Supplementary Information

Direct metal-carbon bonding in symmetric bis(C-H) agostic Nickel(I) complexes
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Supplementary Methods

General Considerations

All experiments were carried out employing standard Schlenk techniques under an atmosphere of dry nitrogen employing degassed, dried solvents. Complex 1-2 used in this study are prepared according to literature procedures\(^1\). Complex 3-4 are referred to Dr. Dawson Beattie’s thesis\(^2\). Celite® was set in an oven at 180°C for at least 24 hours, then brought into a glovebox overnight following standard procedures. Nujol was dried over activated molecular sieves, then degassed by three freeze-pump-thaw cycles. Pyridine and acetonitrile were purchased from Sigma-Aldrich, dried over CaH\(_2\), and degassed by three freeze-pump-thaw cycles. \(\text{d}_6\)-benzene was purchased from Cambridge Isotope Laboratories Inc., dried over sodium metal, and degassed by three freeze-pump-thaw cycles. THF and Et\(_2\)O were dried over sodium metal, and degassed by three freeze-pump-thaw cycles. Hexanes and toluene were either dried over sodium metal or passed over activated alumina columns into Teflon sealed Schlenk flasks, and degassed by three freeze-pump-thaw cycles. NMR spectra were recorded on Bruker Avance 300, 400, or 600 MHz spectrometers. \(^1\)H NMR spectra are reported in parts per million (ppm) and were referenced\(^3\) to residual solvent: \(^1\)H(C\(_6\)D\(_6\)): \(\delta\) 7.16; \(^{13}\)C(C\(_6\)D\(_6\)): \(\delta\) 128.06; coupling constants are reported in Hz. \(^{13}\)C NMR spectra were performed as proton-decoupled experiments and are reported in ppm. The multiplicities are abbreviated as follows: \(s\) = singlet, \(d\) = doublet, \(dd\) = doublet of doublets, \(t\) = triplet, \(sept\) = septet. NMR spectra are shown using MestReNova 6.0.2 NMR processing software. Integrations of paramagnetic compounds 1-4 were not possible. EI-MS data were obtained using a Kratos MS-50 spectrometer (70 eV source). Elemental analyses were recorded on a Carlo Erba EA 1108 elemental analyzer. IR spectroscopy was performed using Nujol mulls between two NaCl salt plates on a Thermo Electron Corporation Nicolet 4700 FT-IR spectrometer.
Synthesis and Isolation of 3

**Complex 3:** In a glovebox, Sigman’s Dimer (70 mg, 0.066 mmol) was added as a solid at room temperature to a 20 mL vial containing a stirring solution of Na[MeCyAm] (27.2 mg, 0.132 mmol) in toluene (5 mL). The contents were stirred overnight (~12 h), and in the morning removed from the stir plate and allowed to settle for 5 minutes. The supernatant was filtered through Celite®, and the remaining solids were dissolved in toluene (5 mL) and filtered until no solid remained. The filtered toluene was divided equally into 2 vials (5 mL each) and layered with hexanes. Paramagnetic yellow crystals of 3 formed overnight at -35°C (67.1 mg, 0.107 mmol, 81% - multiple crops) and were collected by decanting the vials, washing with cold hexanes (0.5 mL), and removal of volatiles *in vacuo*. X-ray quality crystals were prepared by slow diffusion of hexanes into toluene solutions of 3 in toluene at -35°C. \(^1\)H NMR (400 MHz, 25°C, d\(_8\)-tol): \(\delta = 28.01, 17.51, 14.98, 9.11, 8.26, 5.12, 4.22, 2.36, 1.81, 1.24, 0.04, -0.99.\) Evans Method (C\(_6\)D\(_6\), 27°C): \(\overline{\gamma} = 2.17\) \(\overline{\gamma} = \) a. EI-MS (m/z): 628 [M]+. *Anal. Calcd.* for C\(_{38}\)H\(_{56}\)N\(_3\)NiO (628). C, 72.50%; H, 8.97%; N, 6.67%. Found: C, 72.24%; H, 9.00%; N, 6.45%.

Supplementary Figure 1. \(^1\)H NMR (400 MHz, 25°C, d\(_8\)-tol) of complex 3
Formation of 4

"Sigman's Dimer"  
0.5 equiv.  
\[ \text{Ni-Br} \]  
\[ \text{IPr-Ni-Ni-IPr} \]  
\[ \text{H} \]  
\[ \text{Na} \]  
\[ \text{toluene, r.t.} \]  
\[ -\text{NaBr} \]  
45%  

Complex 4: In a glovebox, Sigman's Dimer (50 mg, 0.0474 mmol) was added as a solid at room temperature to a 20 mL vial containing a stirring solution of Na[CyAm] (18.1 mg, 0.0948 mmol) in toluene (5 mL). The contents were stirred overnight (~12 h), and in the morning removed from the stir plate and allowed to settle for 5 minutes. The supernatant was filtered through Celite®, and the remaining solids were dissolved in toluene (10 mL) and filtered until no solid remained. The filtered toluene was divided equally into 2 vials (10 mL each) and layered with hexanes. Paramagnetic yellow crystals of 4 formed overnight at -35°C (26.2 mg, 45% - single crop) and were collected by decanting the vials, washing with cold hexanes (2 x 0.5 mL), and removal of volatiles in vacuo. X-ray quality crystals were prepared by slow diffusion of hexanes into a concentrated solution of 4 in toluene at -35°C. ¹H NMR (300 MHz, 25°C, C₆D₆): δ(ppm) = 52.46, 32.35, 31.04, 27.01, 20.49, 15.20, 7.16, 4.96, 3.55, 2.79, 2.30, 1.90, 0.44, 0.29, -1.09, -2.28, -4.65, -5.14, -5.53, -5.77, -6.41, -15.35, -20.90. Evans Method (C₆D₆, 24°C): g_eff = 2.12. EI-MS (m/z): 614 [M]⁺. Anal. Calcd. for C₃7H₅₄N₆NiO (614). C, 72.20%; H, 8.84%; N, 6.83%. Found: C, 71.97%; H, 8.55%; N, 6.75%.

Supplementary Figure 2 ¹H NMR (400 MHz, 25°C, d₈-tol) of complex 4
Supplementary Data

Ni K edge X-ray Absorption Spectroscopy (XAS)

All XAS samples were analyzed as solids under anaerobic conditions and diluted in boron nitride (20-50% by weight). All samples were quickly frozen under liquid nitrogen environment. XAS Ni K-edges were acquired at the SSRL beamline 7-3, which is equipped with a Si(220) ϕ = 90° double crystal monochromator, a 9 keV cutoff mirror, and a He cryostat (at 20 K). Data were collected using a Canberra 30-element Ge solid-state detector with a 3mm Co filter. Data averaging and energy calibration were performed using SixPack^4. The AUTOBK algorithm available in the Athena software package^5 was employed for data reduction and normalization.

Supplementary Figure 3. The first derivative (left) and second derivative (right) of normalized Ni K-edge PFY XANES edge spectra for agostic complexes (1), (3) and their control group complexes non-agostic complexes (2), (4). The local minimum of second derivative were carefully selected as an initial guess of the pre-edge features for the fitting work in Supplementary Figure 4-7.
TD-DFT of Ni K edge XAS

XAS TD-DFT (X-ray absorption Time dependent DFT) calculation were performed with a dense intergration grid (Gird6) for better implementing Scalar relativisitic effects by using ZORA\textsuperscript{8} corrections, and reduced by using MOanlayzer software. All the Molecular orbitals information and their contribution to the TD-DFT calculated pre-edge features are provided. Only the molecular orbitals with pronounced Ni contribution are considered to contribute the Ni K edge spectrum and function as the acceptors for quick identifying the character of major molecular orbitals (> 5%, labelled in bold), but the rest molecular orbitals are still provided as a record. The calculated energies are all shifted by + 180.19 eV for a better comparison with the experimental data.

![Image of calculated Ni K edge XAS spectrum](image)

Supplementary Figure 4 TD-DFT calculated Ni K edge XAS spectrum of 1-4.
|    | Energy(eV) | Intensity  | MO-1 | MO-2 Cont. | MO-3 Cont. | MO-4 Cont. |
|----|------------|------------|------|------------|------------|------------|
| A  | 8330.48    | 6.36E-06   | 159b | 52.4%      | 163b       | 18.4%      | 162b       | 13.0%      |
| B  | 8335.12    | 8.25E-05   | 164b | 56.8%      | 161b       | 26.7%      | 160b       | 11.8%      |
|    | 8335.27    | 9.27E-05   | 164a | 50.8%      | 162a       | 27.4%      | 160a       | 17.2%      |
|    | 8336.86    | 2.89E-05   | 166a | 45.2%      | 176a       | 5.9%       |            |            |
|    | 8337.44    | 5.41E-05   | 166a | 38.9%      | 176a       | 12.9%      | 170a       | 11.2%  167a 10.30% |
|    | 8337.55    | 2.87E-05   | 167b | 71.4%      | 174b       | 12.7%      |            |            |
|    | 8337.58    | 2.28E-05   | 167a | 65.6%      |            |            |            |            |
| C  | 8337.6     | 1.07E-05   | 166b | 28.0%      | 172b       | 21.0%      | 176b       | 2.7%       |
|    | 8337.68    | 5.31E-05   | 168a | 64.1%      | 174a       | 5.1%       | 176a       | 5.4%       |
|    | 8337.72    | 6.70E-05   | 168b | 69.7%      | 174b       | 4.2%       | 176b       | 7.0%       |
|    | **8337.84**| **8.84E-05**| **174a** | **32.5%** | **169a** | **25.8%** | **167a** | **19.0%** |
|    | 8337.84    | 5.73E-05   | 174b | 30.0%      | 169b       | 24.8%      | 167b       | 16.3%      |
|    | 8337.93    | 2.20E-05   | 169a | 56.9%      | 174a       |            |            |            |
|    | 8338.05    | 3.36E-05   | 170a | 28.6%      | 172a       | 23.7%      | 168a       | 16.6%  174a 4.66% |
| D  | 8338.11    | 4.26E-05   | 170a | 44.0%      | 176a       | 16.8%      | 168a       | 11.1%      |
|    | 8338.24    | 1.06E-05   | 171b | 64.6%      | 174b       | 1.4%       | 176b       | 11.7%      |
|    | 8338.31    | 1.65E-05   | 173b | 76.8%      | 176b       | 5.4%       |            |            |

