Supporting Information

Reductive Binding and Ligand-Based Redox Transformations of Nitrosobenzene at a Dinickel(II) Core

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A Experimental Section

A.1 General Information and Methods

All experiments and manipulations were carried out under dry oxygen-free Argon using standard Schlenk techniques, or in a glovebox filled with dinitrogen (O_2 < 0.1 ppm, H_2O < 0.1 ppm). Solvents were dried by standard methods and freshly distilled prior use. THF, pentane and hexane were dried over sodium in the presence of benzophenone; THF–d_8 was also dried over sodium in the presence of benzophenone and stored over 3 Å molecular sieves. Chemicals used were either present in the working group or purchased from commercial sources. The starting material $KL(NiH)_2$ (**1**) and labeled $Ph^{15}NO$ were prepared by following the literature procedures.[1,2] UV–vis spectra were recorded in quartz cuvettes using an Agilent Cary 60 equipped with an Unisoku Cryostat (CoolSpek) and magnetic stirrer, or in a glovebox with a BWTek Exemplar LS spectrophotometer. Cyclic voltammetry (CV) experiments were performed with an Interface 1000B potentiostat using a three electrode setup consisting of a glassy carbon working electrode, a platinum wire counter electrode, and Ag wire as pseudo-reference electrode; data were analyzed by Gamry Framework software. CV experiments were performed in deoxygenated THF containing NBu_4PF_6 (0.1 M) as supporting electrolyte; ferrocene was used as an internal standard. At the beginning of the experiment the open circuit potential of the sample was measured in order to obtain the voltage of the solution when only a minimal current is present. For spectroelectrochemical experiments platinum mesh was used as working electrode. Infrared spectra were recorded inside a glovebox on a Cary 630 FTIR spectrometer equipped with Dial Path Technology and analyzed by FTIR MicroLab software. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance 300 or 400 spectrometers. Chemical shifts are reported in parts per million relative to residual proton and carbon signals of the solvent THF (δ_H = 1.73 and 3.59 ppm; δ_C = 25.31 and 67.21 ppm) or toluene (δ_H = 2.08, 6.97, 7.01 and 7.09 ppm; δ_C = 20.43, 125.13, 127.96, 128.87 and 137.48 ppm).

EPR Spectroscopy. EPR spectra were measured with a Bruker E500 ELEXSYS X-band spectrometer equipped with a standard cavity (ER4102ST, 9.45 GHz). The sample temperature was maintained constant with an Oxford instrument nitrogen flow cryostat (ESP910) and an Oxford temperature controller (ITC-4). The microwave frequency was measured with the built-in frequency counter, and the magnetic field was calibrated by using an NMR field probe (Bruker ER035M). EPR spectra were simulated using Easy-Spin.42

DFT Calculations. The ORCA package (version 3.0.3) was employed.[3] Geometry optimizations were performed based on the coordinates of from the crystallographic structure determinations in case of **2**, **3** and **5** (BP86 functional, def2-tzvp and def2-tzvp/J basis sets,[4] RI approximation, D3 dispersion correction with zero damping,[5] tight convergence and optimization criteria). Selected geometric parameters are listed in Table S5, S6 and S8. The calculated structures (Figure S29, S30 and S32) are in reasonable agreement with the molecular structures in solid state determined by X-ray crystallography. Frequency calculations (Figure S33, S34 and S36) yielded no imaginary frequencies. Unrestricted DFT calculations were carried out on the optimized coordinates of **4** (Figure S31, Table S7) to obtain the spin density (Figure S37) using the B3LYP functional and the RIJCOSX approximation (def2-tzvp and def2-tzvp/J basis sets). A frequency calculation (Figure S35) yielded no imaginary frequencies.

X-ray Crystallography. Crystal data and details of the data collections are given in Table S4. X-ray data were collected on a STOE IPDS II diffractometer (graphite monochromated Mo-Kα radiation, λ = 0.71073 Å) by use of ω scans at –140 °C. The structures were solved with SHELXT[6a] and refined on F^2 using all reflections with SHELXL-2014/17/18.[6b] Non-hydrogen atoms were refined anisotropically. The unit cell of **2** contains highly

disordered solvent molecules (MeCN and pentane) for which no satisfactory model for a disorder could be found. The solvent contribution to the structure factors was calculated with PLATON SQUEEZE[6c] and the resulting .fab file was processed with SHELXL using the ABIN instruction. The empirical formula and derived values are in accordance with the calculated cell content. The PhNO moiety in **2** was found to be disordered about the mirror plane and was refined at ½ occupancy. **2** was furthermore twinned (twin law: 0 0 –1, 0 –1 0, –1 0 0; BASF: 0.471(2)). In case of **3** a THF solvent molecule was found to be disordered about three positions (occupancy factors: 0.474(3)/ 0.196(3)/ 0.331(3)). RIGU (**2**,**3**), SIMU (**2**), DELU(**2**), ISOR (**2**), SAME (**3**), BUMP (**3**) restraints EADP constraints (**3**) were applied to model the disordered parts. Face-indexed absorption corrections were performed numerically with the program X-RED.[6d]

A.2 Synthetic Protocols

$KLNi_2(PhNO)$ (2). A solution of PhNO (4.1 mg, $3.8\cdot10^{-2}$ mmol, 1 eq) in THF (1 mL) was added dropwise to an orange solution of **1** (29 mg, $3.8 \cdot 10^{-2}$ mmol, 1 eq) in THF (2 mL) at 0°C. The color turned immediately to black and the mixture was stirred for 2 hours at room temperature. The volatile materials were removed under reduced pressure. The resulting black solid was washed with pentane (3 × 2 mL) and crystallized by layering Et_2O onto a THF solution of the crude product. Single crystals suitable for X-ray diffraction were obtained by diffusion of Et_2O onto a concentrated solution of **2** in THF/MeCN at -30°C. Yield = 19 mg, 60%.
^{1}H NMR (toluene-d_8, 400 MHz, 298 K) δ = 11.03 (br, 1H, Ph-H^o), 10.78 (br, 1H, Ph-H^o), 7.39 (br, 2H, Ph-H^m), 6.84−6.80 (m, 2H, Ph-H^m + Ar-H^p), 6.79 (m, 1H, Ph-H^p), 6.74 (d, 1H, Ar-H^m), 6.67 (d, 1H, Ar-H^m), 6.57 (d, 1H, Ar-H^m), 6.50 (d, 1H, Ar-H^m), 5.35 (s, 1H, H-Pz), 5.21 (sept, 1H, CH-iPr), 4.83 (s, 1H, CH), 4.74 (s, 1H, CH), 4.67 (sept, 1H, CH-iPr), 3.70 (sept, 1H, CH-iPr), 3.64 (m, 1H, CH-iPr), 3.63−3.52 (m, 4H, CH_2), 2.31 (d, J_{H-H} = 7 Hz, 3H, CH_3- iPr), 2.13 (d, J_{H-H} = 7 Hz, 3H, CH_3- iPr), 1.75 (d, J_{H-H} = 7 Hz, 3H, CH_3- iPr),1.58 (s, 3H, CH_3), 1.73 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.19 (d, J_{H-H} = 7 Hz, 3H, CH_3- iPr), 1.14 (d, J_{H-H} = 7 Hz, 3H, CH_3- iPr), 1.01 (d, J_{H-H} = 7 Hz, 3H, CH_3-iPr), 0.84 (d, J_{H-H} = 7 Hz, 3H, CH_3- iPr), 0.51 (d, J_{H-H} = 7 Hz, 3H, CH_3- iPr) ppm. ^{13}C-NMR (toluene-d_8, 100 MHz, 298 K) δ = 180.9 (C-H^o), 166.8 (C-CH^p), 164.9 (Ar), 161.4 (C-Me), 160.6 (C-Pz), 160.4 (C-Me), 158.8 (C-Me), 158.0 (C-Me), 151.5 (Ar), 148.8 (Ar), 148.7 (Ar), 147.0 (Ar), 146.7 (Ar), 145.6 (Ar), 141.5 (Ar), 125.0 (Ar), 124.3 (Ar), 123.7 (Ar), 123.4 (Ar), 123.3 (Ar), 122.9 (Ar), 122.6 (Ar), 113.5 (C-H^m), 98.0 (CH), 97.6 (CH), 91.0 (C-Pz), 54.4 (CH_2), 51.4 (CH_2), 28.8 (CH-iPr), 28.5 (CH-iPr), 27.2 (CH-iPr), 27.0 (CH_3-iPr), 26.9 (CH_3-iPr), 26.8 (CH-iPr), 25.8 (CH_3-iPr), 25.2 (CH_3-iPr), 24.3 (CH_3-iPr), 24.2 (CH_3), 23.9 (CH_3), 23.8 (CH_3-iPr), 23.6 (CH_3-iPr), 22.8 (CH_3-iPr), 21.4 (CH_3), 20.9 (CH_3) ppm. ATR-IR ($\tilde{\nu}$/cm^{-1}) = 3036 (w), 2660 (m), 2922 (m), 2861 (m), 1576 (m), 1560 (m), 1537 (w), 1519 (vs), 1462 (s), 1428 (s), 1402 (vs), 1366 (w), 1337 (w), 1312 (s), 1290 (w), 1273 (m), 1244 (m), 1227 (m), 1213 (m), 1187 (m), 1163 (s), 1088 (m), 1069 (m), 1052 (m), 1030 (m), 1023 (s), 1013 (m), 976 (s), 948 (w), 933 (w), 911 (w), 907 (w, NO), 853 (w), 804 (s), 772 (s), 754 (m), 746 (w), 734 (vs), 693 (s), 656 (w), 634 (w), 597 (w), 549 (m), 522 (s), 492 (w), 473 (w), 464 (w), 458 (w), 447 (w), 439 (w), 432 (s). UV-Vis (THF, λ/nm (ε/M^{-1}cm^{-1})) = 271 (20400), 374 (9800), 611 (2000), 721 (1400). MS (ESI$^+$, THF/MeOH) *m/z* (%) = 867.3 [LNi_2(PhNO) + K]$^+$, 851.3 [LNi_2(PhNO) + Na]$^+$. Anal. Calcd for $C_{45}H_{58}N_7OKNi_2$: C 62.16 H 6.62 N 11.28. Found: C 61.10, H 6.83; N 10.51 (deviations may be due to trace amounts of solvents, or trace amounts of stable [LNi_2(OH)] which is a well known side product in any chemistry based on the {LNi_2} scaffold). **2-^{15}NO.** The synthesis of **2-^{15}NO** was achieved by the same procedure as described above for **2** but using Ph^{15}NO. ATR-IR ($\tilde{\nu}$/cm^{-1}) = 894 (m, ^{15}NO).

[LNi_2(PhNO)][K(crypt)] (3). Complex **2** (15 mg, $1.7 \cdot 10^{-5}$ mmol, 1 eq) was dissolved in THF (1 mL) and treated with [2.2.2]-cryptand (6.8 mg, $1.8 \cdot 10^{-5}$ mmol, 1.05 eq) at room temperature. After stirring for 2 hours, the

solution was layered with hexane and kept at −30°C for 3 days. The product was then isolated as dark green powder that was washed with pentane (3 × 2 mL). Single crystals suitable for X-ray diffraction were obtained by diffusion of pentane into a concentrated solution of **3** in THF at −30 °C. Yield = 12 mg, 58 %.

^{1}H-NMR (THF-d_8, 400 MHz, 298 K) δ = 9.73 (br, Ph-H^{o}), 6.88−6.44 (m, 8H, Ph + Ar), 5.91 (t, J_{H-H} = 7 Hz, 1H, Ph-H^{p}), 5.22 (s, 1H, H-Pz), 4.59 (sept, 1H, CH-iPr), 4.39 (s, 1H, CH), 4.36 (s, 1H, CH), 4.00−3.73 (m, 4H, CH_2), 3.41 (sept, 1H, CH-iPr), 3.11 (sept, 1H, CH-iPr), 3.02 (sept, 1H, CH-iPr), 2.17 (d, J_{H-H} = 7 Hz, 3H, CH_3-Ar), 1.77 (s, 3H, CH_3), 1.63 (s, 3H, CH_3), 1.42 (d, J_{H-H} = 7 Hz, 3H, CH_3-Ar), 1.63 (s, 3H, CH_3), 1.42 (d, J_{H-H} = 7 Hz, 3H, CH_3-Ar), 1.23 (s, 3H, CH_3), 1.18 (s, 3H, CH_3),1.05 (d, J_{H-H} = 7 Hz, 3H, CH_3-Ar), 0.98 (d, J_{H-H} = 7 Hz, 3H, CH_3-Ar), 0.85 (d, J_{H-H} = 4 Hz, 3H, CH_3-Ar), 0.82 (d, J_{H-H} = 4 Hz, 3H, CH_3-Ar) ppm. ^{13}C-NMR (THF-d_8, 100 MHz) δ = 180.4 (C-H^{o}), 165.2 (C-CH^{p}), 160.4 (C-Pz), 158.4 (C-Me), 157.3 (C-Me), 156.6 (C-Me), 150.5 (C-Pz), 148.8 (Ar), 146.0 (Ar), 145.0 (C-Me), 142.5 (Ar), 141.9 (Ar) 126.0 (Ar), 125.0 (Ar), 124.3 (Ar), 122.6 (Ar), 122.3 (Ar), 122.1 (Ar), 121.8 (Ar), 121.2 (Ar), 114.1 (C-H^{m}), 111.7 (Ar), 105.6 (C-H^{p}), 96.0 (CH), 95.3 (CH), 89.1 (C-Pz), 54.4 (CH_2), 50.9 (CH_2), 31.6 (Me), 28.5 (CH-iPr), 28.1 (CH-iPr), 27.8 (CH-iPr), 26.7 (CH-iPr), 26.2 (CH_3), 26.0 (CH_3), 25.8 (CH_3), 25.1 (CH_3), 25.0 (CH_3), 24.7 (CH_3), 24.3 (CH_3), 23.9 (CH_3), 23.8 (CH_3), 23.2 (CH_3), 23.1 (CH_3) ppm. ATR-IR ($\tilde{\nu}$/cm^{-1}) = 2953 (w), 2922 (m), 2865 (m), 2814 (m), 1580 (m), 1550 (m), 1521 (m), 1468 (m), 1443 (m) 1403 (m), 1354 (m), 1298 (m), 1233 (m), 1134 (m), 1101 (vs), 1081 (m), 1061 (m), 1022 (w), 982 (m), 973 (m), 949 (s), 933 (m), 833 (m), 799 (m), 759 (m), 723 (m), 694 (w), 568 (w), 524 (m), 508 (m), 480 (w), 464 (w), 452 (w), 444 (w), 435 (w), 425 (vs). UV-Vis (THF, λ/nm (ε/M^{-1}cm^{-1})) = 270 (19607), 378 (7826). MS (ESI+, THF/MeOH) *m/z* (%) = 867.3 [LNi_2(PhNO) + K]$^{+}$

3-^{15}NO. The synthesis of **3-^{15}NO** was achieved by the same procedure as described above for **3** but using **2-^{15}NO**. ^{15}N-NMR (THF-d_8, 50 MHz) δ = −213.8 (s, ^{15}NO) ppm.

LNi_2(PhNO) (**4**): Complex **2** (20 mg, 2.3 · 10^{-2} mmol, 1 eq) was dissolved in THF (1 mL) and treated with [Fe(Cp*)$_2$][PF_6] (12 mg, 2.5 · 10^{-2} mmol, 1.1 eq) at room temperature. After stirring for 2 hours, the resulting red suspension was filtered and stored at −30°C overnight. The solution was filtered again while cold and the solvent was then removed under reduced pressure. The obtained dark red powder was washed with cold pentane (2 × 2 mL) and the final product was dried under vacuum. Yield = 6.5 mg, 34 %. ATR-IR ($\tilde{\nu}$/cm^{-1}) =3051 (w), 2957 (m), 2954 (m), 2865 (m), 1615 (br), 1582 (m), 1555 (m), 1525 (m), 1461 (m), 1434 (m), 1397 (m), 1367 (w), 1344 (w), 1314 (m), 1276 (w), 1251 (w), 1230 (w), 1185 (w), 1165 (w), 1155 (w, NO), 1149 (w, PF), 1104 (br) 1090 (m), 1071 (m), 1054 (m), 1032 (m), 1024 (m), 1018 (m), 979 (m), 908 (br), 828 (vs, PF), 805 (m), 797 (m), 756 (m), 751 (m), 744 (m), 734 (m), 715 (m), 796 (m), 678 (m), 661 (w), 643 (w), 596 (w), 561 (w). UV-Vis (THF, λ/nm (ε/M^{-1}cm^{-1})) = 270 (19607), 378 (7826).

LNi_2(Ph^{15}NO) (4-^{15}NO): The synthesis of **4-^{15}NO** was achieved by the same procedure as described above for **4** but using **2-^{15}NO**. ATR-IR ($\tilde{\nu}$/cm^{-1}) = 1135 (m, ^{15}NO).

LNi_2(PhN(H)O) (5): Complex **2** (15 mg, 1.72 · 10^{-5} mmol, 1 eq) was dissolved in THF (1 mL) and treated with [LutH][OTf] (4.8 mg, 1.89 · 10^{-5} mmol, 1.1 eq) at room temperature. After stirring for one hour, the resulting red suspension was filtered and the solvent was removed under reduced pressure. The product was extracted with hexane (3 × 2 mL) and the solvent was removed again under reduced pressure. Single crystals of **5** suitable for X-ray diffraction were grown by diffusion of hexane into a concentrated THF solution of **5** at room temperature. Yield = 7 mg, 47 %. ATR-IR ($\tilde{\nu}$/cm^{-1}) = 3147 (w, NH), 3142 (w), 2955 (m), 2921 (m), 2863 (m), 1644 (vw), 1553 (s), 1523 (s), 1492 (w), 1454 (s), 1433 (s), 1398 (vs), 1377 (s), 1309 (s), 1276 (m), 1251 (m), 1227 (m), 1182 (m), 1175 (m), 1137 (w), 1086 (m), 1052 (w), 1038 (s, NO), 981 (m), 953 (w), 933 (m), 920 (m), 880 (m), 864 (w), 794 (s), 784 (m), 758 (vs), 731 (vs), 714 (s), 694 (m), 632 (m), 600 (m), 522 (m), 492 (s).

LNi_2(μ-Ph^{15}NHO) (5-^{15}NO): The synthesis of **5-^{15}NO** was achieved by the same procedure as described above for **5** but using **2-^{15}NO**. ATR-IR ($\tilde{\nu}$/cm^{-1}) = 3138 (w, ^{15}NH), 1018 (s, ^{15}NO).

