (s, 1H), 54.15 (s, 1H), 44.67 (s, 1H), 24.37 (s, 1H), 17.19 (s, 3H, -CH$_3$), 11.91 (s, 2H), 9.36 (s, 1H), 8.28 (s, 2H).
ESI-MS(+): 373.89: [(HL)NiBr]$^+$, [M-Br]$^+$

Synthesis of [(L⁻)NiBr]₂
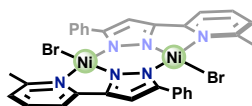
In a 20 mL scintillation vial in a glove box, (HL)NiBr₂ (0.337 g, 0.83 mmol) was dissolved in 5 mL of THF solvent and cooled to -78 °C. To this, a pre-cooled solution of LiHMDS (0.146 g, 0.87 mmol, in 2 mL of THF) was added dropwise, which caused a color change from orange to green in 10 minutes of stirring. The reaction was stirred at -78 °C for a total of two hours and was then warmed slowly to room temperature (over the course of 4 more hours) with no additional color changes. The crude reaction mixture was then filtered over a plug of celite to remove byproduct LiBr, and all volatile material was removed, giving rise to a light green powder. The crude material was then recrystallized by adding 5x excess Et₂O to a concentrated THF solution, and upon collection of the precipitate, a green product was isolated (0.223 g, 72% yield). The product was characterized by ^{1}H NMR, IR spectroscopy and mass spectrometry. Single crystals suitable for Xray diffraction were grown from a concentrated MeCN solution at -35 °C.

^{1}H NMR (Fig S12) (400 MHz, CD₃CN, 298K): δ(ppm): 60.86 (s, 2H), 42.45 (s, 2H), 38.43 (s, 2H), 16.48 (s, 2H), 11.03 (s, 4H), 8.38 (s, 4H), 8.01 (s, 6H, -CH₃ groups), 4.31 (s, 2H).
ESI-MS(+): 663.00: [(L⁻)₂Ni₂Br]⁺, [M-Br]⁺

