Supplementary Information

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

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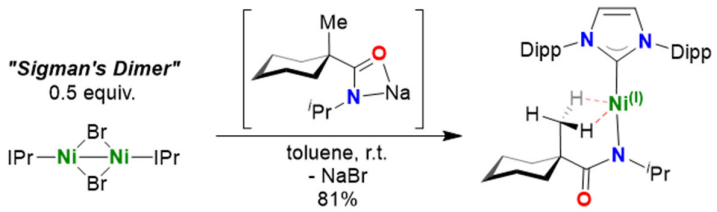
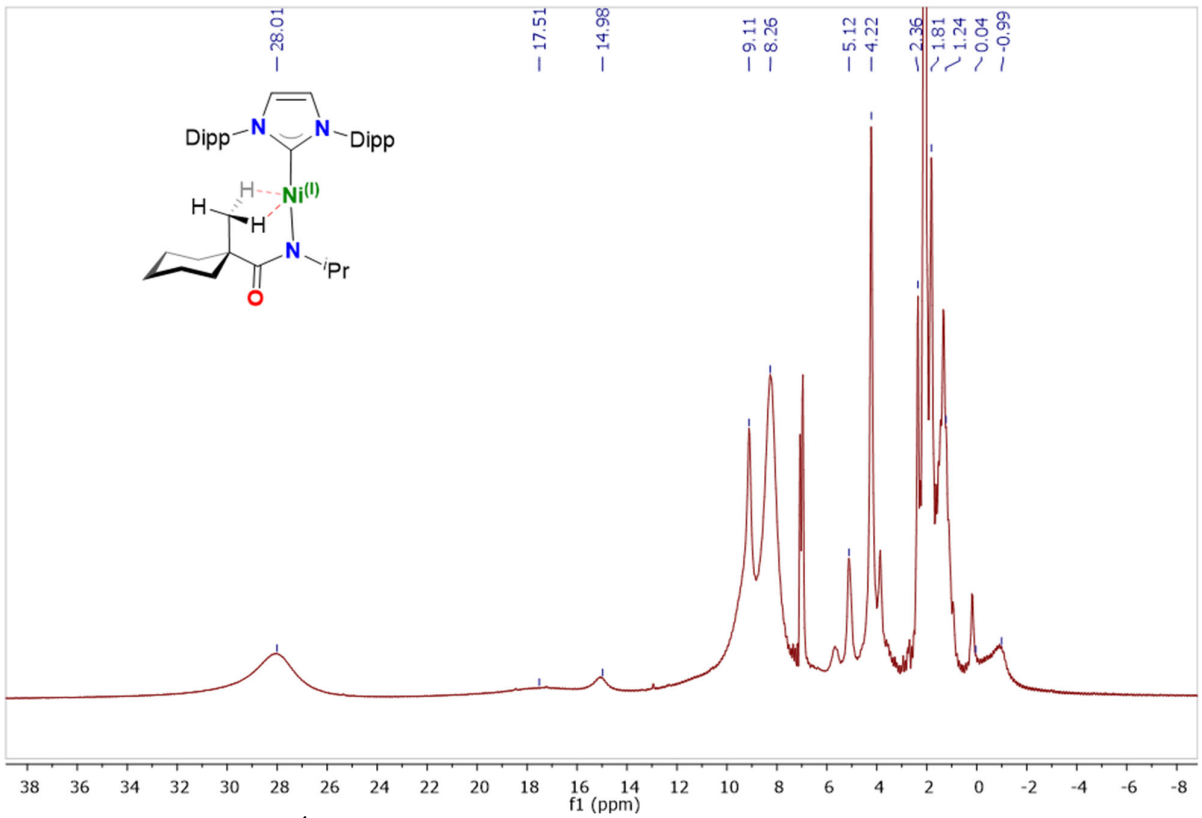
Contents

1. Supplementary Methods

Synthesis and Isolation of 3

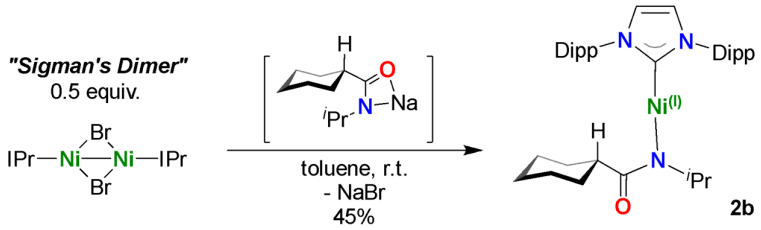


Complex 3: In a glovebox, Sigman's Dimer (70 mg, 0.066 mmol) was added as a solid at room temperature to a 20 mL vial containing a stirring solution of Na[MeCyAm] (27.2 mg, 0.132 mmol) in toluene (5 mL). The contents were stirred overnight (~12 h), and in the morning removed from the stir plate and allowed 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):** δ = 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_6D_6, 27°C):** μ_{eff} = 2.17 μ_B. **EI-MS (m/z):** 628 $[M]^+$. **Anal. Calcd.** for $C_{38}H_{56}N_3NiO$ (628). C, 72.50%; H, 8.97%; N, 6.67%. Found: C, 72.24%; H, 9.00%; N, 6.45%.

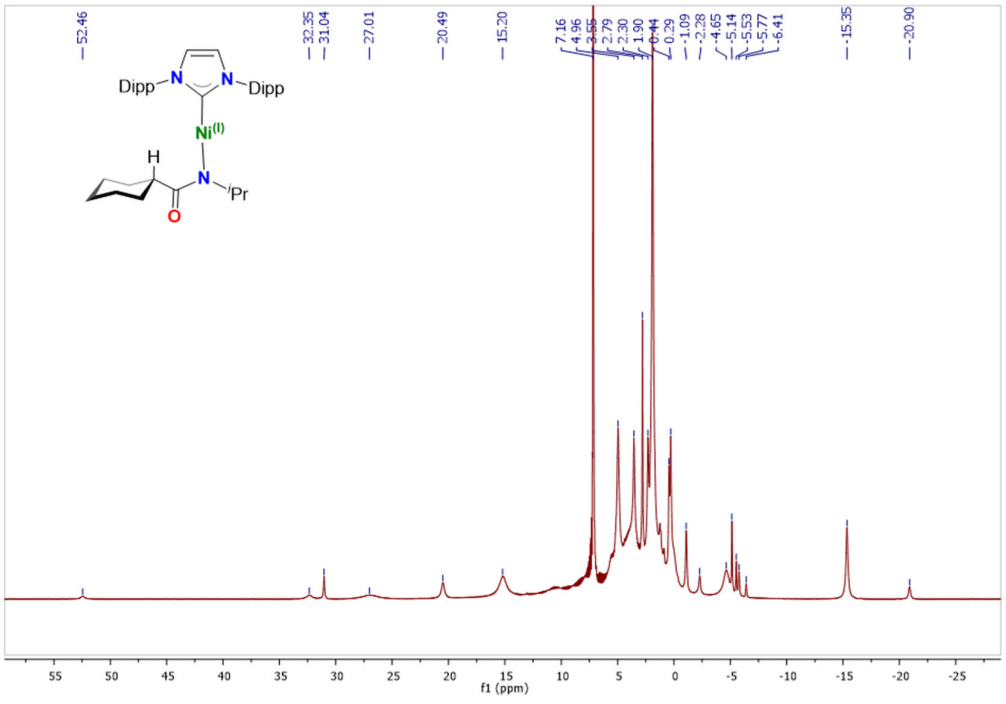


Supplementary Figure 1. ^{1}H NMR (400 MHz, 25°C, d_8-tol) of complex 3

Formation of 4

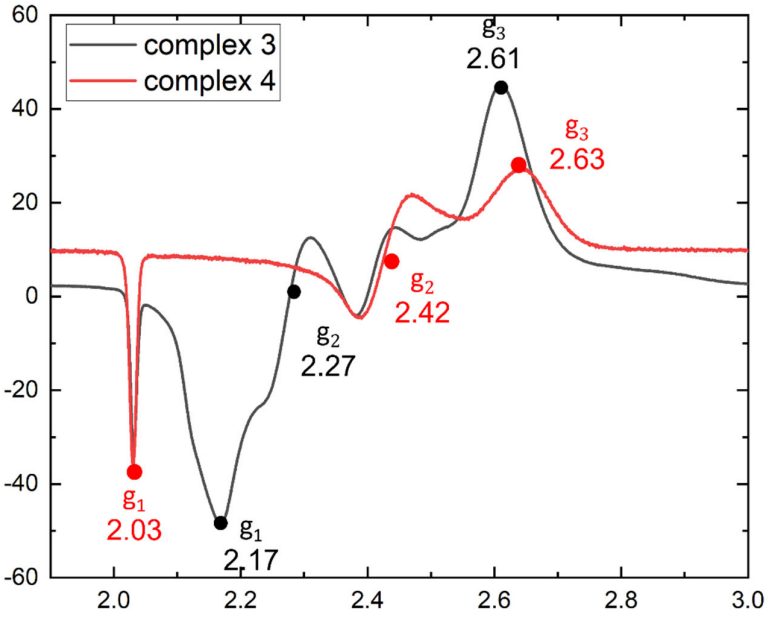


Complex 4: In a glovebox, Sigman's Dimer (50 mg, 0.0474 mmol) was added as a solid at room temperature to a 20 mL vial containing a stirring solution of Na[CyAm] (18.1 mg, 0.0948 mmol) in toluene (5 mL). The contents were stirred overnight (~12 h), and in the morning removed from the stir plate and allowed 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. **^{1}H NMR (300 MHz, 25°C, C_6D_6):** 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 (C_6D_6, 24°C):** μ_{eff} = 2.12 μ_B. **EI-MS (*m/z*):** 614 $[M]^+$. **Anal. Calcd.** for $C_{37}H_{54}N_3NiO$ (614). C, 72.20%; H, 8.84%; N, 6.83%. Found: C, 71.97%; H, 8.55%; N, 6.75%.



Supplementary Figure 2. ^{1}H NMR (400 MHz, 25°C, d_8-tol) of complex 4

EPR Spectrum of 3 & 4

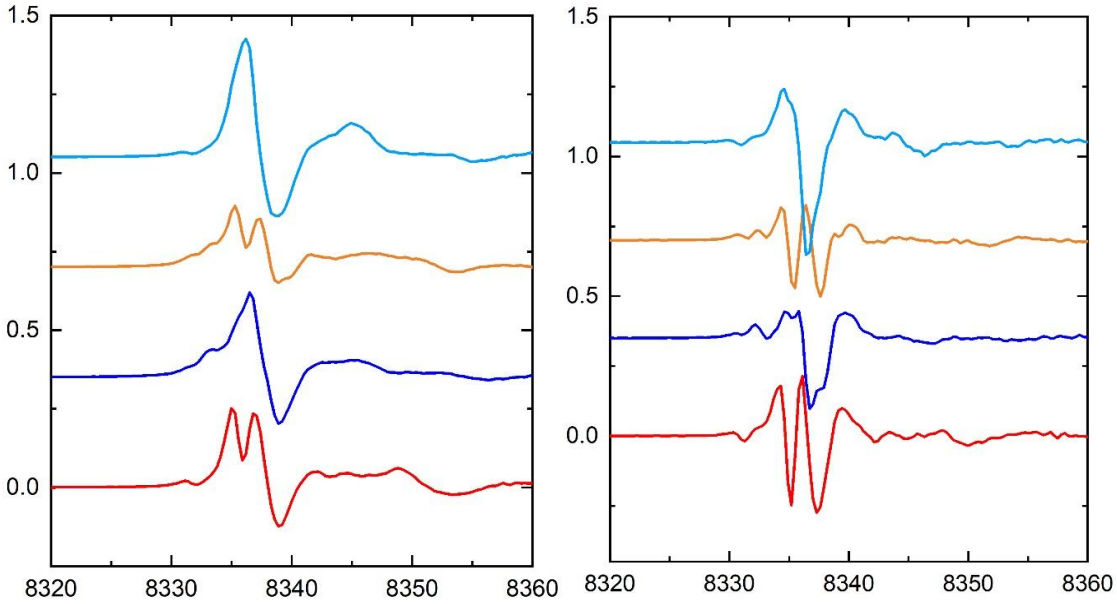


Supplementary Figure 3. X-band EPR spectrum of complex 3 and 4 in dry toluene solution at 7 K, g factors are labelled. The extra secondary features of complex 4's spectrum are from mixtures of its non-agostic configuration, as they are showing at the identical position in the spectrum of non-agostic complex 4, are therefore not labelled.

2. Supplementary Data

2.1 Ni K edge X-ray Absorption Spectroscopy (XAS)

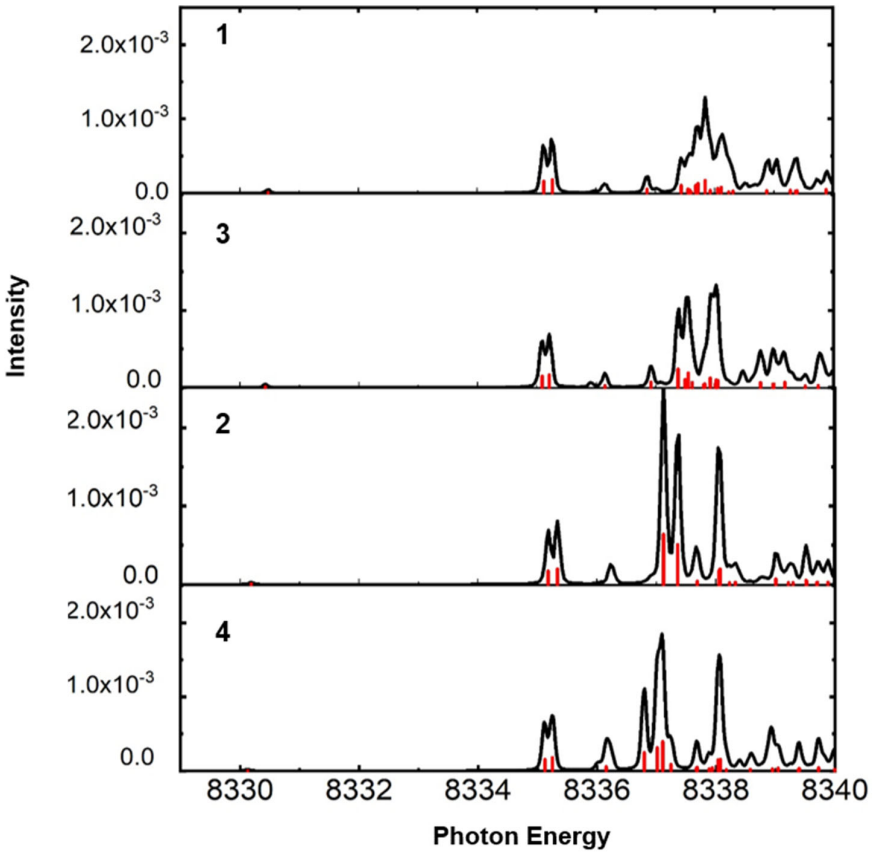
All XAS samples were analyzed as solids under anaerobic conditions and diluted in boron nitride (20-50% by weight). All samples were quickly frozen under a liquid nitrogen environment. XAS Ni K-edges were acquired at the SSRL beamline 7-3, which is equipped with a Si(220) ϕ = 90° double crystal monochromator, 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[1],The AUTOBK algorithm available in the Athena software package[2] was employed for data reduction and normalization.



Supplementary Figure 4. 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).

2.2 TD-DFT of Ni K edge XAS

XAS TD-DFT (X-ray absorption Time-dependent DFT) calculations were performed with a dense integration grid (Gird6) for better implementing Scalar relativistic effects by using ZORA[3] corrections and reduced by using MOanalyzer[4] 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 to the Ni K edge spectrum, and function as the acceptors for quickly identifying the character of major molecular orbitals (> 5%, labelled in bold), but the rest of 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.