B Complex 2

B.1 Further Analytical Data

B.1.1. NMR Spectroscopy

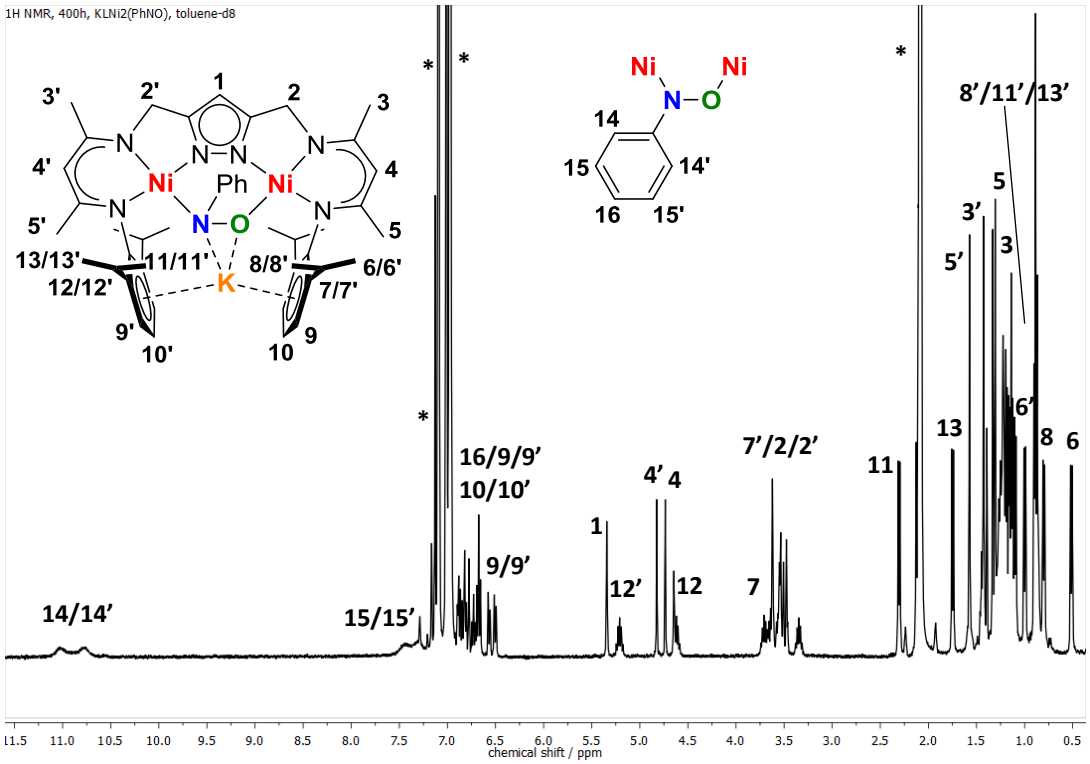


Figure S1: ^{1}H NMR spectrum of complex **2** in toluene-d_8. Solvent signals are marked with an asterisk (*).

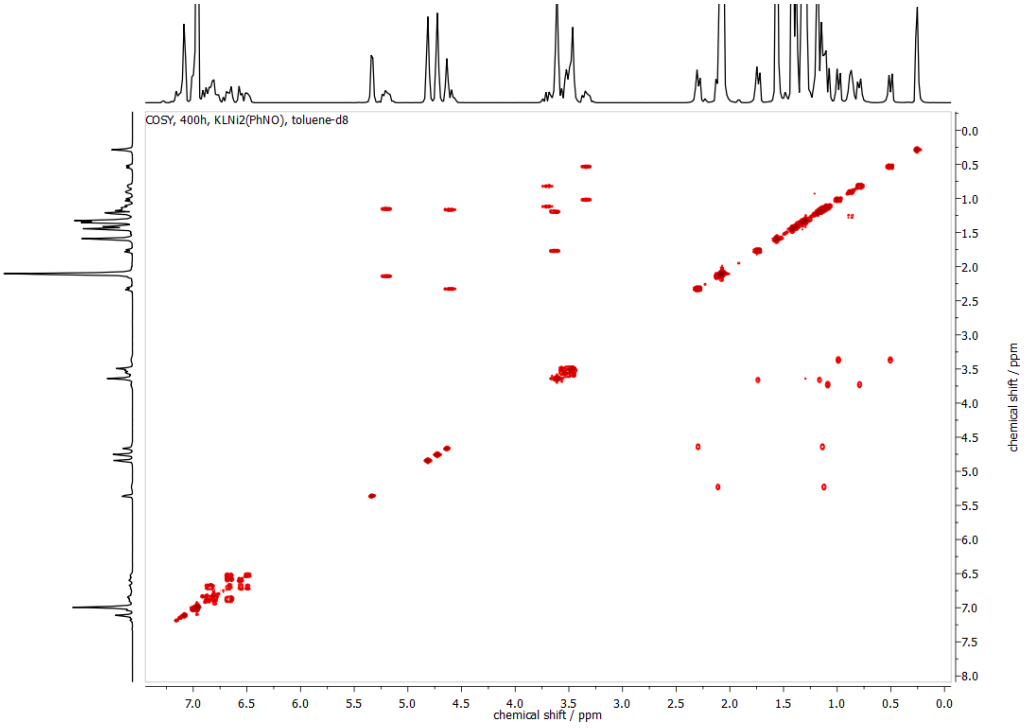


Figure S2: ^{1}H-^{1}H COSY spectrum of complex **2** in toluene-d_8.

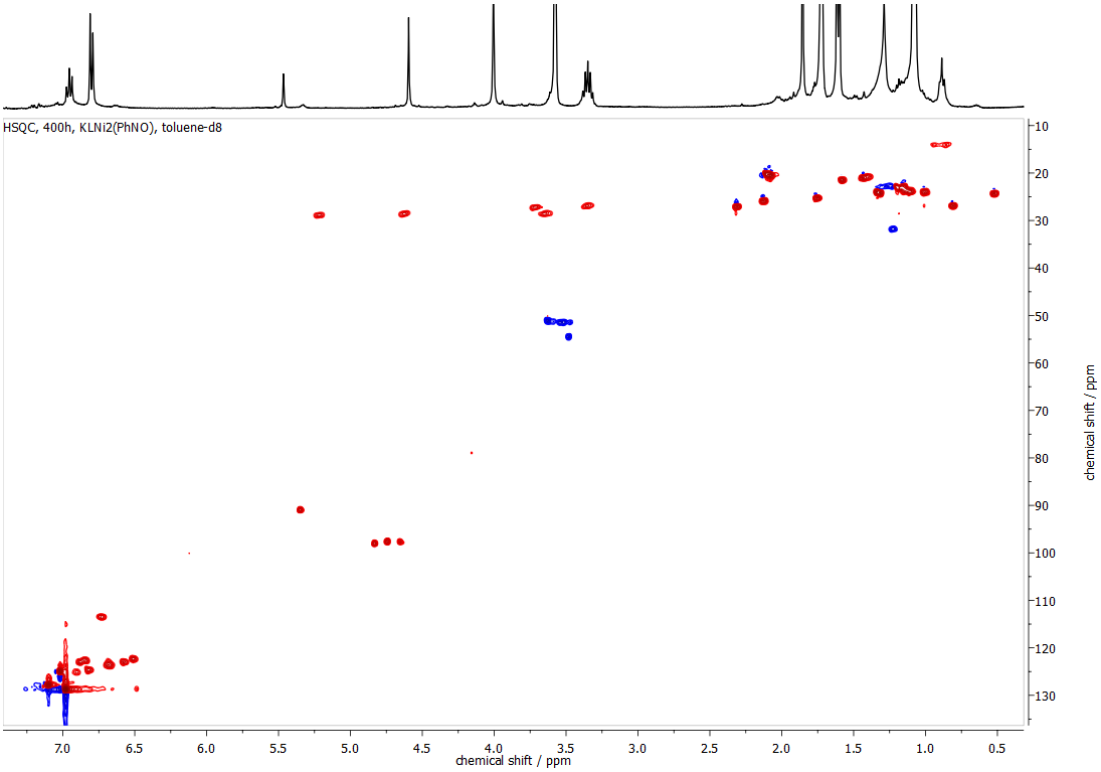


Figure S3: HSQC spectrum of complex **2** in toluene-d_8.

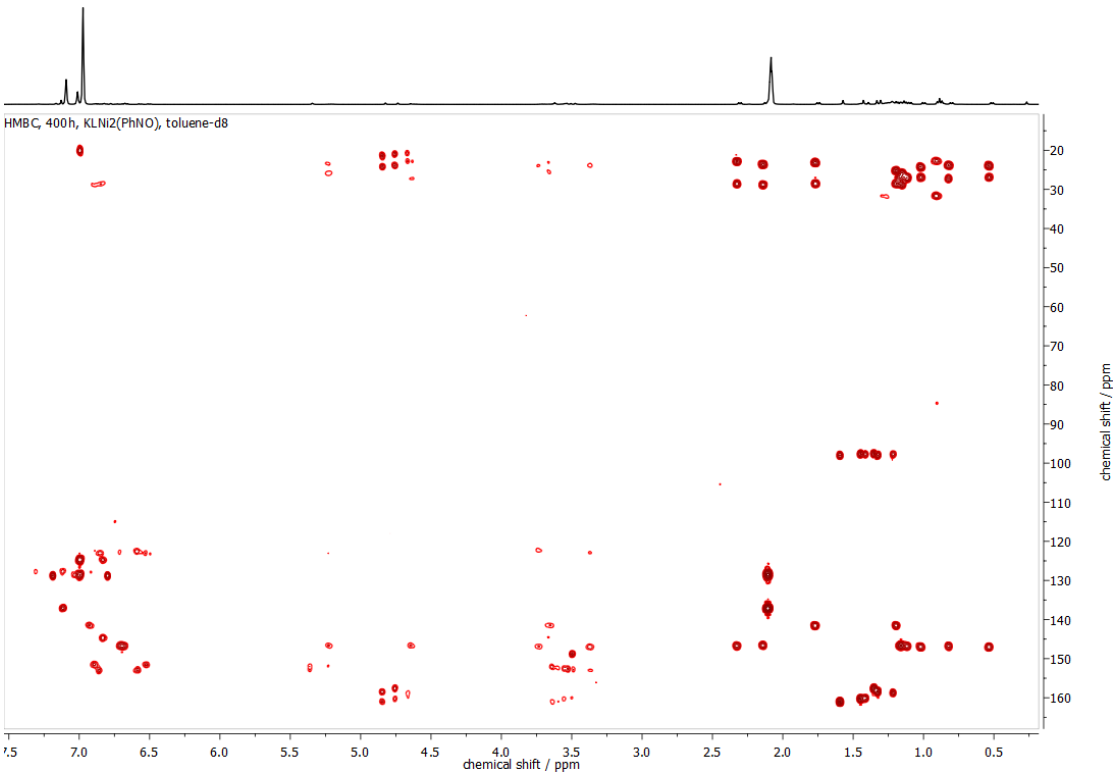


Figure S4: HMBC spectrum of complex **2** in toluene-d_8.

B.1.2. Mass Spectrometry

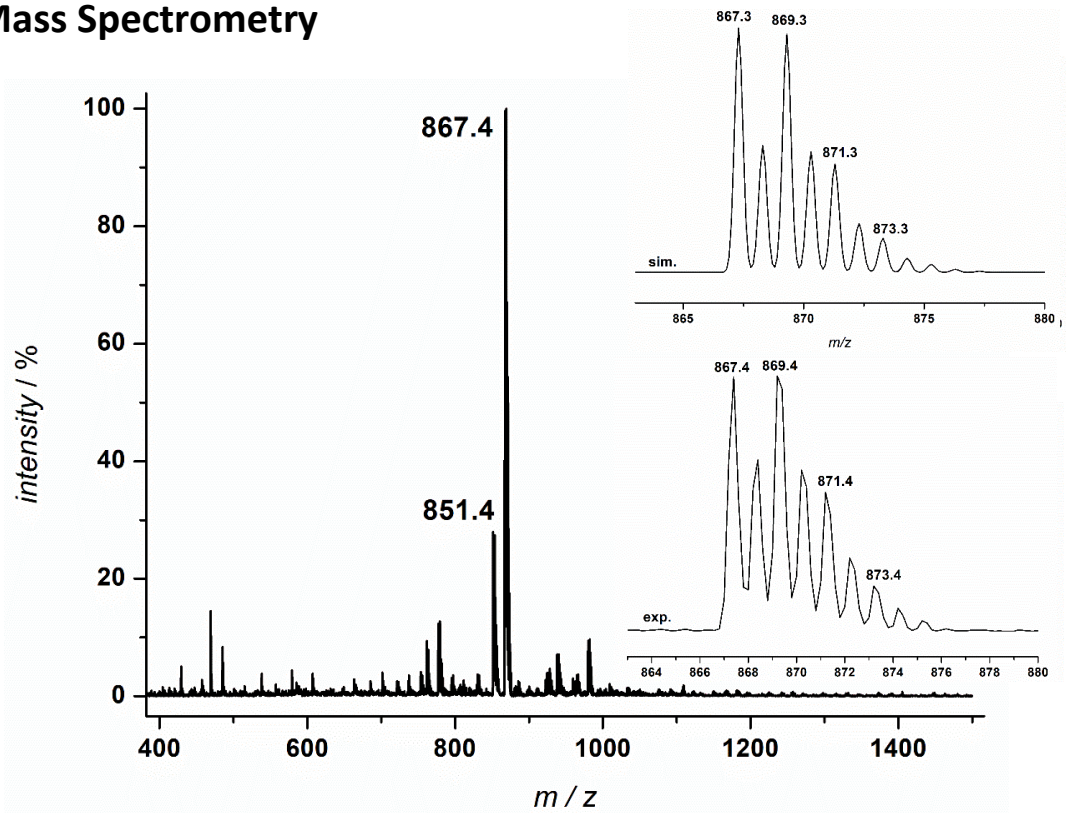


Figure S5: ESI mass spectrum of complex **2** in THF/MeOH (10:1). The inset shows the experimental (bottom) and simulated (top) isotope pattern for the major peak around *m/z* = 867.3 (100) $[M+K]^+$.

B.1.3. UV-vis Spectroscopy

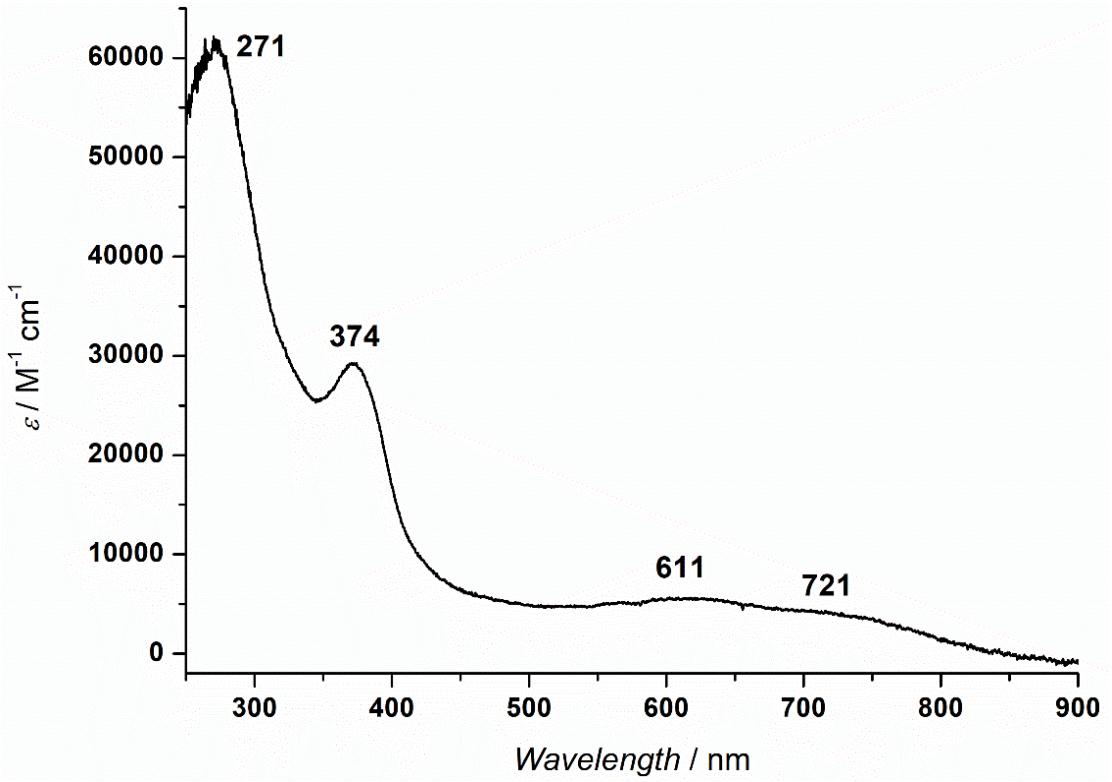


Figure S6: UV-vis spectrum of complex **2** in THF recorded at room temperature.

B.2 Variable Temperature (VT) NMR

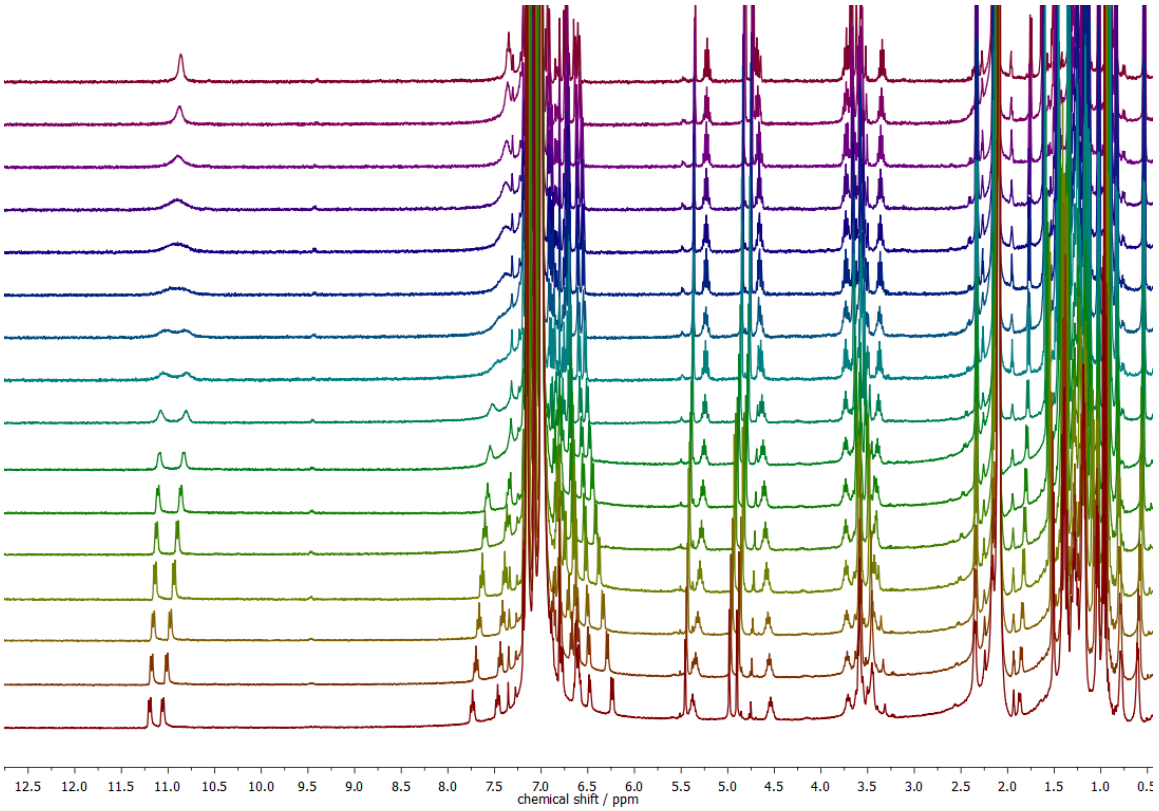


Figure S7: VT ^{1}H NMR spectra of complex **2** in toluene-d_8 in the range 338K (top)-218K (bottom).