Spectral data.
IR details: All IR spectra were obtained by using a KBr press.
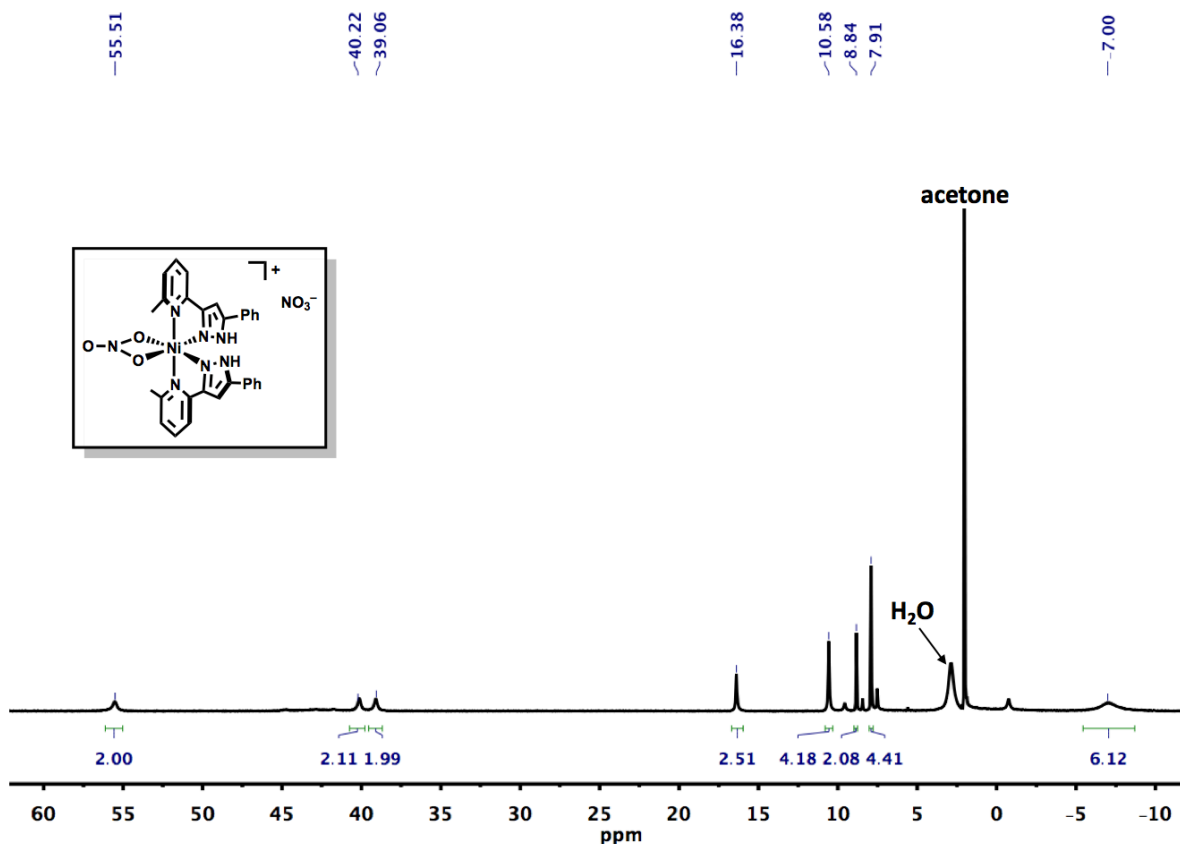
Figure S2. ^{1}H NMR (400 MHz, CD₃CN, 298K) of [(HL)₂Ni(NO₃)]NO₃. The -NH resonance could not be resolved due to broadening from hydrogen bonding with solvent.
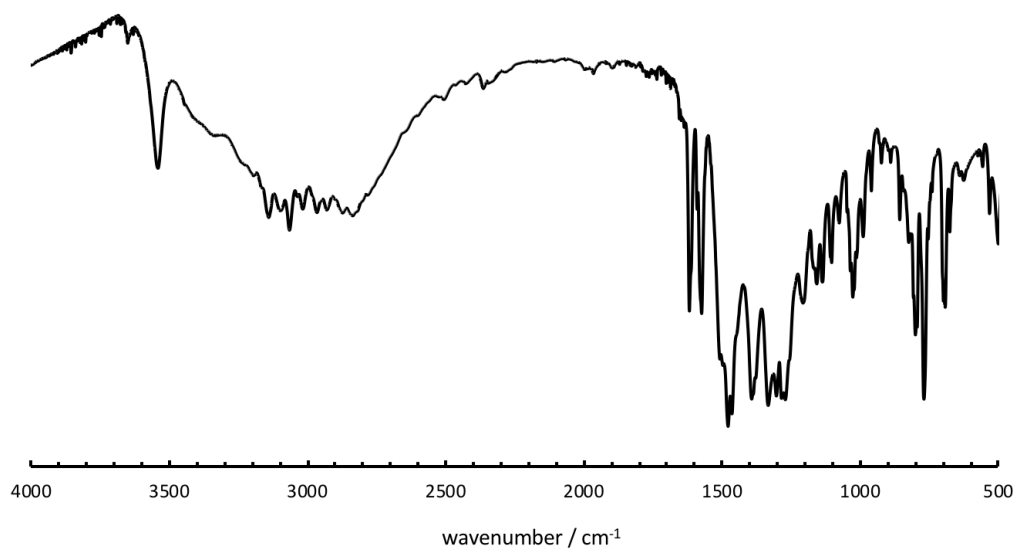
Figure S3. FT-IR spectrum of [(HL)₂Ni(NO₃)]NO₃
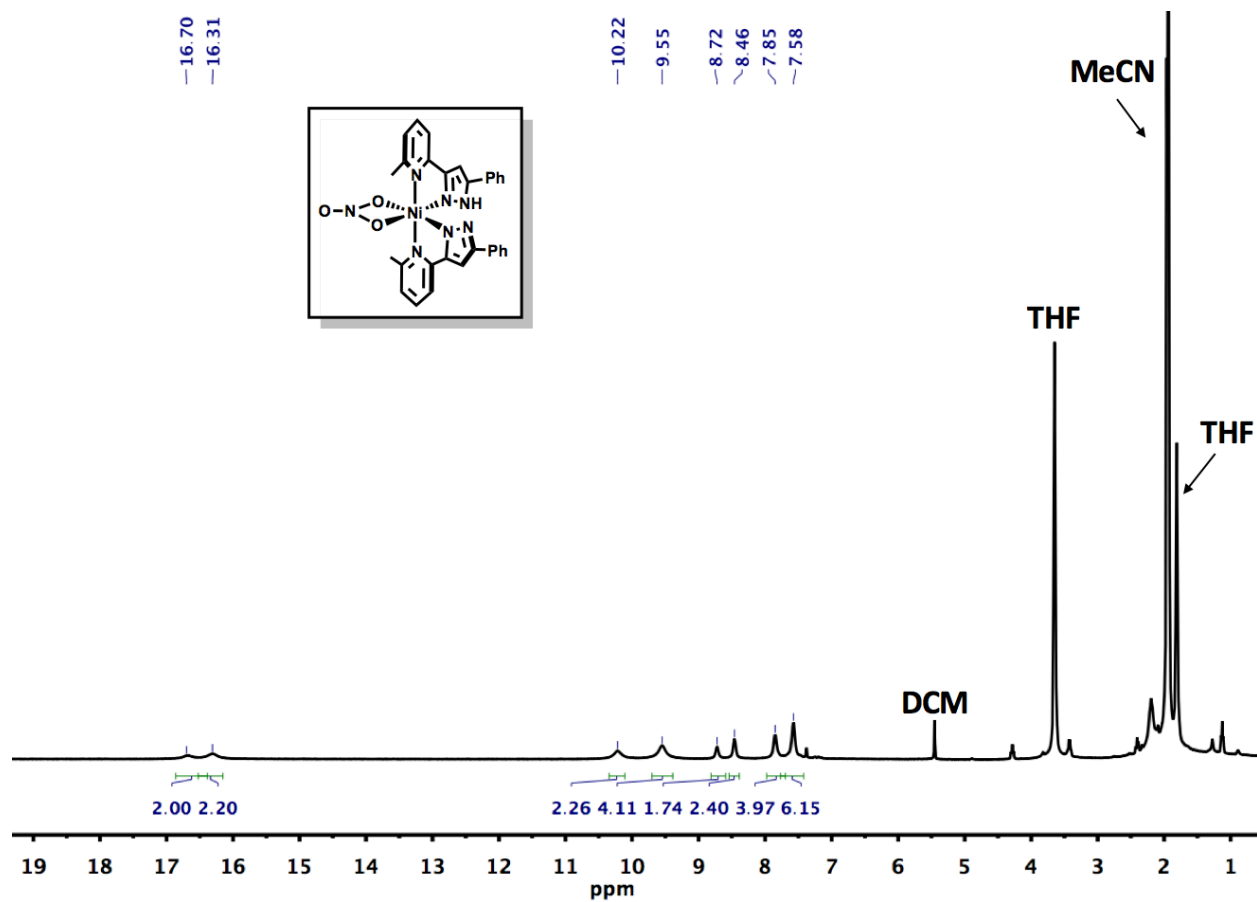