Supplementary Figure 5 TD-DFT calculated Ni K edge XAS spectrum of 1-4.

	complex 1									
	Energy(eV)	**Intensity**	**MO-1**	**Cont.**	**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%**		
C	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%						
	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%		
D	8337.93	2.20E-05	169a	56.9%	174a	16.4%				
	8338.05	3.36E-05	170a	28.6%	172a	23.7%	168a	16.6%	174a	4.66%
	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	76.6%	176b	5.4%				

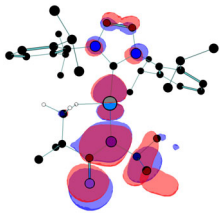
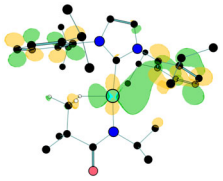
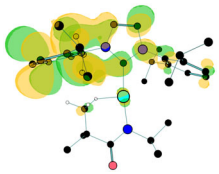
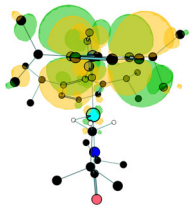
Supplementary Table 1 TD-DFT calculation of the pre-edge features (A-D) and the Molecular orbital contribution of complex 1. highest calculated features are labeled in bold. Important orbitals with Ni character (>5%) are labeled in bold.

complex 1	Nickel Centre				CH_3					NHC ligand				
	Ni				C			H		N			C	
Orbital	Total	s (%)	p (%)	d (%)	Total	s (%)	p (%)	s (%)	p (%)	Total	s (%)	p (%)	s (%)	p (%)
159,a	**23.4**	**0**	**2**	**21.4**	**0.2**	**0**	**0.2**	**0**	**0**	**1.6**	**0**	**1.5**	**0**	**0.1**
160,a	1.4	0	0.9	0.5	0.6	0	0.4	0.2	0	4.3	0	2.3	0	2
161,a	0.2	0	0.1	0.1	0	0	0	0	0	1.4	0	0.3	0.6	0.5
162,a	2.9	0	2	0.9	0.1	0	0.1	0	0	7.7	0	3.7	0	4
163,a	0.2	0	0.2	0	0	0	0	0	0	1.3	0	0.5	0	0.8
164,a	**11.3**	**0.1**	**7.9**	**3.3**	**1**	**0.1**	**0.5**	**0.3**	**0.1**	**35.3**	**0**	**13.3**	**0**	**22**
166,a	1.7	0.7	0.3	0.7	0.9	0.2	0.1	0.5	0.1	1.4	0	0.4	0.3	0.7
167,a	1.6	0	1.3	0.3	0.2	0	0.1	0.1	0	5	0	1.4	0	3.6
168,a	2.1	0.1	2	0	2.1	0.5	0.3	1	0.3	0.7	0.2	0.3	0	0.2
169,a	1.5	0.3	1.1	0.1	0.1	0	0.1	0	0	0.9	0.4	0.4	0	0.1
170,a	1.8	0.4	1.2	0.2	0.5	0.1	0.1	0.3	0	1.2	0.1	0.4	0	0.7
171,a	3.1	1.1	1.3	0.7	1.3	0.3	0.2	0.5	0.3	1	0.1	0.5	0.1	0.3
172,a	**5.9**	**1.8**	**3.1**	**1**	**3.2**	**0.8**	**0.5**	**1.1**	**0.8**	**0.9**	**0**	**0.3**	**0.2**	**0.4**
173,a	0.1	0	0.1	0	0.3	0	0.2	0.1	0	0.6	0	0.5	0	0.1
174,a	**19.4**	**0.2**	**18.8**	**0.4**	**3.1**	**0**	**1.9**	**0.7**	**0.5**	**5.4**	**0**	**1.5**	**0**	**3.9**
176,a	**12.1**	**0.5**	**10.5**	**1.1**	**5.5**	**1.5**	**0.8**	**2.2**	**1**	**2.2**	**0.5**	**0.2**	**0**	**1.5**
159,b	**44.3**	**6.8**	**2.4**	**35.1**	**1.9**	**0.3**	**0.7**	**0.8**	**0.1**	**3**	**0**	**0.4**	**0.7**	**1.9**
160,b	1	0	0.5	0.5	0.3	0	0.2	0.1	0	3	0	1.7	0	1.3
161,b	4.8	0.3	1.8	2.7	0.3	0	0.2	0.1	0	6.7	0	3	0	3.7
162,b	**12.2**	**1.7**	**0.9**	**9.6**	**0.4**	**0.1**	**0.1**	**0.2**	**0**	**1.7**	**0**	**0.8**	**0.2**	**0.7**
163,b	**17.1**	**2.4**	**0.4**	**14.3**	**0.8**	**0.2**	**0.4**	**0.2**	**0**	**1.4**	**0**	**0.3**	**0.2**	**0.9**
164,b	**13.4**	**0.1**	**7.8**	**5.5**	**1.1**	**0.1**	**0.6**	**0.3**	**0.1**	**35.9**	**0**	**13.4**	**0**	**22.5**
166,b	2.8	0.3	0.3	2.2	0.5	0.1	0.1	0.3	0	1.3	0	0.4	0.2	0.7
167,b	1.5	0	1.2	0.3	0.4	0	0.3	0.1	0	5	0	1.4	0	3.6
168,b	1.8	0.1	1.7	0	2.1	0.5	0.3	1	0.3	0.6	0.2	0.2	0	0.2
169,b	1.2	0.1	0.8	0.3	0.1	0	0.1	0	0	0.8	0.3	0.4	0	0.1
170,b	0.9	0.1	0.7	0.1	0.2	0	0.1	0.1	0	1.2	0.2	0.4	0	0.6
171,b	0.1	0	0	0.1	0.2	0	0.1	0.1	0	0.8	0.1	0.7	0	0
172,b	**7.9**	**1.5**	**4.6**	**1.8**	**3.6**	**0.9**	**0.6**	**1.3**	**0.8**	**1**	**0**	**0.3**	**0**	**0.7**
173,b	1.3	0.2	0.6	0.5	0.9	0.2	0.2	0.4	0.1	0.3	0	0.3	0	0
174,b	**18.7**	**0.1**	**18.1**	**0.5**	**3.1**	**0**	**1.8**	**0.8**	**0.5**	**4.7**	**0**	**1.2**	**0**	**3.5**
176,b	**7.9**	**0**	**6.4**	**1.5**	**5.9**	**1.4**	**0.8**	**2.7**	**1**	**0.9**	**0.2**	**0.2**	**0**	**0.5**

Supplementary Table 2. Atomic Character Contribution in Acceptor Molecular Orbital from Ni centre, pendant CH_3 substitute and NHC ligand in complex 1. Important Molecular Orbitals with Ni character (>5%) are labeled in bold.

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	8337.93	2.20E-05	3.2%	0.0%	3.1%	0.1%	1.0%	96.9%	2.1%	4.8%	83.8%	11.3%
	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%			

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%).

Molecular Orbitals of Complex 1			
			
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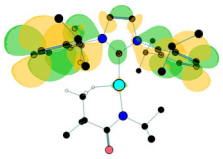	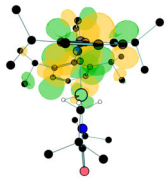	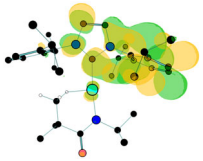	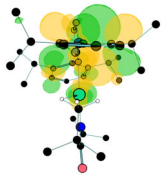
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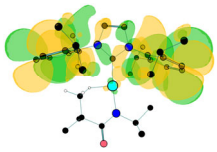	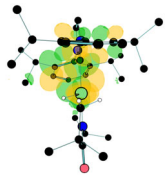	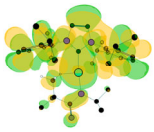	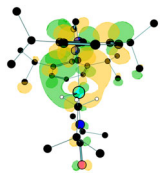
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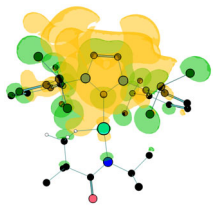
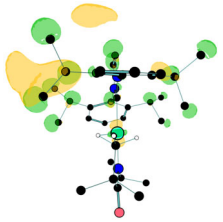
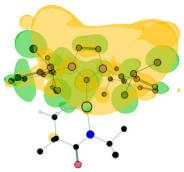
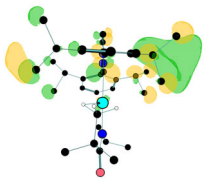
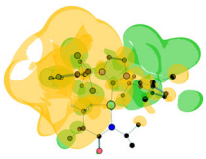
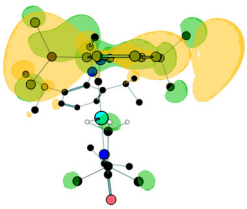
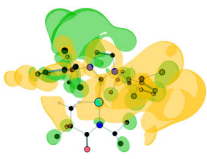
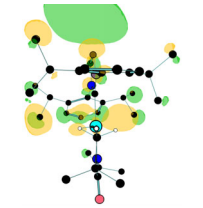
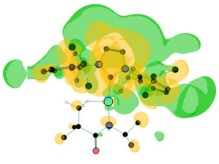
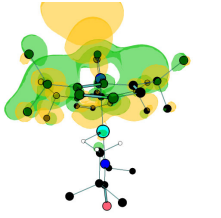
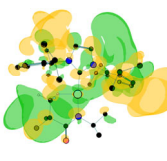
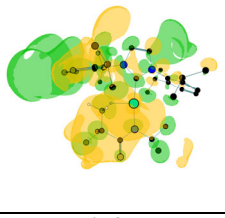
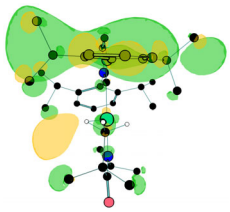
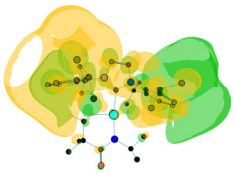
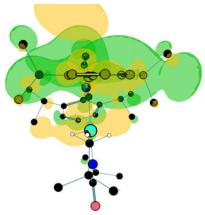
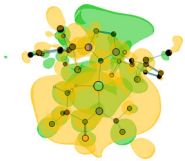
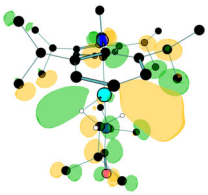
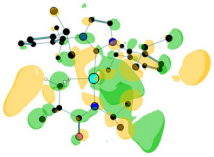
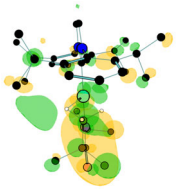
			
166α	166β	167α	167β
			
168α	168β	169α	169β
			
170α (Nip_x)	170β (Nip_x)	171α	171β

			
172α	172β	173α	173β
			
174α (Nip_y)	174β (Nip_y)	176α	176β

Supplementary Figure 6. 3D view of Molecular Orbital Acceptors in Complex 1.

	Complex 2									
	Energy(eV)	**Intensity**	**MO-1**	**Cont.**	**MO-2**	**Cont.**	**MO-3**	**Cont.**	**MO-4**	**Cont.**
A	**8330.19**	**3.33E-06**	**155b**	**81.76%**						
B	8335.18	8.66E-05	160b	54.29%	156b	18.21%				
	8335.34	**9.90E-05**	**160a**	**47.84%**	**156a**	**23.54%**	**157a**	**17.06%**	**158a**	**9.54%**
C	**8337.12**	**3.20E-04**	**164a**	**33.30%**	**170a**	**24.10%**	**167a**	**13.73%**		
	8337.36	2.53E-04	164b	31.48%	170b	31.02%	167b	9.77%		
	8337.69	2.24E-05	163a	74.33%	172a	9.38%				
	8338.05	8.42E-05	172a	35.24%	163a	16.43%	169a	14.46%		
	8338.06	2.61E-05	164a	50.24%	167a	16.16%	166a	10.30%		
D	8338.06	3.25E-05	164b	51.67%	170b	14.79%	166b	11.77%	167b	10.28%
	8338.07	**9.87E-05**	**172b**	**37.14%**	**169b**	**19.55%**	**163b**	**10.47%**		
	8338.23	1.26E-05	166b	54.57%	167b	11.22%	172b	8.87%		
	8338.33	1.17E-05	167a	41.74%	170a	26.82%	168a	16.02%		
	8338.33	1.38E-05	167b	58.49%	170b	17.83%				

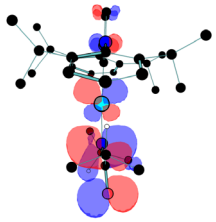
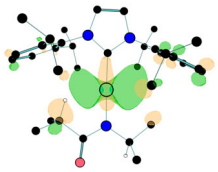
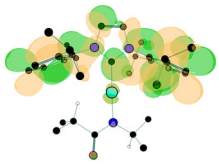
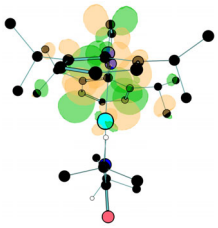
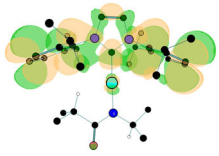
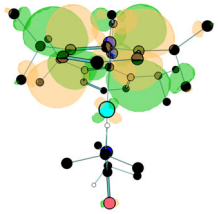
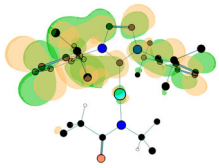
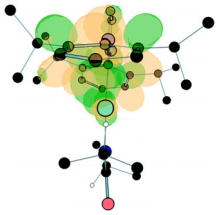
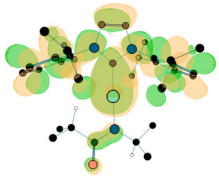
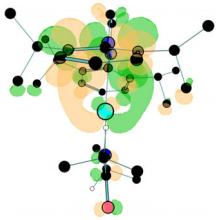
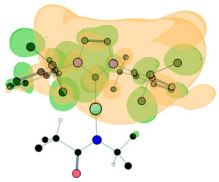
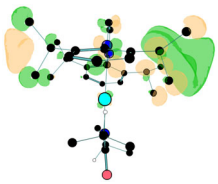
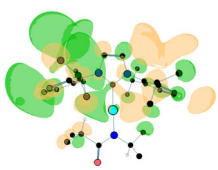
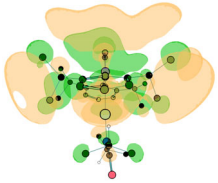
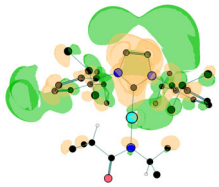
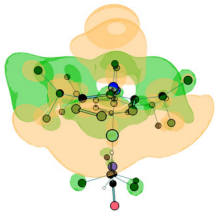
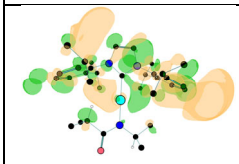
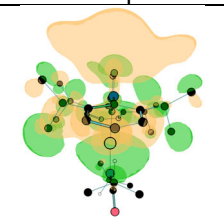
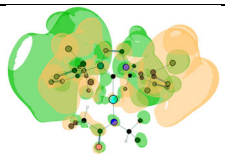
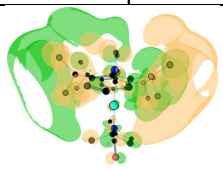
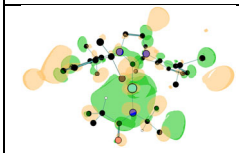
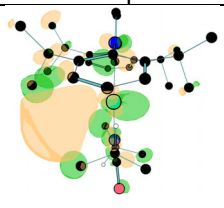
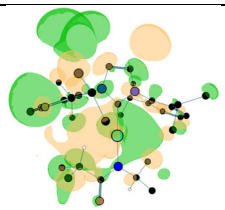
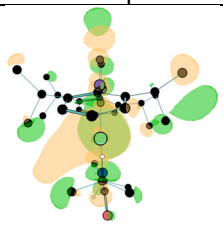
Supplementary Table 4. TD-DFT calculation of the pre-edge features and the Molecular orbital contribution of complex 2.