Supplementary Table 1 TD-DFT calculation of the pre-edge features (A-D) and the Molecular orbital contribution of complex 1. highest calculated features are labeled in bold. Important orbitals with Ni character (>5%) are labeled in bold.
| Complex 1 | Nickel Centre | CH₃ | NHC ligand |
|-----------|---------------|-----|------------|
|           | Ni            | C   | H          | N | C |
| Orbital   | Total s (%)   | p (%) | d (%)     | Total s (%) | p (%) | d (%) | Total s (%) | p (%) | d (%) |
| 159,a     | 23.4          | 0.2  | 0.2        | 21.4 | 0.2  | 0.2  | 0          | 1.6  | 0.1  |
| 160,a     | 1.4           | 0.6  | 0.4        | 0.5  | 0.6  | 0.4  | 0          | 4.3  | 0.2  |
| 161,a     | 0.2           | 0    | 0          | 0.1  | 0    | 0    | 0          | 1.4  | 0.3  |
| 162,a     | 2.9           | 0.1  | 0.1        | 2    | 0.1  | 0.1  | 0          | 7.7  | 0.3  |
| 163,a     | 0.2           | 0    | 0          | 0.2  | 0    | 0    | 0          | 1.3  | 0.0  |
| 164,a     | 11.3          | 1    | 0.1        | 7.9  | 0.1  | 0.5  | 3.3        | 0    | 0.3  |
| 166,a     | 1.7           | 0.9  | 0.2        | 0.7  | 0.9  | 0.2  | 0.5        | 0.1  | 0.3  |
| 167,a     | 1.6           | 0.2  | 0.1        | 0.3  | 0.2  | 0.1  | 0.0        | 5    | 0.1  |
| 168,a     | 2.1           | 0.5  | 0.3        | 0    | 2.1  | 0.5  | 0.3        | 0.7  | 0.2  |
| 169,a     | 1.5           | 0.1  | 0.1        | 1.1  | 0.1  | 0.1  | 0          | 0.9  | 0.0  |
| 170,a     | 1.8           | 0.5  | 0.1        | 1.2  | 0.5  | 0.1  | 0.3        | 1.2  | 0.1  |
| 171,a     | 3.1           | 1.3  | 0.3        | 1.3  | 0.3  | 0.3  | 0.5        | 1    | 0.1  |
| 172,a     | 5.9           | 3.2  | 0.8        | 3.1  | 3.2  | 0.8  | 0.5        | 0.9  | 0.0  |
| 173,a     | 0.1           | 0.3  | 0.2        | 0    | 0.1  | 0.3  | 0.2        | 0.6  | 0.0  |
| 174,a     | 19.4          | 3.1  | 0.1        | 18.8 | 3.1  | 0.1  | 1.9        | 5.4  | 0.1  |
| 176,a     | 12.1          | 5.5  | 1.5        | 10.5 | 5.5  | 1.5  | 0.8        | 2.2  | 1    |
| 159,b     | 44.3          | 1.9  | 0.3        | 6.8  | 1.9  | 0.3  | 0.7        | 0    | 0.3  |
| 160,b     | 1             | 0.3  | 0.2        | 0.5  | 0.3  | 0.2  | 0.1        | 3    | 0    |
| 161,b     | 4.8           | 0.3  | 0.2        | 1.8  | 0.3  | 0.2  | 0.1        | 6.7  | 0    |
| 162,b     | 12.2          | 0.4  | 0.1        | 1.7  | 0.4  | 0.1  | 0.1        | 1.7  | 0    |
| 163,b     | 17.1          | 0.8  | 0.2        | 2.4  | 0.8  | 0.2  | 0.4        | 1.4  | 0    |
| 164,b     | 13.4          | 1.1  | 0.1        | 0.7  | 1.1  | 0.1  | 0.6        | 3.2  | 0.1  |
| 166,b     | 2.8           | 0.5  | 0.1        | 0.3  | 0.5  | 0.1  | 0.1        | 0.5  | 0    |
| 167,b     | 1.5           | 0.4  | 0.3        | 1.2  | 0.4  | 0.3  | 0.1        | 0    | 0.4  |
| 168,b     | 1.8           | 2.1  | 0.5        | 1.7  | 2.1  | 0.5  | 0.3        | 0.6  | 0.2  |
| 169,b     | 1.2           | 0.1  | 0.1        | 0.8  | 0.1  | 0.1  | 0.0        | 0.8  | 0    |
| 170,b     | 0.9           | 0.2  | 0.1        | 0.7  | 0.2  | 0.1  | 0.1        | 1.2  | 0    |
| 171,b     | 0.1           | 0.2  | 0.1        | 0    | 0.1  | 0.2  | 0.1        | 0.8  | 0    |
| 172,b     | 7.9           | 3.6  | 0.9        | 1.5  | 3.6  | 0.9  | 0.6        | 1    | 0    |
| 173,b     | 1.3           | 0.9  | 0.2        | 0.2  | 0.9  | 0.2  | 0.2        | 0.3  | 0    |
| 174,b     | 18.7          | 3.1  | 0.1        | 18.1 | 3.1  | 0.1  | 1.8        | 4.7  | 0    |
| 176,b     | 7.9           | 5.9  | 1.4        | 6.4  | 5.9  | 1.4  | 0.8        | 2.7  | 1    |

Supplementary Table 2. Atomic Character Contribution in Acceptor Molecular Orbital from Ni centre, pendant CH₃ substitute and NHC ligand in complex 1. Important Molecular Orbitals with Ni character (>5%) are labeled in bold.
Supplementary Table 3. The contribution of atomic orbital character of Ni centre to the TD-DFT calculated transition states in each pre-edge feature of complex 1 Ni K edge. Only the molecular orbitals with pronounced Ni contribution are considered (> 5%).

| Feature | Energy(eV) | Intensity | sum | s   | p   | d   | s   | p   | d   | s   | p   | d   |
|---------|------------|-----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| A       | 8330.48    | 6.36E-06  | 12.3% | 0.0% | 1.0% | 11.2% | 0.0% | 8.5% | 91.5% | 0.0% | 8.5% | 91.5% |
| B       | 8335.12    | 8.25E-05  | 7.6% | 0.1% | 4.4% | 3.1% | 0.7% | 58.2% | 41.0% | 0.8% | 64.1% | 35.1% |
|         | 8335.27    | 9.27E-05  | 5.7% | 0.1% | 4.0% | 1.7% | 0.9% | 69.9% | 29.2% |
| C       | 8336.86    | 2.89E-05  | 0.7% | 0.0% | 0.6% | 0.1% | 4.1% | 86.8% | 9.1% | 2.8% | 89.8% | 7.3% |
|         | 8337.44    | 5.41E-05  | 1.6% | 0.1% | 1.4% | 0.1% | 4.1% | 86.8% | 9.1% |
|         | 8337.55    | 2.87E-05  | 2.4% | 0.0% | 2.3% | 0.1% | 0.5% | 96.8% | 2.7% |
|         | 8337.6     | 1.07E-05  | 3.3% | 0.3% | 2.3% | 0.7% | 9.5% | 69.6% | 20.9% |
|         | 8337.68    | 5.31E-05  | 1.6% | 0.0% | 1.5% | 0.1% | 2.3% | 92.9% | 4.8% |
|         | 8337.72    | 6.70E-05  | 1.1% | 0.0% | 1.0% | 0.1% | 0.4% | 92.1% | 7.5% |
|         | 8337.84    | 8.84E-05  | 6.3% | 0.1% | 6.1% | 0.1% | 1.0% | 96.9% | 2.1% |
|         | 8337.84    | 5.73E-05  | 5.6% | 0.0% | 5.4% | 0.2% | 0.5% | 96.8% | 2.7% |
| D       | 8338.05    | 3.36E-05  | 2.3% | 0.4% | 1.6% | 0.3% | 18.9% | 70.0% | 11.1% |
|         | 8338.11    | 4.26E-05  | 2.0% | 0.1% | 1.8% | 0.2% | 4.1% | 86.8% | 9.1% |
|         | 8338.24    | 1.06E-05  | 1.2% | 0.0% | 1.0% | 0.2% | 0.1% | 84.5% | 15.4% |
|         | 8338.31    | 1.65E-05  | 0.4% | 0.0% | 0.3% | 0.1% | 0.0% | 81.0% | 19.0% |
Molecular Orbitals of Complex 1
| 170α (Nipα) | 170β (Nipβ) | 171α | 171β |
|--------------|--------------|------|------|
| ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) | ![Image](image4.png) |
| 172α | 172β | 173α | 173β |
| ![Image](image5.png) | ![Image](image6.png) | ![Image](image7.png) | ![Image](image8.png) |
| 174α (Nipα) | 174β (Nipβ) | 176α | 176β |
| ![Image](image9.png) | ![Image](image10.png) | ![Image](image11.png) | ![Image](image12.png) |

Supplementary Figure 5. 3D view of Molecular Orbital Acceptors in Complex 1.
|    | Energy(eV) | Intensity   | MO-1 | MO-2 | MO-3 | MO-4 |
|----|------------|-------------|------|------|------|------|
| A  | 8330.19    | 3.33E-06    | 155b | 81.76%|      |      |
|    | 8335.18    | 8.66E-05    | 160b | 54.29%| 156b | 18.21%|
|    | 8335.34    | 9.90E-05    | 160a | 47.84%| 156a | 23.54%|
|    | 8337.12    | 3.20E-04    | 164a | 33.30%| 170a | 24.10%|
|    | 8337.36    | 2.53E-04    | 164b | 31.48%| 170b | 31.02%|
| B  | 8335.18    | 8.66E-05    | 160b | 54.29%| 156b | 18.21%|
|    | 8335.34    | 9.90E-05    | 160a | 47.84%| 156a | 23.54%|
|    | 8337.12    | 3.20E-04    | 164a | 33.30%| 170a | 24.10%|
|    | 8337.36    | 2.53E-04    | 164b | 31.48%| 170b | 31.02%|
|    | 8337.69    | 2.24E-05    | 163a | 74.33%| 172a | 9.38% |
|    | 8338.05    | 8.42E-05    | 172a | 35.24%| 163a | 16.43%|
|    | 8338.06    | 2.61E-05    | 164a | 50.24%| 167a | 16.16%|
|    | 8338.06    | 3.25E-05    | 164b | 51.67%| 170b | 14.79%|
|    | 8338.07    | 9.87E-05    | 172b | 37.14%| 169b | 19.55%|
|    | 8338.23    | 1.26E-05    | 166b | 54.57%| 167b | 11.22%|
|    | 8338.33    | 1.17E-05    | 167a | 41.74%| 170a | 26.82%|
|    | 8338.33    | 1.38E-05    | 167b | 58.49%| 170b | 17.83%|

Supplementary Table 4. TD-DFT calculation of the pre-edge features and the Molecular orbital contribution of complex 2.
Supplementary Table 5. Atomic Character Contribution in Acceptor Molecular Orbital from Ni centre, pendant CH$_3$ substitute and NHC ligand in complex 2. Important Molecular Orbitals with Ni character (>5%) are labeled in bold.