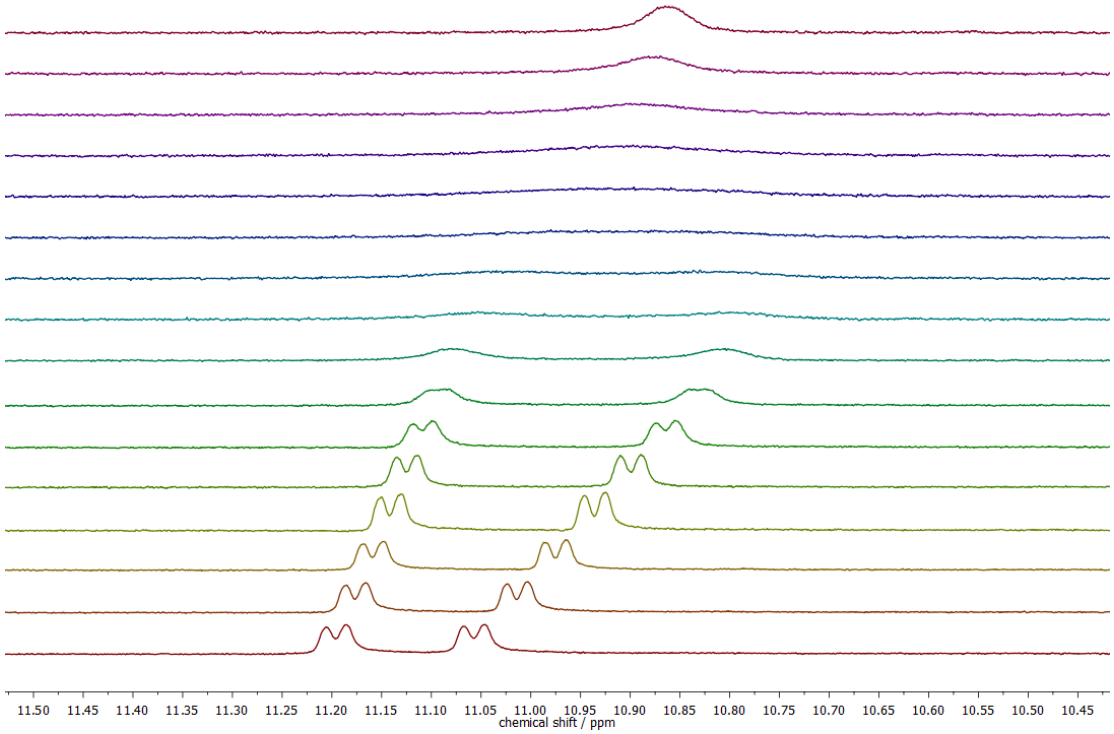


Figure S8: VT ^{1}H NMR spectra of complex **2** (11.5-10.5 ppm) in toluene-d_8 in the range 338 K (top) – 218 K (bottom). The resonance for H^{ortho} of the phenyl group of the nitrosobenzene ligand splits and shifts its position upon cooling.

C Complex 3

C.1 Further Analytical Data

C.1.1 UV-vis Spectroscopy

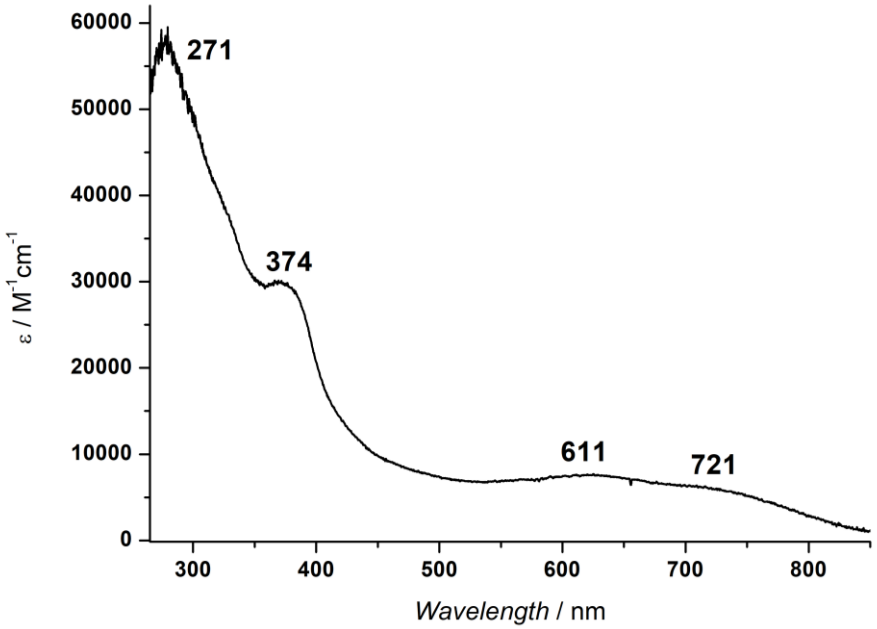


Figure S9: UV-vis spectrum of complex **3** in THF recorded at room temperature.

C.1.2 Cyclic Voltammetry

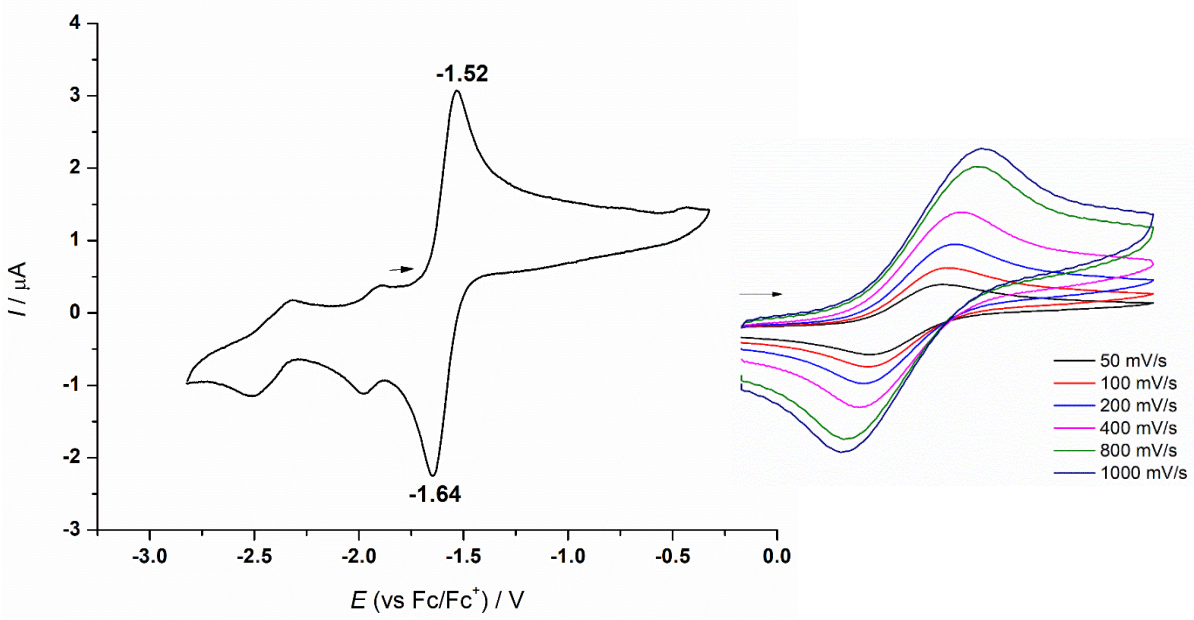


Figure S10: Cyclic voltammogram of compound **3** recorded in THF at room temperature; the inset shows the main reversible peak at $E_{½}$ = −1.58 V measured at different scan rates.

C.1.3 NMR Spectroscopy

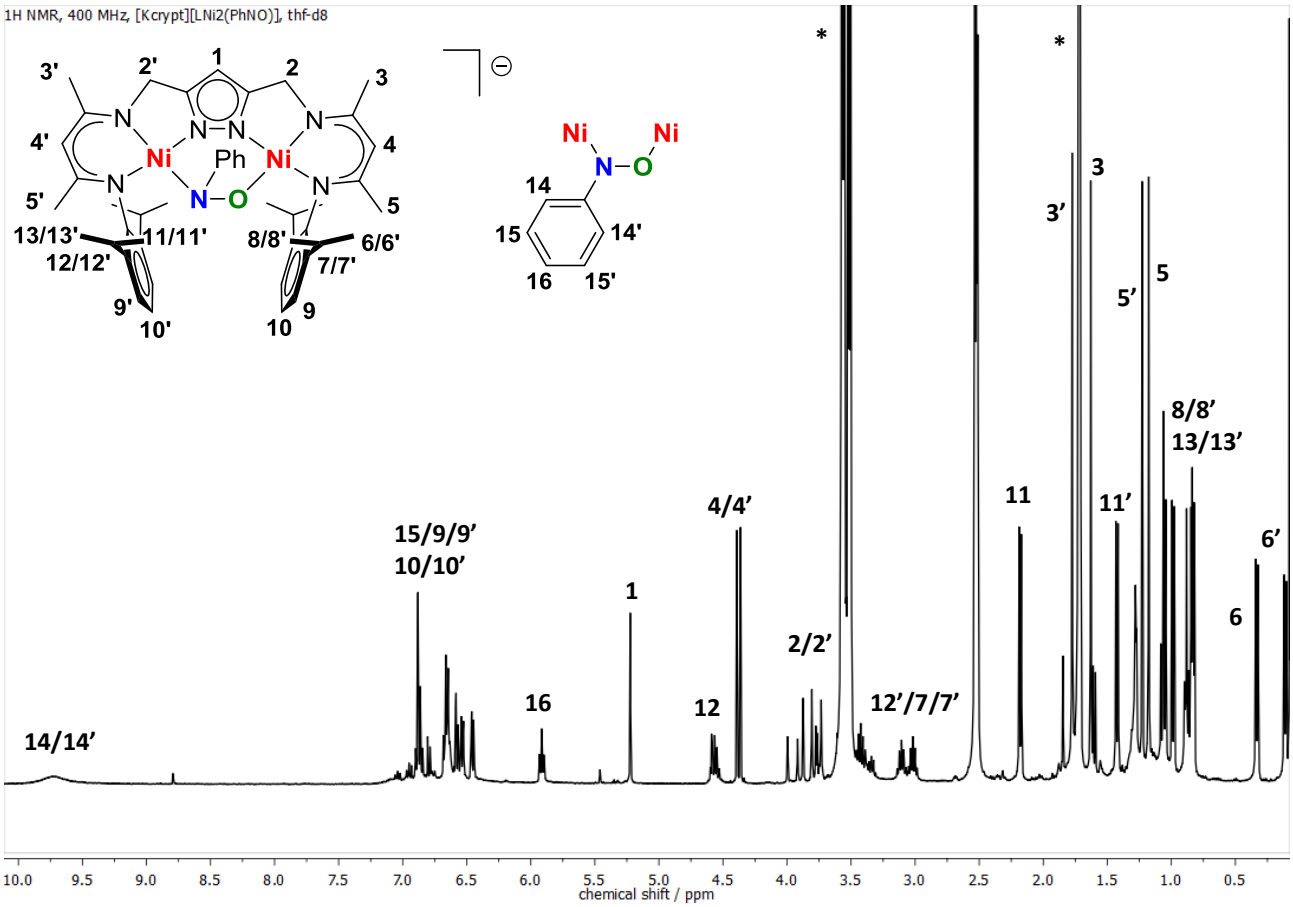


Figure S11: ^{1}H NMR spectrum of complex **3** in thf-d_8. Solvent signals are marked with an asterisk (*).

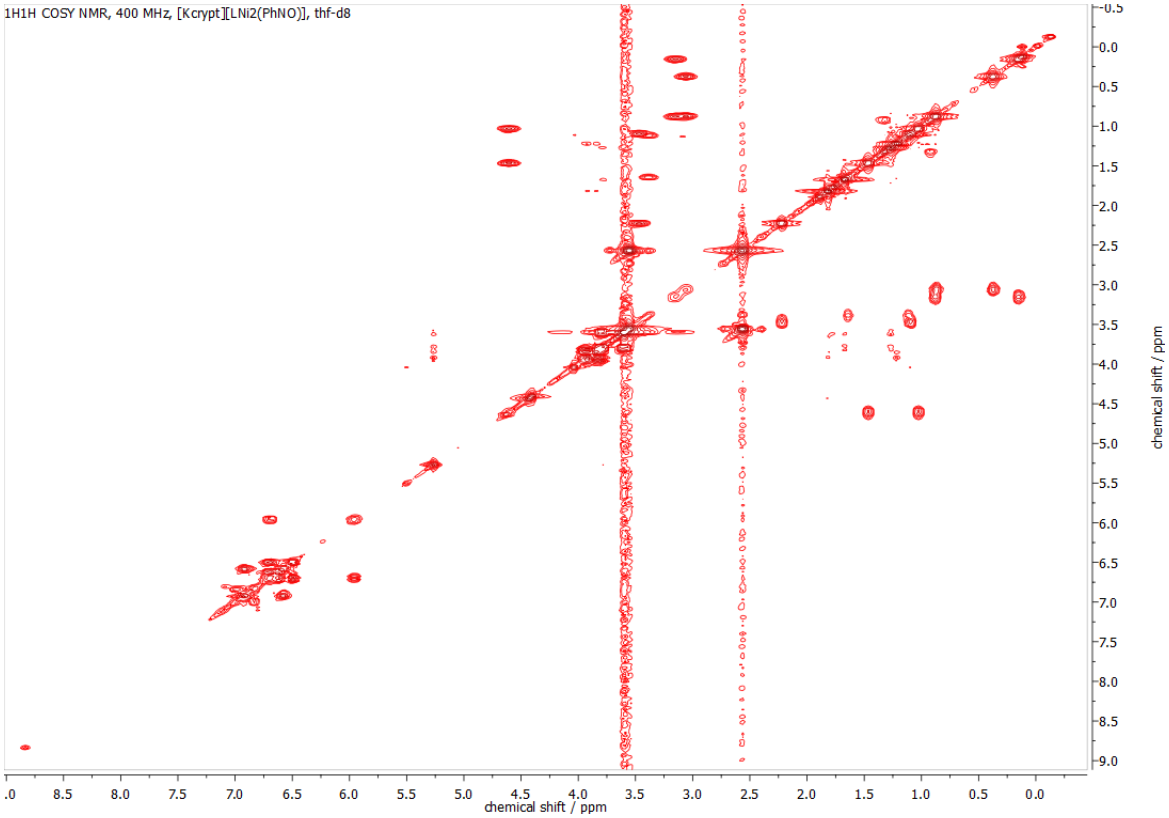


Figure S12: ^{1}H-^{1}H COSY spectrum of complex **3** in thf-d_8.

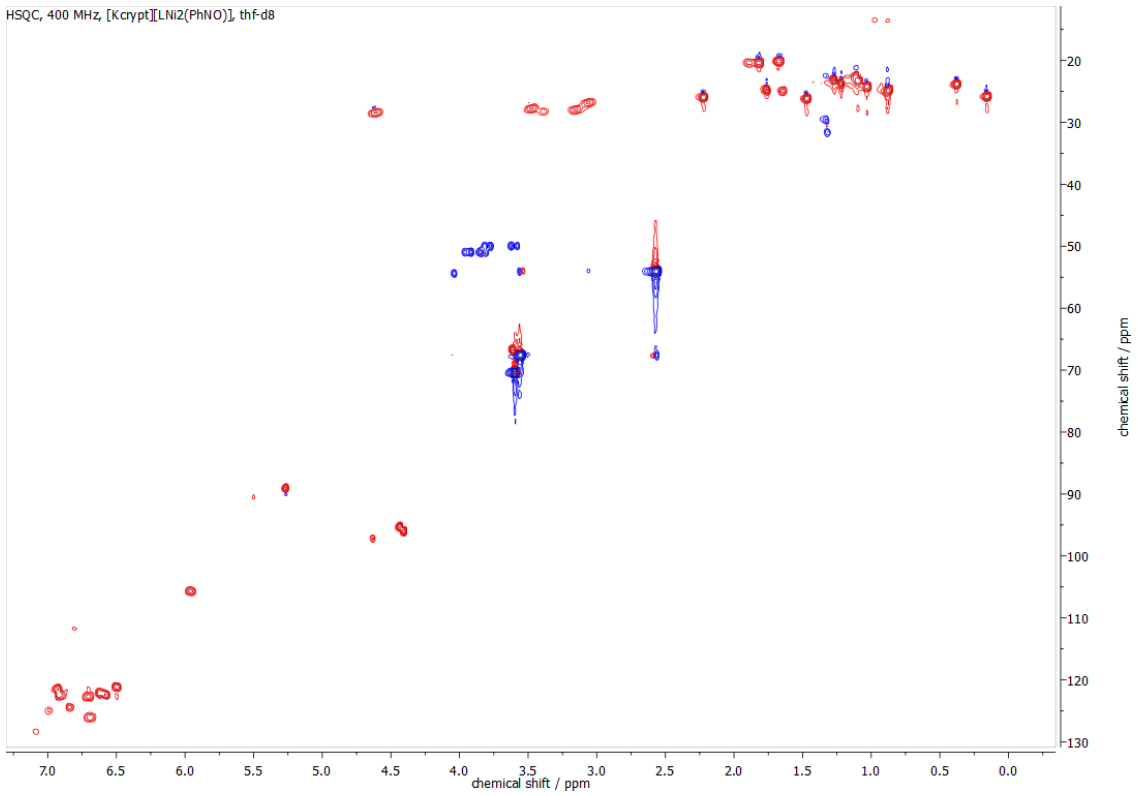


Figure S13: HSQC spectrum of complex **3** in thf-d_8.