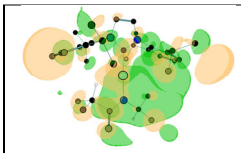
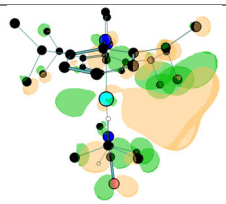
complex 2	Nickel Center				NHC ligand				
	Ni				N			C	
Orbital	Total	s (%)	p (%)	d (%)	Total	s (%)	p (%)	s (%)	p (%)
155,a	**26.6**	**0.1**	**2.5**	**24**	**2**	**0**	**1.8**	**0**	**0.2**
156,a	2.6	0	1.8	0.8	5.8	0	2.7	0.3	2.8
157,a	2	0	1.4	0.6	4.6	0	1.9	0.3	2.4
158,a	1.3	0	0.8	0.5	3.4	0	2	0.1	1.3
160,a	**11.8**	**0**	**8.3**	**3.5**	**34.8**	**0**	**13.1**	**0**	**21.7**
163,a	2.1	0	1.8	0.3	4.7	0	1.2	0.1	3.4
164,a	**7.6**	**0**	**7.5**	**0.1**	**1.6**	**0.2**	**0.6**	**0**	**0.8**
166,a	3.9	0.5	3.1	0.3	1.6	0.2	0.7	0	0.7
167,a	**6**	**0.2**	**5.5**	**0.3**	**1.8**	**0.4**	**0.5**	**0**	**0.9**
168,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**	**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**

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.

			absolute				normalized			average		
Feature	**Energy(eV)**	**Intensity**	sum	s	p	d	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%**	0.4%	9.4%	90.2%
B	8335.18	8.66E-05	**7.6%**	0.1%	4.5%	3.0%	**0.7%**	**59.3%**	**40.0%**	0.4%	64.8%	34.8%
	8335.34	**9.90E-05**	**5.6%**	0.0%	4.0%	1.7%	**0.0%**	**70.3%**	**29.7%**			
C	**8337.12**	**3.20E-04**	**7.6%**	0.3%	7.0%	0.3%	**3.5%**	**92.9%**	**3.5%**	5.5%	75.4%	19.0%
	8337.36	2.53E-04	**6.3%**	0.1%	5.8%	0.3%	**2.0%**	**93.1%**	**5.0%**			
	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%**	2.7%	91.5%	5.7%
	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
			
169α	169β	170α	170β

			
172α	172β		

Supplementary Figure 7. 3D view of Molecular Orbital Acceptors in Complex 2.

complex 3										
	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%
	8335.21	**8.25E-05**	**175a**	**41.45%**	**171a**	**40.12%**	**172a**	**11.44%**		
C	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	35.75%	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%	179b	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%		

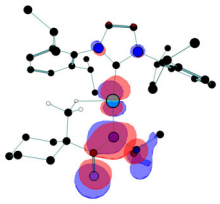
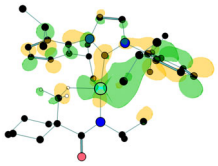
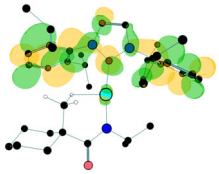
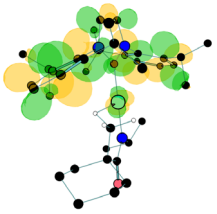
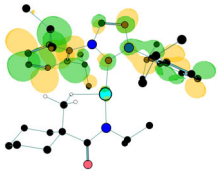
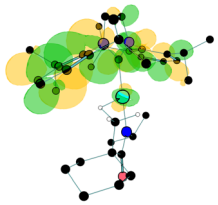
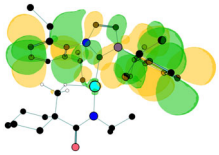
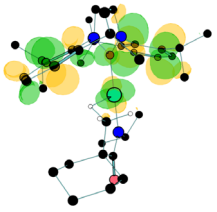
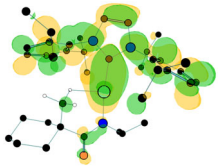
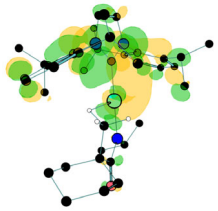
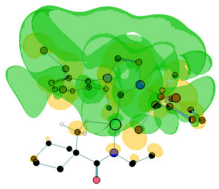
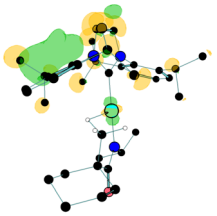
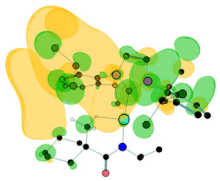
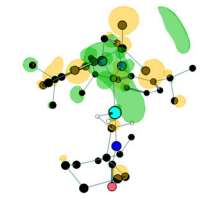
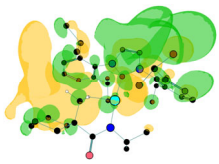
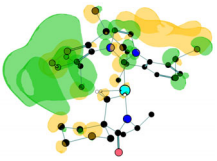
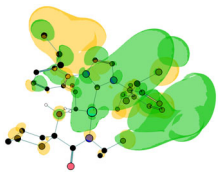
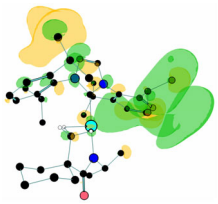
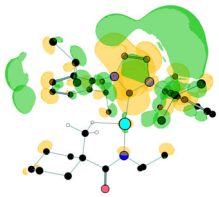
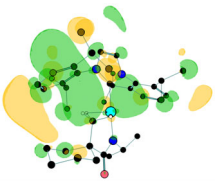
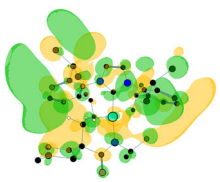
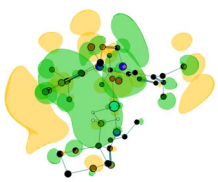
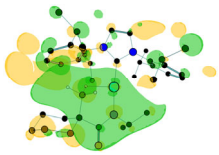
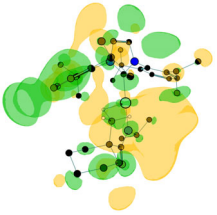
Supplementary Table 7 TD-DFT calculation of the pre-edge features and the Molecular orbital contribution of complex 3.

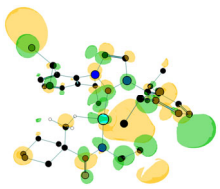
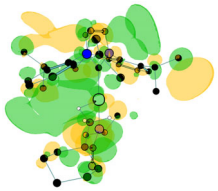
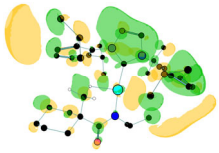
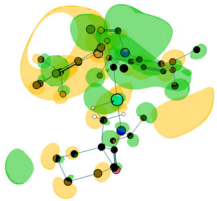
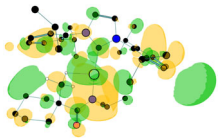
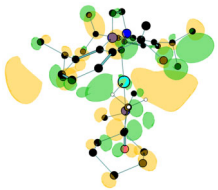
complex 3	Nickel Center				CH3					NHC ligand				
	Ni				C			H		N			C	
Orbital	Total	s (%)	p (%)	d (%)	Total	s (%)	p (%)	s (%)	p (%)	Total	s (%)	p (%)	s (%)	p (%)
170,a	**23.4**	**0**	**1.7**	**21.7**	**0.2**	**0**	**0.2**	**0**	**0**	**1.4**	**0**	**1.2**	**0**	**0.2**
171,a	**2.9**	**0**	**1.8**	**1.1**	**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	**8.5**	**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 labelled in bold.

				absolute			normalized			average		
Feature	**Energy(eV)**	**Intensity**	sum	s	p	d	s	p	d	s	p	d
A	**8330.43**	**5.47E-06**	**28.30%**	**4.4%**	**2.0%**	**21.9%**	**15.4%**	**7.1%**	**77.5%**	15.4%	7.1%	77.5%
B	8335.09	7.31E-05	**11.30%**	0.9%	3.1%	7.3%	**8.2%**	**27.5%**	**64.3%**	4.1%	47.2%	48.7%
	8335.21	**8.25E-05**	**5.30%**	**0.0%**	**3.6%**	**1.8%**	**0.0%**	**67.0%**	**33.0%**			
C	8336.15	1.40E-05	**0.70%**	0.1%	0.6%	0.1%	**8.2%**	**81.2%**	**10.6%**	9.7%	78.5%	11.9%
	8336.92	3.42E-05	**0.70%**	0.1%	0.6%	0.1%	**8.2%**	**81.2%**	**10.6%**			
	8337.38	**1.21E-04**	**0.80%**	0.1%	0.7%	0.1%	**8.2%**	**81.2%**	**10.6%**			
	8337.55	9.41E-05	**0.40%**	0.0%	0.3%	0.1%	**1.9%**	**78.8%**	**19.2%**			
	8337.62	3.32E-05	**0.80%**	0.2%	0.5%	0.1%	**21.7%**	**70.0%**	**8.3%**			
	8337.92	**6.26E-05**	**1.10%**	**0.2%**	**0.8%**	**0.1%**	**21.7%**	**70.0%**	**8.3%**	8.7%	85.5%	5.9%
D	8338.01	2.30E-05	**1.80%**	0.0%	1.7%	0.0%	**0.9%**	**97.3%**	**1.8%**			
	8338.02	5.06E-05	**1.30%**	0.0%	1.3%	0.0%	**0.9%**	**98.2%**	**0.9%**			
	8338.04	3.70E-05	**4.60%**	0.4%	3.8%	0.4%	**8.4%**	**83.5%**	**8.1%**			
	8338.05	4.72E-05	**1.80%**	0.2%	1.4%	0.2%	**11.5%**	**78.2%**	**10.3%**			

Supplementary Table 9. The contribution of the 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			
			
170α	170β	171α	171β
			
172α	172β	174α	174β
			
175α	175β	177α	177β
			
178α	178β	179α	179β
			
180α	180β	181α	181β
			

183α	183β	184α	184β
			
185α	185β	186α	186β
			
187α	187β		

Supplementary Figure 8. 3D view of Molecular Orbital Acceptors in Complex 3.

	complex 4									
	Energy(eV)	Intensity	MO-1	Cont.	MO-2	Cont.	MO-3	Cont.	MO-4	Cont.
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%**				
C	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	175a	51.48%	174a	21.66%				
	8337.88	1.35E-05	175b	42.62%	176b	40.52%				
D	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%

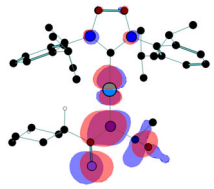
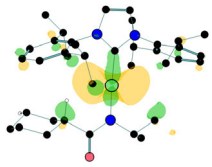
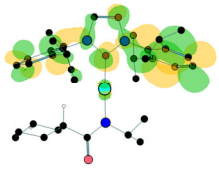
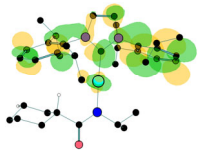
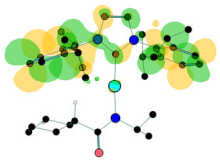
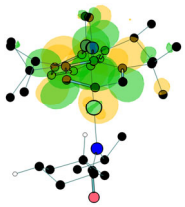
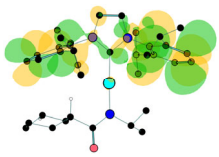
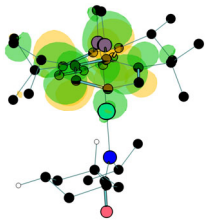
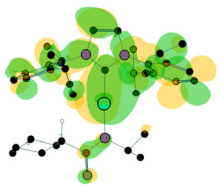
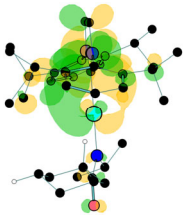
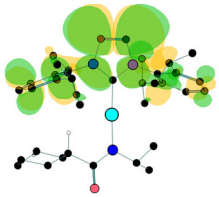
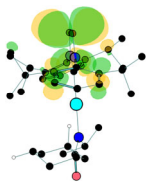
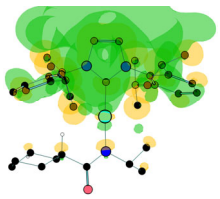
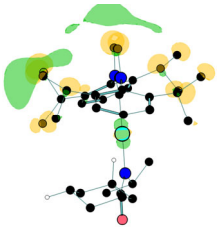
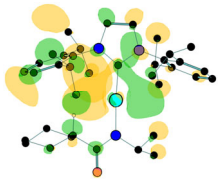
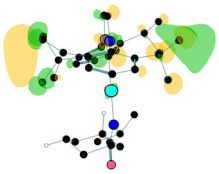
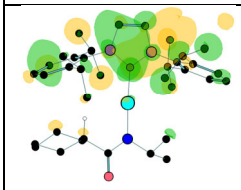
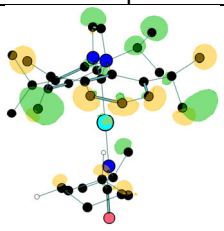
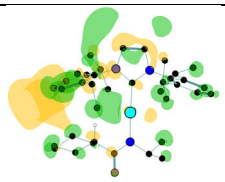
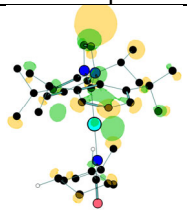
Supplementary Table 10. TD-DFT calculation of the pre-edge features and the Molecular orbital contribution of complex 4.

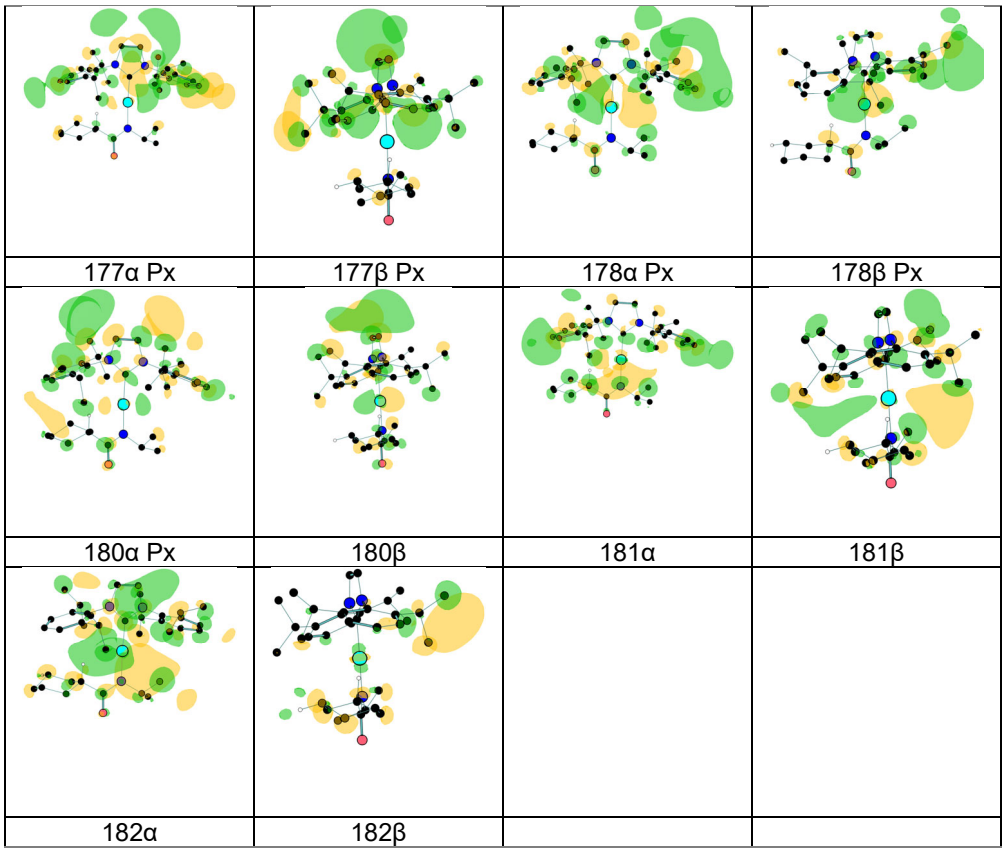
Complex 4	Nickel Center				NHC ligand				
	Ni				N			C	
Orbital	Total	s (%)	p (%)	d (%)	Total	s (%)	p (%)	s (%)	p (%)
166,a	**24.9**	**0**	**2.3**	**22.6**	**1.6**	**0**	**1.4**	**0**	**0.2**
167,a	3.2	0	1.8	1.4	9.7	0	3.5	0.3	5.9
169,a	1.1	0	0.8	0.3	2.8	0	1.2	0	1.6
170,a	0.6	0	0.5	0.1	0.8	0	0.3	0	0.5
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 CH_3 substitute and NHC ligand in complex 4. Important Molecular Orbitals with Ni character (>5%) are labelled in bold.