| complex | Nickel Center | NHC ligand |
|---------|---------------|------------|
|         | Ni            | N          | C          |
|         | Total s (%) p (%) d (%) | s (%) p (%) s (%) p (%) |
| 155,a   | 26.6 0.1 2.5 24 | 2 0 1.8 0 0.2 |
| 156,a   | 2.6 0 1.8 0.8 | 5.8 0 2.7 0.3 2.8 |
| 157,a   | 2 0 1.4 0.6 | 4.6 0 1.9 0.3 2.4 |
| 158,a   | 1.3 0 0.8 0.5 | 3.4 0 2 0.1 1.3 |
| 160,a   | 11.8 0 8.3 3.5 | 34.8 0 13.1 0 21.7 |
| 163,a   | 7.6 0 7.5 0.1 | 1.6 0.2 0.6 0 0.8 |
| 164,a   | 3.9 0.5 3.1 0.3 | 1.6 0.2 0.7 0 0.7 |
| 166,a   | 6 0.2 5.5 0.3 | 1.8 0.4 0.5 0 0.9 |
| 167,a   | 1.6 0.1 1.4 0.1 | 0.6 0 0.4 0 0.2 |
| 169,a   | 14.9 2 11.5 1.4 | 3.2 0.1 0.6 0.3 2.2 |
| 170,a   | 17.5 1 15.7 0.8 | 3.3 0.6 0.3 0.2 2.2 |
| 172,a   | 12.5 0.3 11.7 0.5 | 3.5 0 0.5 0 0.3 |
| 155,b   | 70.2 13.4 0.2 56.6 | 3.9 0 0.1 0.8 3 |
| 156,b   | 2.4 0 1.3 1.1 | 4.4 0 2.2 0 2.2 |
| 157,b   | 3.3 0 1.9 1.4 | 6.2 0 3 0 3.2 |
| 158,b   | 5.2 0.9 0 4.3 | 0.7 0 0.2 0.4 0.1 |
| 160,b   | 14 0.1 8.3 5.6 | 35.6 0 13.2 0 22.4 |
| 163,b   | 1.7 0 1.3 0.4 | 4.9 0 1.2 0 3.7 |
| 164,b   | 4.6 0 4.6 0 | 0.8 0.2 0.3 0 0.3 |
| 166,b   | 1.8 0.1 1.3 0.4 | 0.9 0 0.5 0 0.4 |
| 167,b   | 2.8 0 2.7 0.1 | 1.2 0.3 0.5 0 0.4 |
| 168,b   | 0.5 0 0.4 0.1 | 0.6 0 0.5 0 0.1 |
| 169,b   | 17.6 0.9 14.6 2.1 | 3.2 0.1 0.7 0.1 2.3 |
| 170,b   | 20.2 0.4 18.8 1 | 3.6 0.7 0.4 0.1 2.4 |
| 172,b   | 12.3 0.2 11.4 0.7 | 3.1 0 0.5 0 2.6 |
| Feature | Energy(eV) | Intensity | absolute | normalized | average |
|---------|------------|-----------|----------|------------|---------|
|         |            |           | sum      | s          | p       | d       | s          | p          | d       |
| **A**   | 8330.19    | 3.33E-06  | 21.7%    | 0.1%      | 2.0%    | 19.6%   | 0.4%      | 9.4%      | 90.2%   |
|         | 8335.18    | 8.66E-05  | 7.6%     | 0.1%      | 4.5%    | 3.0%    | 0.7%      | 59.3%     | 40.0%   |
|         | 8335.34    | 9.90E-05  | 5.6%     | 0.0%      | 4.0%    | 1.7%    | 0.0%      | 70.3%     | 29.7%   |
| **B**   | 8337.12    | 3.20E-04  | 7.6%     | 0.3%      | 7.0%    | 0.3%    | 3.5%      | 92.9%     | 3.5%    |
|         | 8337.36    | 2.53E-04  | 6.3%     | 0.1%      | 5.8%    | 0.3%    | 2.0%      | 93.1%     | 5.0%    |
| **C**   | 8337.69    | 2.24E-05  | 1.2%     | 0.0%      | 1.1%    | 0.0%    | 2.4%      | 93.6%     | 4.0%    |
|         | 8338.05    | 8.42E-05  | 24.7%    | 4.7%      | 0.1%    | 19.9%   | 19.1%     | 0.3%      | 80.6%   |
|         | 8338.06    | 2.61E-05  | 4.8%     | 0.0%      | 4.7%    | 0.1%    | 0.7%      | 97.3%     | 2.1%    |
| **D**   | 8338.06    | 3.25E-05  | 3.0%     | 0.1%      | 2.8%    | 0.1%    | 2.0%      | 93.1%     | 5.0%    |
|         | 8338.07    | 9.87E-05  | 8.0%     | 0.3%      | 7.1%    | 0.7%    | 3.1%      | 88.5%     | 8.4%    |
|         | 8338.23    | 1.26E-05  | 1.1%     | 0.0%      | 1.0%    | 0.1%    | 1.6%      | 92.7%     | 5.7%    |
|         | 8338.33    | 1.17E-05  | 7.2%     | 0.4%      | 6.5%    | 0.3%    | 4.9%      | 90.4%     | 4.7%    |
|         | 8338.33    | 1.38E-05  | 3.6%     | 0.1%      | 3.4%    | 0.2%    | 2.0%      | 93.1%     | 5.0%    |

Supplementary Table 6. The contribution of atomic orbital character of Ni centre to the TD-DFT calculated transition states in each pre-edge feature of complex 2's Ni K edge. Only the molecular orbitals with pronounced Ni contribution are considered (> 5%).
Molecular Orbitals of Complex 2

155α  155β  156α  156β

157α  157β  158α  158β

160α  160β  163α  163β

164α  164β  166α  166β

167α  167β  168α  168β
**Supplementary Figure 6.** 3D view of Molecular Orbital Acceptors in Complex 2.
|    | Energy(eV) | Intensity | MO-1 | Cont.  | MO-2 | Cont.  | MO-3 | Cont.  | MO-4 | Cont.  |
|----|------------|-----------|------|-------|------|-------|------|-------|------|-------|
| A  | 8330.43    | 5.47E-06  | 170b | 55.60%| 174b | 11.80%|      |       |      |       |
| B  | 8335.09    | 7.31E-05  | 175b | 45.81%| 172b | 30.88%| 171b | 10.06%| 170b | 9.56% |
| C  | 8335.21    | 8.25E-05  | 175a | 41.45%| 171a | 40.12%| 172a | 11.44%|      |       |
|    | 8336.15    | 1.40E-05  | 177a | 49.45%| 185a | 8.09% | 183a | 6.42% |      |       |
|    | 8336.92    | 3.42E-05  | 177a | 49.45%| 185a | 8.09% |      |       |      |       |
|    | **8337.38**| **1.21E-04**| 177a | 36.75%| 179a | 10.79%| 185a | 9.45% |      |       |
|    | **8337.5** | **5.28E-05**| 178b | 33.65%| 179b | 23.53%| 180b | 10.92%| 177b | 8.79% |
|    | **8337.52**| **1.07E-05**| 178a | 78.59%| 179a | 7.60% |      |       |      |       |
|    | **8337.55**| **9.41E-05**| 178b | 52.50%| 179a | 7.72% | 186b | 7.64% |      |       |
|    | **8337.62**| **3.32E-05**| 179a | 42.65%| 184a | 12.61%| 177a | 8.57% |      |       |
|    | **8337.81**| **1.83E-05**| 180a | 63.30%| 181a | 8.87% | 179a | 8.72% |      |       |
| D  | **8337.83**| **2.50E-05**| 180b | 50.40%| 181b | 13.04%| 179b | 7.38% |      |       |
|    | **8337.92**| **6.26E-05**| 179a | 24.19%| 184a | 19.13%| 181a | 9.69% |      |       |
|    | **8338.01**| **2.30E-05**| 181b | 26.81%| 180b | 18.15%| 187b | 15.78%|      |       |
|    | **8338.02**| **5.06E-05**| 181a | 30.87%| 180a | 14.68%| 187a | 11.78%|      |       |
|    | **8338.04**| **3.70E-05**| 185a | 34.98%| 181a | 26.58%| 184a | 10.04%| 187a | 9.09% |
|    | **8338.05**| **4.72E-05**| 185b | 24.93%| 184b | 23.07%| 181b | 21.85%|      |       |

**Supplementary Table 7** TD-DFT calculation of the pre-edge features and the Molecular orbital contribution of complex 3.
| complex 3 | Nickel Center | CH3 | NHC ligand |
|----------|--------------|-----|-----------|
|          |              | C   | H         |
|          |              | s (%) | p (%) | d (%) | Total s (%) | p (%) | s (%) | p (%) |
| 170,a    | 23.4 0 1.7 21.7 | 0.2 0 0.2 0 0 | 1.4 0 1.2 0 0 |
| 171,a    | 2.9 0 1.8 1.1 | 0.1 0 0.1 0 0 | 9.9 0 3.9 0.3 5.7 |
| 172,a    | 1.4 0 0.9 0.5 | 0.5 0 0.2 0.3 0 | 3.5 0 1.8 0 1.7 |
| 174,a    | 0.1 0 0 0.1 | 0.3 0 0.1 0.2 0 | 1.7 0 0.5 0 1.2 |
| 175,a    | 10.1 0 6.9 3.2 | 0.3 0.1 0.2 0 0 | 35.3 0 13.5 0 21.8 |
| 177,a    | 1.3 0.6 0.2 0.5 | 0.5 0.1 0.1 0.3 0 | 0.6 0 0.2 0.3 0.1 |
| 178,a    | 1.7 0.1 1.4 0.2 | 1.9 0.3 0.4 0.8 0.4 | 3.7 0 1 0 2.7 |
| 179,a    | 1.6 0 1.6 0 | 1.2 0.1 0.2 0.7 0.2 | 1.7 0 0.4 0.1 1.2 |
| 180,a    | 2 0.2 1.6 0.2 | 0.6 0 0.5 0.1 0 | 0.7 0.3 0.2 0 0.2 |
| 181,a    | 1.4 0.2 1.1 0.1 | 0.3 0 0.1 0.2 0 | 1.2 0 0.6 0 0.6 |
| 183,a    | 2.7 0.8 1.4 0.5 | 1.1 0 0.4 0.5 0.2 | 0.6 0 0.3 0 0.3 |
| 184,a    | 6 1.3 4.2 0.5 | 4 1.3 1.1 0.9 0.7 | 0.4 0 0.2 0.1 0.1 |
| 185,a    | 0.5 0.7 6.9 0.9 | 2.1 0.5 0.2 0.8 0.6 | 2.3 0.2 0.5 0.2 1.4 |
| 186,a    | 5 0 4.7 0.3 | 0.7 0.1 0.4 0.1 0.1 | 1.9 0.2 0.8 0 0.9 |
| 187,a    | 11.3 0.1 11.1 0.1 | 3.8 0 1.8 1.2 0.8 | 3 0.2 0.3 0 2.5 |
| 170,b    | 48.5 7.5 3.5 37.5 | 2.6 0.3 1 0.9 0.4 | 5.8 0 1.5 0.8 3.5 |
| 171,b    | 5.8 0.7 0.3 4.8 | 0.6 0.1 0.1 0.4 0 | 3 0 1.3 0 1.7 |
| 172,b    | 4.8 0.3 1.6 2.9 | 0.3 0 0.2 0.1 0 | 7.1 0 2.8 0 4.3 |
| 174,b    | 11.4 1.6 0.6 9.2 | 0.3 0.1 0.2 0 0 | 2.1 0 0.3 0.1 1.7 |
| 175,b    | 13.3 0.3 6 7 | 1 0.2 0.5 0.3 0 | 35.4 0 13.4 0 22 |
| 177,b    | 2.4 0.2 0.3 1.9 | 0.4 0.1 0 0.3 0 | 0.6 0 0.2 0.2 0.2 |
| 178,b    | 2 0.1 1.5 0.4 | 1.9 0.3 0.4 0.8 0.4 | 3.8 0 1 0 2.8 |
| 179,b    | 1.6 0 1.3 0.3 | 1.3 0.2 0.2 0.7 0.2 | 1.6 0 0.4 0 1.2 |
| 180,b    | 1.8 0.1 1.4 0.3 | 0.6 0 0.5 0.1 0 | 0.4 0.2 0 0 0.2 |
| 181,b    | 0.9 0.1 0.6 0.2 | 0.3 0 0.1 0.2 0 | 0.8 0 0.5 0 0.3 |
| 183,b    | 0.9 0.1 0.4 0.4 | 1 0 0.3 0.5 0.2 | 0.2 0 0.2 0 0 |
| 184,b    | 7.8 0.9 6.1 0.8 | 4.4 1.4 1.1 1 0.9 | 0.1 0 0.1 0 0 |
| 185,b    | 4.4 0.5 2.5 1.4 | 1.1 0.1 0.2 0.6 0.2 | 1.1 0 0.6 0 0.5 |
| 186,b    | 5.2 0.1 4.1 1 | 1.6 0.2 0.4 0.6 0.4 | 1.2 0.2 0.4 0 0.6 |
| 187,b    | 11.2 0.1 10.9 0.2 | 3.5 0 1.8 1.2 0.5 | 3 0.2 0.3 0 2.5 |