Figure S4. ^{1}H NMR (400 MHz, CD$_3$CN, 298K) of (HL)(L$^-$)Ni(NO$_3$).
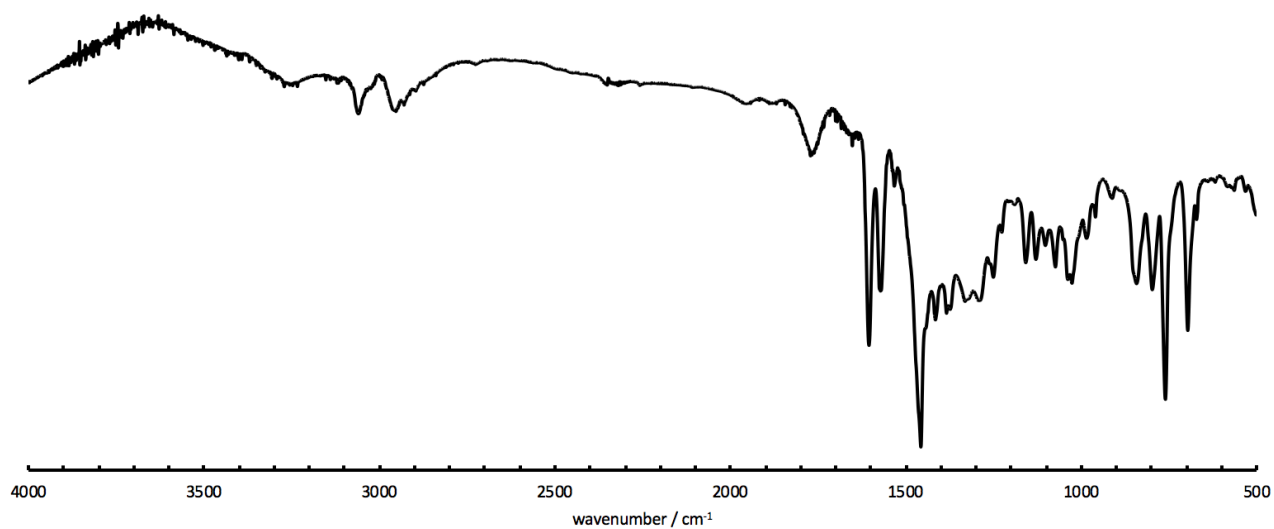
Figure S5. FT-IR spectrum of (HL)(L$^-$)Ni(NO$_3$)
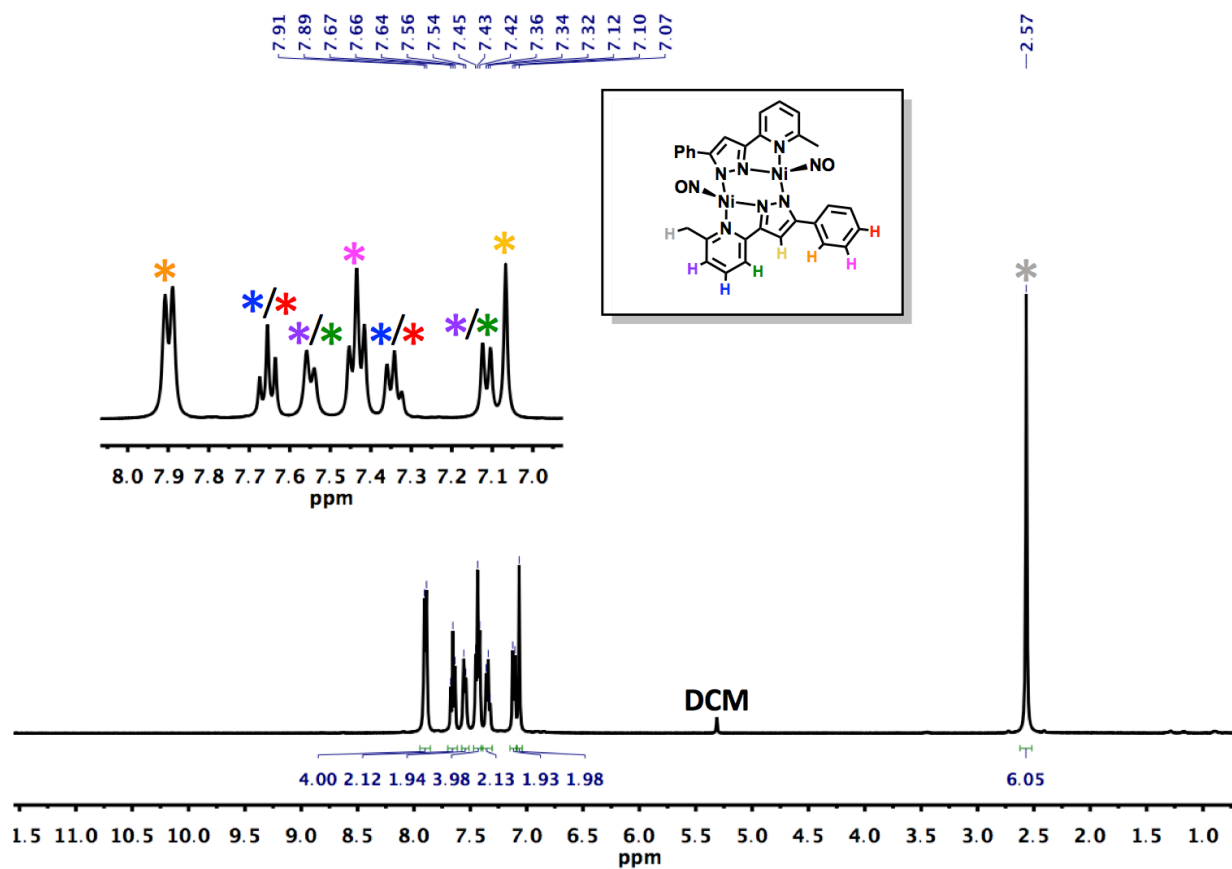
Figure S6. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 298K) of [(L$^-$)Ni(NO)]$_2$.
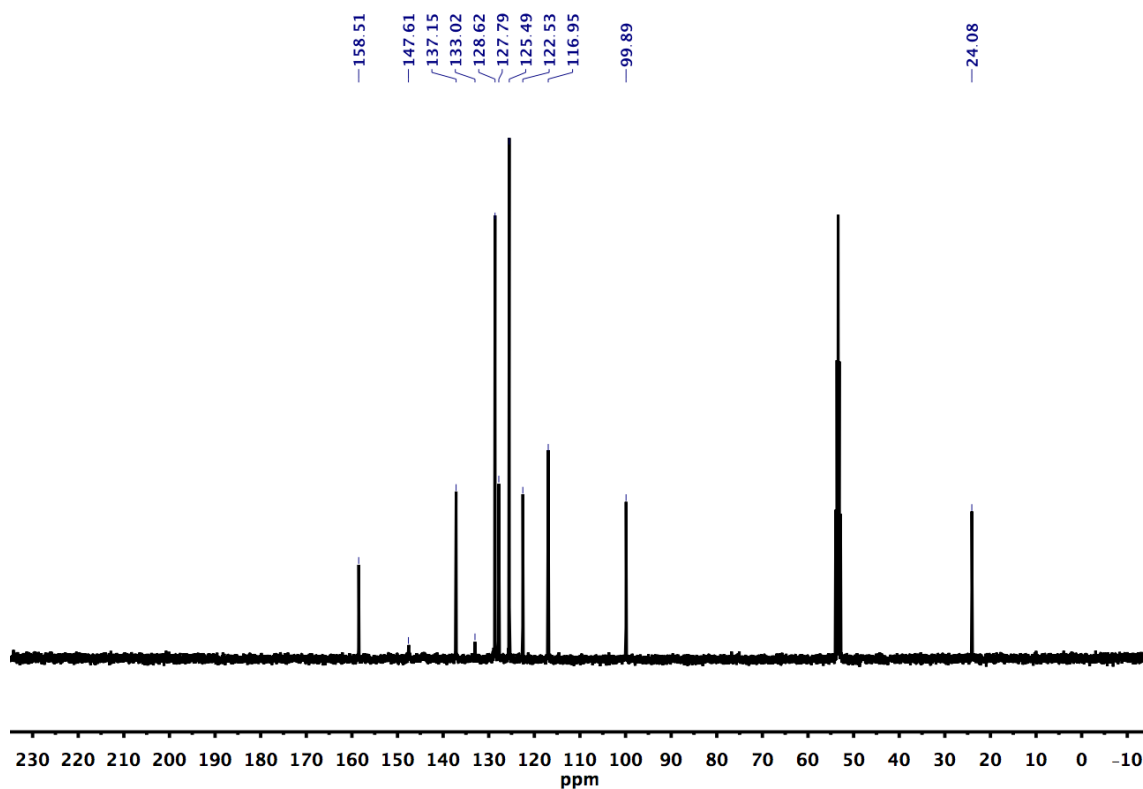
Figure S7. ^{13}C NMR (400 MHz, CD$_2$Cl$_2$, 298K) of [(L$^-$)Ni(NO)]$_2$.