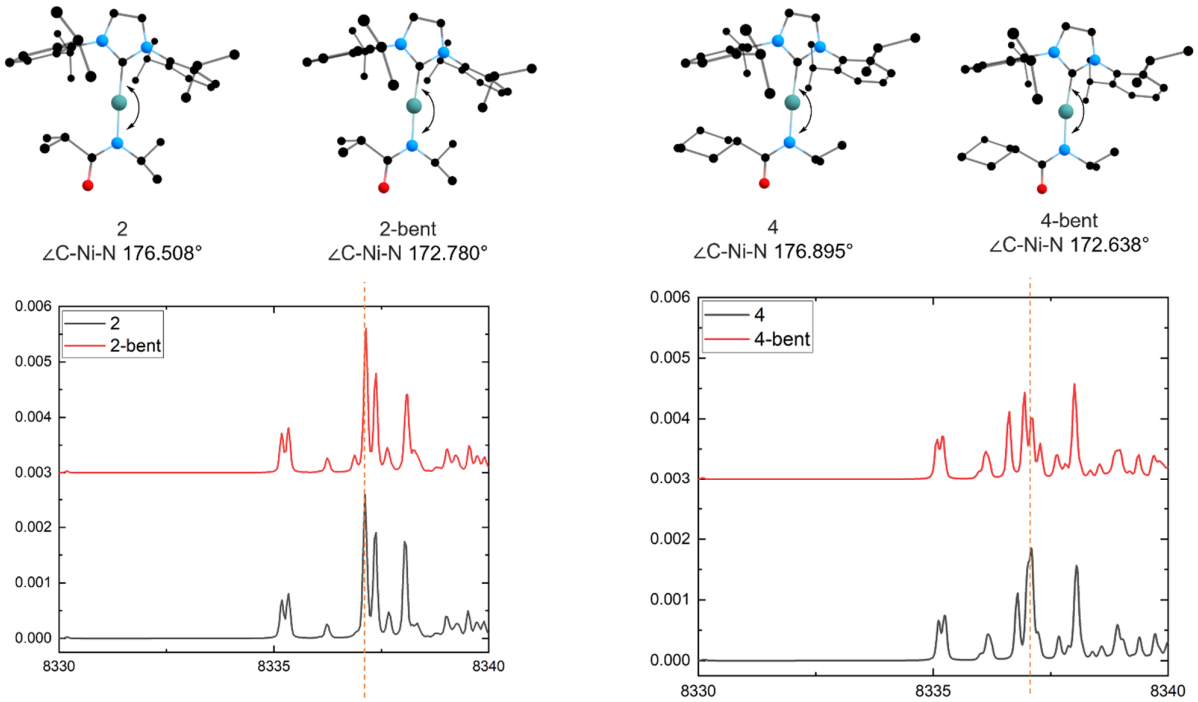
				absolute			normalized			average		
Feature	**Energy(eV)**	**Intensity**	sum	s	p	d	s	p	d	s	p	d
A	**8330.13**	**2.00E-06**	**59.10%**	12.9%	0.0%	46.2%	**21.9%**	**0.0%**	**78.1%**	21.9%	0.0%	78.1%
B	8335.12	7.93E-05	**6.70%**	0.1%	3.8%	2.8%	**0.7%**	**57.4%**	**41.8%**	0.4%	64.7%	34.9%
	8335.25	**9.21E-05**	**5.00%**	0.0%	3.6%	1.4%	**0.0%**	**72.0%**	**28.0%**			
C	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%**			

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%).

Molecular Orbitals of Complex 4			
			
166α	166β	167α	167β
			
169α	169β	170α	170β
			
171α	171β	172α	172β
			
173α	173β	174α	174β
			
175α	175β	176α Px	176β Px



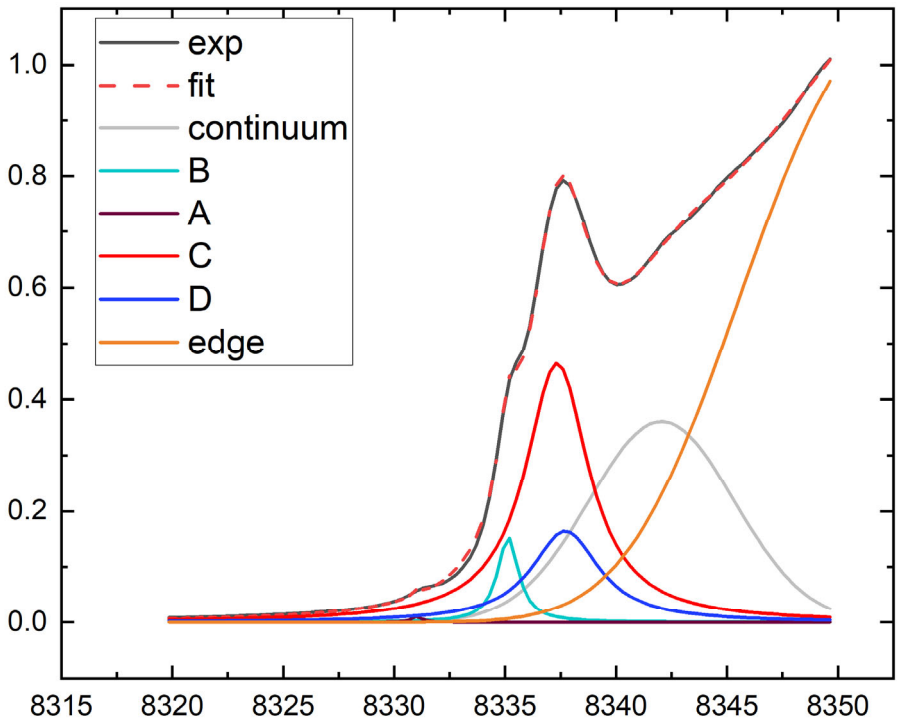
Supplementary Figure 9. 3D view of Molecular Orbital Acceptors in Complex 4.



Supplementary Figure 10. TD-DFT calculated Ni K edge XAS spectrum of 2, 2-bent, 4 and 4-bent. Calculated complex 2's bond angle (∠C-Ni-N 176.508°) is manually adapted to its agostic version of the calculated complex 1's bond angle (∠C-Ni-N 176.508°) and named 2-bent. Calculated complex 4's bond angle (∠C-Ni-N 176.895°) is manually adapted to its agostic version of the calculated complex 3's bond angle (∠C-Ni-N 172.638°) and named 2-bent. The TD-DFT calculation indicates no energy shift of the primary features between 2 and 2-bent, and a small energy shift (-0.02 eV) from 4 to 4-bent is found and considered negligible.

2.3 Simulation of Ni K edge XAS

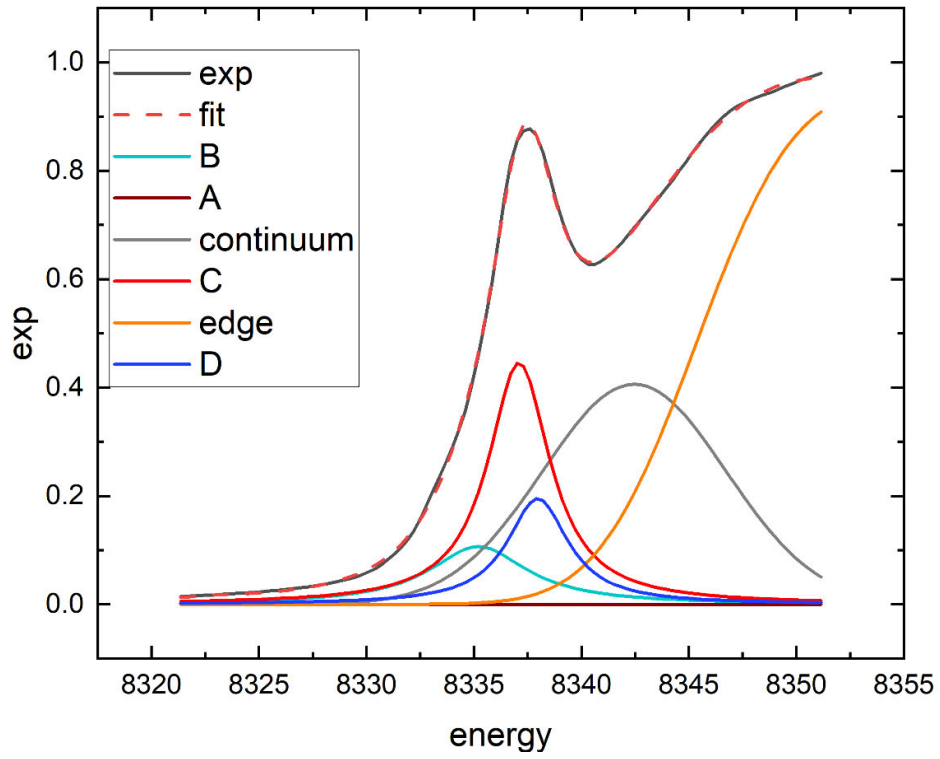
Calibrated and normalized experimental spectra were further stimulated with Athena software. Assumption of the number of the pre-edge features was made from the time-dependant DFT calculation and the assignment of each feature by the DFT MO calculation. Four Lorentzian function curves were applied for 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 the Gaussian curve and error function constitutes 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 11. Ni K edge XAS spectrum fitting of complex 1 in solid state.

complex 1					
	R-factor	0.000071			
	Chi-square	0.00202	Reduced chi-square	0.0000246	
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
	Function	step	e0	width	
Edge	error fun	0.576(0.305)	8345.51(5.57)	5.806(4.568)	

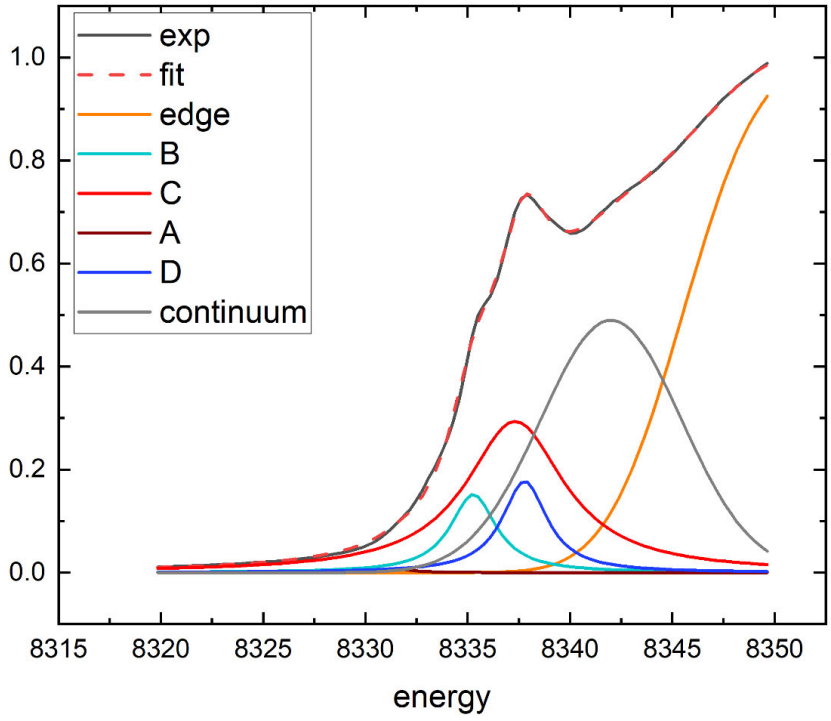
Supplementary Table 13. Ni K edge XAS spectrum fitting results of complex 1 in solid state. The uncertainty of each simulating value is listed within bracket.



Supplementary Figure 12. Ni K edge XAS spectrum fitting of complex 2 in solid state.

complex 2					
	R-factor	0.0000587			
	Chi-square	0.00212	Reduced chi-square	0.0000258	
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
	Function	step	e0	width	
Edge	error fun	0.480(0.093)	8345.33(11.08)	5.113(4.845)	

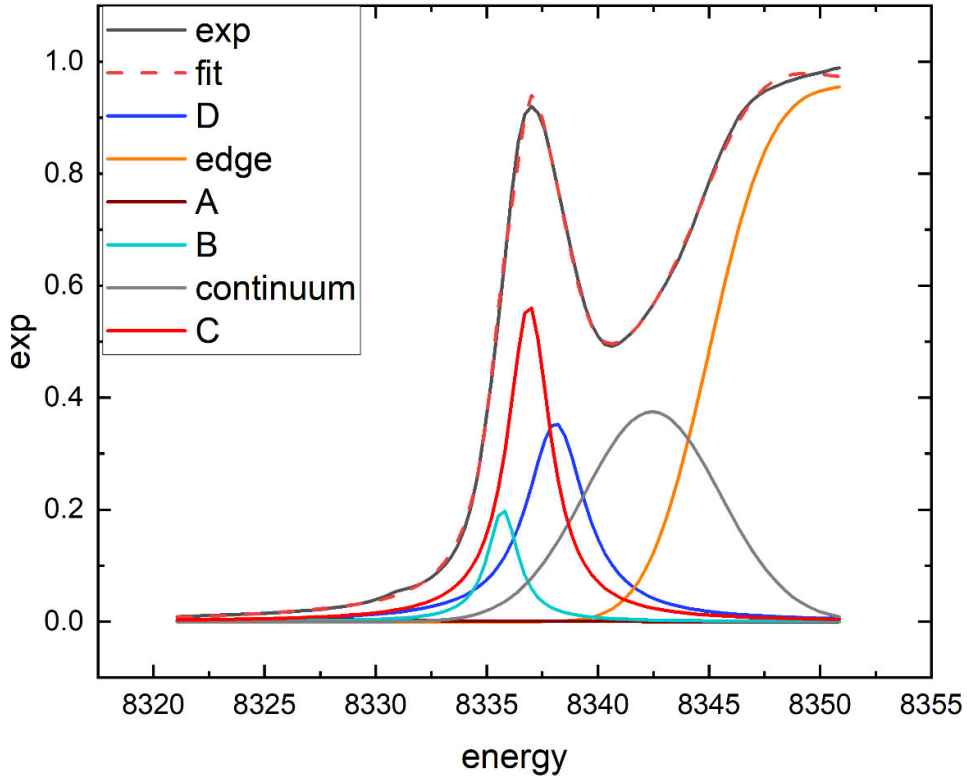
Supplementary Table 14. Ni K edge XAS spectrum fitting results of complex 2 in solid state. The uncertainty of each simulating value is listed within bracket.