**Supplementary Table 8.** Atomic Character Contribution in Acceptor Molecular Orbital from Ni centre, pendant CH$_3$ substitute and NHC ligand in complex 3. Important Molecular Orbitals with Ni character (>5%) are labeled in bold.
Supplementary Table 9. The contribution of atomic orbital character of Ni centre to the TD-DFT calculated transition states in each pre-edge feature of complex 2’s Ni K edge. Only the molecular orbitals with pronounced Ni contribution are considered (> 5%).
| Molecular Orbitals of Complex 3 |
|--------------------------------|
| ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) | ![Image](image4.png) |
| 170α                  | 170β                  | 171α                  | 171β                  |
| ![Image](image5.png) | ![Image](image6.png) | ![Image](image7.png) | ![Image](image8.png) |
| 172α                  | 172β                  | 174α                  | 174β                  |
| ![Image](image9.png) | ![Image](image10.png) | ![Image](image11.png) | ![Image](image12.png) |
| 175α                  | 175β                  | 177α                  | 177β                  |
| ![Image](image13.png) | ![Image](image14.png) | ![Image](image15.png) | ![Image](image16.png) |
| 178α                  | 178β                  | 179α                  | 179β                  |
| ![Image](image17.png) | ![Image](image18.png) | ![Image](image19.png) | ![Image](image20.png) |
| 180α                  | 180β                  | 181α                  | 181β                  |
Supplementary Figure 7. 3D view of Molecular Orbital Acceptors in Complex 3.
|     | Energy (eV) | Intensity | MO-1 | MO-2 | MO-3 | MO-4 |
|-----|-------------|-----------|------|------|------|------|
| A   | 8330.13     | 2.00E-06  | 166b | 82.35% |      |      |
| B   | 8335.12     | 7.93E-05  | 171b | 47.30% | 167b | 42.24% |
|     | 8335.25     | 9.21E-05  | 167a | 44.79% | 171a | 42.79% |
|     | 8336.15     | 2.95E-05  | 169a | 49.94% | 170a | 25.29% | 171a | 15.75% |
|     | 8336.79     | 1.26E-04  | 174a | 20.88% | 172a | 19.95% | 173a | 14.43% | 179a | 9.68% |
|     | 8337.01     | 1.59E-04  | 174a | 26.08% | 173a | 16.21% | 178a | 10.53% |
|     | 8337.1      | 2.00E-04  | 175b | 23.16% | 176b | 11.19% | 178b | 10.68% | 174b | 10.13% |
|     | 8337.24     | 4.58E-05  | 173b | 48.67% |      |      |      |      |
|     | 8337.67     | 2.17E-05  | 174b | 69.27% |      |      |      |      |
|     | 8337.68     | 2.40E-05  | 175b | 51.48% | 174a | 21.66% |      |      |
|     | 8337.88     | 1.35E-05  | 175b | 42.62% | 176b | 40.52% |      |      |
| C   | 8338.03     | 7.67E-05  | 182a | 32.00% | 176a | 18.10% | 177a | 11.26% |
|     | 8338.07     | 1.52E-05  | 177a | 56.19% | 174a | 15.38% |      |      |
|     | 8338.07     | 7.93E-05  | 181b | 24.80% | 177b | 22.75% | 180b | 11.20% | 174b | 10.43% |
|     | 8338.17     | 1.07E-05  | 178b | 38.30% | 177b | 31.60% | 180b | 9.70%  | 176b | 9.26%  |

Supplementary Table 10. TD-DFT calculation of the pre-edge features and the Molecular orbital contribution of complex 4.
| Complex 4 | Nickel Center | NHC ligand |  |
|-----------|---------------|------------|---------------|
|           | Ni            | Total      | s (%) | p (%) | d (%) | Total     | s (%) | p (%) | s (%) | p (%) |
| 166,a     | 24.9          | 0          | 2.3   | 22.6  |       | 1.6       | 0      | 1.4   | 0     | 0.2   |
| 167,a     | 3.2           | 0          | 1.8   | 1.4   |       | 9.7       | 0      | 3.5   | 0.3   | 5.9   |
| 169,a     | 1.1           | 0          | 0.8   | 0.3   |       | 2.8       | 0      | 1.2   | 0     | 1.6   |
| 170,a     | 0.6           | 0          | 0.5   | 0.1   |       | 0.8       | 0      | 0.3   | 0     | 0.5   |
| 171,a     | 11.8          | 0          | 8.5   | 3.3   |       | 34.2      | 0      | 13.6  | 0     | 20.6  |
| 173,a     | 1.5           | 0.8       | 0.2   | 0.5   |       | 0.5       | 0      | 0.1   | 0.3   | 0.1   |
| 174,a     | 15.6          | 0          | 15.5  | 0.1   |       | 2        | 0.2    | 0.5   | 0     | 1.3   |
| 175,a     | 2.7           | 0          | 2.5   | 0.2   |       | 3.5       | 0      | 1.2   | 0     | 2.3   |
| 176,a     | 4.8           | 0.1       | 4.7   | 0     |       | 1        | 0.4    | 0.2   | 0     | 0.4   |
| 177,a     | 4             | 0          | 4     | 0     |       | 1.2       | 0.2    | 0.4   | 0     | 0.6   |
| 178,a     | 6.9           | 0.2       | 6.6   | 0.1   |       | 1.2       | 0.3    | 0.3   | 0     | 0.6   |
| 179,a     | 6.5           | 2.2       | 2.9   | 1.4   |       | 1.4       | 0.1    | 0.4   | 0.1   | 0.8   |
| 180,a     | 3.4           | 0          | 3.4   | 0     |       | 1.5       | 0.1    | 0.7   | 0     | 0.7   |
| 181,a     | 5.4           | 1.6       | 2.8   | 1     |       | 0.9       | 0      | 0.2   | 0.2   | 0.5   |
| 182,a     | 10.4          | 0          | 10.2  | 0.2   |       | 2.8       | 0.1    | 0.9   | 0     | 1.8   |
| 166,b     | 71.8          | 15.7      | 0     | 56.1  |       | 4.6       | 0      | 0.2   | 0.8   | 3.6   |
| 167,b     | 4.3           | 0.2       | 1.5   | 2.6   |       | 9.4       | 0      | 3.4   | 0.2   | 5.8   |
| 169,b     | 1.6           | 0.1       | 0.7   | 0.8   |       | 2.6       | 0      | 1.1   | 0     | 1.5   |
| 170,b     | 0.7           | 0          | 0.4   | 0.3   |       | 0.7       | 0      | 0.3   | 0     | 0.4   |
| 171,b     | 14.1          | 0.1       | 8.1   | 5.9   |       | 34.7      | 0      | 13.6  | 0     | 21.1  |
| 173,b     | 2.1           | 0.2       | 0.2   | 1.7   |       | 0.4       | 0      | 0.2   | 0.1   | 0.1   |
| 174,b     | 3.8           | 0          | 3.5   | 0.3   |       | 3.7       | 0      | 1     | 0     | 2.7   |
| 175,b     | 6.7           | 0          | 6.6   | 0.1   |       | 1        | 0.1    | 0.3   | 0     | 0.6   |
| 176,b     | 5.2           | 0.1       | 5.1   | 0     |       | 0.9       | 0.4    | 0.2   | 0     | 0.3   |
| 177,b     | 2.1           | 0          | 2.1   | 0     |       | 1        | 0.1    | 0.5   | 0     | 0.4   |
| 178,b     | 8.9           | 0.2       | 8.6   | 0.1   |       | 1.4       | 0.4    | 0.3   | 0     | 0.7   |
| 179,b     | 3.1           | 0.3       | 1.7   | 1.1   |       | 0.4       | 0.1    | 0.2   | 0     | 0.1   |
| 180,b     | 5.9           | 0          | 5.8   | 0.1   |       | 1.6       | 0.2    | 0.5   | 0     | 0.9   |
| 181,b     | 10.4          | 0.1       | 10.1  | 0.2   |       | 2.1       | 0.1    | 0.5   | 0     | 1.5   |
| 182,b     | 6.3           | 0.6       | 4.2   | 1.5   |       | 0.5       | 0.1    | 0.1   | 0     | 0.3   |

Supplementary Table 11. Atomic Character Contribution in Acceptor Molecular Orbital from Ni centre, pendant CH₃ substitute and NHC ligand in complex 4. Important Molecular Orbitals with Ni character (>5%) are labeled in bold.
Supplementary Table 12. The contribution of atomic orbital character of Ni centre to the TD-DFT calculated transition states in each pre-edge feature of complex 2’s Ni K edge. Only the molecular orbitals with pronounced Ni contribution are considered (> 5%).

| Feature | Energy(eV) | Intensity | s  | p  | d  | s  | p  | d  | s  | p  | d  |
|---------|------------|-----------|----|----|----|----|----|----|----|----|----|
| A       | 8330.13    | 2.00E-06  | 59.10% | 12.9% | 0.0% | 46.2% | 21.9% | 0.0% | 78.1% | 21.9% | 0.0% | 78.1% |
| B       | 8335.12    | 7.93E-05  | 6.70% | 0.1% | 3.8% | 2.8% | 0.7% | 57.4% | 41.8% | 0.4% | 64.7% | 34.9% |
| C       | 8335.25    | 9.21E-05  | 5.00% | 0.0% | 3.6% | 1.4% | 0.0% | 72.0% | 28.0% |
|         | 8336.15    | 2.95E-05  | 1.90% | 0.0% | 1.3% | 0.5% | 0.0% | 72.0% | 28.0% | 1.3% | 92.8% | 5.9% |
|         | 8336.79    | 1.26E-04  | 3.90% | 0.2% | 3.5% | 0.2% | 5.5% | 90.5% | 4.0% |
|         | 8337.01    | 1.59E-04  | 4.80% | 0.0% | 4.7% | 0.0% | 0.4% | 98.8% | 0.8% |
|         | 8337.1     | 2.00E-04  | 3.10% | 0.0% | 3.0% | 0.0% | 1.1% | 97.8% | 1.1% |
|         | 8337.68    | 2.40E-05  | 3.40% | 0.0% | 3.4% | 0.0% | 0.0% | 99.4% | 0.6% |
|         | 8337.88    | 1.35E-05  | 5.00% | 0.0% | 4.9% | 0.0% | 0.8% | 98.3% | 0.9% |
| D       | 8338.07    | 1.52E-05  | 2.40% | 0.0% | 2.4% | 0.0% | 0.0% | 99.4% | 0.6% | 1.0% | 97.8% | 1.2% |
|         | 8338.07    | 7.93E-05  | 2.60% | 0.0% | 2.5% | 0.1% | 1.0% | 97.1% | 1.9% |
|         | 8338.17    | 1.07E-05  | 4.50% | 0.1% | 4.3% | 0.1% | 1.9% | 97.0% | 1.1% |
| Molecular Orbitals of Complex 4 |
|--------------------------------|
| ![Molecular Orbital 166α](image1) | ![Molecular Orbital 166β](image2) | ![Molecular Orbital 167α](image3) | ![Molecular Orbital 167β](image4) |
| ![Molecular Orbital 169α](image5) | ![Molecular Orbital 169β](image6) | ![Molecular Orbital 170α](image7) | ![Molecular Orbital 170β](image8) |
| ![Molecular Orbital 171α](image9) | ![Molecular Orbital 171β](image10) | ![Molecular Orbital 172α](image11) | ![Molecular Orbital 172β](image12) |
| ![Molecular Orbital 173α](image13) | ![Molecular Orbital 173β](image14) | ![Molecular Orbital 174α](image15) | ![Molecular Orbital 174β](image16) |
| ![Molecular Orbital 175α](image17) | ![Molecular Orbital 175β](image18) | ![Molecular Orbital 176α Px](image19) | ![Molecular Orbital 176β Px](image20) |
| ![Molecular Orbital 177α Px](image21) | ![Molecular Orbital 177β Px](image22) | ![Molecular Orbital 178α Px](image23) | ![Molecular Orbital 178β Px](image24) |
Supplementary Figure 8. 3D view of Molecular Orbital Acceptors in Complex 4.
Simulation of Ni K edge XAS