expected integrations:

3H (methyl)
9H (aromatic)

3H (methyl)
9H (aromatic)

8H

36H
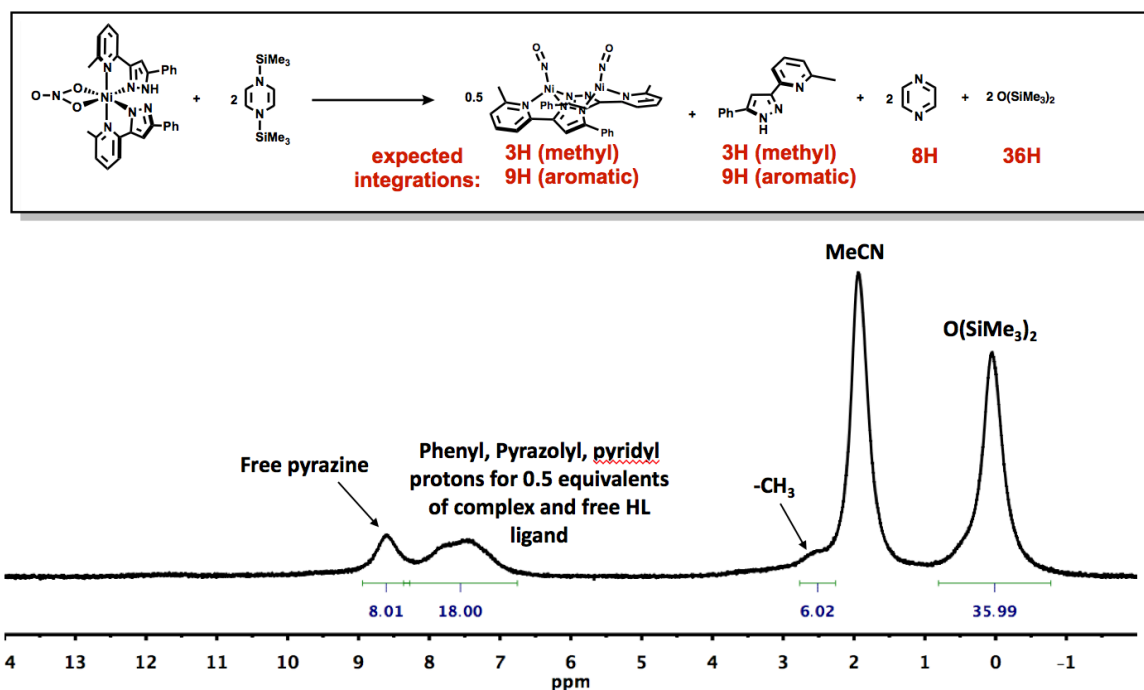
Figure S8. ^{1}H NMR (400 MHz, CD$_3$CN, 298K) tracking the reaction progress for formation of [(L$^-$)Ni(NO)]$_2$ with concomitant loss of HL free ligand. Broad signals are attributed to the presence of residual paramagnetic (HL)(L$^-$)Ni(NO$_3$).
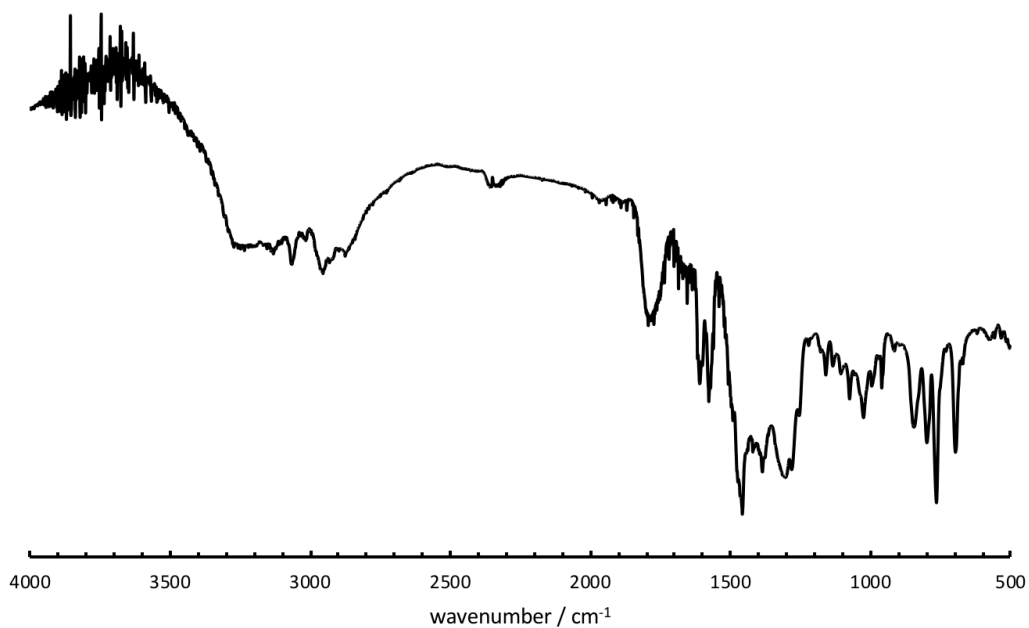
Figure S9. FT-IR spectrum of [(L⁻)Ni(NO)]₂.
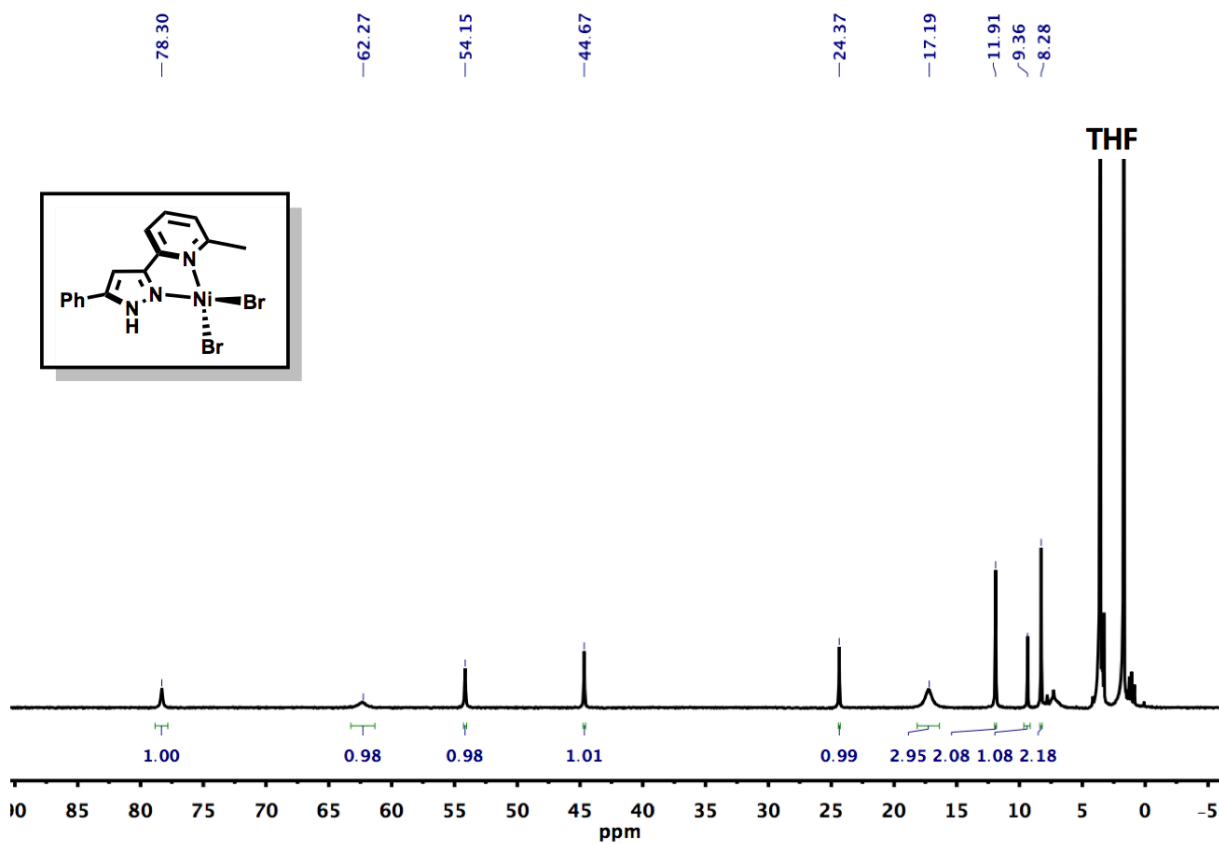
Figure S10. ¹H NMR (400 MHz, d₈-THF, 298K) of (HL)NiBr₂
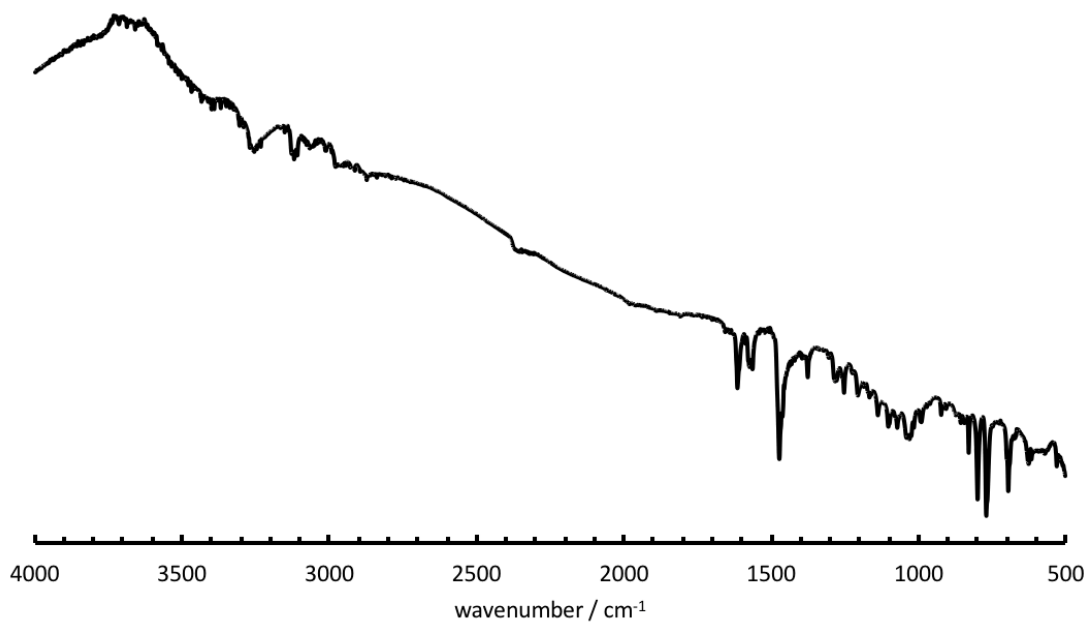
Figure S11. FT-IR spectrum of (HL)NiBr$_2$
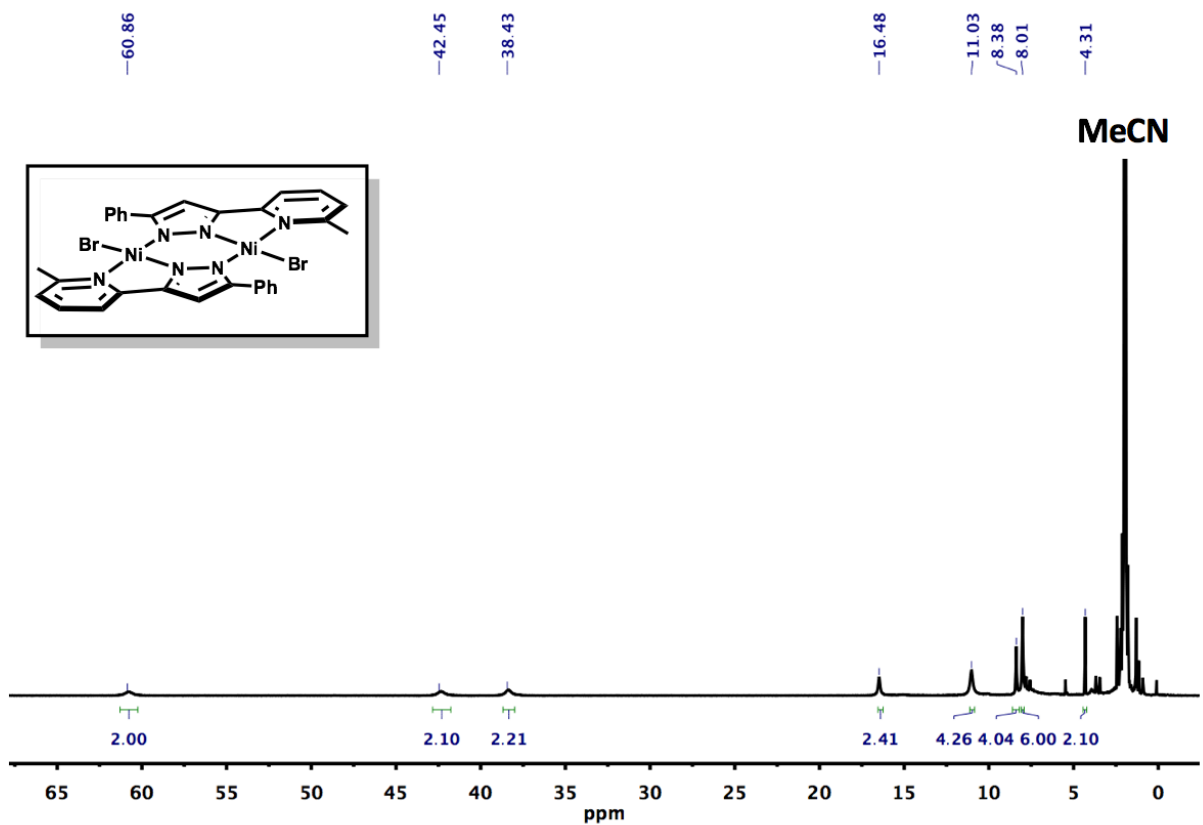
Figure S12. ^{1}H NMR (400 MHz, CD$_3$CN, 298K) of [(L$^-$)NiBr]$_2$.
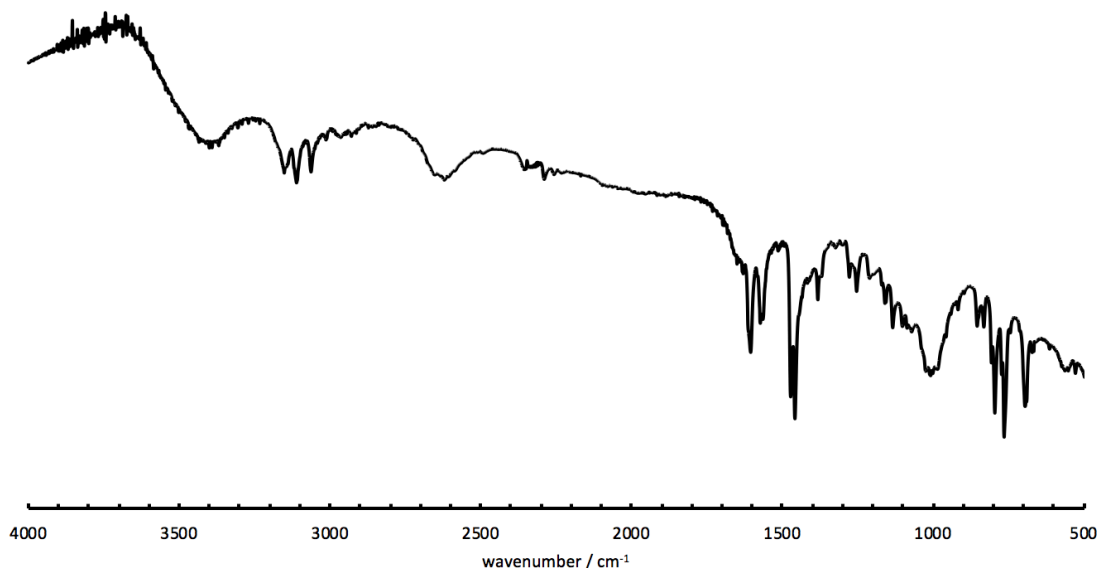
Figure S13. FT-IR spectrum of $[(L^-)NiBr]_2$.