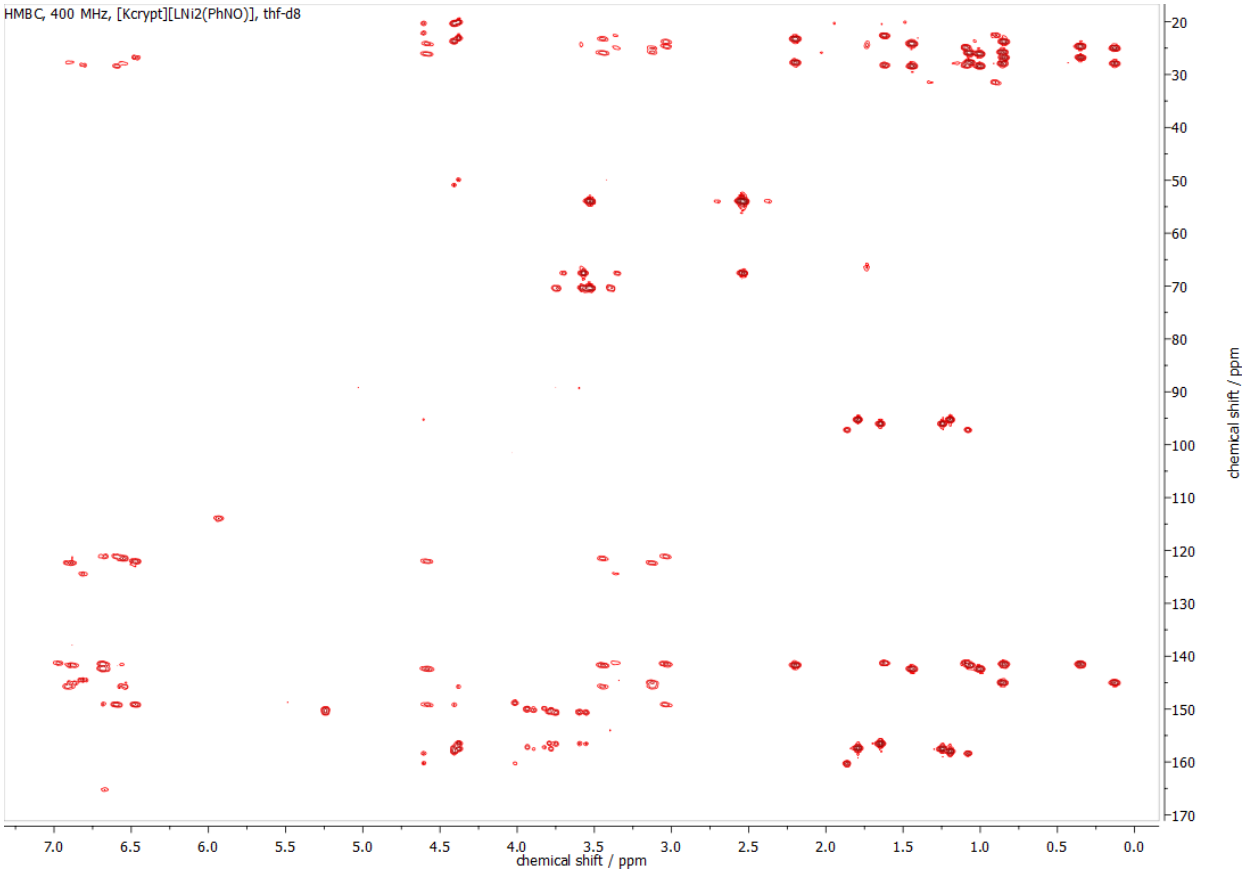


Figure S14: HMBC spectrum of complex **3** in thf-d_8.

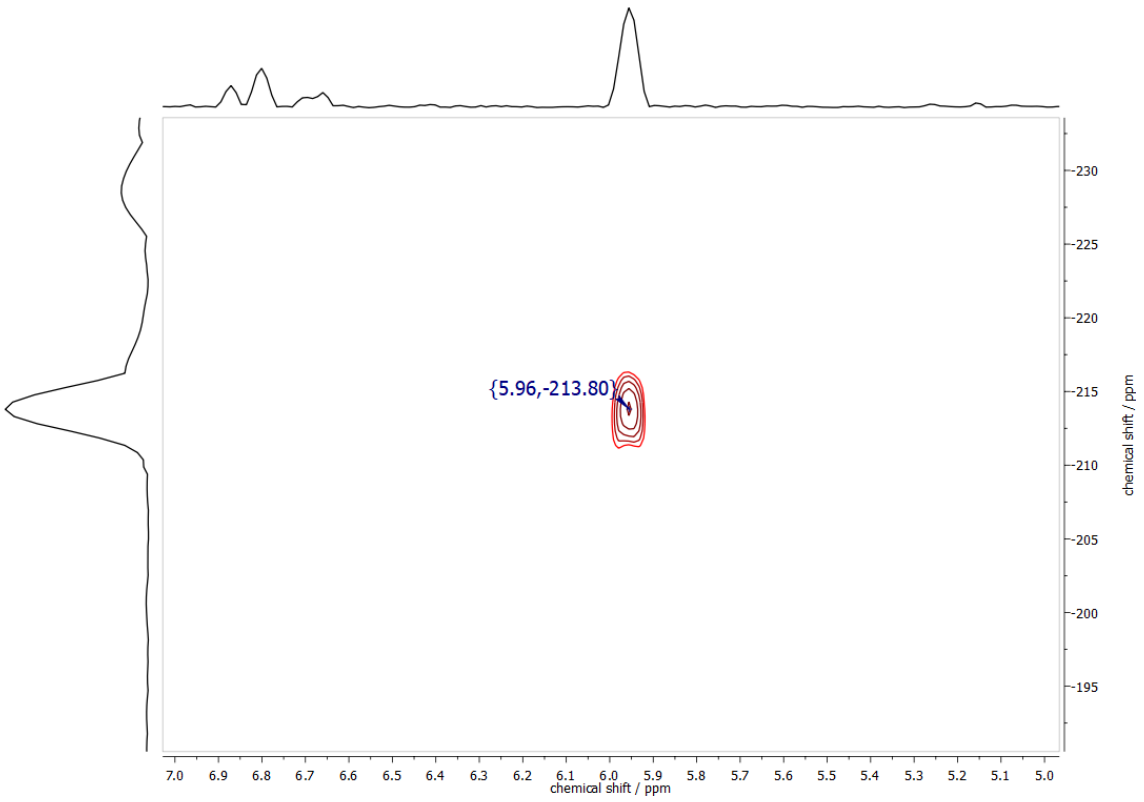


Figure S15: ^{1}H-^{15}N HMBC spectrum of complex **3** in thf-d_8. A correlation between the para-H at the phenyl group of the nitrosobenzene ligand and the nitrogen atom is observed.

C.2 Variable Temperature (VT) ^{1}H-NMR Spectroscopy

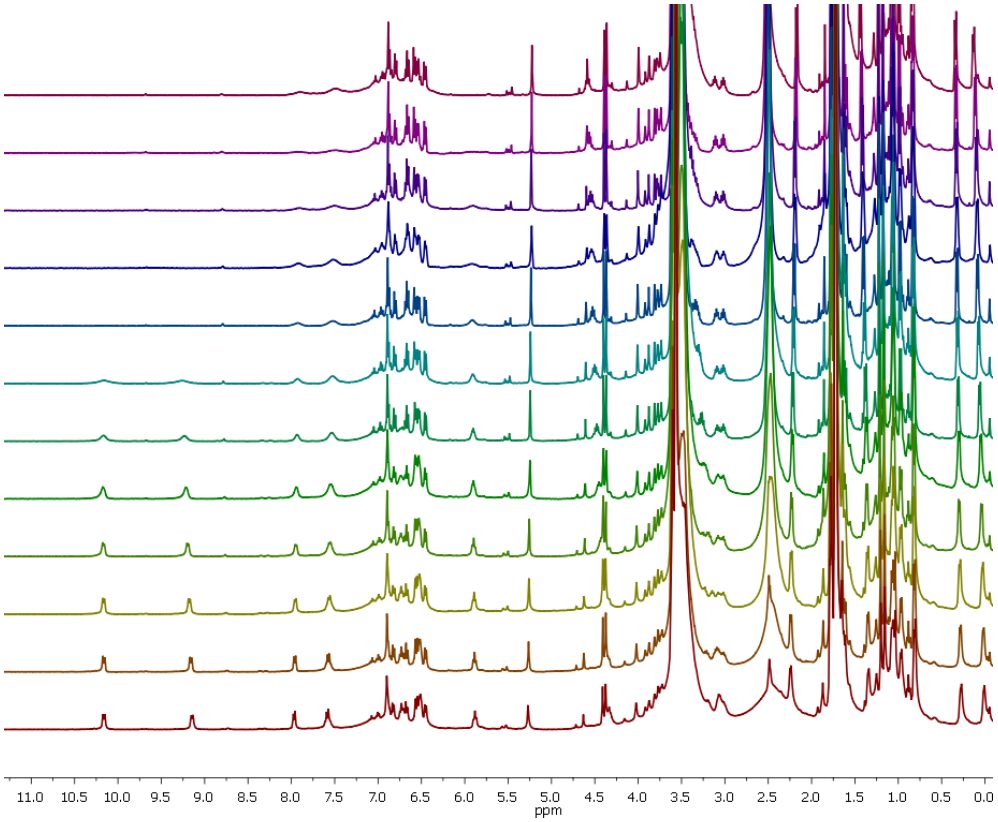


Figure S16: VT ^{1}H NMR spectra of complex **3** in thf-d_8 in the range 308K (top)-208K (bottom).

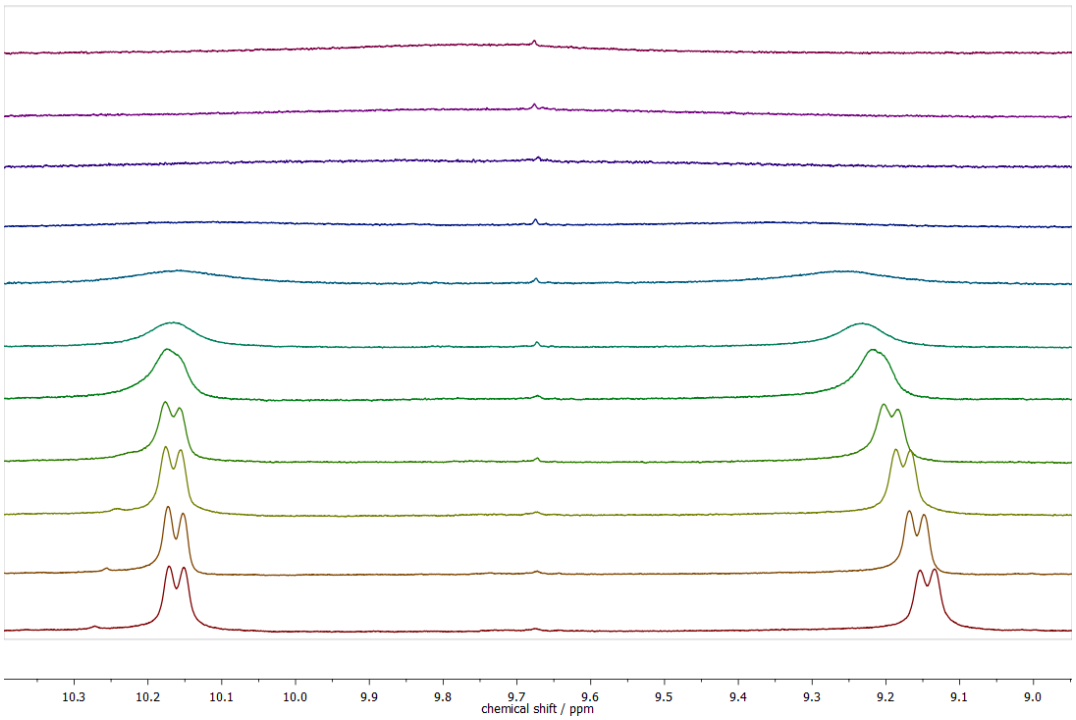


Figure S17: Section of the variable temperature ^{1}H NMR spectra (400 MHz) of **3** measured in the range 208-308 K. The two resonances for the ortho-H atoms of the phenyl ring are depicted.

Table S1. Exchange rate constants derived from the experimental NMR spectra (lineshape analysis).

T / K	k / s^{-1}
208	0
218	0.25
228	1.06
238	5.56
248	23.40
258	46.84
268	429.92
278	665.02
283 (T_c)	903.54
288	1060.04

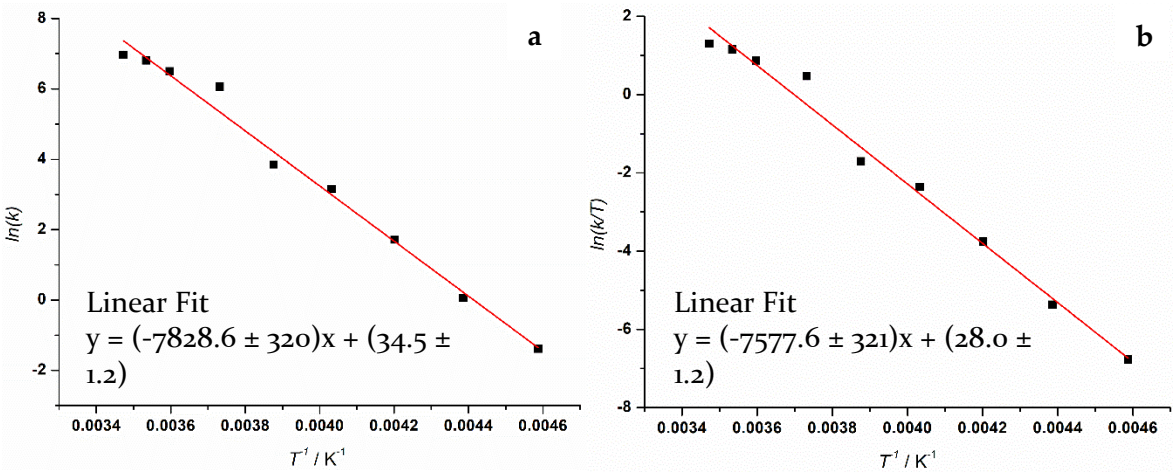


Figure S18. Arrhenius (a) and Eyring (b) plot for the obtained exchange constants. The linear fit is represented by the red line.

Table S2. Activation parameters for the rotation of the phenyl ring of complex **3** determined by the variable temperature NMR experiment.

E_a		$\Delta H^{\ddagger}$		$\Delta S^{\ddagger}$		$\Delta G_{298}{}^{\ddagger}$	
kJ mol^{-1}	kcal mol^{-1}	kJ mol^{-1}	kcal mol^{-1}	J K^{-1} mol^{-1}	cal K^{-1} mol^{-1}	kJ mol^{-1}	kcal mol^{-1}
65.1±2.7	15.6±0.6	62.7±2.7	15.0±0.6	35±9	8.3±2.1	52.1±1.0	12.5±0.3

D Complex 4

D.1 Further Analytical Data

D.1.1 UV-vis Spectroscopy

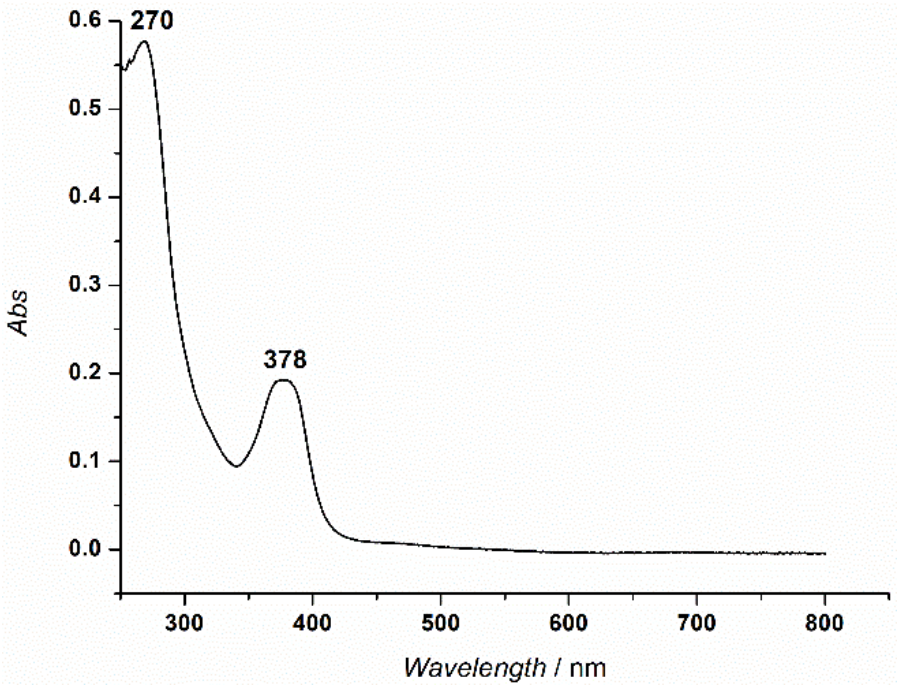


Figure S19. UV-vis spectrum of complex **4** in THF at room temperature.

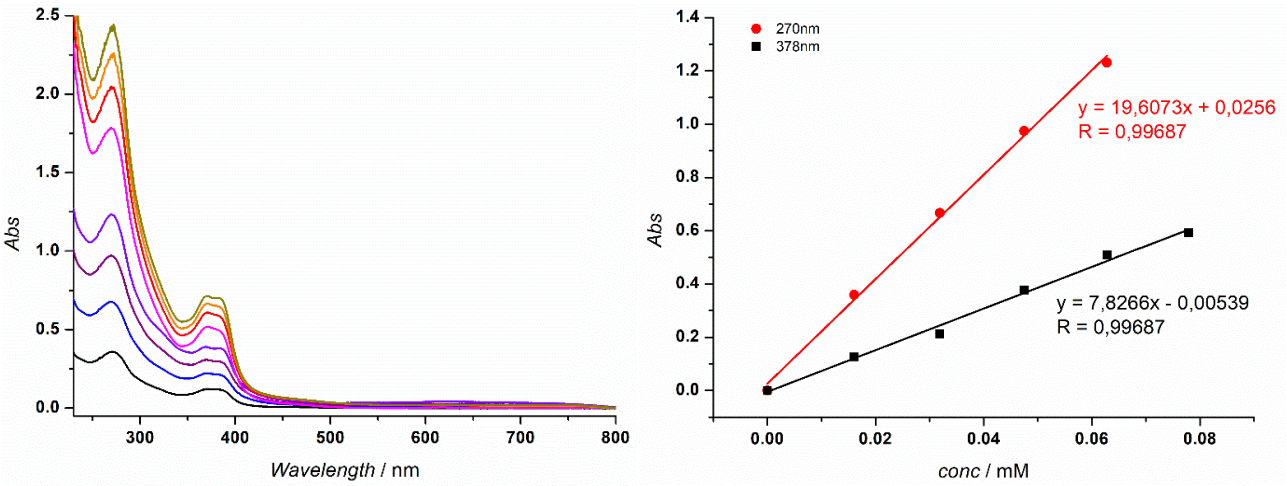


Figure S20. UV-vis spectra of complex **4** in THF at room temperature at different concentrations (left) and Beer's law plot of **4** that shows λ_{max} / nm (ε / M^{-1} cm^{-1}) = 270 (19610), 378 (7825).