Calibrated and normalized experimental spectra were further simulated with Athena software. Assumption of number of the pre-edge features was made from the time-dependant DFT calculation and the assignment of each feature by the DFT MO calculation. Four Lorentzian function curves were applied for the four identified pre-edge features. One Gaussian feature was used to simulate the broad background continuum comprised of a series of satellite features. An error function was used for simulating the edge jump of XAS. Both of the Gaussian curve and error function constitute the background of the simulated spectrum. The simulating results indicated that the pre-edge feature A is extremely hard to track and evaluate due to the large uncertain and small peak height. Therefore, the details of the consideration of 3d feature will be discussed by the Ni L edge spectra.
Supplementary Figure 9. Ni K edge XAS spectrum fitting of complex 1 in solid state.

| Feature | Function | height  | center    | sigma    | area   |
|---------|----------|---------|-----------|----------|--------|
| A       | lorentzian | 0.009(0.009) | 8331.04(5.56) | 0.538(0.441) | 0.009  |
| B       | lorentzian | 0.277(0.034) | 8335.13(0.39) | 1.149(0.092) | 0.277  |
| C       | lorentzian | 2.548(0.585) | 8337.34(0.53) | 3.492(0.288) | 2.548  |
| D       | lorentzian | 0.957(0.606) | 8337.72(1.50) | 3.711(0.803) | 0.957  |
| Continuum | gaussian | 2.958(1.140) | 8342.05(5.14) | 3.271(0.176) | 2.958  |
| Edge    | error fun | 0.576(0.305) | 8345.51(5.57) | 5.806(4.568) |        |

Supplementary Table 13. Ni K edge XAS spectrum fitting results of complex 1 in solid state. The uncertainty of each simulating value is listed within bracket.
Supplementary Figure 10. Ni K edge XAS spectrum fitting of complex 2 in solid state.

| Feature | Function | height    | center    | sigma   | area   |
|---------|----------|-----------|-----------|---------|--------|
| A       | lorentzian| 0.012(0.030) | 8333.11(15.44) | 2.482(4.660) | 0.012  |
| B       | lorentzian| 0.930(0.873) | 8335.20(7.52)  | 5.557(0.557) | 0.93   |
| C       | lorentzian| 2.459(0.318) | 8337.10(0.38)  | 3.510(0.185) | 2.459  |
| D       | lorentzian| 1.054(0.496) | 8337.97(0.84)  | 3.439(0.610) | 1.054  |
| Continuum | gaussian| 4.333(9.793) | 8342.46(13.87) | 4.256(0.646) | 4.333  |
| Edge    | error fun| 0.480(0.093) | 8345.33(11.08) | 5.113(4.845) |        |

Supplementary Table 14. Ni K edge XAS spectrum fitting results of complex 2 in solid state. The uncertainty of each simulating value is listed within bracket.
Supplementary Figure 11. Ni K edge XAS spectrum fitting of complex 3 in solid state.

Supplementary Table 15. Ni K edge XAS spectrum fitting results of complex 3 in solid state. The uncertainty of each simulating value is listed within bracket.
Supplementary Figure 12. Ni K edge XAS spectrum fitting of complex 3 in solid state.

Supplementary Table 16. Ni K edge XAS spectrum fitting results of complex 4 in solid state. The uncertainty of each simulating value is listed within bracket.

Extended X-ray absorption fine structure (EXAFS) of complex 1
The EXAFS oscillations $\chi (k)$ were quantitatively analyzed by curve fitting using Artemis suite of computer programs as previously described, using *ab initio* theoretical phase and amplitude functions calculated using the program FEFF version 6.0. No smoothing, filtering, or related operations were performed on the data. Single scattering paths as well as a multiple scattering model used in the fitting procedure were obtained from the single crystal structure from solid complex 1.

Supplementary Figure 13. Ni K edge XAS spectrum of complex 1 in solid state (red solid line) and toluene solution (red dash line).

Supplementary Figure 14. Experimental (black) and calculated (blue) EXAFS spectra of the 1 (in toluene solution), in k space (left) and reduced distance space (right) with Model 1.
Supplementary Table 17. Structural parameters obtained from best EXAFS fitting for complex 1 (in toluene solution). Degeneracy (coordination number) N, internuclear separations R, Debye-Waller factors $\sigma^2$, and threshold energy shift $\Delta E_0$, derived from EXAFS curve fitting. *Fit parameters: $\Delta k = 3.0 - 12.0 \text{Å}^{-1}, \quad dk = 1.0 \text{Å}^{-1}, \quad R = 1 - 4.4 \text{Å}, \quad S_0^2 = 1.20$. Goodness of fit value, $R = 0.006$. The degeneracy for Ni-C at 2.41 Å was set as a floating number. *Fit parameters: $\Delta k = 3.0 - 12.0 \text{Å}^{-1}, \quad dk = 1.0 \text{Å}^{-1}, \quad R = 1 - 4.4 \text{Å}, \quad S_0^2 = 1.20$. Goodness of fit value, $R = 0.007$. The degeneracy for Ni-C at 2.41 Å was set as a fixed number.

| Scattering Path | Degeneracy | R (Å) | $\sigma^2$ (Å$^2$) | $\Delta E_0$ (eV) |
|----------------|------------|-------|-------------------|------------------|
| Ni-N           | 1          | 1.89  | 0.004             | -1.13            |
| Ni-C           | 1          | 1.90  | 0.004             | -1.13            |
| Ni-C           | 0.59       | 2.41  | 0.002             | -1.13            |
| Ni-C/N         | 6          | 2.93  | 0.011             | -1.13            |
| Ni-C-N         | 8          | 3.15  | 0.005             | -1.13            |
| Ni-C           | 1          | 3.54  | 0.005             | -1.13            |
| Ni-C           | 6          | 3.25  | 0.026             | -1.13            |
| Ni-C/O         | 8          | 4.05  | 0.010             | -1.13            |
| Ni-C-O         | 2          | 4.04  | 0.010             | -1.13            |
| Ni-C-C/N       | 6          | 4.17  | 0.005             | -1.13            |

In order to obtain metrical information from the peaks in the Fourier-transformed data, a shell model method was utilized for EXAFS fitting. It was first started with the model optimized by DFT calculations, and the simulated EXAFS spectrum of complex 1 (in toluene solution) agrees well with the experimental results (Figure S10). The first coordination shell at around 1.5 Å (R + $\Delta$, without phase correction) consists of the contributions from a single Ni-N bond at 1.89 Å, a single Ni-C bond at 1.90 Å, as well as another Ni-C bond at 2.41 Å. It should be noteworthy that the fitting results was slightly improved (R =0.007 to R = 0.006) when we set the coordination number of Ni-C bond at 2.41 Å as a floating number (Model 1 in Table S6). Based the fitting results, it suggests the coordination number of Ni-C at 2.41 Å is 0.59 rather than 1, indicating the flexibility of CH$_3$ group when 1 is dissolved in toluene. The second coordination shell at around 2.7 Å to 3.0 Å (R + $\Delta$, without phase correction) consists of the single scattering from neighbouring C or N atom at distance 2.93 Å to 3.54 Å. Multiple scattering at 4.04 Å and 4.17 Å contributes to the third shell in EXAFS spectrum.
Ni L edge X-ray Absorbance Spectroscopy

Supplementary Figure 15. Experimental Ni L edge XAS of complex 1 and 2 and the simulating function curves of each pre-edge feature.
Supplementary Table 18. Simulation data of Ni L edge XAS. The most pronounced pre-edge feature 1 lies in the energy region of 3d← 2p, which is supported by the following TD-DFT calculation.
Supplementary Figure 16. TD-DFT calculated Ni L-edge XAS. See feature info in Supplementary Table 10 & 11.
| Region   | Energy   | Intensity  | MO  | MO-1  | MO-2  | MO-3  |
|----------|----------|------------|-----|-------|-------|-------|
| 3d$^{2}$-$y^{2}$ ← 2p | 844.57   | 1.18E-03   | orbital | 159b  | 163b  | 162b  |
|          |          |            | contribution | 52.01% | 19.41% | 12.65%|
|          | 844.63   | 4.27E-02   | orbital | 159b  | 163b  | 162b  |
|          |          |            | contribution | 51.91% | 19.40% | 12.63%|
|          | 844.79   | 4.42E-02   | orbital | 159b  | 163b  | 162b  |
|          |          |            | contribution | 51.80% | 19.36% | 12.61%|
| $\pi^{*}$CNiN← 2p | 849.43   | 4.04E-03   | orbital | 164b  | 161b  | 160b  |
|          |          |            | contribution | 56.25% | 26.00% | 11.90%|
|          | 851.33   | 2.30E-03   | orbital | 166b  | 172b  | 193b  |
|          |          |            | contribution | 53.86% | 11.12% |       |
|          | 849.18   | 3.62E-03   | orbital | 164b  | 161b  |       |
|          |          |            | contribution | 54.56% | 25.29% | 11.57%|
|          | 849.57   | 5.36E-03   | orbital | 164a  | 162a  | 160a  |
|          |          |            | contribution | 47.89% | 26.57% | 17.05%|
|          | 850.2    | 2.43E-03   | orbital | 164a  | 162a  | 160a  |
|          |          |            | contribution | 41.89% | 22.68% | 14.42%|
|          | 851.16   | 8.74E-03   | orbital | 166a  | 164a  |       |
|          |          |            | contribution | 21.55% | 5.50%  |       |
|          | 851.2    | 1.01E-03   | orbital | 166b  | 172b  |       |
|          |          |            | contribution | 56.04% | 10.68% |       |
|          | 851.68   | 1.20E-03   | orbital | 166b  | 172b  | 167b  |
|          |          |            | contribution | 21.21% | 15.45% | 15.79%|
|          | 851.7    | 1.65E-03   | orbital | 166a  | 176a  | 170a  |
|          |          |            | contribution | 29.99% | 9.99%  | 9.10%  |
| 4p← 2p  | 852.36   | 1.52E-03   | orbital | 171b  | 166a  | 170b  |
|          |          |            | contribution | 18.25% | 12.94% | 10.31%|
|          | 851.85   | 8.65E-05   | orbital | 167a  | 174a  | 166a  |
|          |          |            | contribution | 59.37% | 7.68%  |       |
|          | 851.89   | 1.61E-03   | orbital | 167b  | 174b  |       |
|          |          |            | contribution | 54.51% | 11.36% |       |
|          | 851.94   | 3.12E-03   | orbital | 168a  | 166b  |       |
|          |          |            | contribution | 15.50% | 12.45% | 9.83%  |
|          | 851.96   | 1.99E-03   | orbital | 168a  | 169b  | 172a  |
|          |          |            | contribution | 45.15% | 6.42%  | 5.72%  |
|          | 852.78   | 1.84E-03   | orbital | 176b  | 172b  | 183b  |
|          |          |            | contribution | 19.66% | 12.35% | 11.45%|
**Supplementary Table 19. TD-DFT calculated Ni L-edge XAS and each Molecular Orbital Acceptors Contribution of complex 1.** See the details of each MO acceptor's atomic character and 3d graphics in Supplementary Table 1 and Supplementary Table 5.