Supplementary Figure 13. Ni K edge XAS spectrum fitting of complex 3 in solid state.

complex 3					
	R-factor	0.0000684			
	Chi-square	0.00202	Reduced chi-square	0.0000247	
Feature	Function	height	center	sigma	area
A	lorentzian	0.019(0.052)	8331.57(17.38)	1.854(2.282)	0.019
B	lorentzian	0.649(0.302)	8335.27(1.16)	2.724(0.392)	0.649
C	lorentzian	2.694(0.658)	8337.32(2.88)	5.840(0.420)	2.694
D	lorentzian	0.744(0.373)	8337.78(0.76)	2.667(0.476)	0.744
Continuum	gaussian	4.222(3.869)	8342.01(7.17)	3.437(0.420)	4.222
	Function	step	e0	width	
Edge	error fun	0.503(0.301)	8345.52(4.81)	4.168(1.026)	

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.



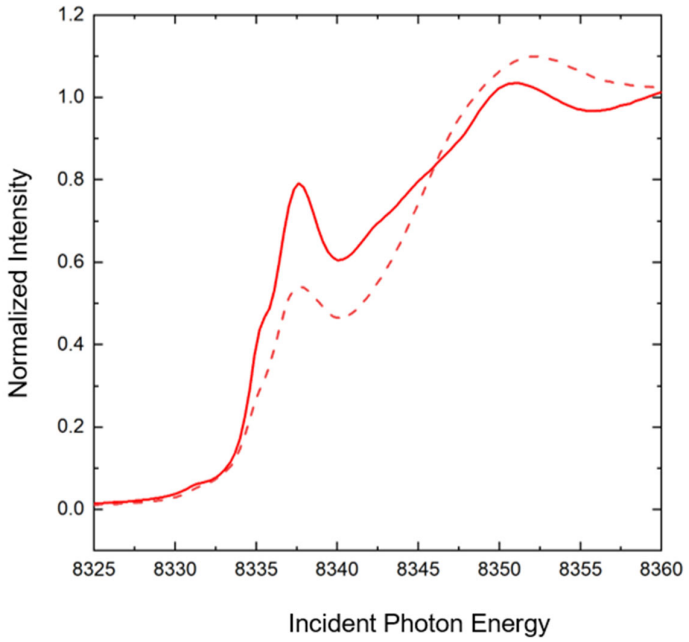
Supplementary Figure 14. Ni K edge XAS spectrum fitting of complex 3 in solid state.

complex 4					
	R-factor	0.0001512			
	Chi-square	0.00492	Reduced chi-square	0.0000593	
Feature	Function	height	center	sigma	area
A	lorentzian	0.058(0.293)	8327.81(41.86)	8.088(9.376)	0.058
B	lorentzian	0.523(0.143)	8335.72(0.73)	1.664(0.182)	0.523
C	lorentzian	2.090(0.309)	8336.90(0.23)	2.355(0.217)	2.09
D	lorentzian	1.788(0.593)	8338.10(0.65)	3.212(0.523)	1.788
Continuum	gaussian	2.880(1.354)	8342.44(2.09)	3.064(0.717)	2.88
	Function	step	e0	width	
Edge	error fun	0.479(0.090)	8344.98(1.40)	3.094(0.575)	

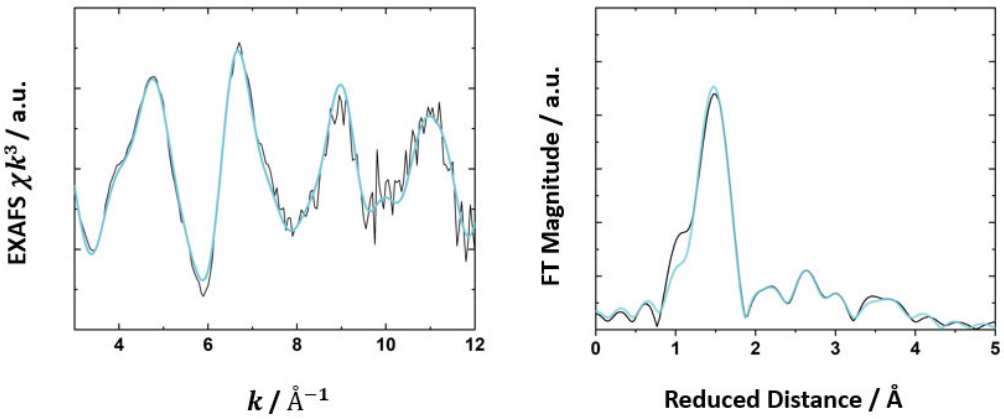
Supplementary Table 16. Ni K edge XAS spectrum fitting results of complex 4 in solid state. The uncertainty of each simulating value is listed within bracket.

2.4 Extended X-ray absorption fine structure (EXAFS) of complex 1

The EXAFS oscillations χ (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.[5] 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 15. Ni K edge XAS spectrum of complex 1 in solid-state (solid red line) and toluene solution (red dash line).



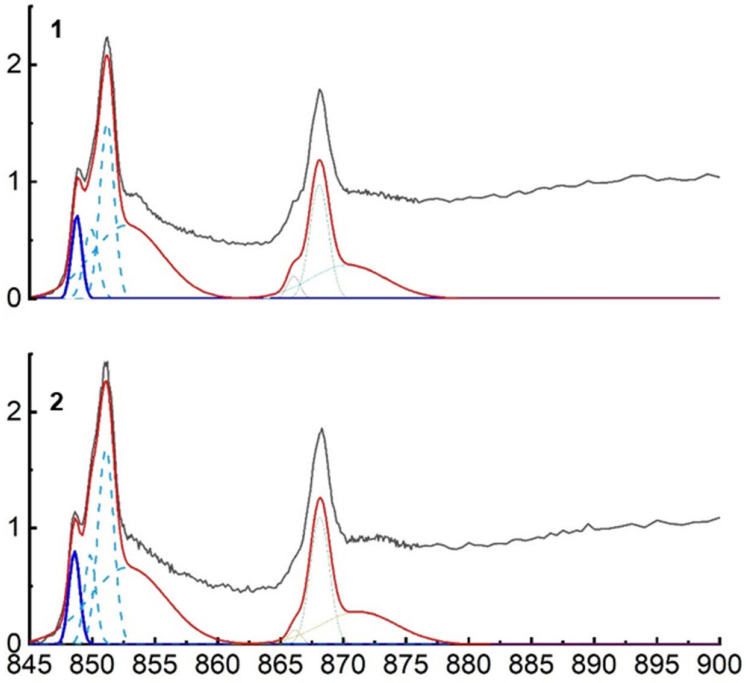
Supplementary Figure 16. Experimental (black) and calculated (blue) EXAFS spectra of the 1 (in toluene solution), in k space (left)and reduced distance space (right) with Model 1.

Scattering Path	Degeneracy	R (Å)	σ^2 (Å^2)	ΔE_0 (eV)
		Model 1[a]		
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
		Model 2[b]		
Ni-N	1	1.88	0.004	-2.10
Ni-C	1	1.90	0.004	-2.10
Ni-C	1	2.41	0.006	-2.10
Ni-C/N	6	2.93	0.012	-2.10
Ni-C-N	8	3.14	0.004	-2.10
Ni-C	1	3.54	0.004	-2.10
Ni-C	6	3.27	0.026	-2.10
Ni-C/O	8	4.04	0.010	-2.10
Ni-C-O	2	4.04	0.010	-2.10
Ni-C-C/N	6	4.16	0.005	-2.10

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 σ2, and threshold energy shift ΔE_0, $derived\ from\ EXAFS\ curve\ fitting$. [a]Fit parameters: $\Delta k = 3.0 - 12.0$ Å^{-1}, $dk = 1.0$ Å^{-1}, $R = 1 - 4.4$ Å, $S_0{}^2 = 1.20$. Goodness of fit value, $R = 0.006$. The degeneracy for Ni-C at 2.41 Å was set as a floating number. [b]Fit parameters: $\Delta k = 3.0 - 12.0$ Å^{-1}, $dk = 1.0$ Å^{-1}, $R = 1 - 4.4$ Å, $S_0{}^2 = 1.20$. Goodness of fit value, $R = 0.007$. The degeneracy for Ni-C at 2.41 Å was set as a fixed number.

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 S16). The first coordination shell at around 1.5 Å (R + Δ, 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 were slightly improved (R =0.007 to R = 0.006) when we set the coordination number of the Ni-C bond at 2.41 Å as a floating number (Model 1 in Table S6). Based on 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 the CH_3 group when 1 is dissolved in toluene. The second coordination shell at around 2.7 Å to 3.0 Å (R + Δ, without phase correction) consists of the single scattering from neighbouring C or N atom at a distance of 2.93 Å to 3.54 Å. Multiple scattering at 4.04 Å and 4.17 Å contributes to the third shell in the EXAFS spectrum.

2.5 Ni L edge X-ray Absorbance Spectroscopy

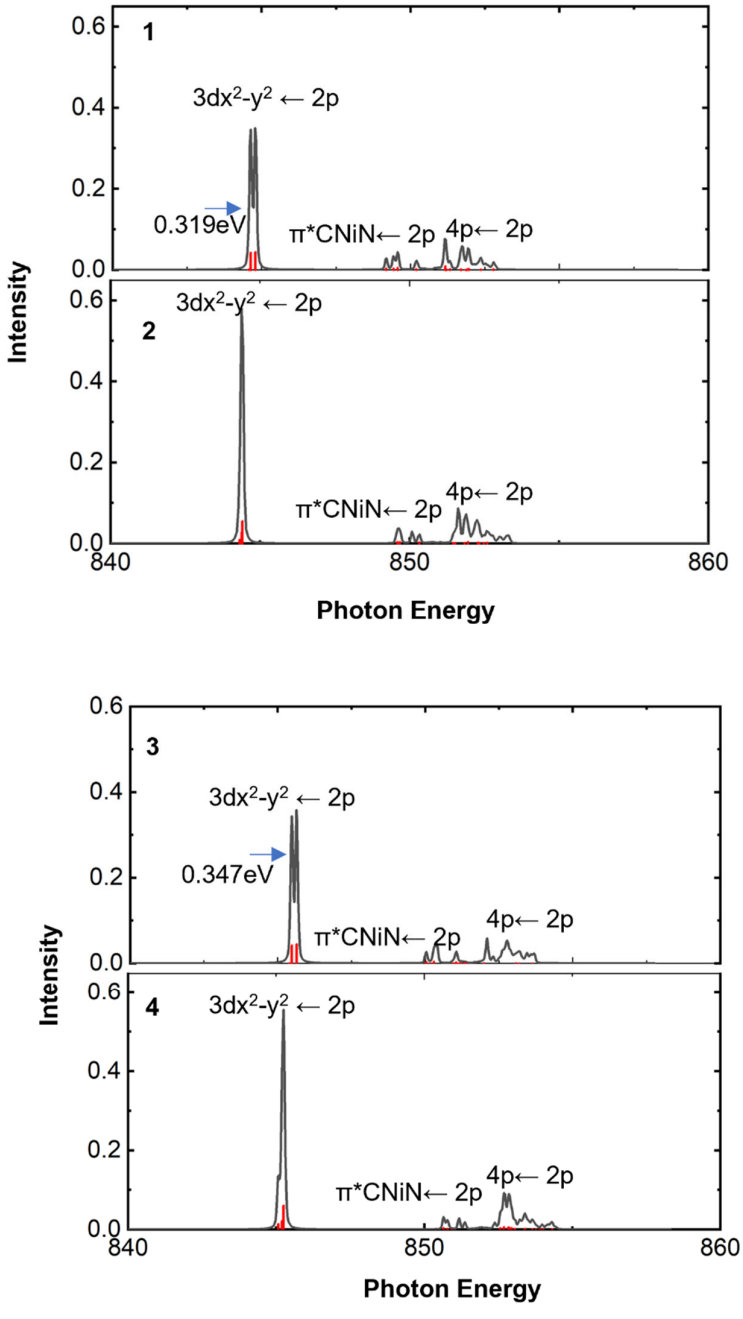


Supplementary Figure 17. Experimental Ni L edge XAS of complex 1 and 2 and the simulating function curves of each pre-edge feature.

complex 1 (agostic)							
	gaussian	Transition	height	centre	hwhm	area	FWHM
L_3 edge	1	$3d_{x^2-y^2} \leftarrow 2p$	0.72	848.75	0.47	0.72	0.94
	2	$\pi^*_{CNiN} \leftarrow 2p$	0.6	849.89	0.66	0.84	1.31
	3	$4p \leftarrow 2p$	1.51	851.17	0.67	2.14	1.33
	4	continuum	0.63	852.76	3.34	4.46	6.67
L_2 edge	1	$3dx^2\text{-}y^2 \leftarrow 2p$	0.19	866.04	0.59	0.25	1.19
	2	$\pi^*_{CNiN} \leftarrow 2p$	0.98	868.08	0.88	1.83	1.76
	3	$4p \leftarrow 2p$	0.29	870.39	3.49	2.14	6.98
complex 2 (non-agostic)							
	gaussian	Transition	height	centre	hwhm	**area**	FWHM
L_3 edge	1	$3d_{x^2-y^2} \leftarrow 2p$	0.8	848.57	0.5	0.86	1.01
	2	$\pi^*_{CNiN} \leftarrow 2p$	0.77	849.83	0.56	0.91	1.11
	3	$4p \leftarrow 2p$	1.68	851.07	0.73	2.63	1.47
	4	continum	0.66	852.81	3.61	5.09	7.22
L_2 edge	1	$3d_{x^2-y^2} \leftarrow 2p$	0.13	866.14	0.57	0.16	1.15
	2	$\pi^*_{CNiN} \leftarrow 2p$	1.1	868.13	0.9	2.1	1.8
	3	$4p \leftarrow 2p$	0.28	871.23	3.53	2.1	7.07

Supplementary Table 18. Simulation data of Ni L edge XAS. The most pronounced pre-edge feature 1 lies in the energy region of $3d \leftarrow 2p$, which is supported by the following TD-DFT calculation.

2.6 TD-DFT calculation of Ni L edge XAS



Supplementary Figure 18. Top. TD-DFT calculated Ni L-edge XAS of 1 and 2. Bottom. TD-DFT calculated Ni-L edge XAS of 3 and 4. Only the 2p to 3d transition features are dipole allowed and therefore have much intensed features used for analysis. See feature info in Supplementary Table 19 & 22.

complex 1

Region	Energy	Intensity	MO	MO-1	MO-2	MO-3
$3dx^2\text{-}y^2 \leftarrow 2p$	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%
$\pi^*CNiN \leftarrow 2p$	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%
$4p \leftarrow 2p$	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%
	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.