D.1.2 IR Spectroscopy

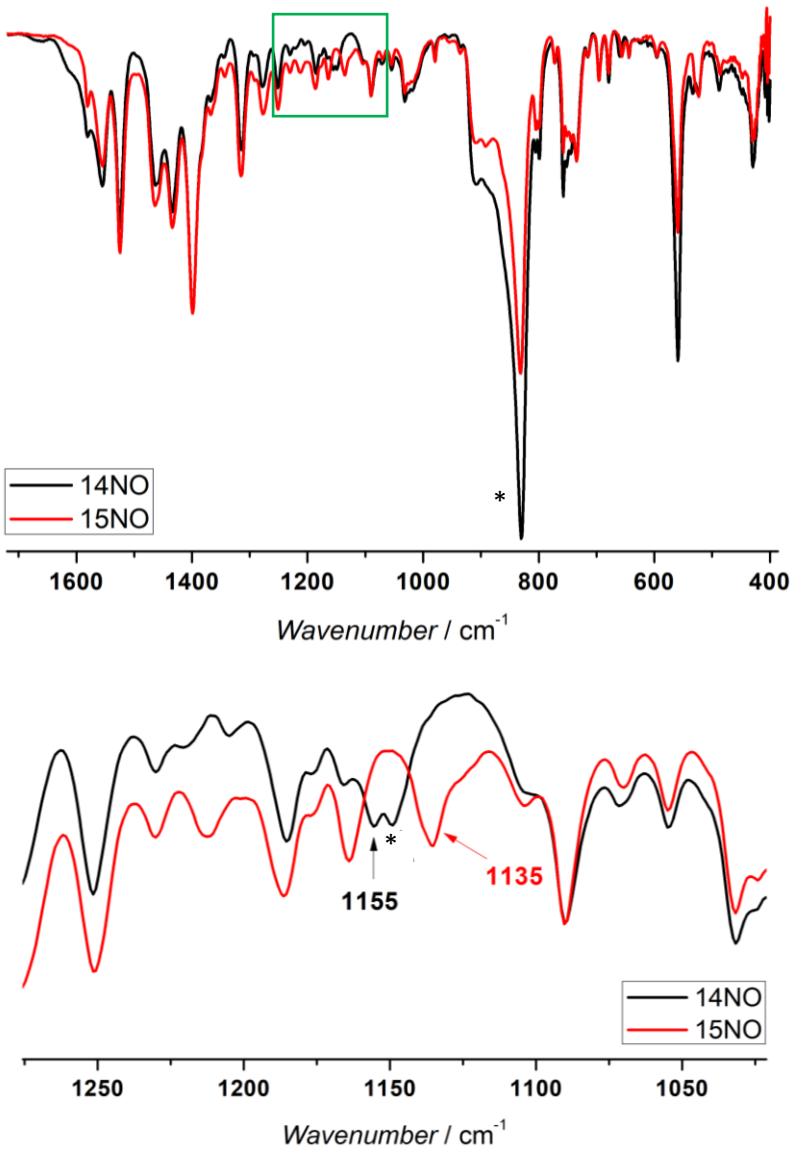
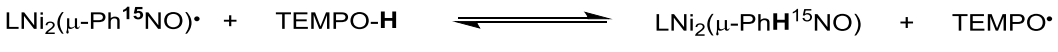


Figure S21. IR spectra of solid **4** (black line) and **4-^{15}NO** (red line). Top: IR spectra in the region 1700 cm^{-1} – 400 cm^{-1}; bottom: zoom into in the region 1300 cm^{-1} – 1000 cm^{-1}. Traces of KPF_6 found in the samples are marked with an asterisk (*).

D.2 Reactivity of 4-^{15}NO with TEMPO-H monitored by EPR spectroscopy



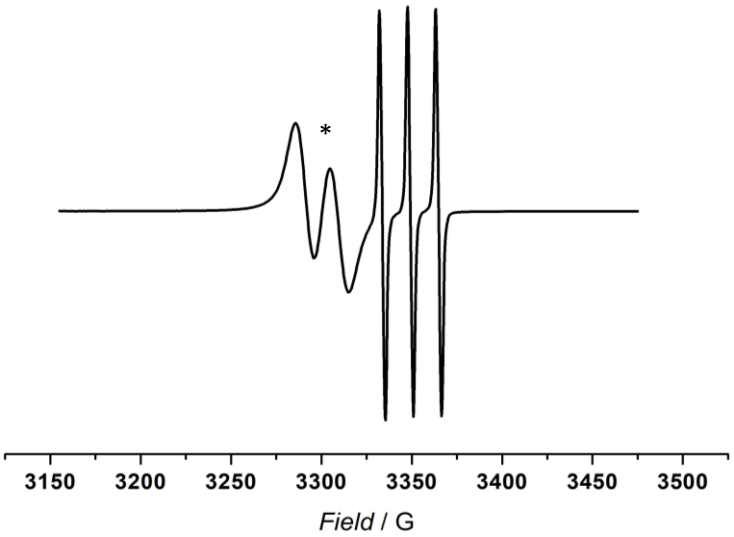


Figure S22. X-band EPR spectrum in THF recorded at room temperature of complex **4-^{15}NO** treated with TEMPO-H, showing formation of TEMPO· next to unreacted starting material **4** (marked with an asterisk (*)).

E Complex 5

E.1 IR Spectroscopy

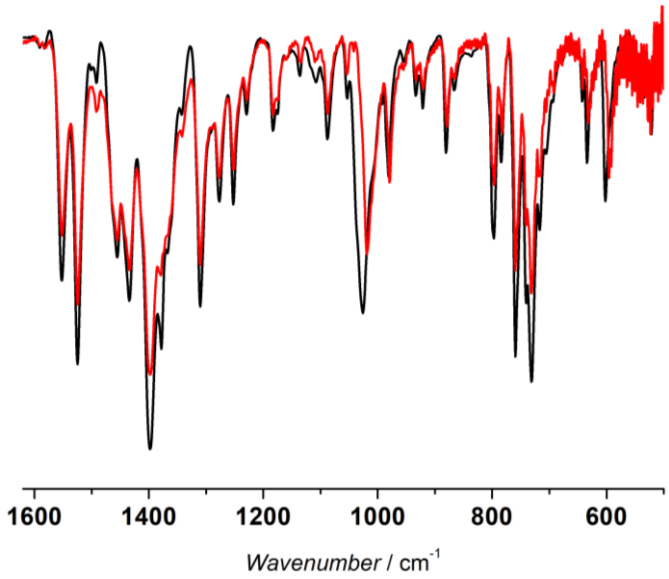


Figure S23. IR spectra of solid **5** (black line) and **5-^{15}NO** (red line).

E.2 Reactivity towards Verkade's base monitored by UV-vis spectroscopy

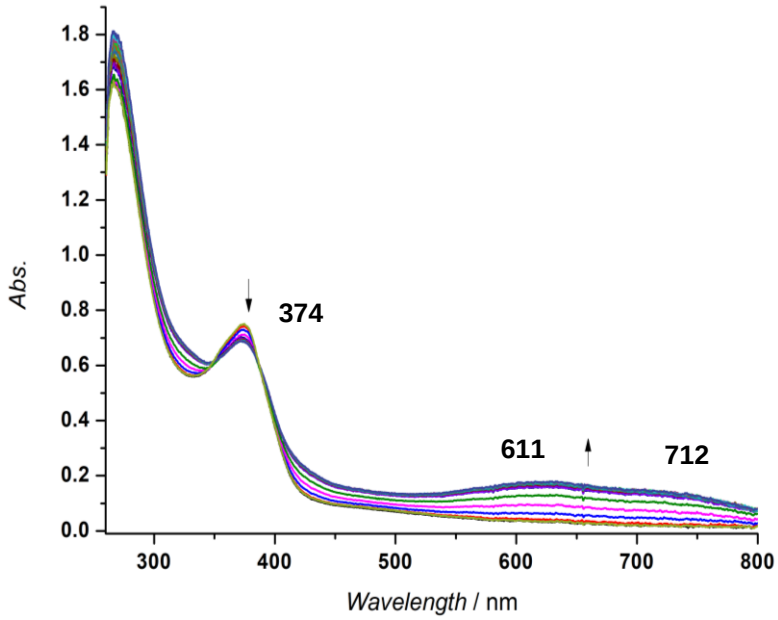


Figure S24. Deprotonation of complex **5** with Verkade's base in THF at room temperature followed by UV-vis spectroscopy that shows the formation of complex **2**.

E.3 Reactivity towards phenoxyl radical monitored by EPR spectroscopy

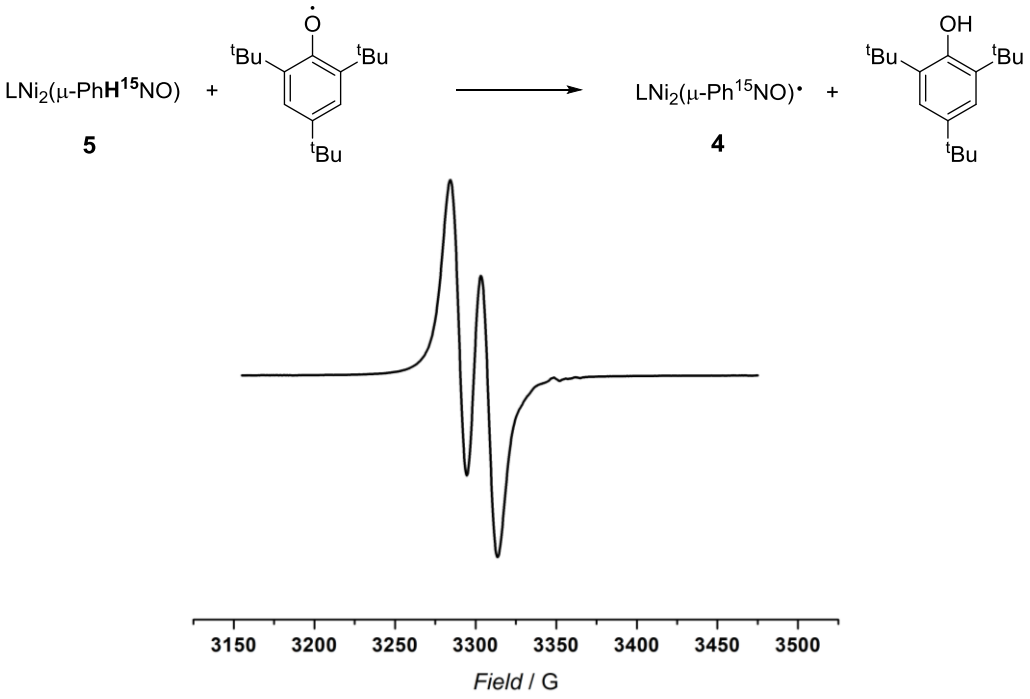


Figure S25. X-band EPR spectrum in THF recorded at room temperature of complex **5** treated with 1 equiv. of 2,4,6-tri-*tert*-butyl phenoxy radical, showing the formation of **4**.

F X-ray Crystallography

Table S3. Crystal data and refinement details for **2**, **3** and **5**.

compound	**2**	**3**	**5**
empirical formula	C_{47} H_{61} K N_8 Ni_2 O	C_{71} H_{110} K N_9 Ni_2 O_9	C_{45} H_{59} N_7 Ni_2 O
formula weight	910.55	1390.19	831.41
crystal size [mm^3]	0.360 x 0.340 x 0.280 mm^3	0.255 x 0.252 x 0.187 mm^3	0.486 x 0.314 x 0.173 mm^3
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	*P* $2_1/m$	*P* $2_1/c$	*P* $2_1/n$
a [Å]	11.6350(7)	25.3445(7)	10.6925(3)
b [Å]	18.2506(13)	12.9108(5)	23.5112(7)
c [Å]	11.6398(9)	22.8413(8)	16.6922(4)
α [°]	90	90	90
β [°]	91.616(6)	106.782(2)	101.387(2)
γ [°]	90	90	90
V [$Å^3$]	2470.7(3)	7155.8(4)	4113.7(2)
Z	2	4	4
ρ [g/cm^3]	1.244	1.290	1.342
F(000)	964	2984	1768
μ [mm^{-1}]	0.887	0.645	0.959
T_{min} / T_{max}	0.6692 / 0.8708	0.7290 / 0.8782	0.5781 / 0.8278
Θ-range [°]	1.750-25.775	1.678-25.670	1.516-25.785
hkl-range	±14 ±22 ±14	±30 ±15 -27, 23	-11,12 ±28 ±20
measured refl.	27929	69092	37123
unique refl. [R_{int}]	4854 [0.1346]	13156 [0.1435]	7701 [0.0301]
Data/restrains/param.	4854 / 164 / 305	13156 / 158 / 916	7701 / 0 / 512
Goodness-of-fit F^2	1.098	0.918	1.084
*R*1, w*R*2 [*I*>2σ(*I*)]	0.0824, 0.1798	0.0627, 0.0797	0.0287, 0.0702
*R*1, w*R*2 (all data)	0.0961, 0.1873	0.1281, 0.0930	0.0378, 0.0754
resid. el .dens [$e/Å^3$]	1.841/-0.481	0.482/-0.280	0.606/-0.422

Table S4. Geometric and spectroscopic features of relevant nitrosobenzene PhNO complexes reported so far. The compounds described in this work are included.

Compound	Binding mode	*d*(N-O) / Å	IR $\tilde{\nu}$(N-O)/ cm^{-1} ($\Delta[^{15}NO]$)	Reference
PhNO (nitrosobenzene)	--	1.21-1.23[1]	1506	[7]
PhNHOH (N-phenylhydroxylamine)	--	--	$\tilde{\nu}$(N-H)/ cm^{-1} = 3041	[8]
NH_2OH (hydroxylamine)	--	1.47 (±0.03)	895 912 (876, ND_2OD)	[9]
N-(quinolin-6-yl)hydroxylamine	--	1.42	--	[10]
2-Hydroxylamino-4,6-dinitrotoluene	--	1.43	--	[11]
$[KLNi_2(\mu\text{-PhNO})]$ **(2)**	$\mu\text{-}\eta^1\text{:}\eta^1$	1.48	907 (894) [DFT: 936 (921)]	this work
$[LNi_2(\mu\text{-PhNO})]$ [Kcryptand] **(3)**	$\mu\text{-}\eta^1\text{:}\eta^1$	1.37	-- [DFT: 1007 (991)]	this work
(CF_3-nacnac)Ni(PhNO) **(A)**	η^2	1.32	968 (950)	[12]
[(CF_3-nacnac)Ni(PhNO)][K(18C6)] **(B)**	$\mu\text{-}\eta^2\text{:}\eta^2$	1.38	765 (751)	[12]
$[(nacnac)Ni]_2$(ArNO) **(C)**	$\mu\text{-}\eta^2\text{:}\eta^2$	1.44	--	[2]
$[(nacnac)Ni]_2$(PhNO) **(C^{PhNO})**	$\mu\text{-}\eta^2\text{:}\eta^2$	--	915 (901)	[2]
(nacnac)Cu(PhNO) **(D)**	η^2	1.33	1113 (1093)	[2]
$[(nacnac)Cu]_2$(PhNO)	$\mu\text{-}\eta^2\text{:}\eta^1$	1.37	1040 (1029)	[2]
$[(Cp^*Rh)_2(\mu\text{-Cl})(PhNO)][BF_4]$	$\mu\text{-}\eta^2\text{:}\eta^2$	1.422	1001	[13]
$[\{Cp^*Ru(S(iPr))\}_2(PhNO)][OTf]$	$\mu\text{-}\eta^1\text{:}\eta^1$	1.35	--	[14]
$[\{Cp^*Rh(S(iPr))\}_2(PhNO)][BPh_4]$	$\mu\text{-}\eta^1\text{:}\eta^1$	1.33	--	[14]
$[\{Cp^*Ir(S(iPr))\}_2(PhNO)][BPh_4]$	$\mu\text{-}\eta^1\text{:}\eta^1$	1.34	--	[14]
$[CpCo(PhNO)]_2$	$\mu\text{-}\eta^2\text{:}\eta^1$	1.38	1047	[15]

[1] Free nitrosoarenes exist in both monomeric and dimeric form.

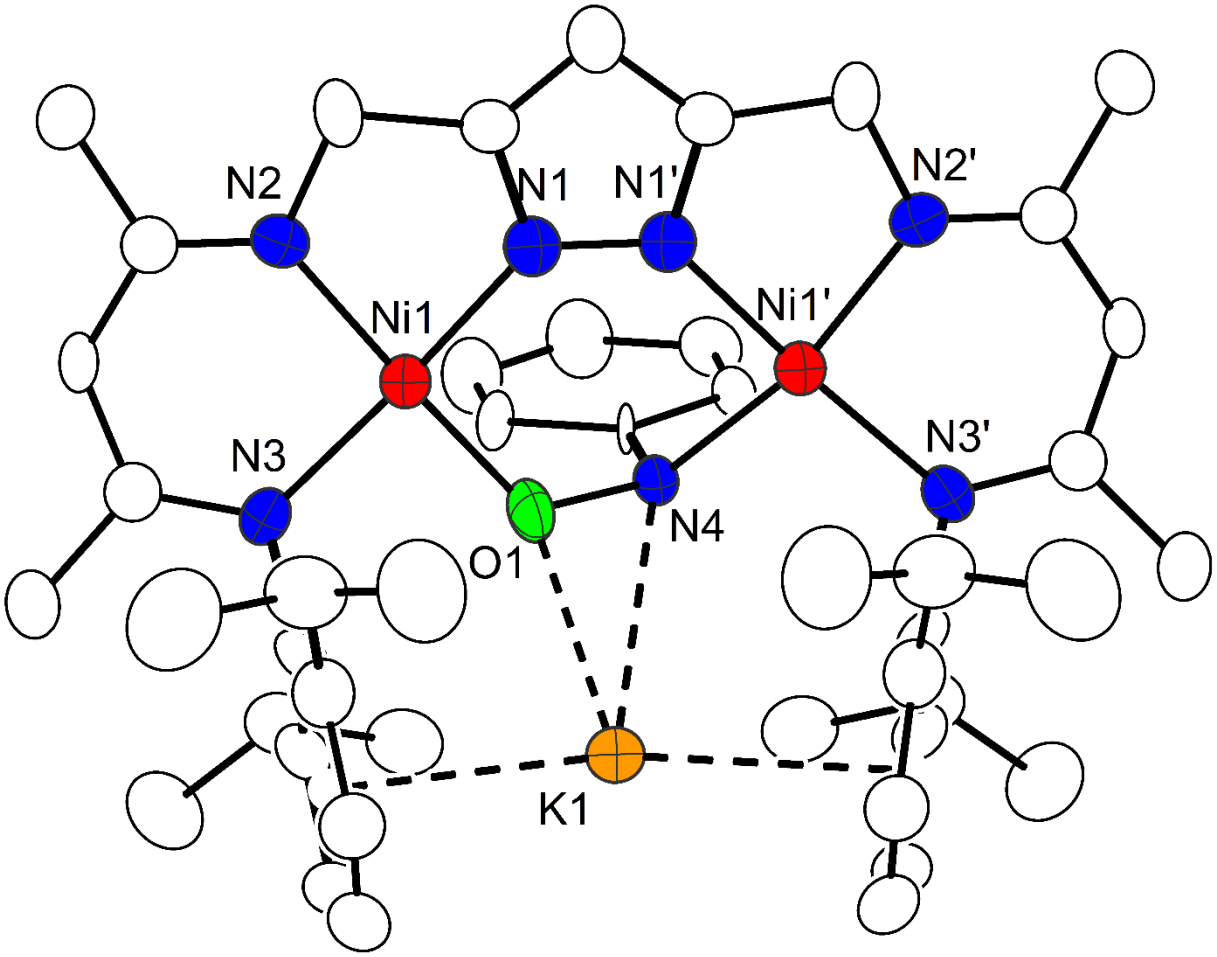


Figure S26: Plot (50% probability thermal ellipsoids) of the molecular structure of **2** (solvent molecules and hydrogen atoms omitted for clarity). Cg is the centroid of the six ring atoms of the $iPr_2C_6H_3$ group. Selected bond lengths [Å] and angles [°]: Ni(1)-O(1) 1.798(10), Ni(1)-N(1) 1.862(5), Ni(1)-N(2) 1.913(5), Ni(1)-N(3) 1.931(5), Ni(1)-N(4) 1.992(9), N(4)-O(1) 1.487(12), K(1)-Cg 2.9173(5), K(1)-O(1) 2.570(10), K(1)-N(4) 2.909(11), Ni(1)··· Ni(1)' 3.9217(8); O(1)-Ni(1)-N1 93.8(3), O(1)-Ni(1)-N(2) 174.2(4), N(1)-Ni(1)-N(2) 83.1(2), O(1)-Ni(1)-N(3) 89.9(3), N(1)-Ni(1)-N(3) 172.5(2), N(2)-Ni(1)-N(3) 92.7(2), N(4)-O(1)-Ni(1) 119.9(7), O(1)-N4-Ni(1)' 120.1(7), Cg-K(1)-Cg' 159.85(1). Symmetry transformation used to generate equivalent atoms: (') *x*, 1/2-*y*, *z*. The rather long contact from K(1) to an MeCN molecule is not shown; K(1)-N(5) 2.896(12) Å.