| Region          | Energy | Intensity | MO acceptor | MO-1  | MO-2  | MO-3  |
|-----------------|--------|-----------|-------------|-------|-------|-------|
| 3d_{x^2-y^2} ← 2p |        |           | Orbital     | 160b  | 156b  | 157b  |
| 849.59          | 3.70E-03 |          | Contribution | 50.56% | 26.07% | 17.91% |
| 850.324         | 3.05E-03 |          | Orbital     | 160, a| 156, a| 157, a|
|                 |         |          | Contribution | 44.86% | 29.54% | 18.04% |
| π^*CNiN←2p      |        |           | Orbital     | 162b  | 158a  | 170b  |
| 851.526         | 1.99E-03 |          | Contribution | 24.03% | 20.87% | 6.44%  |
| 851.455         | 1.39E-03 |          | Orbital     | 162b  | 170b  | 186b  |
| 851.839         | 2.04E-03 |          | Contribution | 29.80% | 7.91%  | 6.53%  |
| 851.954         | 4.22E-03 |          | Orbital     | 164b  | 170b  | 167b  |
| 852.285         | 2.62E-03 |          | Contribution | 26.30% | 23.42% | 9.04%  |
|                 |         |           | Orbital     | 162a  | 163b  | 170a  |
|                 |         |           | Contribution | 18.68% | 17.26% | 10.20% |
| 852.341         | 1.53E-03 |          | Orbital     | 162a  | 170a  | 166a  |
| 852.6           | 2.71E-03 |          | Contribution | 56.73% | 10.77% | 9.47%  |
| 852.458         | 1.63E-03 |          | Orbital     | 164a  | 172b  | 169a  |
|                 |         |           | Contribution | 16.47% | 16.36% | 7.91%  |
| 844.312         | 9.20E-03 |          | Orbital     | 155, b| 158, b|       |
|                 |         |           | Contribution | 84.02% | 6.91%  |       |
| 844.386         | 2.83E-02 |          | Orbital     | 155, b| 158, b|       |
|                 |         |           | Contribution | 81.29% | 6.68%  |       |
| 844.406         | 5.50E-02 |          | Orbital     | 155, b| 160, b|       |
|                 |         |           | Contribution | 81.34% | 5.06%  |       |
| 849.674         | 3.94E-03 |          | Orbital     | 160, b| 156, b| 157, b|
|                 |         |           | Contribution | 51.27% | 26.40% | 18.13% |
| 4p←2p           |        |           | Orbital     | 167b  | 174b  |       |
| 851.89          | 1.61E-03 |          | Contribution | 54.51% | 11.36% |       |
| 851.94          | 3.12E-03 |          | Orbital     | 168a  | 166b  |       |
|                 |         |           | Contribution | 15.50% | 12.45% | 9.83%  |
| 851.96          | 1.99E-03 |          | Orbital     | 168a  | 169b  | 172a  |
|                 |         |           | Contribution | 45.15% | 6.42%  | 5.72%  |
| 852.78          | 1.84E-03 |          | Orbital     | 176b  | 172b  | 183b  |
|                 |         |           | Contribution | 19.66% | 12.35% | 11.45% |
Density Functional Calculation

General Consideration

Density Functional Theory Calculations Initial geometries for all molecules were obtained from crystallographic coordinates (where available) or constructed from standard models. Geometry optimizations and numerical frequency calculations were performed using version 4.21 of the ORCA computational chemistry package. Molecular geometries were optimized using the PBE0 functional and all electron basis sets (def2-TZVP) for Ni centre and def2-SVP for all the rest atoms. Statistical mechanics calculations of entropic and thermal effects were performed using the rigid rotor and harmonic oscillator approximations at 298.15 K and 1 atm. Computational efficiency was improved by applying the RI approximation (RIJCOSX) for the hybrid functional. All calculations were performed with integration grid (ORCA Grid4). NBO calculations were calculated with Gaussian 09 program package, AIM calculation were performed in Multiwfn software by using NBO outputs using D3LYP/def2-TZVPP level. All calculations were run on the UBC Chemistry Abacus cluster and on the Cedar of Compute Canada cluster.
Supplementary Figure 17. MO diagram of complex 1 and 2. Only orbitals contribute to the XAS absorption with significant Ni characters are present.
Supplementary Figure 18. MO diagram of complex 3 and 4. Only orbitals contribute to the XAS absorption with significant Ni characters are present.
**DFT-AIM calculation**

Supplementary Figure 19. AIM electron density contour map of complex 1 and its simplified version 1-s. 1° dihedral angle Φ was optimized at 0° and constrained at 10° as comparison.

|               | bcp 98 in 1 | bcp 10 in 1° | bcp 10 in 1° |
|---------------|------------|-------------|-------------|
| Φ(°)          | 4.9        | 0.0         | 10.0        |
| ρ(r)          | 0.040      | 0.030       | 0.030       |
| G(r)          | 0.043      | 0.030       | 0.030       |
| K(r)          | 0.003      | 0.001       | 0.001       |
| V(r)          | -0.046     | -0.031      | -0.032      |
| E(r) or H (r) | -0.003     | -0.001      | -0.001      |
| ∇²ρ(r)        | 0.159      | 0.117       | 0.117       |
| ELF          | 0.095      | 0.075       | 0.076       |
| LOL          | 0.241      | 0.217       | 0.218       |
| ESP from nuclear charges | 53.671 | 27.653 | 27.598 |
| ESP from electrons | -53.440 | -27.445 | -27.390 |
| Total ESP    | 0.232      | 0.208       | 0.207       |

Supplementary Table 21. AIM calculation data. a Dihedral Angle Ni1-N2-C3-C4; b Density of all electrons; c Lagrangian kinetic energy; d Hamiltonian kinetic energy; e Potential energy density; f Energy density; g Laplacian of electron density; h Electron localization function; i Localized orbital locator;
**DFT -NBO Calculation**

![Complex 1 Diagram](image)

|                | B3LYP/Def2SVP |                  |                  |                  |
|----------------|---------------|------------------|------------------|------------------|
| **Donor**      | **Acceptor**  | **E(2)** kcal/mol| **E(j)-E(i)** a.u.| **F(i,j)** a.u.  |
| 85. BD (1) C 71 - H91 | 155. LP*(6)Ni 1 | 1.89             | 0.6              | 0.046            |
|                 | 157. LP*(8)Ni 1 | 4.76             | 0.77             | 0.077            |
| 84. BD (1) C 71 - H90 | 155. LP*(6)Ni 1 | 1.06             | 0.6              | 0.034            |
|                 | 157. LP*(8)Ni 1 | 3.11             | 0.77             | 0.062            |
| **Total**      |               | 10.82            | 2.74             | 0.219            |
| 85. BD (1) C71 - H90 | 156. LP*(7)Ni 1 | 5.51             | 0.59             | 0.073            |
|                 | 157. LP*(8)Ni 1 | 0.74             | 0.7              | 0.029            |
| 86. BD 1) C71 - H91 | 156. LP*(7)Ni 1 | 8.89             | 0.59             | 0.092            |
|                 | 157. LP*(8)Ni 1 | 1.06             | 0.7              | 0.035            |
| **Total**      |               | 16.2             | 2.58             | 0.229            |

| **Donor**      | **Acceptor**  | **E(2)** kcal/mol| **E(j)-E(i)** a.u.| **F(i,j)** a.u.  |
| H1             | σC71 - H90    | 10.42            | 2.66             | 0.198            |
| H2             | σC71 - H91    | 16.6             | 2.66             | 0.25             |

**α spin**

|                |                  |                  |                  |
| 84. (0.98497) BD (1) C71 – H90 | (61.21%) C 71 s(22.93%) p 3.36(77.02%) d 0.00(0.04%) |
|                 | (38.79%) H 90 s(99.92%) p 0.00(0.08%) |
| 85. (0.98081) BD (1)C71 - H91 | (60.28%) C 71 s(22.37%) p 3.47(77.59%) d 0.00(0.05%) |
|                 | (39.72%) H 91 s(99.92%) p 0.00(0.08%) |
| 155. (0.16568) LP*(6)Ni1 | s(87.97%) p 0.05(4.11%) d 0.09(7.93%) |
| 157. (0.01818) LP*(8)Ni1 | s(1.99%) p48.57(96.75%) d 0.63(1.25%) |

**β spin**

|                |                  |                  |                  |
| 85. (0.97987) BD (1) C71 - H90 | (61.16%) C 71 s(22.63%) p 3.42(77.32%) d 0.00(0.04%) |
|                 | (38.84%) H 90 s(99.93%) p 0.00(0.07%) |
| 86. (0.97184) BD (1) C71 - H91 | (59.97%) C 71 s(21.93%) p 3.56(78.02%) d 0.00(0.04%) |
|                 | (40.03%) H 91 s(99.93%) p 0.00(0.07%) |
| 155. (0.07809) LP*(6)Ni1 | s(0.10%) p99.99(98.76%) d11.26(1.12%) |
| 157. (0.00789) LP*(8)Ni1 | s(6.46%) p12.86(83.04%) d 1.63(10.50%) |

**Supplementary Table 22. NBO calculation of complex 1 at UB3LYP/defs-SVP theory level.**
| Donor | Acceptor | \(E(2)\) kcal/mol | \(E(i)-E(i)\) a.u. | \(F(i,j)\) a.u. |
|-------|----------|---------------------|---------------------|------------------|
| 84. BD (1) C71 - H90 | 155. LP*(6)Ni 1 | 1.14 | 0.61 | 0.036 |
| 85. BD (1) C71 - H91 | 155. LP*(6)Ni 1 | 4.14 | 0.86 | 0.075 |
| 85. BD (1) C71 - H91 | 157. LP*(8)Ni 1 | 2.11 | 0.61 | 0.049 |
| | 157. LP*(8)Ni 1 | 6.14 | 0.86 | 0.092 |
| Total | | 13.53 | 2.94 | 0.252 |
| 86. BD (1) C71 - H90 | 158. LP*(8)Ni 1 | 1.07 | 0.8 | 0.037 |
| 87. BD (1) C71 - H91 | 157. LP*(7)Ni 1 | 7.76 | 0.63 | 0.09 |
| | 158. LP*(8)Ni 1 | 11.7 | 0.63 | 0.109 |
| Total | | 22.19 | 2.86 | 0.283 |

\(\alpha\) spin

| 84. (0.98224) BD (1) C71 - H90 | C71 s (23.66%) p 3.22(76.20%) d 0.01(0.14%) |
| | H90 s(99.97%) p 0.00(0.03%) |
| 85. (0.97697) BD (1) C71 - H91 | 0.7731* C 71 s(23.06%)p 3.33(76.78%) d 0.0(0.15%) |
| | 0.6343* H 91 s(99.96%)p 0.00(0.04%) |
| 155. (0.17706) LP*(6)Ni1 | s(88.35%) p 0.08(6.75%) d 0.06(4.90%) |
| 157. (0.02359) LP*(8)Ni 1 | s(1.69%) p57.45(97.23%) d 0.63(1.07%) |

\(\beta\) spin

| 86. (0.97271) BD (1) C71 - H90 | C71 s(23.32%) p 3.28(76.53%) d 0.01(0.14%) |
| | H90 s(99.97%) p 0.00(0.03%) |
| 87. (0.96183) BD (1) C71 - H91 | 0.7731* C 71 s(22.59%)p 3.32(77.25%) d 0.01(0.15%) |
| | 0.6343* H 91 s(99.96%)p 0.00(0.03%) |
| 157. (0.05668) LP*(7)Ni 1 | s(54.15%) p 0.37(19.97%) d 0.48(25.88%) |
| 158. (0.01122) LP*(8)Ni 1 | s(6.84%) p12.23(83.71%) d 1.38(9.45%) |

Supplementary Table 23. NBO calculation of complex 1 at UB3LYP/def2-TZVP theory level.
**complex 1**