Complex 2

Region	Energy	Intensity	MO accpetor	MO-1	MO-2	MO-3
$3dx^2\text{-}y^2 \leftarrow 2p$	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%	
$\pi^*CNiN \leftarrow 2p$	849.674	3.94E-03	orbital	160, b	156, b	157, b
			contribution	51.27%	26.40%	18.13%
	849.59	3.70E-03	Orbital	160b	156b	157b
			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%
$4p \leftarrow 2p$	851.526	1.99E-03	Orbital	162b	158a	170b
			Contribution	24.03%	20.87%	6.44%
	851.455	1.39E-03	Orbital	162b	170b	186b
			Contribution	29.80%	7.91%	6.53%
	851.839	2.04E-03	Orbital	164b	170b	167b
			Contribution	26.30%	23.42%	9.04%
	851.954	4.22E-03	Orbital	164b	170b	169b
			Contribution	26.71%	20.12%	7.80%
	852.285	2.62E-03	Orbital	162a	163b	170a
			Contribution	18.68%	17.26%	10.20%
	852.341	1.53E-03	Orbital	162a	170a	166a
			Contribution	56.73%	10.77%	9.47%
	852.6	2.71E-03	Orbital	162a	172b	170a
			Contribution	32.57%	12.55%	7.89%
	852.485	1.63E-03	Orbital	164a	172b	169a
			Contribution	16.47%	16.36%	7.91%
	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 20. TD-DFT calculated Ni L-edge XAS and each Molecular Orbital Acceptors Contribution of complex 2. See the details of each MO acceptor's atomic character and 3d graphics in Supplementary Table 4 and Supplementary Table 6.

complex 3						
Region	Energy	Intensity	MO	MO-1	MO-2	MO-3
$3dx^2\text{-}y^2 \leftarrow 2p$	845.396	4.68E-04	orbital	170b	174b	
			contribution	56.02%	12.11%	
	845.475	4.22E-02	orbital	170b	174b	
			contribution	55.91%	12.10%	
	845.638	4.47E-02	orbital	170b	172b	
			contribution	55.66%	27.94%	
$\pi^*CNiN \leftarrow 2p$	850.029	3.34E-03	orbital	175a	171a	
			contribution	1.71%	1.27%	
	850.155	2.39E-04	orbital	175b	172b	171b
			contribution	45.44%	28.91%	11.98%
	850.297	4.14E-03	orbital	175b	172b	171b
			contribution	45.52%	28.83%	11.90%
	850.938	3.44E-04	orbital	175a	171a	
			contribution	36.67%	35.93%	
	850.943	2.33E-04	orbital	175a	171a	
			contribution	4.30%	4.20%	
$4p \leftarrow 2p$	851.042	2.34E-03	orbital	175a	171a	
			contribution	33.53%	32.48%	
	851.06	1.09E-04	orbital	174b	173b	171b
			contribution	37.79%	32.18%	10.46%
	851.125	1.55E-04	orbital	175b	172b	171b
			contribution	47.72%	35.91%	14.95%
	851.177	1.97E-05	orbital	174b	173b	
			contribution	72.81%	19.47%	
	851.211	5.35E-05	orbital	173b	172b	
			contribution	59.73%	34.81%	
	851.306	1.61E-04	orbital	175a	171a	
			contribution	4.75%	4.81%	
	851.33	8.92E-05	orbital	174b	173b	
			contribution	72.53%	19.40%	
	851.393	2.88E-04	orbital	175b	172b	171b
			contribution	47.51%	36.15%	15.03%
	851.985	1.81E-04	orbital	175a	171a	172a
			contribution	52.91%	24.98%	11.60%
	853.071	4.82E-04	orbital	184a	179a	
			contribution	20.14%	19.97%	
	853.189	1.32E-04	orbital	185a	181a	187a
			contribution	24.40%	13.00%	10.65%
	853.626	1.34E-04	orbital	186a	187a	
			contribution	48.29%	21.32%	

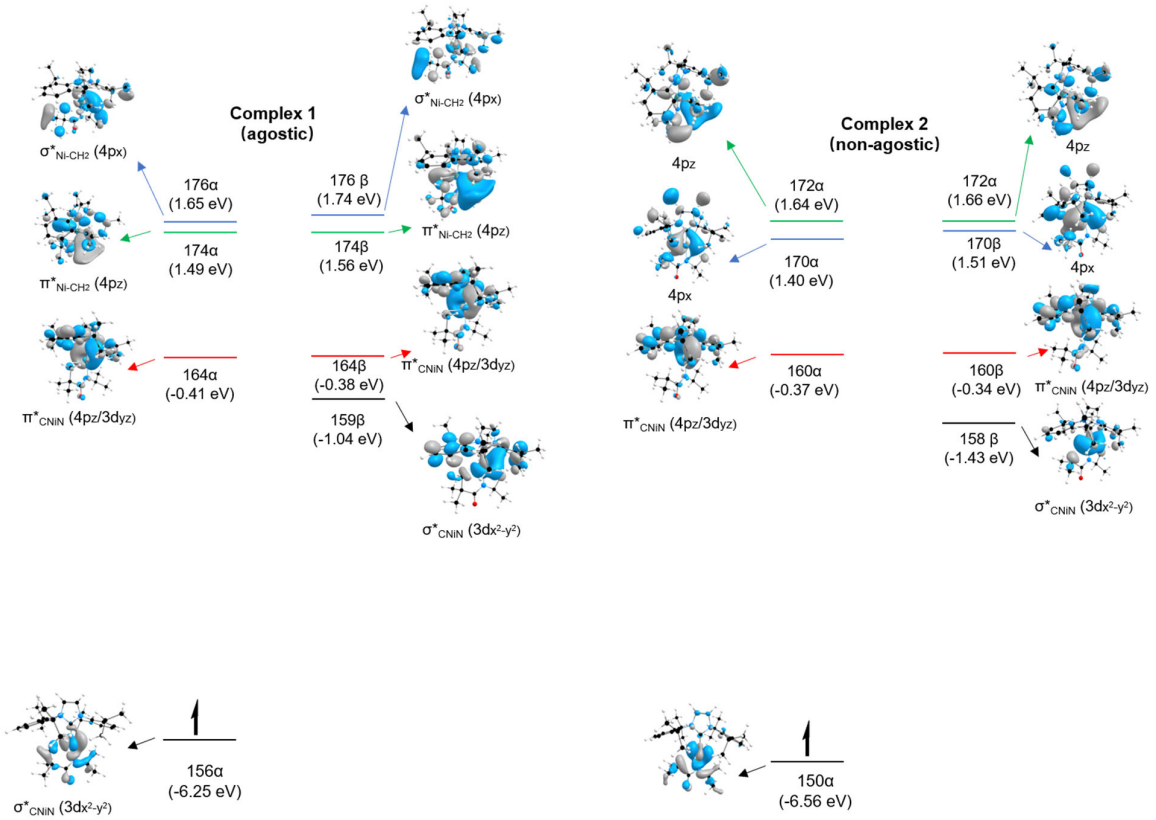
Supplementary Table 21. TD-DFT calculated Ni L-edge XAS and each Molecular Orbital Acceptors Contribution of complex 3. See the details of each MO acceptor's atomic character and 3d graphics in Supplementary Table 5 and Supplementary Table 7.

complex 4						
Region	Energy	Intensity	MO	MO-1	MO-2	MO-3
$3dx^2\text{-}y^2 \leftarrow 2p$	845.07	1.42E-02	orbital	166b		
			contribution	0.87%		
	845.192	2.19E-02	orbital	166b		
			contribution	86.81%		
	845.251	6.05E-02	orbital	166b		
			contribution	86.64%		
$\pi^*CNiN \leftarrow 2p$	850.651	3.86E-03	orbital	167b	171b	
			contribution	45.91%	42.35%	
	850.782	2.80E-03	orbital	167b	171b	
			contribution	45.95%	42.12%	
	850.922	1.83E-04	orbital	167b	171b	
			contribution	46.65%	42.59%	
$4p \leftarrow 2p$	852.567	3.85E-03	orbital	174b	173b	178b
			contribution	29.88%	21.67%	10.49%
	852.953	3.98E-03	orbital	171a		
			contribution	13.46%		
	852.688	6.45E-03	orbital	174a		
			contribution	20.62%		
	852.837	5.25E-03	orbital	174a		
			contribution	18.25%		
	852.875	4.85E-03	orbital	174a		
			contribution	22.37%		
	853.063	2.29E-03	orbital	174a		
			contribution	36.23%		
	853.399	2.31E-03	orbital	174a		
			contribution	11.86%		
	853.646	1.31E-03	orbital	174a		
			contribution	37.49%		
	853.768	5.47E-05	orbital	178b	177b	174b
			contribution	59.26%	19.59%	14.33%
	853.895	3.47E-05	orbital	178b	177b	
			contribution	56.03%	17.46%	
	854.025	2.84E-05	orbital	178b	177b	179b
			contribution	60.05%	19.01%	10.63%
	853.884	5.94E-05	orbital	181b	176b	
			contribution	34.60%	14.65%	
	853.953	3.34E-04	orbital	182a	176a	177a
			contribution	21.45%	15.80%	15.03%
	854.312	8.13E-04	orbital	179a	181a	
			contribution	45.28%	18.17%	

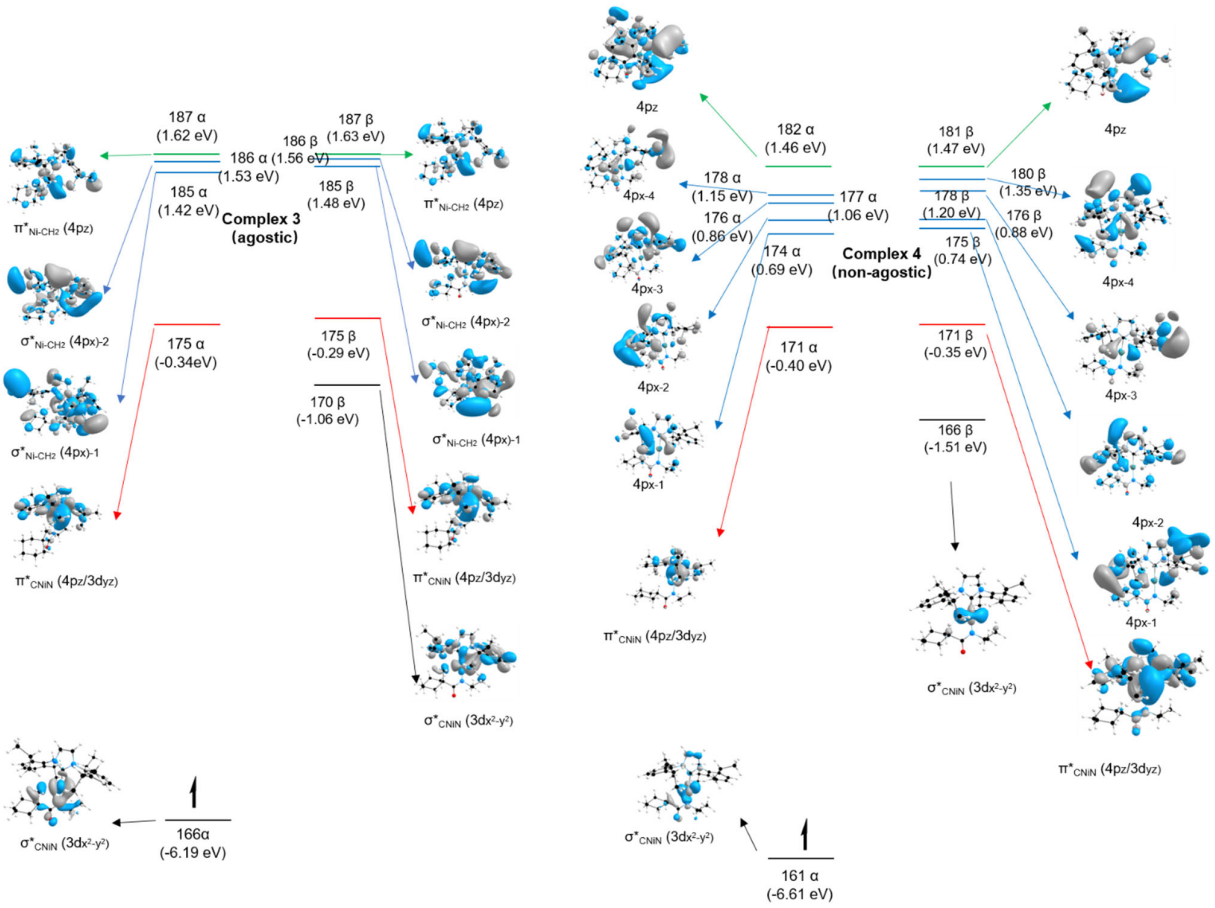
Supplementary Table 22. TD-DFT calculated Ni L-edge XAS and each Molecular Orbital Acceptors Contribution of complex 4. See the details of each MO acceptor's atomic character and 3d graphics in Supplementary Table 5 and Supplementary Table 7.

3. Density Functional Calculation

3.1 Molecular Orbital

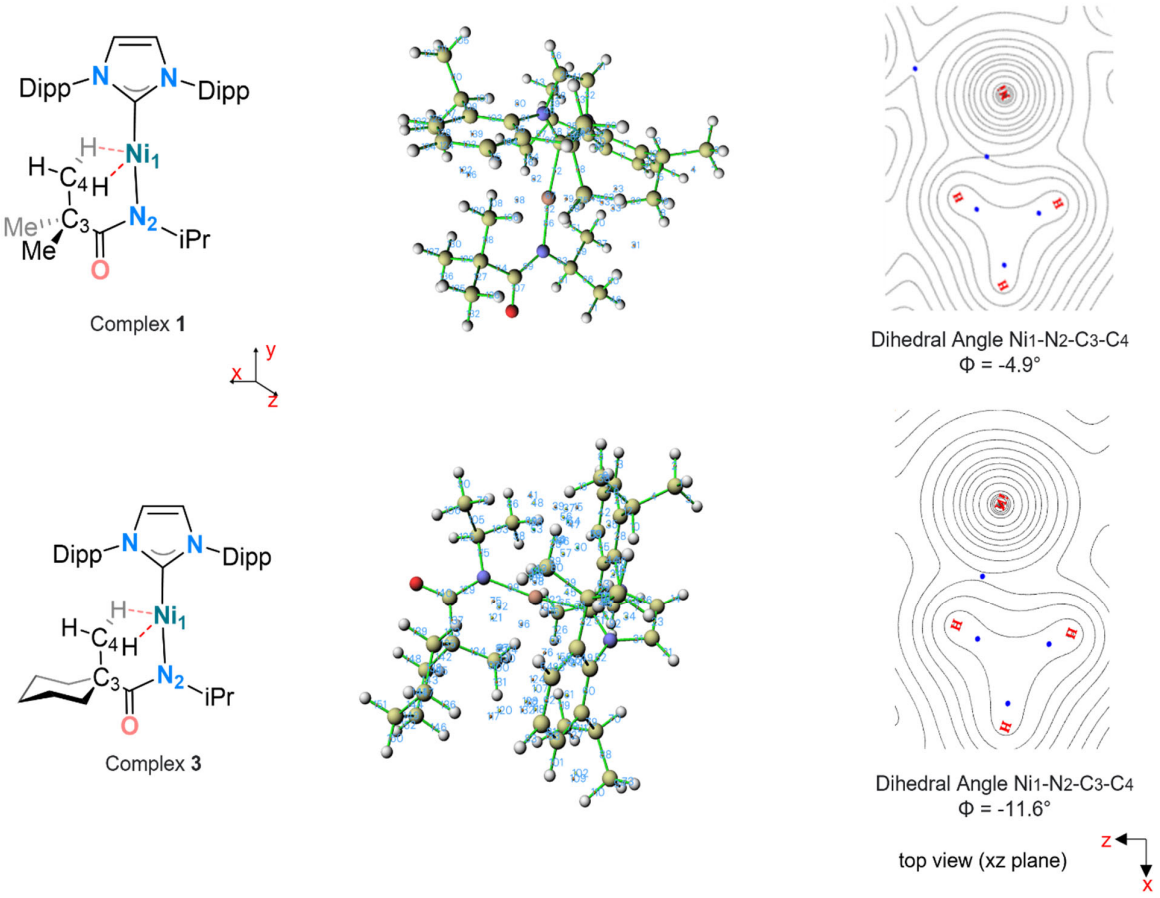


Supplementary Figure 19. MO diagram of complex 1 and 2. Only orbitals contribute to the XAS absorption with significant Ni characters are present.