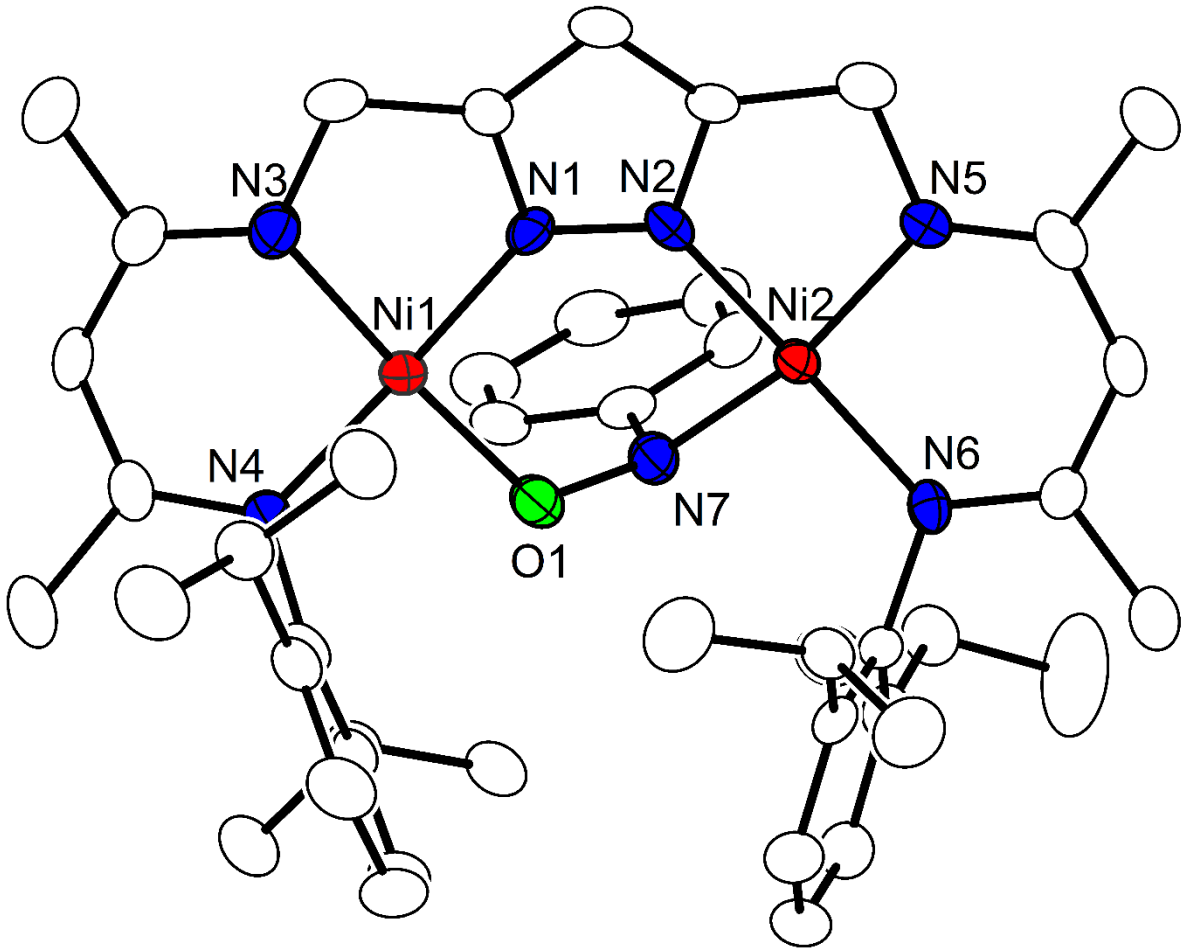


Figure S27: Plot (50% probability thermal ellipsoids) of the molecular structure of **3** (anionic part, solvent molecules and hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ni(1)-N(1) 1.861(3), Ni(1)-N(3) 1.908(4), Ni(1)-N(4) 1.909(3), Ni(1)-O(1) 1.865(3), Ni(2)-N(2) 1.842(4), Ni(2)-N(5)1.917(5), Ni(2)-N(6) 1.909(3), Ni(2)-N(7) 1.895(3), N(7)-O(1) 1.374(4), Ni(1)···Ni(2) 3.8266(7), N(1)-Ni(1)-N(3) 82.48(1), N(1)-Ni(1)-O(1) 93.86(1), N(3)-Ni(1)-N(4) 93.41(1), N(3)-Ni(1)-O(1) 175.26(14), N(1)-Ni(1)-N(4) 170.82(14), N(2)-Ni(2)-N(5) 82.99(14), N(2)-Ni(2)-N(7) 87.78(14), N(7)-Ni(2)-N(6) 95.60(14), Ni(1)-O(1)-N(7) 119.77(23), O(1)-N(7)-Ni(2) 121.92(25).

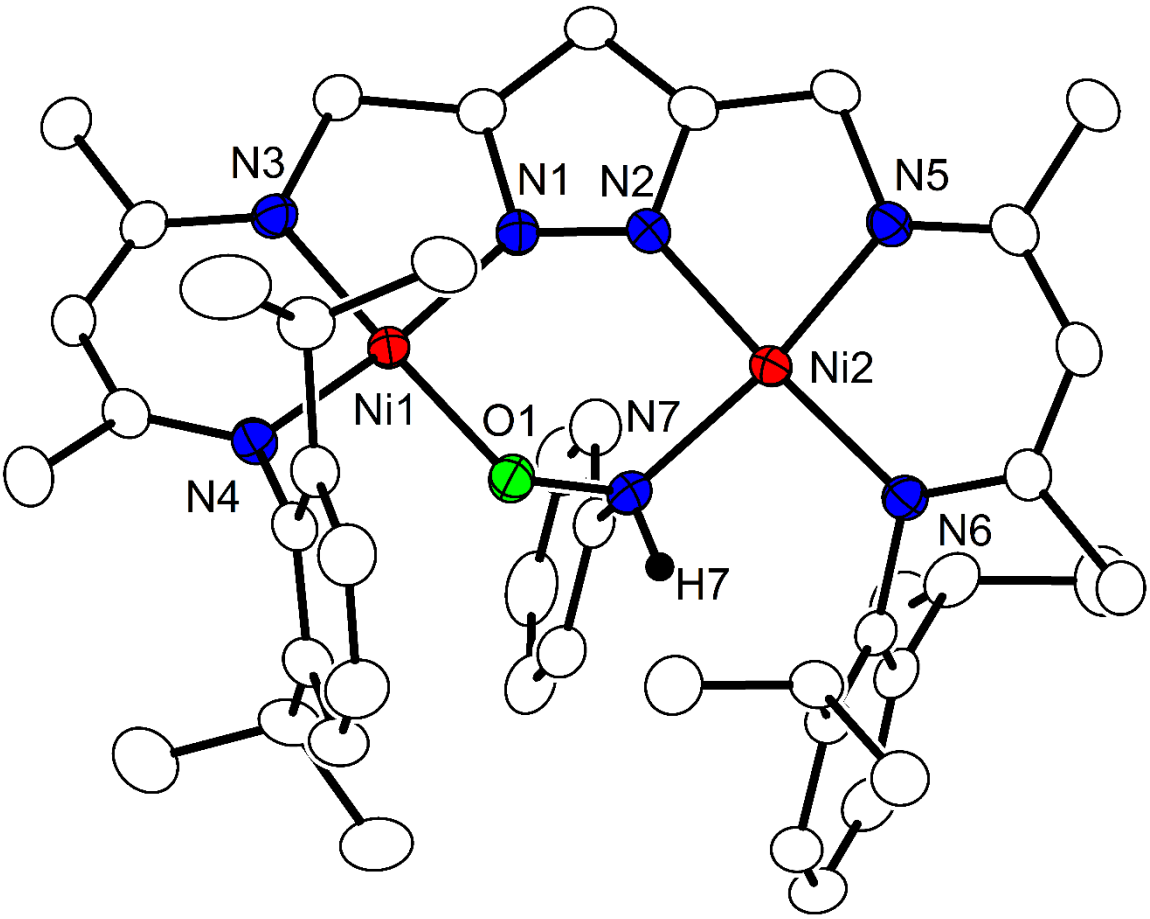


Figure S28: Plot (50% probability thermal ellipsoids) of the molecular structure of **5** (solvent molecules and most hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ni(1)-N(1) 1.8410(16), Ni(1)-N(3) 1.8696(13), Ni(1)-N(4) 1.9023(16), Ni(1)-O(1) 1.8696(13), Ni(2)-N(7) 1.9450(16), Ni(2)-N(5) 1.8857(16), Ni(2)-N(6) 1.9141(15), Ni(2)-N(2) 1.8560(16), N(7)-O(1) 1.464(2), N(7)-H(7) 0.867(25), Ni(1)···Ni(2) 3.8866(6), N(1)-Ni(1)-N(3) 83.23(7), N(3)-Ni(1)-N(4) 167.07(7), N(1)-Ni(1)-O(1) 92.56(6) N(4)-Ni(1)-O(1) 90.80(6), N(2)-Ni(2)-N(5) 82.64(7), N(5)-Ni(2)-N(6) 94.05(7), N(6)-Ni(2)-N(7) 94.25(7), N(2)-Ni(2)-N(7) 89.04(7), Ni(1)-O(1)-N(7) 119.32(10), Ni(2)-N(7)-O(1) 117.36(11), Ni(1)-O(1)-N(7)-Ni(2) 77.15(14).

G DFT Calculations

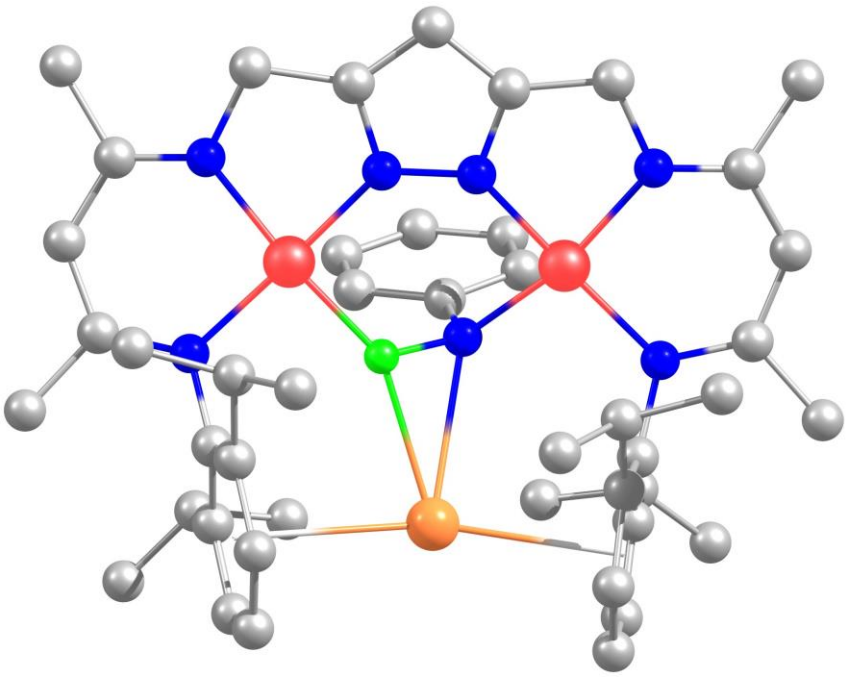


Figure S29: DFT optimized molecular structure of K[$LNi_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-PhNO})$] (**2**) (Ni = red, K = orange, N = blue, O = green, C = grey). (Spin restricted DFT calculations with ORCA 3.0.3, BP86 functional, def2-tzvp basis set, RI approximation using the auxiliary def2-tzvp/J basis set, D3 dispersion correction with zero damping, tight convergence and optimization criteria).

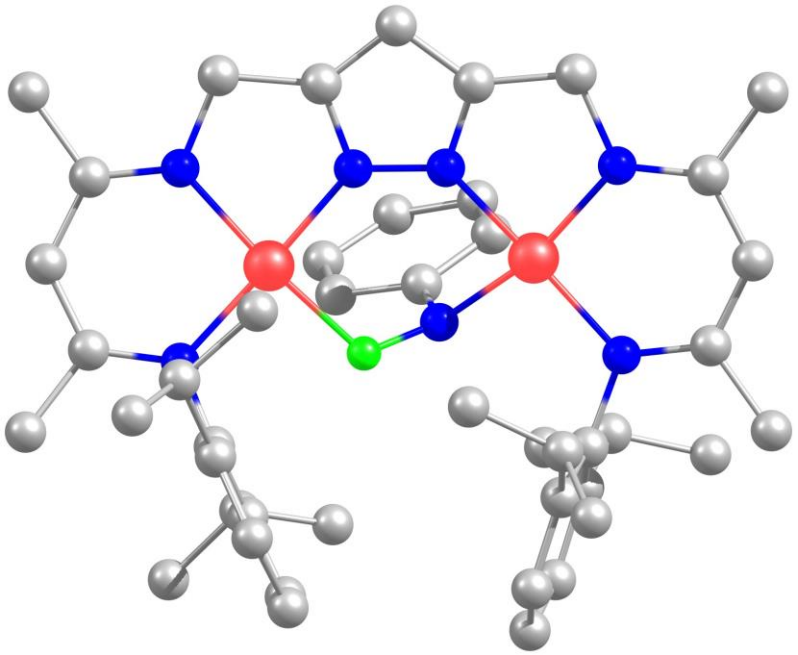


Figure S30: DFT optimized molecular structure of $[LNi_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-PhNO})]^-$ (anion of **3**) (Ni = red, N = blue, O = green, C = grey). (Spin restricted DFT calculations with ORCA 3.0.3, BP86 functional, def2-tzvp basis set, RI approximation using the auxiliary def2-tzvp/J basis set, D3 dispersion correction with zero damping, tight convergence and optimization criteria).

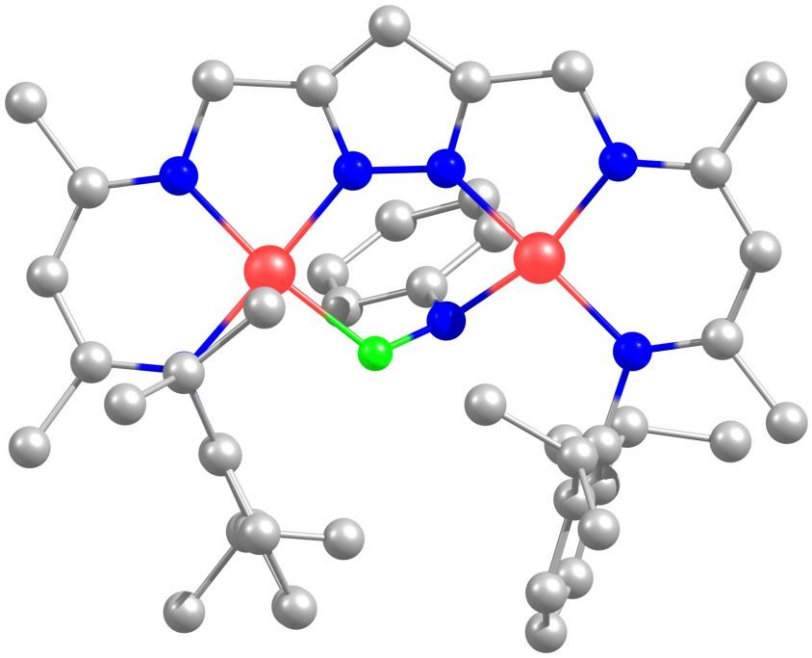


Figure S31: DFT optimized molecular structure of [$LNi_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-PhNO})$] (**4**) (Ni = red, N = blue, O = green, C = grey). (Spin unrestricted DFT calculations with ORCA 3.0.3, BP86 functional, def2-tzvp basis set, RI approximation using the auxiliary def2-tzvp/J basis set, D3 dispersion correction with zero damping, tight convergence and optimization criteria).

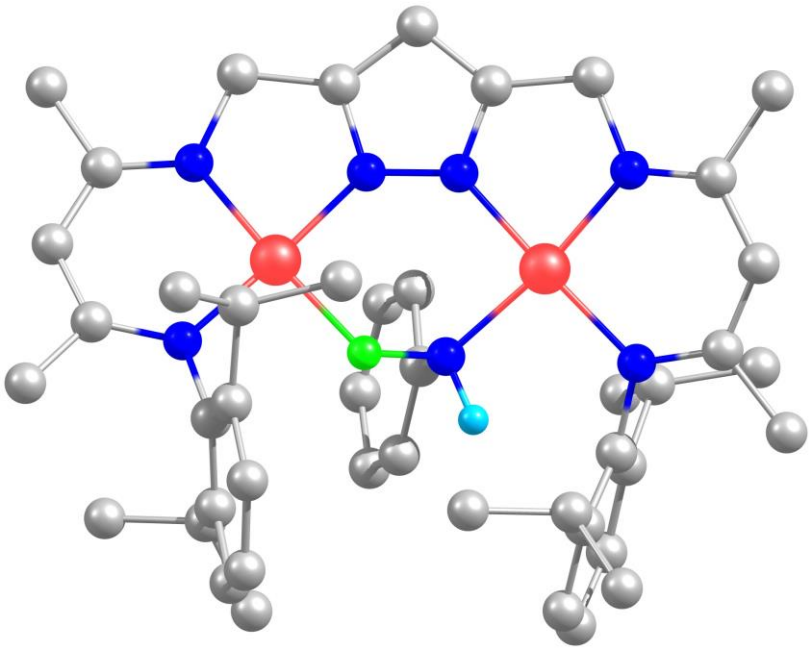


Figure S32: DFT optimized molecular structure of [$LNi_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-PhN(H)O)}$] (**5**) (Ni = red, N = blue, O = green, C = grey, H = turquoise). (Spin restricted DFT calculations with ORCA 3.0.3, BP86 functional, def2-tzvp basis set, RI approximation using the auxiliary def2-tzvp/J basis set, D3 dispersion correction with zero damping, tight convergence and optimization criteria).