![Chemical structure of complex 1](image)

| Donor | Acceptor | E(2) kcal/mol | E(\(j\))-E(\(i\)) a.u. | F(\(i,j\)) a.u. |
|-------|----------|----------------|--------------------------|-----------------|
| 84. BD (1) C71 - H90 | 155. LP*(6)Ni | 1 | 0.83 | 0.59 | 0.03 |
| 156. LP*(7)Ni | 1 | 0.31 | 0.92 | 0.022 |
| 157. LP*(8)Ni | 1 | 8.26 | 0.87 | 0.107 |
| α | 155. LP*(6)Ni | 1 | 1.65 | 0.59 | 0.043 |
| 156. LP*(7)Ni | 1 | 0.34 | 0.92 | 0.023 |
| 157. LP*(8)Ni | 1 | 10.06 | 0.87 | 0.118 |
| Total | | | 21.45 | 4.76 | 0.343 |
| 86. BD (1) C71 - H91 | 155. LP*(6)Ni | 1 | 0.31 | 0.88 | 0.021 |
| 156. LP*(7)Ni | 1 | 10.73 | 0.67 | 0.108 |
| 157. LP*(8)Ni | 1 | 2.41 | 0.74 | 0.054 |
| β | 155. LP*(6)Ni | 1 | 0.61 | 0.88 | 0.03 |
| 156. LP*(7)Ni | 1 | 14.23 | 0.67 | 0.124 |
| 157. LP*(8)Ni | 1 | 2.5 | 0.74 | 0.054 |
| Total | | | 30.79 | 4.58 | 0.391 |
| H 1 | σ C71 - H90 | | 24.65 | 4.67 | 0.342 |
| H 2 | σ C71 - H91 | | 27.59 | 4.67 | 0.392 |

**α spin**

| 84. (0.97610) BD (1) C71 - H90 | (60.72%) C71 s(23.77%) p 3.20(76.08%) d 0.01(0.15%) |
| (39.28%) H90 s(99.95%) p 0.00(0.05%) d 0.00(0.00%) |
| 85. (0.97199) BD (1) C71 - H91 | (59.74%) C71 s(23.12%) p 3.32(76.72%) d 0.01(0.16%) |
| (40.26%) H91 s(99.95%) p 0.00(0.05%) d 0.00(0.00%) |
| 155. (0.17905) LP*(6)Ni1 | s(89.15%) p 0.06(6.67%) d 0.06(5.67%) |
| 156. (0.06951) LP*(7)Ni1 | s(2.64%) p36.77(97.15%) d 0.07(0.20%) |
| 157. (0.03664) LP*(8)Ni1 | s(2.46%) p36.97(96.05%) d 0.60(1.47%) |

**β spin**

| 86. (0.96711) BD (1) C71 - H90 | (60.69%) C71 s(23.43%) p 3.26(76.42%) d 0.01(0.14%) |
| (39.31%) H90 s(99.95%) p 0.00(0.04%) d 0.00(0.00%) |
| 87. (0.95755) BD (1) C71 - H91 | (59.43%) C71 s(22.63%) p 3.41(77.21%) d 0.01(0.15%) |
| (40.57%) H91 s(99.95%) p 0.00(0.05%) d 0.00(0.00%) |
| 156. (0.07142) LP*(6)Ni | s(4.49%) p19.57(87.92%) d 1.68(7.57%) |
| 157. (0.05801) LP*(7)Ni | s(47.59%) p 0.68(32.47%) d 0.42(19.94%) |
| 158. (0.02297) LP*(8)Ni | s(10.13%) p 7.54(76.31%) d 1.34(13.56%) |

Supplementary Table 24. NBO calculation of complex 1 at UB3LYP/defs-TZVPP theory level
| Donor       | Acceptor     | \(E(2)\) kcal/mol | \(E(j)-E(i)\) a.u. | \(F(i,j)\) a.u. |
|-------------|--------------|-------------------|-------------------|-----------------|
| 11. BD (1)C5-H7 | 52. LP*(6)Ni 12 | 0.68              | 0.61              | 0.026           |
|             | 52. LP*(6)Ni 12 | 5.22              | 0.67              | 0.075           |
|             | 52. LP*(7)Ni 12 | 0.68              | 0.61              | 0.026           |
|             | 52. LP*(7)Ni 12 | 5.22              | 0.67              | 0.075           |
| Total       | 11.8         | 2.56              | 0.202             |                 |
| 11. BD (1)C5-H7 | 51. LP*(5)Ni 12 | 8.55              | 0.59              | 0.091           |
|             | 52. LP*(6)Ni 12 | 0.7               | 0.61              | 0.026           |
|             | 53. LP*(7)Ni 12 | 0.36              | 0.62              | 0.019           |
| b           | 51. LP*(5)Ni 12 | 8.55              | 0.59              | 0.091           |
| 13. BD (1)C5-H10 | 52. LP*(6)Ni 12 | 0.7               | 0.61              | 0.026           |
|             | 53. LP*(7)Ni 12 | 0.36              | 0.62              | 0.019           |
| Total       | 19.22        | 3.64              | 0.272             |                 |
| H1          | \(\sigma\) C5 - H7 | 15.51             | 3.1               | 0.237           |
| H1          | \(\sigma\) C5 - H10 | 15.51             | 3.1               | 0.237           |

\textbf{Supplementary Table 25.} NBO calculation of complex 1* at UB3LYP/defs-TZVPP theory level
DFT calculation of rotation scan

Supplementary Figure 20. AIM electron density contour map of complex 1 and its simplified version 1-s. 1-s’s dihedral angle Φ was optimized at 0° and constrained at 10° as comparison.
**X-ray diffraction**

The crystal structure details are referred to previous reports.\textsuperscript{1,2}

**Supplementary Figure 21.** ORTEP depiction of the solid-state structure of 3 (ellipsoids at 50% probability, H1 and H2 were freely located and refined from the electron density map.)

**Supplementary Figure 22.** ORTEP depiction of the solid-state structure of 4 (ellipsoids at 50% probability, H1 and H2 were freely located and refined from the electron density map.)
| Compound | 3 | 4 |
|----------|---|---|
| Empirical formula | C_{38}H_{56}N_{3}NiO | C_{37}H_{54}N_{3}NiO |
| Formula weight | 629.56 | 615.54 |
| Temperature/K | 90 | 90 |
| Crystal system | monoclinic | monoclinic |
| Space group | P2_1/c | P2_1/n |
| a/Å | 9.3273(13) | 9.4012(6) |
| b/Å | 17.223(2) | 20.5882(13) |
| c/Å | 21.432(3) | 18.0158(13) |
| α/° | 90 | 90 |
| β/° | 94.644(3) | 94.096(2) |
| γ/° | 90 | 90 |
| Volume/Å³ | 3431.7(8) | 3478.1(4) |
| Z | 4 | 4 |
| ρ_cal g/cm³ | 1.219 | 1.175 |
| μ/mm⁻¹ | 0.598 | 0.589 |
| F(000) | 1364 | 1332 |
| Crystal size/mm³ | 0.57 x 0.12 x 0.04 | 0.19 x 0.17 x 0.17 |
| Radiation | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| 2θ range for data collection/° | 3.038 to 56.018 | 3.956 to 58.254 |
| Index ranges | -10 ≤ h ≤ 12, -22 ≤ k ≤ 22, -27 ≤ l ≤ 28 | -12 ≤ h ≤ 12, -28 ≤ k ≤ 20, -24 ≤ l ≤ 24 |
| Reflections collected | 32923 | 39295 |
| Independent reflections | 8266 [R_{int} = 0.0536, R_{sigma} = 0.0468] | 9351 [R_{int} = 0.0521, R_{sigma} = 0.0472] |
| Data/restraints/parameters | 8266/0/399 | 9351/6/419 |
| Goodness-of-fit on F² | 1.02 | 1.008 |
| Final R indexes [I>=2σ(I)] | R₁ = 0.0374, wR₂ = 0.0808 | R₁ = 0.0378, wR₂ = 0.0798 |
| Final R indexes [all data] | R₁ = 0.0610, wR₂ = 0.0897 | R₁ = 0.0612, wR₂ = 0.0877 |
| Largest diff. peak/hole / e Å⁻³ | 0.47/-0.37 | 0.48/-0.26 |

**Supplementary Table 26. Crystallographic data for complex 3 and 4.**
| complex      | Ni1-H1 (Å) | N1-H2 (Å) | Ni1-C1 (Å) | Ni1-H1-C1 (°) | Ni1-H2-C1 (°) | ΔNi-H (Å) | ΔNi-H-C (°) |
|-------------|------------|-----------|------------|---------------|---------------|-----------|------------|
| 6.1a(XRD)   | 2.159(15)  | 2.024(15) | 2.4476(10) | 101.8(10)     | 94.3(10)      | 7.5       | -0.135     |
| 6.2a(XRD)   | 1.94(2)    | 2.15(2)   | 2.4007(2)  | 106.18(3)     | 92.60(8)      | 13.575    | 0.21       |
| 6.1a(DFT)   | 1.98       | 2.133     | 2.394      | 97.384        | 89.488        | 7.896     | 0.152      |
| 6.2a(DFT)   | 1.97       | 2.263     | 2.461      | 102.276       | 86.734        | 15.542    | 0.294      |

Supplementary Table 27. The comparison of Distances and Angles of agnostic complexes 6.1a-6.2a in XRD and DFT structures.
## Appendix – Calculation Coordinates

**Complex 1**

![Complex 1 Diagram](image_url)