Crystallographic data.

Data for $[(HL)_2Ni(NO_3)]NO_3$ (MSC#19072) (CCDC: 2042062)

General details. A light blue crystal (approximate dimensions $0.19 \times 0.16 \times 0.1$ mm^3) was placed onto the tip of a MiTeGen pin and mounted on a Bruker Kappa Duo diffractometer equipped with an ApexII CCD detector at 173 K.

Data collection. The data collection was carried out using Mo Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator) with a frame time of 90 seconds and a detector distance of 40 mm. A collection strategy was calculated and complete data to a resolution of 0.84 Å with a redundancy of 4 were collected. Two major sections of frames were collected with 0.50° ω and ϕ scans. The total exposure time was 20.03 hours. The frames were integrated with the Bruker SAINT[1] software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 18548 reflections to a maximum θ angle of 25.00° (0.84 Å resolution). The final cell constants of a = 14.1621(7) Å, b = 13.3400(6) Å, c = 15.5762(7) Å, β = 92.7960(19)°, volume = 2939.2(4) Å3, are based upon the refinement of the XYZ-centroids of 4731 reflections above 20 $\sigma(I)$ with 6.062° < 2θ < 49.13°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[2] The ratio of minimum to maximum apparent transmission was 0.905. Please refer to Table S1 for additional crystal and refinement information.