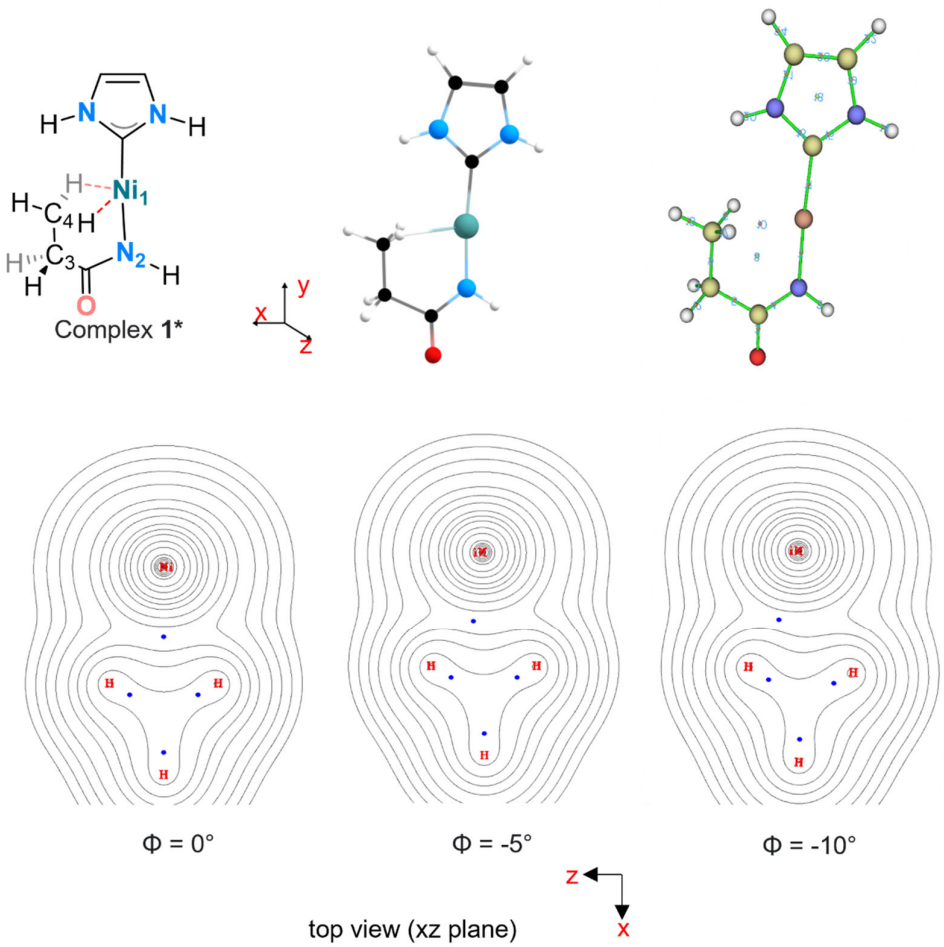


Supplementary Figure 20. MO diagram of complex 3 and 4. Only orbitals contribute to the XAS absorption with significant Ni characters are present.

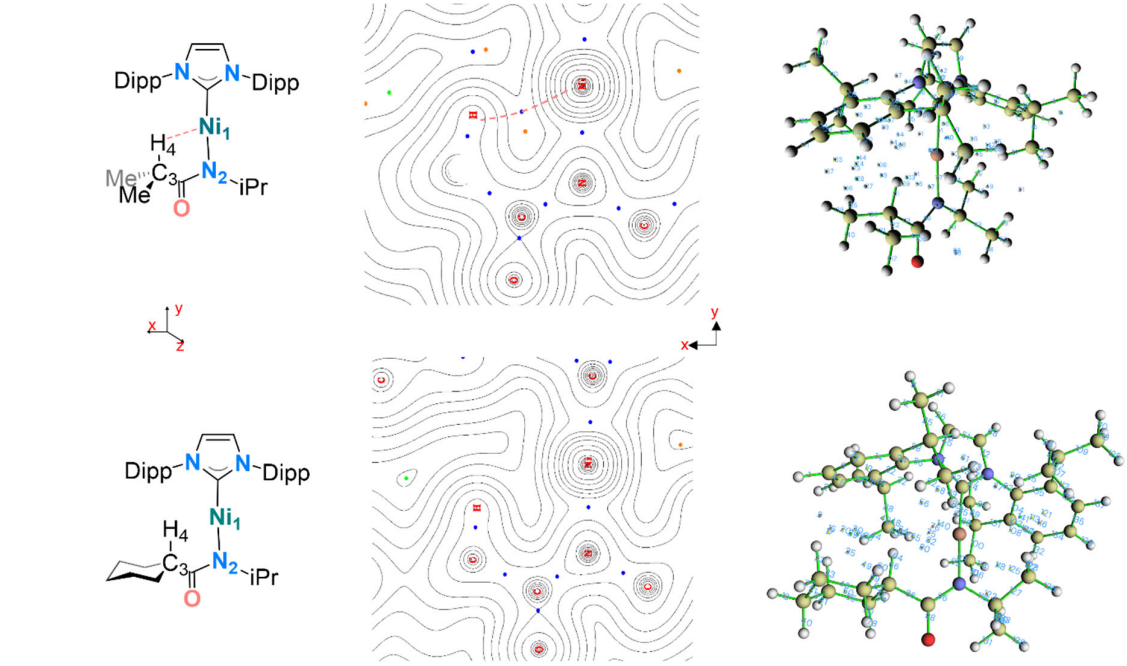
3.2 DFT-AIM calculation



Supplementary Figure 21. AIM electron density contour map(right) and 3D rendering (middle) with bonding critical points (bcp) labelled in blue of complex 1 and 3.



Supplementary Figure 22. AIM electron density contour map with bonding critical points (bcp) labelled in blue of the simplified version 1* .1* dihedral angle Ni1-N2-C3-C4 Φ was optimized at 0° and constrained at 5° and 10° as a comparison.

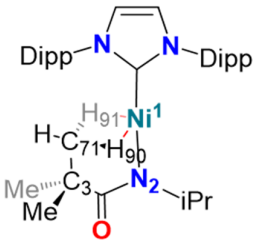


Supplementary Figure 23. AIM electron density contour map (Middle) with bonding critical points (bcp) labelled in blue of the complex 3 and 4, and the 3D AIM path rendering.

	bcp 98 in 1	bcp 96 in 3	bcp 10 in 1*	bcp 10 in 1*-5	bcp 10 in 1*-10	bcp 91 in complex 2
Φ(°)[a]	-4.866	-11.595	0	-5	-10	N/A
ρ(r)[b]	**0.04**	**0.04**	**0.03**	**0.03**	**0.03**	**0.022**
G(r)[c]	0.043	0.041	0.03	0.03	0.03	0.019
K(r)[d]	0.003	0.003	0.001	0.001	0.001	0.001
V(r)[e]	-0.046	-0.044	-0.031	-0.031	-0.033	-0.020
E(r) or H (r)[f]	-0.003	-0.003	-0.001	-0.001	-0.001	-0.001
$\nabla^2\rho(r)$[g]	**0.159**	**0.152**	**0.117**	**0.117**	**0.121**	**0.070**
ELF[h]	0.095	0.091	0.075	0.075	0.078	0.074
LOL[i]	0.241	0.236	0.217	0.218	0.220	0.217
ESP from nuclear charges	53.671	56.317	27.653	27.596	27.505	50.896
ESP from electrons	-53.44	-56.083	-27.445	-27.389	-27.289	-50.754
Total ESP	0.232	0.234	0.208	0.207	0.216	0.142

Supplementary Table 23. AIM calculation data.[a]Dihedral Angle Ni_1-N_2-C_3-C_4; [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.

3.3 DFT -NBO Calculation



complex 1

			B3LYP/Def2SVP		
	Donor	Acceptor	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
α	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
β	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
H1	σC71 - H90		10.42	2.66	0.198
H2	σC71 - H91		16.6	2.66	0.25

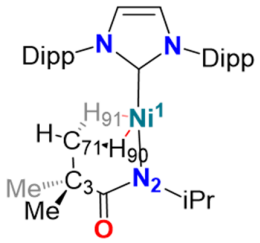
α spin

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)Ni 1	s(0.10%) p99.99(98.76%) d11.26(1.12%)
157. (0.00789) LP*(8)Ni 1	s(6.46%) p12.86(83.04%) d 1.63(10.50%)

Supplementary Table 24. NBO calculation of complex 1 at UB3LYP/defs-SVP theory level.



complex 1

			B3LYP/Def2TZVP		
	Donor	Acceptor	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
α	84. BD (1) C71 - H90	155. LP*(6)Ni 1	1.14	0.61	0.036
		157. LP*(8)Ni 1	4.14	0.86	0.075
	85. BD (1) C71 - H91	155. LP*(6)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
β	86. BD (1) C71 - H90	158. LP*(8)Ni 1	1.07	0.8	0.037
		157. LP*(7)Ni 1	7.76	0.63	0.09
	87. BD (1) C71 - H91	157. LP*(7)Ni 1	11.7	0.63	0.109
		158. LP*(8)Ni 1	1.66	0.8	0.047
	Total		22.19	2.86	0.283
H 1	σ C71 - H90		14.11	2.9	0.238
H 2	σ C71 - H91		21.61	2.9	0.297

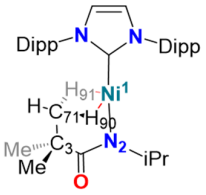
α spin

84. (0.98224) BD (1) C71 - H90	(60.70%) C 71 s(23.66%) p 3.22(76.20%) d 0.01(0.14%)
	(39.30%) H90 s(99.97%) p 0.00(0.03%)
85. (0.97697) BD (1) C71 - H91	(59.76%) 0.7731* C 71 s(23.06%)p 3.33(76.78%) d 0.0(0.15%)
	(40.24%) 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%)

β spin

86. (0.97271) BD (1) C71 - H90	(60.69%) C71 s(23.32%) p 3.28(76.53%) d 0.01(0.14%)
	(39.31%) H90 s(99.97%) p 0.00(0.03%)
87. (0.96183) BD (1) C71 - H91	(59.47%) C71 s(22.59%) p 3.42(77.25%) d 0.01(0.15%)
	(40.53%) H91 s(99.97%) p 0.00(0.03%)
157. (0.05668) LP*(7)Ni1	s(54.15%) p 0.37(19.97%) d 0.48(25.88%)
158. (0.01122) LP*(8)Ni1	s(6.84%) p12.23(83.71%) d 1.38(9.45%)

Supplementary Table 25. NBO calculation of complex 1 at UB3LYP/defs-TZVP theory level.



complex 1

			B3LYP/Def2TZVPP		
	Donor	Acceptor	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
α	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
	85. BD (1) C71 - H91	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
β	86. BD (1) C71 - H90	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
	87. BD (1) C71 - H91	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

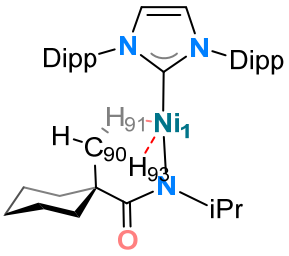
α spin

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%)H 91 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(5.67%) d 0.06(5.17%)
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%) p38.97(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%)H 91 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 26. NBO calculation of complex 1 at UB3LYP/defs-TZVPP theory leve



		B3LYP/Def2TZVPP			
	Donor	Acceptor	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
α	105. BD (1) C 90 - H 91	168. LP*(6)Ni 1	1.07	0.61	0.035
		169. LP*(7)Ni 1	0.26	0.94	0.02
		170. LP*(8)Ni 1	10.67	0.87	0.122
	107. BD (1) C 90 - H 93	168. LP*(6)Ni 1	1.41	0.6	0.04
		169. LP*(7)Ni 1	0.87	0.93	0.037
		170. LP*(8)Ni 1	5.49	0.86	0.087
	Total		19.77	4.81	0.341
β	105. BD (1) C 90 - H 91	168. LP*(6)Ni 1	0.36	0.9	0.023
		169. LP*(7)Ni 1	14.29	0.67	0.124
		170. LP*(8)Ni 1	3.1	0.74	0.061
	107. BD (1) C 90 - H 93	169. LP*(7)Ni 1	8.95	0.67	0.099
		170. LP*(8)Ni 1	1.32	0.74	0.039
	Total		28.02	3.72	0.346
H 1	σ C90 - H91		29.75	4.73	0.385
H 2	σ C90 - H93		18.04	3.8	0.302

α spin

105. (0.97228) BD (1) C 90 - H 91	(59.89%) 0.7739* C 90 s(23.11%)p 3.32(76.73%)d 0.01(0.15%)
	(40.11%) 0.6333* H 91 s(99.95%)p 0.00(0.05%)d 0.00(0.00%)
107. (0.97828) BD (1) C 90 - H 93	(60.72%) 0.7792*C 90 s(23.47%) p 3.25(76.39%) d 0.01(0.14%)
	(39.28%) 0.6267*H 93 s(99.96%) p 0.00(0.04%) d 0.00(0.00%)
168. (0.16807) LP*(6)Ni1	s(85.04%) p 0.12(10.27%) d 0.05(4.67%)
169. (0.06818) LP*(7)Ni1	s(3.04%) p31.83(96.73%) d 0.07(0.21%)
170. (0.03490) LP*(8)Ni1	s(1.98%) p48.79(96.54%) d 0.74(1.46%)

β spin

105. (0.95460) BD(1) C 90 - H 91	(59.24%)0.7697* C90 s(22.52%) p 3.43(77.32%) d 0.01(0.15%)
	40.76%)0.6384* H91 s(99.95%)p 0.00(0.05%)d 0.00(0.00%)
107.(0.97420) BD(1) C 90 - H 93	(60.74%) 0.7793* C90 s(23.27%) p 3.29(76.59%) d 0.01(0.13%)
	(39.26%)0.6266* H93 s(99.96%) p0.00(0.04%) d0.00(0.00%)
168. (0.07000) LP*(6)Ni1	s(2.77%)p32.93(91.32%)d 2.12(5.89%)
169. (0.05597) LP*(7)Ni1	s(48.22%)p 0.65(31.29%)d 0.42(20.49%)
170. (0.02220) LP*(8)Ni1	s(10.34%)p 7.42(76.76%)d 1.25(12.90%)

Supplementary Table 27. NBO calculation of complex 3 at UB3LYP/defs-TZVPP theory level

Complex **1***

complex 1*

	B3LYP/Def2TZVPP Donor	Acceptor	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
a	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
	13. BD (1)C5-H10	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
b	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
	13. BD (1)C5-H10	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
	Total		19.22	3.64	0.272
	H1	σ C5 - H7	15.51	3.1	0.237
	H1	σ C5 - H10	15.51	3.1	0.237

alpha

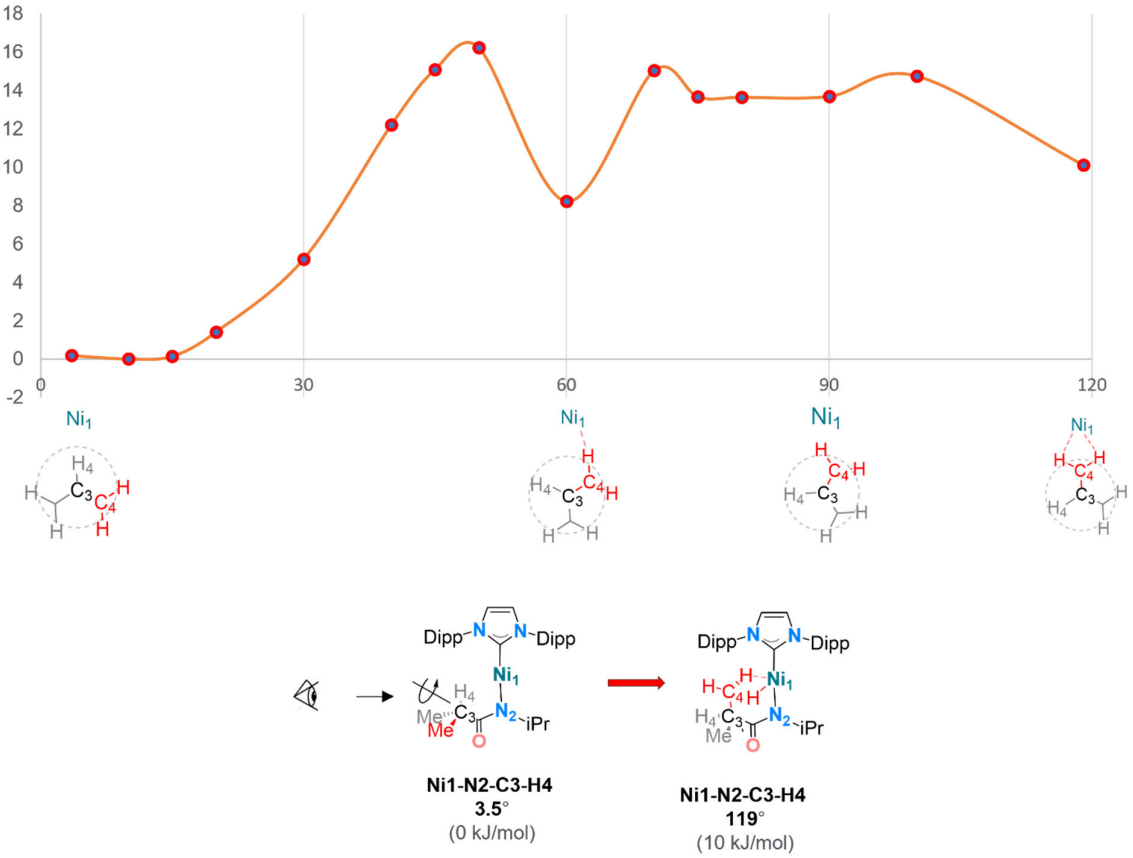
11. (0.97269) BD (1) C 5 - H 7 (59.90%) 0.7739* C 5 s(22.91%)p 3.36(77.02%)d 0.00(0.06%)
13. (0.97268) BD (1) C 5 - H 10 (59.90%) 0.7739* C 5 s(22.91%)p 3.36(77.02%)d 0.00(0.06%)
52. (0.03205) LP*(6)Ni 12 s(0.00%)p 1.00(99.10%)d 0.01(0.86%)
53. (0.00355) LP*(7)Ni 12 s(14.29%)p 4.69(66.98%)d 1.30(18.64%)

beta

52. (0.03180) LP*(6)Ni 12 s(0.00%)p 1.00(99.40%)d 0.01(0.55%)
53. (0.02242) LP*(7)Ni 12 s(1.99%)p48.79(97.30%)d 0.34(0.68%)
11. (0.98137) BD (1) C 5 - H 7 (60.16%) 0.7756* C 5 s(23.32%)p 3.28(76.60%)d 0.00(0.06%)
13. (0.98136) BD (1) C 5 - H 10 (60.16%) 0.7756* C 5 s(23.32%)p 3.28(76.60%)d 0.00(0.06%)