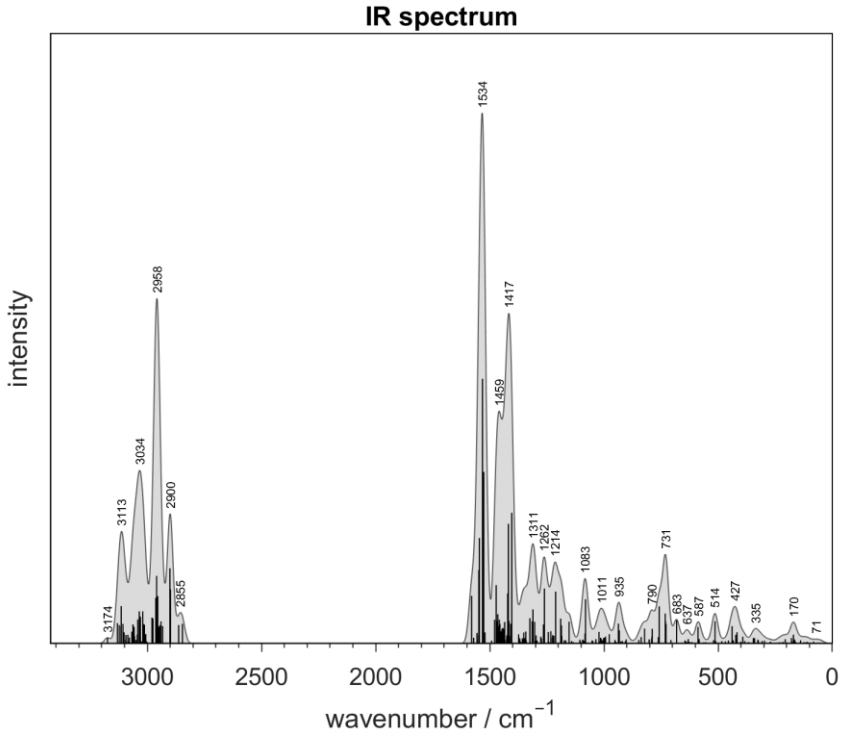


Figure S33. Calculated IR spectrum of K[LNi$_2$(μ-η^1:η^1-PhNO)] (**2**). Predicted NO stretching: 936 cm^{-1}. The spectrum was convoluted using a Gaussian line shape function with a half-width of 15 cm^{-1}.

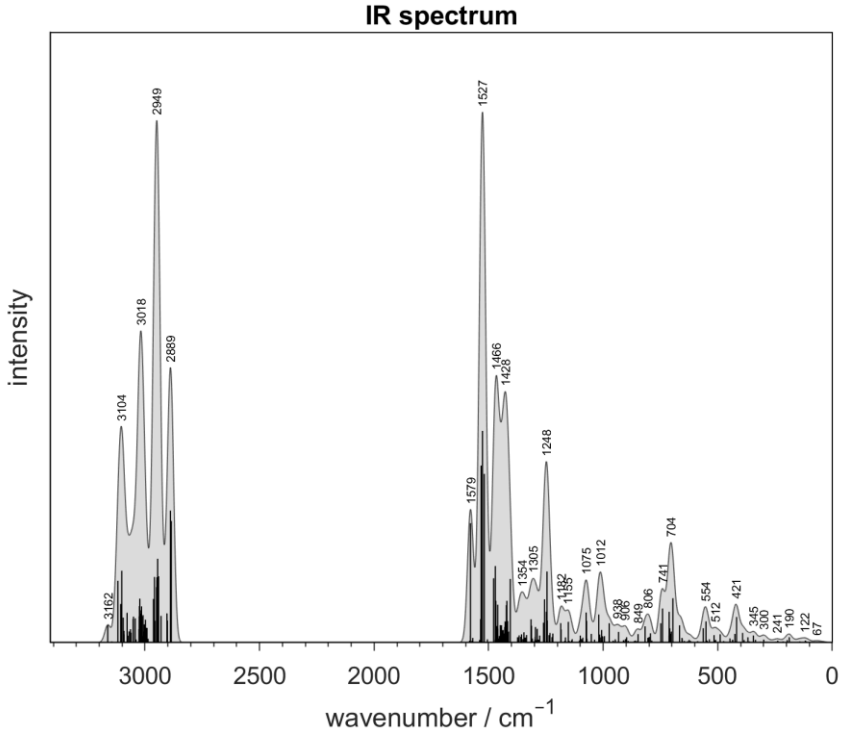


Figure S34. Calculated IR spectrum of [LNi$_2$(μ-η^1:η^1-PhNO)]$^-$ (anion of **3**). Predicted NO stretching: 1007 cm^{-1}. The spectrum was convoluted using a Gaussian line shape function with a half-width of 15 cm^{-1}.

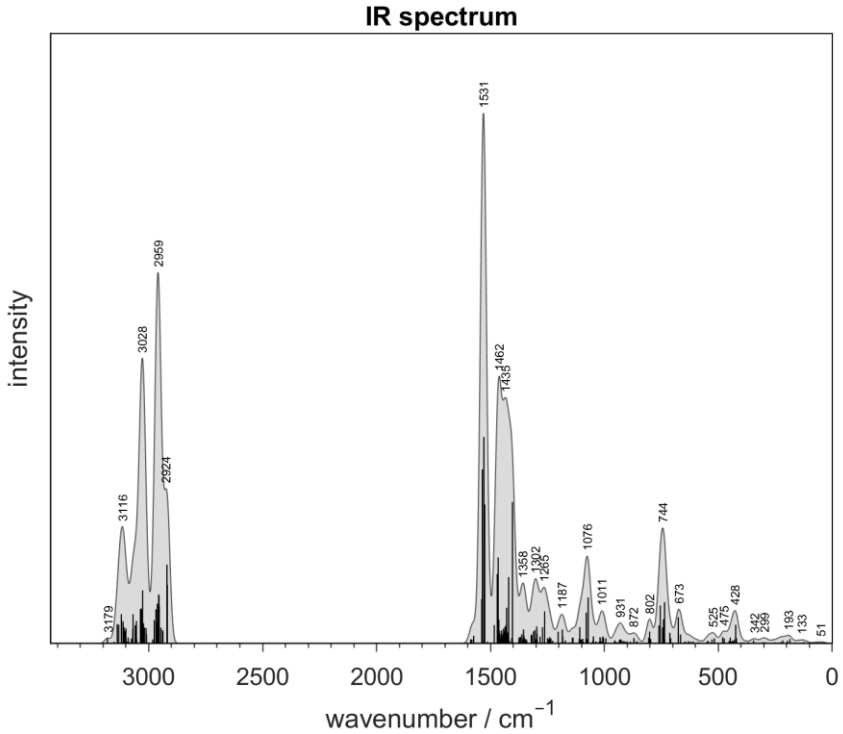


Figure S35. Calculated IR spectrum of [$LNi_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-PhNO})$] (**4**). Predicted NO stretching: 1108 cm^{-1}. The spectrum was convoluted using a Gaussian line shape function with a half-width of 15 cm^{-1}.

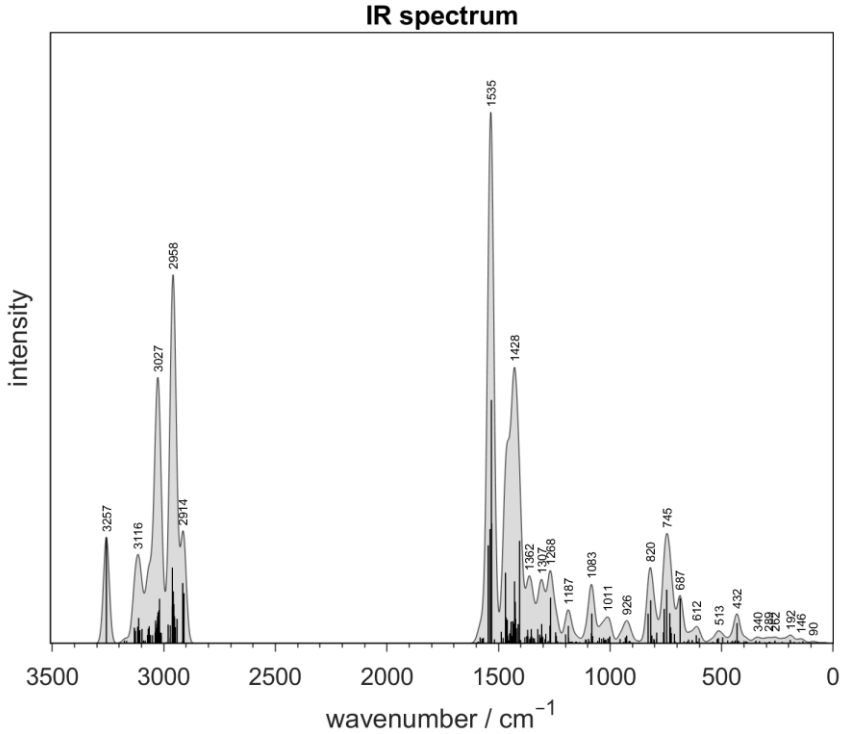


Figure S36. Calculated IR spectrum of [$LNi_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-PhN(H)O})$] (**5**). Predicted NO stretching: 818 cm^{-1}. Predicted NH stretching: 3257 cm^{-1}. The spectrum was convoluted using a Gaussian line shape function with a half-width of 15 cm^{-1}.

Table S5: Comparison of experimental and DFT calculated metric parameters of **2**; selected distances [Å] and angles [°].

	2 (exp)	**2 (calculated)**
Ni–N	1.992(9)	1.933
Ni–O	1.798(10)	1.899
N–O	1.487(12)	1.397
Ni···Ni	3.9217(8)	3.9175
K–N	2.909(11)	2.784
K–O	2.570(10)	2.489
Ni–O–N–Ni	74(1)	77

Table S6: Comparison of experimental and DFT calculated metric parameters of **3**$^{-}$; selected distances [Å] and angles [°].

	3^{-} (exp)	**3^{-} (calculated)**
Ni–N	1.895(3)	1.909
Ni–O	1.864(3)	1.911
N–O	1.374(4)	1.360
Ni···Ni	3.8266(7)	3.8330
Ni–O–N–Ni	73.5(3)	80.4

Table S7: DFT calculated metric parameters of **4**; selected distances [Å] and angles [°].

	4 (calculated)
Ni–N	1.886
Ni–O	1.915
N–O	1.323
Ni···Ni	3.8579
Ni–O–N–Ni	93.3

Table S8: Comparison of experimental and DFT calculated metric parameters of **5**; selected distances [Å] and angles [°].

	5 (exp)	**5 (calculated)**
Ni–N	1.9450(16)	1.9488
Ni–O	1.8696(13)	1.8797
N–O	1.464(2)	1.435
Ni···Ni	3.8866(6)	3.8820
Ni–O–N–Ni	77.15(14)	79.23

Table S9: Comparison of selected experimental and DFT calculated stretching vibrations [cm^{-1}].

compound	$\tilde{\nu}$(NO) / $\tilde{\nu}$(^{15}NO) (exp)	$\tilde{\nu}$(NO) / $\tilde{\nu}$(^{15}NO) (calculated)	$\tilde{\nu}$(NH) / $\tilde{\nu}$(^{15}NH) (exp)	$\tilde{\nu}$(NH) / $\tilde{\nu}$(^{15}NH) (calculated)
2	907 / 894	936 / 921	-	-
3^{-}	-	1007 / 991	-	-
4	1155 / 1135	1108 / 1092	-	-
5	1038 / 1017	818 / 805	3147 / 3138	3257 / 3250

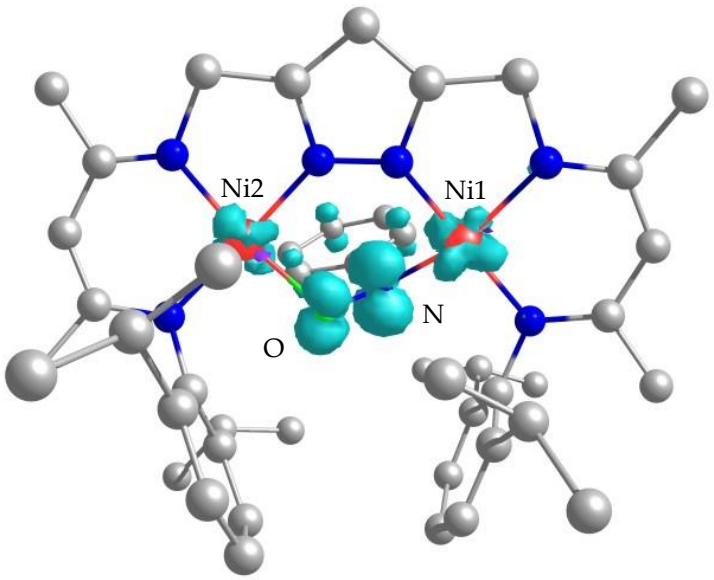


Figure S37: DFT calculated spin density plot of complex **4**. (See Experimental Section of the main manuscript for details). Mulliken spin population: Ni1 = 0.098964, Ni2 = 0.173218, O = 0.172888, N = 0.320570, C(PhNO) = 0.196843.

Coordinates for the energy optimized structure of 2.

Ni	-1.992931706	1.170668937	-0.025128198
Ni	1.921288482	1.200954621	0.132811876
K	0.133946158	-2.507587405	0.226445306
O	-0.634399871	-0.155726201	-0.044461211
N	0.579767399	0.080820544	-0.692565612
N	-0.729341216	2.510121249	0.206563394
N	-3.212671126	2.625218406	-0.117304752
N	-3.370887085	-0.166611518	-0.069198026
N	0.606658734	2.498102404	0.383766372
N	3.116886791	2.650676946	0.523536143
N	3.335878393	-0.127606148	0.065750056
C	0.442622085	0.502041327	-2.021400620
C	-1.180531607	3.770337499	0.390912651
C	-2.643303711	3.942533302	0.202174908
C	-4.471163250	2.563018645	-0.527119207
C	-4.656455303	0.073885604	-0.382537605
C	-3.064660493	-1.425573619	0.517641536
C	-0.796230275	0.543768208	-2.702125429
C	-2.990477679	-0.202145429	2.753443845
C	1.007301805	3.755991268	0.683338300
C	2.468627968	3.921395155	0.875844892
C	4.428975252	2.649983217	0.345998859
C	4.650202601	0.171039388	0.055143272
C	3.026934610	-1.488464551	0.347336429
C	1.604449846	0.867332599	-2.748252636
C	2.532761588	-0.729915379	2.730908914
C	-0.102877131	4.609524035	0.703907680
C	-5.145348119	1.340855333	-0.713843718
C	-5.256898543	3.832848225	-0.760936760
C	-5.674586458	-1.044626450	-0.321307171
C	-2.874850491	-1.473307080	1.927879887
C	-2.957966592	-2.601952979	-0.262722856
C	-0.857646124	0.908468215	-4.047731881
C	-2.239244130	-0.252497335	4.084891051
C	-4.461789511	0.183681513	2.988050279
C	5.154865172	1.473620771	0.078973263
C	5.217964898	3.935257809	0.458591850
C	5.683349690	-0.935718593	0.084898492
C	2.706186328	-1.824308915	1.692574977
C	3.091922500	-2.499658094	-0.643654266
C	1.527073950	1.226062129	-4.088131164
C	1.552138776	-1.108932581	3.843464883
C	3.879476697	-0.281564421	3.322268327
C	-2.606274672	-2.710320429	2.528347664
C	-2.705224080	-3.821865103	0.388079628
C	-3.075716430	-2.580214173	-1.780357744

C	0.295282766	1.248108230	-4.758700022
C	2.551130685	-3.174188521	2.035759187
C	2.923051763	-3.837950683	-0.251017496
C	3.294132262	-2.185991881	-2.116989780
C	-2.533518989	-3.884563546	1.771144923
C	-1.696204240	-2.735636971	-2.438196570
C	-4.030643792	-3.657939343	-2.317268993
C	2.679118945	-4.183527408	1.077537220
C	1.990213322	-2.437933648	-2.893136392
C	4.433626690	-2.994877634	-2.757012842
H	-3.116594449	4.352258288	1.114944647
H	-2.840203497	4.668532793	-0.606156579
H	-1.711772146	0.302915114	-2.162007329
H	-2.537162442	0.601103749	2.139462826
H	2.700506810	4.193056725	1.923653962
H	2.843510284	4.747323358	0.248109276
H	2.567474448	0.864135413	-2.235564481
H	2.112584345	0.140525522	2.186913785
H	-0.121248154	5.675655408	0.903741503
H	-6.185210569	1.397754832	-1.026485708
H	-6.269919581	3.599157468	-1.105651949
H	-4.771437762	4.468518699	-1.517951239
H	-5.335371953	4.431491436	0.159772645
H	-6.688330342	-0.636890183	-0.400704720
H	-5.593250838	-1.604908615	0.620360743
H	-5.531728267	-1.767676090	-1.135739706
H	-1.831435878	0.933834754	-4.542021317
H	-2.255277755	0.741723634	4.553567986
H	-1.190093859	-0.541993115	3.948699641
H	-2.702688685	-0.953934303	4.796678286
H	-4.515620331	1.108409525	3.581750544
H	-4.988384302	-0.608229794	3.542935086
H	-4.991311803	0.363441268	2.044962923
H	6.234183829	1.579036908	-0.010991002
H	6.290277855	3.738635550	0.347983952
H	4.918883304	4.654199499	-0.320666376
H	5.054872967	4.427448745	1.429907599
H	6.685671039	-0.510546929	0.206151735
H	5.497912137	-1.632538284	0.914376683
H	5.675605328	-1.529431896	-0.838023307
H	2.441684723	1.502288736	-4.616259864
H	1.328648616	-0.226239887	4.458713162
H	0.600325186	-1.480226601	3.437864102
H	1.959578488	-1.880427395	4.515933564
H	3.720626732	0.534576522	4.042177101
H	4.369807420	-1.114940112	3.849536528
H	4.556138453	0.088206003	2.542507199
H	-2.464168043	-2.761082151	3.608707283

H	-2.649956370	-4.738702104	-0.202475790
H	-3.456997377	-1.589766084	-2.064125350
H	0.238626134	1.537361237	-5.808318040
H	2.332027059	-3.441708065	3.069855941
H	2.993236751	-4.624391130	-1.004866521
H	3.530460362	-1.116299648	-2.196647568
H	-2.348020449	-4.842608255	2.259990760
H	-1.780609137	-2.726016405	-3.533840756
H	-1.231868834	-3.695468780	-2.154120032
H	-1.036512923	-1.900369502	-2.170563703
H	-4.208398211	-3.505933082	-3.391503195
H	-5.001102275	-3.645415924	-1.803832625
H	-3.604895296	-4.665283503	-2.195876306
H	2.576663320	-5.231126557	1.365267204
H	2.109829711	-2.173918983	-3.952735969
H	1.703864935	-3.499745595	-2.835518436
H	1.172650161	-1.820700102	-2.502042945
H	4.608275634	-2.646380834	-3.784676265
H	5.376802456	-2.901847953	-2.202339835
H	4.184201764	-4.065385299	-2.810429641

Coordinates for the energy optimized structure of the anionic part of 3 (3^{-}).