Structure solution and refinement. The space group P 1 21/c 1 was determined based on intensity statistics and systematic absences. The structure was solved using XT[3] and refined using full-matrix least-squares on F^2 within the OLEX2 suite.[4] An intrinsic phasing solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.0336 and wR2 = 0.0780 (F^2, all data). The goodness-of-fit was 1.009. On the basis of the final model, the calculated density was 1.475 g/cm^3 and F(000), 1352 e$^-$.

Table S1: Crystal data and structure refinement for [(HL)$_2$Ni(NO$_3$)]NO$_3$

Empirical formula	C30 H26 N8 Ni O6
Formula weight	653.30
Crystal color, shape, size	light blue plate, 0.19 × 0.16 × 0.1 mm^3
Temperature	173 K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 1 21/c 1
Unit cell dimensions	a = 15.5799(8) Å α = 90°.
	b = 13.3433(7) Å β = 92.824(2)°.
	c = 14.1660(7) Å γ = 90°.
Volume	2941.4(3) Å^3
Z	4
Density (calculated)	1.475 g/cm^3
Absorption coefficient	0.718 mm^{-1}
F(000)	1352

Data collection

Diffractometer	Kappa Apex II Duo, Bruker
Theta range for data collection	2.435 to 25.096°.
Index ranges	-17<=h<=18, -15<=k<=14, -15<=l<=16
Reflections collected	17798
Independent reflections	5213 [Rint = 0.0395]
Observed Reflections	4034
Completeness to theta = 25.096°	99.4 %

Solution and Refinement

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1 and 0.90
Solution	Intrinsic methods
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	w = [σ^2Fo^2+ AP^2+ BP]$^{-1}$, with
	P = (Fo^2+ 2 Fc^2)/3, A = 0.0312, B = 1.2258
Data / restraints / parameters	5213 / 0 / 408
Goodness-of-fit on F^2	1.009
Final R indices [I>2σ(I)]	R1 = 0.0336, wR2 = 0.0721
R indices (all data)	R1 = 0.0514, wR2 = 0.0780
Extinction coefficient	n/a
Largest diff. peak and hole	0.261 and -0.267 e.Å$^-$

Data for (HL)(L$^-$)Ni(NO$_3$) (MSC#19086) (CCDC: 2042063)

General details. A light blue crystal (plate, approximate dimensions 0.39 × 0.14 × 0.08 mm^3) was placed onto the tip of a MiTeGen pin and mounted on a Bruker Kappa Duo diffractometer equipped with a ApexII CCD detector at 173.15 K.

Data collection. The data collection was carried out using Mo Kα radiation (λ = 0.71073 Å, graphite monochromator) with a frame time of 90 seconds and a detector distance of 40 mm. A collection strategy was calculated and complete data to a resolution of 0.84 Å with a redundancy of 4 were collected. Two sets of frames were collected with 0.50° ω and ϕ scans. The total exposure time was 16.94 hours. The frames were integrated with the Bruker SAINT[1] software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 38993 reflections to a maximum θ angle of 25.14° (0.84 Å resolution), of which 10924 were independent (average redundancy 3.569, completeness = 98.6%, Rint = 13.29%, Rsig = 21.45%)

and 4090 (37.44%) were greater than 2σ(F2). The final cell constants of a = 15.327(3) Å, b = 26.533(6) Å, c = 15.588(4) Å, β = 102.497(7)°, volume = 6189.(2) Å^3, are based upon the refinement of the XYZ-centroids of 2203 reflections above 20 σ(I) with 5.21° < 2θ < 34.38°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[2] The ratio of minimum to maximum apparent transmission was 0.820. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7790 and 0.9480. Please refer to Table S2 for additional crystal and refinement information.

Structure solution and refinement. The space group P 1 21/c 1 was determined based on intensity statistics and systematic absences. The structure was solved using the SHELX suite of programs[3] and refined using full-matrix least-squares on F^2 within the OLEX2 suite.[4] An intrinsic solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.0670 and wR2 = 0.1869 (F^2, all data). The goodness-of-fit was 0.918. On the basis of the final model, the calculated density was 1.267 g/cm^3 and F(000), 2448 e$^-$. Two independent nickel complexes are held together by N-H…N hydrogen bonding, forming a dimer. Disorder was modelled for the phenyl groups and the nitrates. PLATON SQUEEZE[5] was used due to residual electron density generated by disordered THF and diethyl ether molecules (258 A^3 of solvent accessible void per asymmetric unit, 58 electrons).

Table S2: Crystal data and structure refinement for (HL)(L$^-$)Ni(NO$_3$)

Empirical formula	C30 H25 N7 Ni O3
Formula weight	590.28
Crystal color, shape, size	light blue plate, 0.39 × 0.14 × 0.08 mm^3
Temperature	173.15 K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 1 21/c 1
Unit cell dimensions	a = 15.327(3) Å α = 90°.
	b = 26.533(6) Å β = 102.497(7)°.
	c = 15.588(4) Å γ = 90°.
Volume	6189(2) Å^3
Z	8
Density (calculated)	1.267 g/cm^3
Absorption coefficient	0.668 mm^{-1}
F(000)	2448
Data collection	
Diffractometer	Bruker APEX-II CCD
Theta range for data collection	2.036 to 25.138°.
Index ranges	-18<=h<=15, -21<=k<=31, -18<=l<=18
Reflections collected	38979
Independent reflections	10921 [Rint = 0.1329]
Observed Reflections	4088
Completeness to theta = 25.138°	98.6 %
Solution and Refinement	
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.6108
Solution	Intrinsic methods
Refinement method	Full-matrix least-squares on F^2

Weighting scheme	$w = [\sigma^2 Fo^2 + AP^2 + BP]^{-1}$, with
	$P = (Fo^2 + 2\,Fc^2)/3$, A = 0.0787, B = 0.0000
Data / restraints / parameters	10921 / 1112 / 802
Goodness-of-fit on F^2	0.918
Final R indices [I>2σ(I)]	R1 = 0.0670, wR2 = 0.1367
R indices (all data)	R1 = 0.2075, wR2 = 0.1869
Extinction coefficient	n/a
Largest diff. peak and hole	0.284 and -0.326 e.Å^{-3}

Data for [(L$^-$)Ni(NO)]$_2$ (MSC#19099) (CCDC: 2042064)

General details. A dark blue crystal (approximate dimensions 0.25 × 0.24 × 0.2 mm^3) was placed onto the tip of a MiTeGen pin and mounted on a Bruker Kappa Duo diffractometer equipped with a ApexII CCD detector at 173 K.

Data collection. The data collection was carried out using Mo Kα radiation (λ = 0.71073 Å, graphite monochromator) with a frame time of 20 seconds and a detector distance of 40 mm. A collection strategy was calculated and complete data to a resolution of 0.77 Å with a redundancy of 4 were collected. Three major sections of frames were collected with 0.50º ω and ϕ scans. The total exposure time was 5.47 hours. The frames were integrated with the Bruker SAINT[1] software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 21576 reflections to a maximum θ angle of 27.48° (0.77 Å resolution), of which 6256 were independent (average redundancy 3.449, completeness = 99.0%, Rint = 3.44%, Rsig = 3.59%) and 5159 (82.46%) were greater than 2σ(F2). The final cell constants of a = 14.0747(15) Å, b = 8.1646(10) Å, c = 24.161(3) Å, β = 96.931(4)°, volume = 2756.2(5) Å3, are based upon the refinement of the XYZ-centroids of 8622 reflections above 20 σ(I) with 5.275° < 2θ < 55.17°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[2] The ratio of minimum to maximum apparent transmission was 0.811. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7190 and 0.7660. Please refer to Table S3 for additional crystal and refinement information.