**UKS PBE0 D3BJ def2-SVP def2/J RIJCOSX**  
**newgto Ni def2-TZVP**

| Atom | X          | Y          | Z          | Atom | X          | Y          | Z          |
|------|------------|------------|------------|------|------------|------------|------------|
| Ni   | 3.727164   | 9.195253   | 13.992052  | C    | 3.048276   | 5.077815   | 13.820574  |
| O    | 7.277636   | 11.33025   | 14.364541  | H    | 2.225648   | 5.399616   | 13.161702  |
| N    | 5.48843    | 9.710786   | 14.513119  | C    | 3.102184   | 3.553931   | 13.795704  |
| N    | 1.016118   | 8.865216   | 12.726788  | H    | 3.958492   | 3.168817   | 14.369675  |
| N    | 1.408193   | 7.434599   | 14.263826  | H    | 3.230634   | 3.19594    | 12.763219  |
| C    | 1.986116   | 8.481748   | 13.60759   | H    | 2.190384   | 3.100082   | 14.212931  |
| C    | -0.129605  | 8.099015   | 12.852072  | C    | 4.343777   | 5.67682    | 13.267921  |
| H    | -1.004011  | 8.275869   | 12.232826  | H    | 4.298584   | 6.777077   | 13.239147  |
| C    | 0.119016   | 7.191013   | 13.828711  | H    | 4.542161   | 5.316258   | 12.246538  |
| H    | -0.496101  | 6.410374   | 14.267162  | H    | 5.200277   | 5.3967     | 13.899553  |
| C    | 1.161622   | 9.89991    | 11.752266  | C    | 0.985822   | 8.642028   | 16.822892  |
| C    | 0.712155   | 11.195382  | 12.05878   | H    | 0.538637   | 8.893491   | 15.850274  |
| C    | 0.88589    | 12.183485  | 11.085082  | C    | -0.171731  | 8.435076   | 17.795789  |
| H    | 0.550548   | 13.202134  | 11.292249  | H    | -0.849193  | 7.642621   | 17.438279  |
| C    | 1.487599   | 11.892807  | 9.866167   | H    | -0.757987  | 9.360856   | 17.901669  |
| H    | 1.628795   | 12.682657  | 9.125121   | H    | 0.179337   | 8.145797   | 18.798945  |
| C    | 1.909697   | 10.597501  | 9.58476    | C    | 1.886452   | 9.816836   | 17.203842  |
| H    | 2.382065   | 10.378444  | 8.625      | H    | 2.37499    | 9.658367   | 18.178499  |
| C    | 1.744974   | 9.56943    | 10.515264  | H    | 1.301591   | 10.74832   | 17.263661  |
| C    | 2.206491   | 8.160136   | 10.190331  | H    | 2.679269   | 9.958963   | 16.45048   |
| C    | 1.722073   | 7.478021   | 10.906516  | C    | 6.120487   | 10.818185  | 14.077786  |
| C    | 3.717105   | 8.020876   | 10.373556  | C    | 5.318955   | 11.781969  | 13.173247  |
| H    | 4.258188   | 8.730627   | 9.72927    | C    | 3.987607   | 11.211409  | 12.727808  |
| H    | 4.048955   | 7.004568   | 10.110258  | C    | 5.081321   | 13.060589  | 13.98264   |
| C    | 1.784712   | 7.722324   | 8.878508   | H    | 6.042225   | 13.463101  | 14.334471  |
| H    | 2.052672   | 6.667008   | 8.624032   | H    | 4.458012   | 12.852523  | 14.867637  |
| H    | 2.294428   | 8.30763    | 8.007346   | H    | 4.57164    | 13.825716  | 13.373771  |
| C    | 0.028828   | 11.536871  | 13.369749  | C    | 6.174738   | 12.091729  | 11.944559  |
| H    | 0.103404   | 10.65494   | 14.02437   | H    | 6.327429   | 11.188106  | 11.332869  |
| C    | 0.702874   | 12.696179  | 14.101017  | H    | 7.161374   | 12.453245  | 12.264597  |
| H    | 1.755581   | 12.473427  | 14.32539   | H    | 5.691603   | 12.854493  | 11.312487  |
| H    | 0.188447   | 12.895889  | 15.053702  | C    | 6.305923   | 8.816713   | 15.372759  |
| H    | 0.669173   | 13.624732  | 13.510976  | H    | 6.964267   | 9.519483   | 15.966986  |
| C    | -1.453918  | 11.831772  | 13.13069   | C    | 5.419901   | 8.073692   | 16.321138  |
| H    | -1.58244   | 12.675472  | 12.434767  | H    | 4.841868   | 8.748831   | 16.96964   |
|          |          |          |          |          |          |          |          |          |          |          |          |          |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| C        | 2.005736 | 6.793992 | 15.391597| C        | 7.222318 | 7.966058 | 14.542647|
| C        | 1.797763 | 7.374149 | 16.652943| C        | 6.63708  | 7.314907 | 13.874752|
| H        | 3.644965 | 5.149678 | 18.466247| H        | 3.28743  | 11.08291 | 13.584987|
| C        | 0.138763 | 7.123686 | 13.758239| H        | 2.42877  | 3.175425 | 14.219882|
| C        | -0.07221 | 8.049643 | 12.786859| C        | 4.597966 | 5.810832 | 13.498654|
| H        | -0.915966| 8.220989 | 12.124929| H        | 4.528113 | 6.910574 | 14.372513|
| C        | 0.138763 | 7.123686 | 13.758239| H        | 4.894475 | 5.466277 | 12.495199|
| H        | -0.485654| 6.320102 | 14.138031| H        | 5.404308 | 5.546809 | 14.200021|
| C        | 1.273247 | 9.960396 | 11.889243| C        | 0.687983 | 8.506251 | 16.792091|
| C        | 0.918311 | 11.234458| 12.36142 | H        | 0.385301 | 8.800461 | 15.77698 |
| C        | 1.18672 | 12.324391| 11.52895 | C        | -0.593929| 8.146522 | 17.540365|
| H        | 0.93422 | 13.331463| 11.868686| H        | -1.129754| 7.330588 | 17.031781|
| C        | 1.784292 | 12.145016| 10.286977| H        | -1.26768 | 9.015928 | 17.588968|
| C        | 1.999278 | 13.011037| 9.657245 | H        | -0.390679| 7.816134 | 18.571668|
| C        | 2.126188 | 10.870212| 9.846555 | C        | 1.412655 | 9.710882 | 17.390165|
| H        | 2.612479 | 10.745775| 8.876691 | H        | 1.773812 | 9.510235 | 18.411331|
| C        | 1.874169 | 9.746901 | 10.636517| H        | 0.739618 | 10.580718| 17.434009|
| C        | 2.295556 | 8.363636 | 10.18006 | H        | 2.282629 | 9.985838 | 16.773919|
| H        | 1.751381 | 7.631661 | 10.797021| C        | 5.958996 | 10.732585| 13.655393|
| C        | 3.788172 | 8.151266 | 10.426375| C        | 5.000907 | 11.331564| 12.61629 |
| H        | 4.385728 | 8.853888 | 9.828842 | C        | 4.650676 | 12.761055| 13.016402|
| H        | 4.090371 | 7.128841 | 10.151874| H        | 5.57738  | 13.348376| 13.103787|

Complex 2

UKS PBE0 D3BJ def2-SVP def2/J RIJCOSX
newgto Ni def2-TZVP
### Complex 3

![Complex3 Diagram](image)

**UKS PBE0 D3BJ def2-SVP def2/J RIJCOSX**

**newgto Ni def2-TZVP**

| Element | X       | Y       | Z       | X       | Y       | Z       |
|---------|---------|---------|---------|---------|---------|---------|
| Ni      | 3.421346| 11.730938| 15.321682| 1.902363| 9.531025| 17.83243|
| O       | 1.233   | 15.139252| 15.725736| 1.354945| 7.840258| 17.720681|
| N       | 5.147348| 9.368427| 15.670737| 2.056365| 8.438351| 19.235497|
| N       | 4.276215| 9.355061| 13.715053| 0.522941| 13.70932| 13.24637|
| N       | 2.511318| 13.265513| 16.004271| 0.274301| 12.684804| 13.57338|
| C       | 5.38889| 9.6879| 17.04335| -0.171699| 14.387663| 13.765593|
| C       | 4.32319| 10.095646| 14.863808| 0.960475| 13.020045| 17.897575|
| C       | 5.029969| 8.19884| 13.817708| 0.816505| 11.940404| 17.719865|
| H       | 5.0961| 7.480126| 13.006056| 0.809589| 13.224642| 18.970304|
| C       | 1.877913| 14.194095| 15.263299| 0.202488| 13.578926| 17.330888|
| C       | 3.383767| 9.647453| 12.636888| 3.450037| 12.735337| 18.194804|

53
| C    | 2.019782 | 9.35886 | 12.825087 | H    | 4.441588 | 13.094643 | 17.884954 |
| C    | 2.349127 | 13.456562 | 17.440595 | H    | 3.35737 | 12.888905 | 19.281257 |
| H    | 2.424946 | 14.539167 | 17.647595 | H    | 3.41556 | 11.64499 | 18.015668 |
| C    | 5.587299 | 8.210339 | 15.054432 | C    | 0.337304 | 13.854954 | 11.738911 |
| H    | 6.24592 | 7.507783 | 15.556405 | H    | -0.702248 | 13.609057 | 11.463291 |
| C    | 4.604236 | 9.043025 | 18.019793 | H    | 0.971568 | 13.128512 | 11.199818 |
| C    | 3.879434 | 10.233782 | 11.457894 | C    | 8.679397 | 11.409656 | 16.658393 |
| C    | 1.49391 | 8.664765 | 14.066771 | H    | 9.081737 | 10.429675 | 16.957557 |
| H    | 2.357739 | 8.419303 | 14.700902 | H    | 9.264564 | 11.780057 | 15.803151 |
| C    | 1.945268 | 14.065548 | 13.726926 | H    | 8.856276 | 12.110703 | 17.488338 |
| C    | 1.132884 | 9.736255 | 11.813191 | C    | 2.137676 | 15.594577 | 11.672526 |
| H    | 0.065235 | 9.542667 | 11.939248 | H    | 2.819849 | 14.925091 | 11.116069 |
| C    | 6.381975 | 10.630425 | 17.361867 | H    | 2.403224 | 16.617403 | 11.357687 |
| C    | 3.509997 | 8.056972 | 17.646589 | C    | 0.698548 | 15.267108 | 11.290685 |
| H    | 3.460455 | 8.026762 | 16.548948 | H    | 0.02616 | 15.983446 | 11.794903 |
| C    | 0.585948 | 9.58486 | 14.879118 | H    | 0.535962 | 15.394324 | 10.207049 |
| H    | -0.285995 | 9.912931 | 14.292298 | C    | 5.784777 | 10.219195 | 9.806697 |
| H    | 0.211731 | 9.067442 | 15.775342 | H    | 5.318305 | 10.918367 | 9.091049 |
| H    | 1.132631 | 10.484623 | 15.208968 | H    | 6.873662 | 10.341333 | 9.696099 |
| C    | 2.948291 | 10.589866 | 10.477657 | H    | 5.517878 | 9.197723 | 9.48894 |
| H    | 3.294151 | 11.072953 | 9.561975 | C    | 6.638467 | 12.727644 | 16.002216 |
| C    | 7.197334 | 11.333062 | 16.293376 | H    | 6.672412 | 13.361711 | 16.901752 |
| H    | 7.106721 | 10.739369 | 15.370455 | H    | 7.223328 | 13.226552 | 15.214171 |
| C    | 5.357104 | 10.505026 | 11.239058 | H    | 5.586695 | 12.682604 | 15.670705 |
| H    | 5.920839 | 9.819175 | 11.890361 | C    | 3.822124 | 6.64162 | 18.132835 |
| C    | 4.85629 | 9.359131 | 19.357998 | H    | 3.813512 | 6.589599 | 19.23533 |
| H    | 4.266684 | 8.879867 | 20.14355 | H    | 3.06475 | 5.932131 | 17.755777 |
| C    | 6.577981 | 10.924835 | 18.713833 | H    | 4.806755 | 6.294261 | 17.784662 |
| H    | 7.330026 | 11.662978 | 18.998813 | C    | 2.928922 | 13.006119 | 13.275432 |
| C    | 0.804807 | 7.345118 | 13.715361 | H    | 2.577849 | 11.987603 | 13.560088 |
| H    | 1.480165 | 6.671928 | 13.1664 | H    | 3.027009 | 12.951544 | 12.183095 |
| H    | 0.475407 | 6.828971 | 14.630907 | H    | 3.936398 | 13.201753 | 13.680162 |
| H    | -0.087199 | 7.504512 | 13.089608 | C    | 5.744972 | 11.929582 | 11.6434 |
| C    | 5.830051 | 10.293328 | 19.701118 | H    | 5.59381 | 12.099027 | 12.718597 |
| H    | 6.006654 | 10.543039 | 20.75036 | H    | 6.804489 | 12.1179 | 11.408934 |
| C    | 2.345958 | 15.447133 | 13.174214 | H    | 5.141973 | 12.6711 | 11.097919 |
| H    | 3.394915 | 15.656908 | 13.447153 | C    | 1.589255 | 10.356429 | 10.656436 |
| H    | 1.729691 | 16.185076 | 13.711007 | H    | 0.879929 | 10.65385 | 9.881507 |
| C    | 2.13186 | 8.499297 | 18.137962 |
Complex 1*

UKS PBE0 D3BJ def2-SVP def2/J RIJCOSX
newgto Ni def2-TZVP

|  |  |  |  |
|---|---|---|---|
| O | 7.450600555 | 11.08700078 | 14.48790103 |
| N | 5.659100401 | 9.664400718 | 14.63760104 |
| C | 6.307200447 | 10.75800075 | 14.19120103 |
| C | 5.520800403 | 11.65210085 | 13.22550097 |
| C | 4.092500292 | 11.24220079 | 12.91880095 |
| H | 6.280800429 | 9.147200655 | 15.25650109 |
| H | 4.064200295 | 10.24980072 | 12.41680087 |
| H | 3.478500248 | 11.20670083 | 13.84290101 |
| H | 3.583100259 | 11.94160087 | 12.23720086 |
| H | 6.115100427 | 11.70690086 | 12.29930087 |
| H | 5.549700413 | 12.6659009 | 13.65510098 |
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