Ni	-1.856751388	1.107130766	-0.405326911
Ni	1.898539968	0.950878414	0.346240697
O	0.471772287	-0.317172014	0.341756484
N	-3.118325823	-0.282777476	-0.689257903
N	-2.894007026	2.490540595	-1.218434466
N	-0.544196711	2.411585574	-0.368681810
N	-0.742034017	0.109724958	0.783393049
N	3.188132978	-0.446947346	0.385833540
N	3.192720669	2.354612275	0.533091580
N	0.743200212	2.378085156	0.012117759
C	-5.080015696	-1.879094647	1.966935151
C	-2.900751765	-1.844456876	3.240255349
C	-1.908066933	-2.444862916	-4.107906152
C	-0.366038386	-0.915162034	-2.819334699
C	-1.922669779	-4.302827457	-0.202317160
C	-3.576331442	-1.563507164	1.893696224
C	-2.534585784	-3.629037311	0.851883044
C	-1.759478071	-1.559022475	-2.864427503
C	-1.668407080	-3.632012780	-1.397103199
C	2.836218878	-3.727546374	2.530466110
C	0.478851416	-2.907463090	2.198831733
C	2.039197857	-3.879257451	-1.789877015
C	-2.907880958	-2.284638629	0.735864090
C	-2.045538952	-2.295944888	-1.567010349
C	-5.127802404	-1.322642672	-1.682671378
C	-4.913424694	3.598138234	-2.092165438

C	-4.819995030	1.139031654	-1.670328098
C	-0.959954021	1.461130127	4.782709817
C	4.772898233	-1.003772148	-3.521533932
C	-1.998864900	1.711955600	3.873167927
C	1.946919300	-2.684740171	1.831324084
C	1.768401266	-3.802469695	-0.427510928
C	2.725688591	-2.838734560	-2.418680351
C	-2.680925511	-1.631367242	-0.494112084
C	-4.300304070	-0.112658975	-1.296110919
C	-4.151772921	2.375067712	-1.629886084
C	-2.256851188	3.817582952	-1.248872439
C	0.186680789	0.804830468	4.317330031
C	3.825501779	-0.547023940	-2.405088897
C	-1.908079281	1.298970946	2.549943695
C	2.167485494	-2.694625538	0.330985132
C	3.121534201	-1.702557252	-1.706702346
C	5.407388940	-1.478148812	0.662801228
C	5.285398066	3.414440627	1.279496850
C	5.026877617	0.932361767	1.138545305
C	0.279373656	4.481972244	-0.626879084
C	-0.855839621	3.664607070	-0.764779680
C	0.295109800	0.386613718	2.994229014
C	2.808773063	0.475979320	-2.937084188
C	-0.770075838	0.590886056	2.079844122
C	2.825816633	-1.632378970	-0.322144176
C	4.467705772	-0.294292986	0.746619888
C	4.434849928	2.200542074	0.973387594
C	2.708305638	3.712258741	0.240668111
C	1.267720045	3.614468082	-0.128618874
H	-5.605060091	-1.555914804	1.058546599
H	-5.247232795	-2.961006538	2.092987215
H	-5.538181287	-1.359635829	2.822722207
H	-3.361577638	-1.229913686	4.027029861
H	-3.001199039	-2.900981700	3.535476579
H	-1.835327895	-1.592097946	3.203239727
H	-1.806159833	-1.834498370	-5.018351489
H	-1.128140408	-3.221321428	-4.148729030
H	-2.887443310	-2.946589236	-4.137803496
H	-0.232635019	-0.302714326	-1.915867696
H	0.413971796	-1.689760316	-2.798048966
H	-0.206753340	-0.280165811	-3.704748901
H	-1.625668859	-5.347088832	-0.086139883
H	-3.473737521	-0.489132258	1.692459104
H	-2.705983499	-4.150763023	1.795099846
H	-2.489870640	-0.740627303	-2.948088726
H	-1.164043178	-4.154641626	-2.210551433
H	2.702676179	-3.675165398	3.622576345
H	2.571234748	-4.746010035	2.205013011

H	3.903335807	-3.574238057	2.310971869
H	-0.162192244	-2.199249856	1.665976185
H	0.153359903	-3.924616395	1.934773163
H	0.329946995	-2.775308054	3.280948067
H	1.713089542	-4.747405349	-2.366054588
H	-4.735076783	-1.764065740	-2.612630151
H	-5.093659581	-2.114492390	-0.925151775
H	-6.170621813	-1.030204832	-1.859398147
H	-4.415639433	4.085011901	-2.946149705
H	-5.931038110	3.326076919	-2.395177591
H	-4.981709093	4.351853051	-1.291043503
H	-5.828213839	1.142808033	-2.080539069
H	-1.034524096	1.790000991	5.820309972
H	5.485402692	-1.763111647	-3.164554539
H	4.224002932	-1.432016993	-4.374521060
H	5.346108735	-0.145315162	-3.902934017
H	-2.891004722	2.252419100	4.199764707
H	2.247179576	-1.689852103	2.188113609
H	1.227023150	-4.614523533	0.061481434
H	2.938212576	-2.905823545	-3.486916594
H	-2.266724655	4.238608327	-2.272373512
H	-2.815068970	4.531639829	-0.613016692
H	1.022814427	0.621574676	4.997348604
H	4.433559287	-0.025803662	-1.650970513
H	6.312507148	-1.286985824	1.252719214
H	4.934457292	-2.403455612	1.013369792
H	5.710337556	-1.654439264	-0.381238595
H	4.808479900	4.055455964	2.038751197
H	6.271195608	3.110872153	1.650405104
H	5.432279802	4.038066502	0.382685269
H	6.052322524	0.911667377	1.503086815
H	0.373350522	5.538651815	-0.857103186
H	3.322787022	1.367150773	-3.329180630
H	2.207104178	0.035846908	-3.746311934
H	2.839663575	4.378078588	1.114586796
H	3.293599533	4.162170629	-0.584757639
H	-2.705702053	1.534202850	1.841035834
H	1.195853048	-0.105467447	2.637286246
H	2.127281009	0.797163993	-2.133746438

Coordinates for the energy optimized structure of the radical complex 4.

Ni	-1.865024886	-1.039451591	0.519963570
Ni	1.932285921	-0.992351500	-0.159351733
O	0.448038022	0.217479904	-0.187591717
N	-3.163374282	0.325075831	0.509079572
N	-2.916045042	-2.309692158	1.456667296
N	-0.532714480	-2.330054352	0.725873422

N	-0.662571846	-0.272207307	-0.713859025
N	3.188507989	0.393965468	-0.361819519
N	3.204498890	-2.377946493	-0.123254347
N	0.756327556	-2.356853052	0.345712037
C	-4.950814949	1.397528904	-2.452611714
C	-2.721088185	1.301809796	-3.617108833
C	-2.162581692	3.111559650	3.606768724
C	-0.708487234	1.229435266	2.767134614
C	-1.931647476	4.224107799	-0.535875543
C	-3.440735047	1.169081183	-2.268917231
C	-2.470174777	3.382861711	-1.506032707
C	-2.028299405	1.988944615	2.571514261
C	-1.773890272	3.766610346	0.770221262
C	2.977247788	3.649600975	-2.744856028
C	0.673536109	2.669707520	-2.519087788
C	1.935026436	3.976825729	1.492869300
C	-2.854990297	2.073127163	-1.196552671
C	-2.169757008	2.475305080	1.137197565
C	-5.261216852	1.447830932	1.161409325
C	-4.955305728	-3.323640792	2.385556949
C	-4.909014507	-0.976698446	1.553492679
C	-0.506743792	-2.048990382	-4.524379173
C	4.565814752	1.175273434	3.516770507
C	-1.602001108	-2.261692480	-3.677159048
C	2.128190342	2.573008549	-2.047067685
C	1.798402373	3.831245241	0.115858791
C	2.525100459	2.959396469	2.242537442
C	-2.713729909	1.637198908	0.138747551
C	-4.390020952	0.217821050	1.033210483
C	-4.205154661	-2.170183162	1.761157131
C	-2.254936962	-3.590155326	1.772461560
C	0.562576844	-1.261017401	-4.080979828
C	3.570238230	0.658982409	2.470491575
C	-1.638418383	-1.682022483	-2.414753247
C	2.234523358	2.671937025	-0.536717473
C	2.961454734	1.776296704	1.636938581
C	5.396415222	1.407212807	-0.722569491
C	5.285183999	-3.524266988	-0.748730529
C	5.033841857	-1.048074455	-0.929364956
C	0.290407748	-4.332671465	1.305239686
C	-0.846192077	-3.508483134	1.303981948
C	0.543084889	-0.680767914	-2.817453524
C	2.470480379	-0.191968703	3.126702517
C	-0.571379967	-0.871591158	-1.972220482
C	2.794857744	1.635632675	0.237832219
C	4.473296403	0.213539897	-0.685381148
C	4.444451027	-2.278450567	-0.596130818
C	2.726558559	-3.686528715	0.358521753

C	1.281328514	-3.551531378	0.687419386
H	-5.515939651	1.139593549	-1.548555113
H	-5.157865158	2.450070256	-2.699173071
H	-5.333061309	0.773977121	-3.274498352
H	-3.071891495	0.521859708	-4.307313666
H	-2.919769549	2.275482116	-4.091584852
H	-1.635611765	1.191155766	-3.508944787
H	-2.198474175	2.683495981	4.618930430
H	-1.304945338	3.800764403	3.577975634
H	-3.077382502	3.702540889	3.451346702
H	-0.646922304	0.354419799	2.103244940
H	0.150390429	1.872401080	2.532804007
H	-0.616025559	0.879175907	3.805710249
H	-1.628162609	5.238424656	-0.799422170
H	-3.309237936	0.137543501	-1.917844115
H	-2.581407351	3.741317625	-2.529824988
H	-2.842202676	1.271697706	2.759522360
H	-1.344364237	4.428848241	1.521085735
H	2.960469162	3.505124037	-3.835588856
H	2.582123475	4.654668102	-2.533723742
H	4.024716371	3.631084750	-2.412776790
H	0.030117528	1.965670270	-1.983430884
H	0.272919981	3.676684099	-2.338197483
H	0.599167426	2.468590239	-3.598122518
H	1.587361260	4.886367074	1.985171652
H	-4.974211246	2.011337697	2.064266134
H	-5.153047422	2.135116883	0.316155434
H	-6.313642574	1.158623256	1.266945982
H	-4.495554396	-3.630374222	3.337273250
H	-5.995600724	-3.043061788	2.580536862
H	-4.952394382	-4.206428459	1.727595548
H	-5.944831954	-0.956734175	1.883654590
H	-0.484595714	-2.498379982	-5.517368270
H	5.343203826	1.804821476	3.059265985
H	4.068547783	1.770764683	4.297398835
H	5.059963521	0.330070200	4.016975978
H	-2.432882691	-2.888946022	-4.003424692
H	2.530537921	1.590206134	-2.333258562
H	1.341042879	4.630652074	-0.468867277
H	2.639247257	3.084965577	3.320548870
H	-2.290661966	-3.786370705	2.859232985
H	-2.781099198	-4.428837139	1.282515566
H	1.425552670	-1.096922630	-4.728298267
H	4.120400971	-0.002627480	1.786917651
H	6.367940159	1.127835326	-1.145294089
H	4.972616072	2.232140670	-1.308870770
H	5.558553472	1.793160232	0.295009843
H	4.805124481	-4.247301277	-1.426765635

H	6.271453144	-3.273731640	-1.153112526
H	5.427278691	-4.033335334	0.216733430
H	6.058806715	-1.073197067	-1.290889406
H	0.382621200	-5.339426123	1.697065776
H	2.905930793	-1.059930393	3.644018879
H	1.904489747	0.400696009	3.860262733
H	2.877037124	-4.466994069	-0.408346412
H	3.301283012	-4.000522750	1.248848243
H	-2.475420643	-1.863163456	-1.737852542
H	1.375992399	-0.074161477	-2.471820783
H	1.763523102	-0.562028978	2.370057493

Coordinates for the energy optimized structure of 5.

Ni	-1.995989319	0.971131963	-0.388433530
Ni	1.744296579	1.186849838	0.628157933
O	-0.714491963	-0.282026533	0.177742450
N	0.639330293	-0.138620118	-0.277430538
H	1.047061731	-1.040257652	0.014518727
N	-0.801159613	2.377114959	-0.225057131
N	-3.164014474	2.309483671	-1.003516372
N	-3.317593753	-0.370460189	-0.261158178
N	0.429654591	2.457114693	0.313402113
N	2.666662903	2.663087020	1.375422850
N	3.121948847	-0.064397943	1.023986638
C	-1.244169593	3.627270661	-0.478253427
C	-2.609371162	3.673291811	-1.057146032
C	-4.416992757	2.130956326	-1.418963988
C	-4.605573200	-0.212920711	-0.593869457
C	-3.010812677	-1.529449207	0.524453073
C	0.775065567	3.761186847	0.416608765
C	-0.266261402	4.554929255	-0.085067095
C	-5.101607746	0.922217052	-1.249447201
C	-5.164237923	3.277851295	-2.058313403
C	-5.625251222	-1.259183278	-0.196327038
C	-3.136350231	-1.450403952	1.926639335
C	-2.657989970	-2.739348822	-0.115637013
C	2.100948830	3.983962039	1.047165445
C	-3.011580513	-2.627535501	2.674993691
C	-3.354848894	-0.119144282	2.625681352
C	-2.559769598	-3.892459841	0.672352138
C	-2.357350032	-2.771609752	-1.606860832
C	3.740762100	2.614027816	2.154740363
C	4.148823732	0.171143175	1.856800316
C	3.145434481	-1.303834950	0.306087340
C	0.689579949	-0.144909287	-1.737177422
C	-2.759067498	-3.846602399	2.052801220
C	-2.052404026	0.328423722	3.313367461

C	-4.529422300	-0.146793222	3.612249130
C	-1.441903508	-3.940241974	-1.991452203
C	-3.608746892	-2.793759293	-2.502684829
C	4.406451347	1.413215565	2.444041580
C	4.305979960	3.885096848	2.745009497
C	5.118923839	-0.945800243	2.171947573
C	2.591970797	-2.474785868	0.875335085
C	3.683949510	-1.307515656	-1.006159943
C	0.717000639	1.031166309	-2.490558282
C	0.673957003	-1.386791240	-2.372543135
C	2.610048662	-3.653941461	0.114034887
C	1.979011032	-2.479065733	2.268061011
C	3.710097370	-2.516395492	-1.707919160
C	4.188666365	-0.016722070	-1.633458649
C	0.673202541	0.953178566	-3.883543999
C	0.647804723	-1.459816341	-3.764244327
C	3.177558330	-3.682241558	-1.156794531
C	0.450740425	-2.619739316	2.206249014
C	2.574095742	-3.590147947	3.147831329
C	4.139114805	-0.030819467	-3.162847846
C	5.604633852	0.353628895	-1.153704561
C	0.627087447	-0.287730920	-4.524183638
H	-3.248719732	4.375166461	-0.493841201
H	-2.575187363	4.044808380	-2.098305890
H	-0.315740873	5.637609672	-0.134225491
H	-6.140787026	0.894508557	-1.568211369
H	-6.157829267	2.951020169	-2.381622370
H	-4.623058733	3.665390989	-2.934783498
H	-5.289652749	4.119300239	-1.359264438
H	-6.536537927	-1.143974801	-0.794584086
H	-5.894101702	-1.125477921	0.863136408
H	-5.249454054	-2.282801454	-0.298026198
H	2.781275377	4.531078399	0.368725693
H	1.991052735	4.605227690	1.952609162
H	-3.116134334	-2.585514186	3.760733673
H	-3.585196613	0.627343693	1.851841690
H	-2.311093818	-4.845217976	0.204395370
H	-1.823385554	-1.830753944	-1.818305964
H	-2.682738632	-4.759957704	2.645228740
H	-2.181405767	1.317107691	3.779152437
H	-1.233253150	0.390606242	2.583259433
H	-1.760358794	-0.384581335	4.099689475
H	-4.694799244	0.854605224	4.036008199
H	-4.343940571	-0.833002408	4.451921546
H	-5.459913547	-0.464692275	3.120275905
H	-1.085349963	-3.809840397	-3.022981714
H	-1.975280344	-4.902232083	-1.952116383
H	-0.565681227	-4.015236194	-1.330656978

H	-3.309793607	-2.898436614	-3.556546684
H	-4.187925612	-1.867865315	-2.414218572
H	-4.259796091	-3.644593856	-2.248431599
H	5.260251827	1.472150557	3.115110338
H	5.213055910	3.668027305	3.319233158
H	3.580918884	4.371444748	3.415895419
H	4.560342999	4.613396732	1.960292395
H	5.972465091	-0.559009130	2.739216731
H	5.488982717	-1.428877325	1.257801104
H	4.632621331	-1.728706875	2.770220412
H	0.779894271	1.995759206	-1.995987274
H	0.695035375	-2.294453459	-1.770796053
H	2.178374107	-4.564265127	0.533498941
H	2.208380791	-1.507575946	2.729614968
H	4.122534448	-2.539025826	-2.715566971
H	3.506209842	0.776777474	-1.279277364
H	0.687690682	1.872225159	-4.470246301
H	0.648110869	-2.434330109	-4.254452127
H	3.190746519	-4.611825182	-1.727977036
H	0.028332766	-2.639256217	3.220330919
H	0.160814398	-3.555981020	1.708114967
H	-0.037052179	-1.795197916	1.667222490
H	2.192530626	-3.505285814	4.175064132
H	3.672066158	-3.550428852	3.183834025
H	2.291147517	-4.585261659	2.772921314
H	4.346243090	0.978615470	-3.546448500
H	3.155902056	-0.339519784	-3.535668228
H	4.900055579	-0.701238858	-3.591652626
H	5.950989366	1.256956918	-1.677349146
H	6.315038880	-0.458342327	-1.373100911
H	5.630845290	0.563981718	-0.077650898
H	0.598407259	-0.341603557	-5.613504338

H References

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