Structure solution and refinement. The space group P 2$_1$/n was determined based on intensity statistics and systematic absences. The structure was solved using XT (Sheldrick, 2015)[3] and refined using full-matrix least-squares on F^2 within the OLEX2 suite.[4] An intrinsic phasing solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.0319 and wR2 = 0.0868 (F^2, all data). The goodness-of-fit was 1.029. On the basis of the final model, the calculated density was 1.557 g/cm^3 and F(000), 1328 e$^-$. The remaining electron density is minuscule and located along the bonds. The refinement proceeded smoothly, no restraints or constraints were necessary.

Table S3: Crystal data and structure refinement for [(L$^-$)Ni(NO)]$_2$

Empirical formula	C30 H24 N8 Ni2 O2
Formula weight	645.99
Crystal color, shape, size	dark blue block, 0.25 × 0.24 × 0.2 mm^3
Temperature	173 K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 1 21/n 1

Unit cell dimensions	a = 14.0747(15) Å	$\alpha = 90°$.
	b = 8.1646(10) Å	$\beta = 96.931(4)°$.
	c = 24.161(3) Å	$\gamma = 90°$.
Volume	2756.2(5) Å^3	
Z	4	
Density (calculated)	1.557 g/cm^3	
Absorption coefficient	1.411 mm^{-1}	
F(000)	1328	

Data collection

Diffractometer	Kappa Apex II Duo, Bruker
Theta range for data collection	1.698 to 27.483°.
Index ranges	-18<=h<=18, -10<=k<=7, -31<=l<=31
Reflections collected	21576
Independent reflections	6256 [Rint = 0.0344]
Observed Reflections	5159
Completeness to theta = 25.242°	99.7 %

Solution and Refinement

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6049
Solution	Intrinsic methods
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	w = [σ^2Fo^2+ AP^2+ BP]$^{-1}$, with
	P = (Fo^2+ 2 Fc^2)/3, A =0.0412, B = 1.3507
Data / restraints / parameters	6256 / 0 / 381
Goodness-of-fit on F^2	1.029
Final R indices [I>2σ(I)]	R1 = 0.0319, wR2 = 0.0795
R indices (all data)	R1 = 0.0437, wR2 = 0.0868
Extinction coefficient	n/a
Largest diff. peak and hole	0.397 and -0.390 e.Å^{-3}

Data for [(HL)NiBr$_2$]$_2$ (MSC#20121) (CCDC: 2044737)

General details. An orange crystal (plate, approximate dimensions 0.16 × 0.08 × 0.04 mm^3) was placed onto the tip of a MiTeGen pin and mounted on a Bruker Venture D8 diffractometer equipped with a PhotonIII detector at 123.0 K.

Data collection. The data collection was carried out using Mo Kα radiation (λ = 0.71073 Å, graphite monochromator) with a frame time of 8 seconds and a detector distance of 40 mm. A collection strategy was calculated and complete data to a resolution of 0.77 Å with a redundancy of 6 were collected. The frames were integrated with the Bruker SAINT[1] software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 25478 reflections to a maximum θ angle of 27.48° (0.77 Å resolution), of which 3590 were independent (average redundancy 7.097, completeness = 100.0%, Rint = 2.72%, Rsig = 1.58%) and 3334 (92.87%) were greater than 2σ(F^2). The final cell constants of a = 7.1360(3) Å, b = 8.8312(3) Å, c = 13.1888(5) Å, α = 72.909(2)°, β = 79.406(2)°, γ = 87.141(2)°, volume = 780.90(5) Å^3, are based upon the refinement of the XYZ-centroids of 9963 reflections above 20 σ(I) with 4.987° < 2θ < 54.98°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[2] The ratio of minimum to maximum apparent transmission was 0.809. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4300 and 0.7850. Please refer to Table S4 for additional crystal and refinement information.

Structure solution and refinement. The space group P-1 was determined based on intensity statistics and systematic absences. The structure was solved using the SHELX suite of programs[3] and refined using full-matrix least-squares on F^2 within the OLEX2 suite.[4] An intrinsic phasing solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.0176 and wR2 = 0.0384 (F^2, all data). The goodness-of-fit was 1.084. On the basis of the final model, the calculated density was 1.930 g/cm^3 and F(000), 444 e$^-$.

Table S4: Crystal data and structure refinement for [(HL)NiBr$_2$]$_2$

Empirical formula	C30 H26 Br4 N6 Ni2	
Formula weight	907.63	
Crystal color, shape, size	orange plate, 0.16 × 0.08 × 0.04 mm^3	
Temperature	123.0 K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, P-1	
Unit cell dimensions	a = 7.1360(3) Å	α = 72.909(2)°.
	b = 8.8312(3) Å	β = 79.406(2)°.
	c = 13.1888(5) Å	γ = 87.141(2)°.
Volume	780.90(5) Å^3	
Z	1	
Density (calculated)	1.930 g/cm^3	
Absorption coefficient	6.354 mm^{-1}	
F(000)	444	
Data collection		
Diffractometer	Bruker VENTURE D8	
Theta range for data collection	2.413 to 27.485°.	
Index ranges	-9<=h<=9, -11<=k<=11, -17<=l<=17	
Reflections collected	25478	
Independent reflections	3590 [Rint = 0.0272]	
Observed Reflections	3334	
Completeness to theta = 25.242°	100.0 %	
Solution and Refinement		
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6033	
Solution	Intrinsic methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting scheme	w = [$\sigma^2 Fo^2$+ AP^2+ BP]$^{-1}$, with	
	P = (Fo^2+ 2 Fc^2)/3, A = 0.0118, B = 0.634	
Data / restraints / parameters	3590 / 0 / 191	
Goodness-of-fit on F^2	1.084	
Final R indices [I>2σ(I)]	R1 = 0.0176, wR2 = 0.0375	
R indices (all data)	R1 = 0.0203, wR2 = 0.0384	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.402 and -0.345 e.Å^{-3}	

Data for (HL)NiBr₂ (MSC#20123) (CCDC: 2044738)

General details. A pink crystal (block, approximate dimensions 0.14 × 0.09 × 0.04 mm³) was placed onto the tip of a MiTeGen pin and mounted on a Bruker Venture D8 diffractometer equipped with a PhotonIII detector at 123.0 K.

Data collection. The data collection was carried out using Mo Kα radiation (λ = 0.71073 Å, graphite monochromator) with a frame time of 7 seconds and a detector distance of 40 mm. A collection strategy was calculated and complete data to a resolution of 0.77 Å with a redundancy of 5.4 were collected. The frames were integrated with the Bruker SAINT[1] software package using a narrowframe algorithm. The integration of the data using a triclinic unit cell yielded a total of 28003 reflections to a maximum θ angle of 27.48° (0.77 Å resolution), of which 4498 were independent (average redundancy 6.226, completeness = 100.0%, Rint = 5.10%, Rsig = 3.24%) and 3957 (87.97%) were greater than 2σ(F2). The final cell constants of a = 9.3273(4) Å, b = 10.2918(5) Å, c = 10.8763(5) Å, α = 95.137(2)°, β = 95.800(2)°, γ = 107.670(2)°, volume = 981.73(8) Å3 , are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the Multi-Scan method (SADABS).[2] The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5370 and 0.8230. Please refer to Table S5 for additional crystal and refinement information.

Structure solution and refinement. The space group P-1 was determined based on intensity statistics and systematic absences. The structure was solved using the SHELX suite of programs[3] and refined using full-matrix leastsquares on F^2 within the OLEX2 suite.[4] An intrinsic phasing solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.0327 and wR2 = 0.0890 (F^2, all data). The goodness-of-fit was 1.052. On the basis of the final model, the calculated density was 1.779 g/cm³ and F(000), 524 e⁻ .

Table S5: Crystal data and structure refinement for (HL)NiBr₂

Empirical formula	C19 H21 Br2 N3 Ni O	
Formula weight	525.92	
Crystal color, shape, size	pink block, 0.14 × 0.09 × 0.04 mm³	
Temperature	123.0 K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, P-1	
Unit cell dimensions	a = 9.3273(4) Å	α = 95.137(2)°.
	b = 10.2918(5) Å	β = 95.800(2)°.
	c = 10.8763(5) Å	γ = 107.670(2)°.
Volume	981.73(8) Å³	
Z	2	
Density (calculated)	1.779 g/cm³	
Absorption coefficient	5.071 mm⁻¹	
F(000)	524	
Data collection		
Diffractometer	Bruker VENTURE D8	
Theta range for data collection	1.897 to 27.484°.	
Index ranges	-12<=h<=12, -13<=k<=13, -14<=l<=14	
Reflections collected	28003	
Independent reflections	4498 [Rint = 0.0510]	

Observed Reflections	3957
Completeness to theta = 25.242°	100.0 %

Solution and Refinement

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6500
Solution	Intrinsic methods
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$w = [\sigma^2 F_o^2 + AP^2 + BP]^{-1}$, with $P = (F_o^2 + 2F_c^2)/3$, A = 0.0578, B = 0.00
Data / restraints / parameters	4498 / 0 / 237
Goodness-of-fit on F^2	1.052
Final R indices [I>2σ(I)]	R1 = 0.0327, wR2 = 0.0855
R indices (all data)	R1 = 0.0388, wR2 = 0.0890
Extinction coefficient	n/a
Largest diff. peak and hole	1.165 and -0.800 e.Å^{-3}

Figure S14 shows what changes occur to the monomer structure when the dimer forms. This is a least squares fit of the monomer to half the dimer, and shows minimal change in the bidentate ligand, some lengthening of the NiN(pyridine) bond length, and then very modest angular distortion of only one of the two bromines. Dimerization clearly occurs by bringing a new bromine donor trans to pyridine.
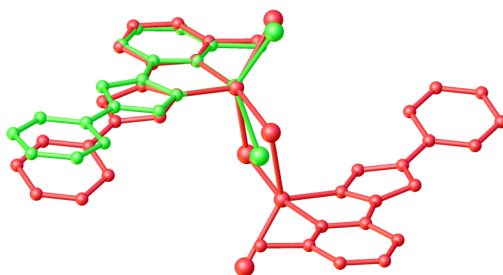

Figure S14: Best least squares fit of (HL)NiBr$_2$ (green) and [(HL)NiBr$_2$]$_2$ (red). RMSD = 0.034.

Data for [(L$^-$)NiBr(MeCN)]$_2$ (MSC#20041) (CCDC: 2042065)

General details. A light blue crystal (plate, approximate dimensions 0.06 × 0.04 × 0.03 mm^3) was placed onto the tip of a MiTeGen pin and mounted on a Bruker Venture D8 diffractometer equipped with a PhotonIII detector at 100.0 K.

Data collection. The data collection was carried out using Mo Kα radiation (λ = 0.71073 Å, graphite monochromator) with a frame time of 2 seconds for low angle and 10 seconds for high angle scans. The detector distance was 120 mm. A collection strategy was calculated and complete data to a resolution of 0.70 Å with a redundancy of 5.5 were collected. The frames were integrated with the Bruker SAINT[1] software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 28559 reflections to a maximum θ angle of 30.57° (0.70 Å resolution), of which 5104 were independent (average redundancy 5.595, completeness = 99.9%, Rint = 8.04%, Rsig = 4.80%) and 3967 (77.72%) were greater than 2σ(F^2). The final cell constants of a = 8.0659(3) Å, b = 9.0221(3) Å, c = 12.1370(5) Å, α = 90.5070(10)°, β = 106.9510(10)°, γ = 100.1250(10)°, volume = 830.00(5) Å^3, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the Multi-Scan method (SADABS).[2] The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8140 and 0.9000. Please refer to Table S6 for additional crystal and refinement information.

Structure solution and refinement. The space group P-1 was determined based on intensity statistics and systematic absences. The structure was solved using the SHELX suite of programs[3] and refined using full-matrix least-squares on F^2 within the OLEX2 suite.[4] An intrinsic phasing solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.0324 and wR2 = 0.0713 (F^2, all data). The goodness-of-fit was 1.008. On the basis of the final model, the calculated density was 1.656 g/cm^3 and F(000), 416 e$^-$. The structure is a Ni dimer and half-a-molecule is the asymmetric unit (Z' = 0.5).

Table S6: Crystal data and structure refinement for $[(L^-)NiBr(MeCN)]_2$

Empirical formula	C34 H30 Br2 N8 Ni2
Formula weight	827.90
Crystal color, shape, size	light blue plate, 0.06 × 0.04 × 0.03 mm^3
Temperature	100.0 K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.0659(3) Å $\qquad$ α = 90.5070(10)°.
	b = 9.0221(3) Å $\qquad$ β = 106.9510(10)°.
	c = 12.1370(5) Å $\qquad$ γ = 100.1250(10)°.
Volume	830.00(5) Å^3
Z	1
Density (calculated)	1.656 g/cm^3
Absorption coefficient	3.579 mm^{-1}
F(000)	416
Data collection	
Diffractometer	Bruker Venture D8
Theta range for data collection	2.298 to 30.571°.
Index ranges	-11<=h<=11, -12<=k<=12, -17<=l<=17
Reflections collected	28559
Independent reflections	5104 [Rint = 0.0804]
Observed Reflections	3967
Completeness to theta = 25.242°	100.0 %
Solution and Refinement	
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.6610
Solution	Intrinsic methods
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	w = $[\sigma^2 Fo^2 + AP^2 + BP]^{-1}$, with
	P = $(Fo^2 + 2\ Fc^2)/3$, A = 0.032, B = 0.00
Data / restraints / parameters	5104 / 0 / 210
Goodness-of-fit on F^2	1.008
Final R indices [I>2σ(I)]	R1 = 0.0324, wR2 = 0.0666
R indices (all data)	R1 = 0.0480, wR2 = 0.0713
Extinction coefficient	n/a
Largest diff. peak and hole	0.586 and -0.658 e.Å^{-3}

References.

1. SAINT, Bruker Analytical X-Ray Systems, Madison, WI, current version.
2. SADABS, Bruker Analytical X-Ray Systems, Madison, WI, current version.
3. G. M. Sheldrick, Acta Cryst. A64, 112 - 122 (2008). Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Crystallogr., 2009, 42, 339–341.
5. Spek, A. L. PLATON SQUEEZE: A Tool for the Calculation of the Disordered Solvent Contribution to the Calculated Structure Factors. Acta Crystallogr. 2015, C71, 9–18.