Supplementary Table 28. NBO calculation of complex 1* at UB3LYP/defs-TZVPP theory level

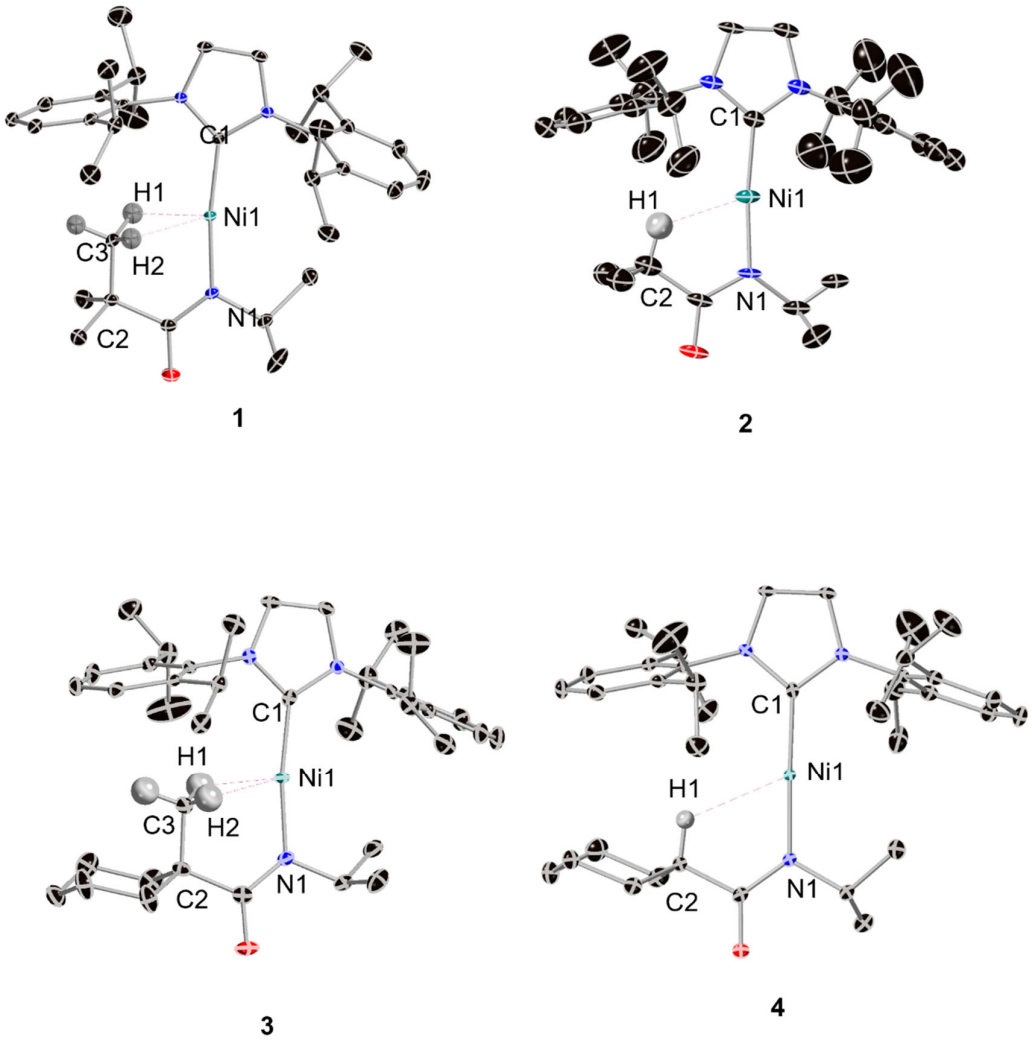
3.4 DFT calculation of rotation scan



Supplementary Figure 24. Energy profile of the Rotational Scan along dihedral angle Ni1-N2-C3-H4.

4. X-ray Diffraction

4.1 Comparison of XRD solid structure and DFT calculated structure



Supplementary Figure 25. ORTEP depiction of the solid-state structure of 1-4 (ellipsoids at 50% probability, H1-H3 were freely located and refined from the electron density map.)

solid state structure						
complex	**bond length(Å)**					
	N1-H1	Ni1-H2	ΔNi-H	Ni1-C30	C1-Ni1	Ni1-N1
1	2.024(15)	2.159(15)	0.135	2.44(8)	1.91(2)	1.91(5)
2	2.28(4)	-	-	-	1.89(4)	1.85(2)
3	1.93(5)	2.14(7)	0.21	2.40(1)	1.89(4)	1.90(0)
4	2.52(6)	-	-	-	1.88(9)	1.88(7)
DFT calculation						
	bond length(Å)					
	N1-H1	Ni1-H2	Δ Ni-H	Ni1-C30	C1-Ni1	Ni1-N1
1	1.980	2.133	0.153	1.920	1.908	1.908
2	2.192	-	-	-	1.894	1.876
3	1.970	2.263	0.294	2.461	1.923	1.910
4	2.531	-	-	-	1.897	1.881

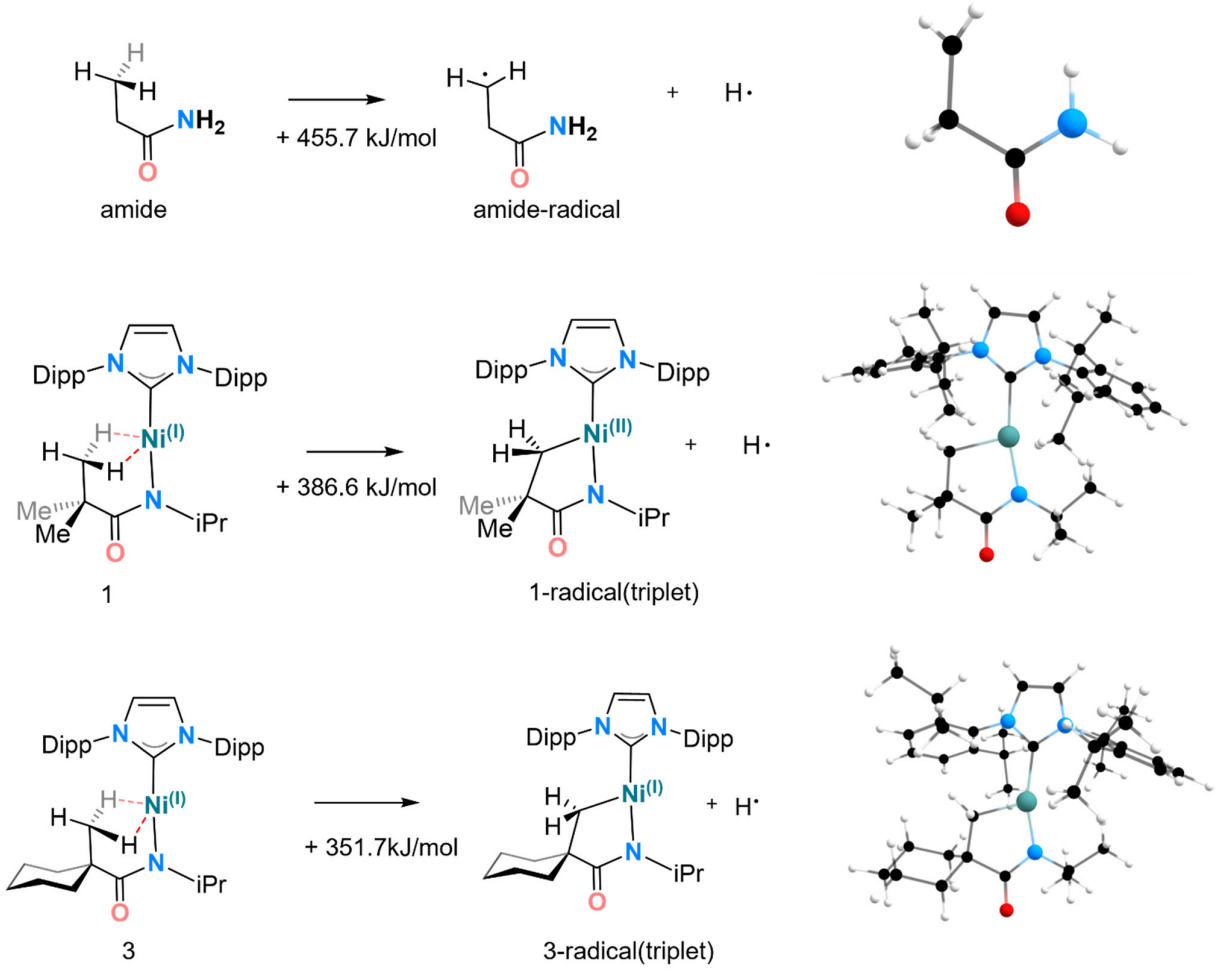
solid state structure					
	bond angle(°)				**dihedral angle (°)**
	C1-Ni1-N1	Ni1-H1-C30	Ni1-H2-C30	ΔNi-H-C	Ni1-N1-C28-C30
1	172.12(7)	101.8(10)	94.3(10)	7.5	-4.57(0)
2	169.00(4)	-	-	-	-
3	171.05(9)	106.18(3)	92.59(2)	13.59	-7.75(2)
4	177.62(0)	-	-	-	-
DFT calculation					
	bond angle(°)				**dihedral angle (°)**
	C1-Ni1-N1	Ni1-H1-C30	Ni1-H2-C30	Δ Ni-H	Ni1-N1-C28-C30
1	172.780	97.384	89.488	7.896	-4.866
2	176.508	-	-	-	-
3	172.638	102.276	86.734	15.542	-11.595
4	176.895	-	-	-	-

Supplementary Table 29. The comparison of important Distances and Angles of agnostic complexes 1, 3 in XRD and DFT structures. The solid structures of complexes 1-2 are referred to the previous work[1,2]. ΔNi-H is the bond length difference between N1-H1 and Ni1-H2, ΔNi-H-C is the bond angle difference between Ni1-H1-C30 and Ni1-H2-C30.

Compound	**3**	**4**
Empirical formula	$C_{38}H_{56}N_3NiO$	$C_{37}H_{54}N_3NiO$
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/Å^3	3431.7(8)	3478.1(4)
Z	4	4
ρ_{calc}g/cm^3	1.219	1.175
μ/mm^{-1}	0.598	0.589
F(000)	1364	1332
Crystal size/mm^3	0.57 × 0.12 × 0.04	0.19 × 0.17 × 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 F^2	1.02	1.008
Final R indexes [I>=2σ (I)]	R_1 = 0.0374, wR_2 = 0.0808	R_1 = 0.0378, wR_2 = 0.0798
Final R indexes [all data]	R_1 = 0.0610, wR_2 = 0.0897	R_1 = 0.0612, wR_2 = 0.0877
Largest diff. peak/hole / e Å^{-3}	0.47/-0.37	0.48/-0.26

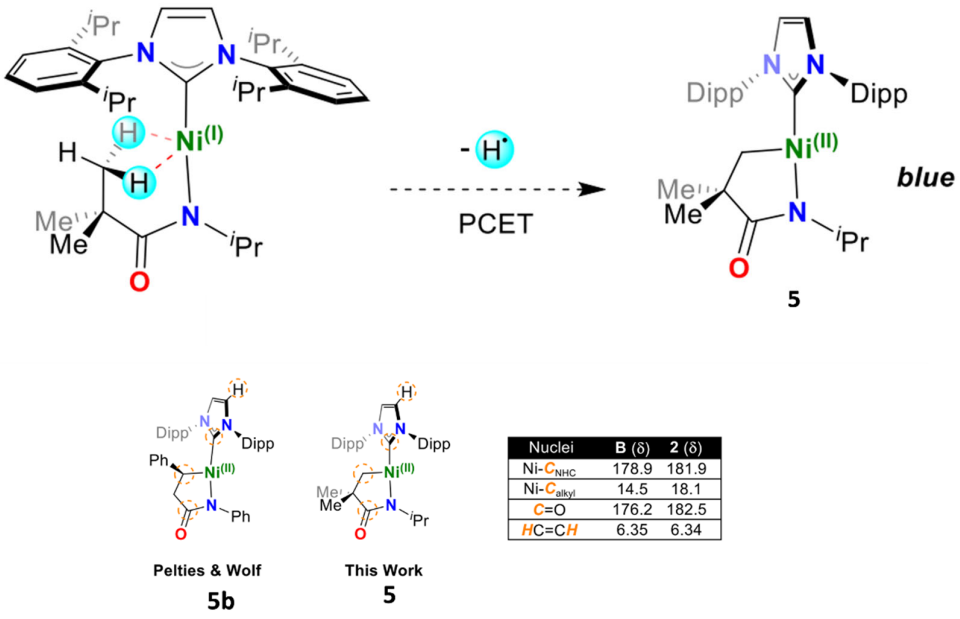
Supplementary Table 30. The information of the crystal 3 and 4.

5. Attempts Towards C-H Activation of Complex 1



Supplementary Figure 26. C-H bond dissociation calculation of non-nickel interacting amide and the agostic contacting C-H bond in complex 1 and 3. Theory Level: M06-2X/def2-TZVP//D3zero//smd-toluene.

We envisioned a PCET (formal H atom abstraction) from one of the agostic C-H interactions by a bulky radical reagent to afford the cyclometallated species **complex 5**. The 1H NMR spectrum of **complex 5** suggests free rotation of the Ni-CNHC bond as evident by only two distinct NHC methyl groups and a single methine resonance. Complex 5 decomposes slowly in both solution or solid-state to afford an insoluble green-blue solid. We speculate that the unsaturated nature of Complex 5 may make it susceptible to oligomerization. The crystal structure of the blue solid **complex 5,** therefore, cannot be obtained due to polymerization. The chemical shift for the Ni-alkyl (C***H***2) is shifted considerably downfield in **complex 5** δ 1.07; Notably, Pelties and Wolf recently reported complex **5b**[5], very structurally similar to **complex 5**, which shows comparable chemical shifts to complex 5. Based on these comparisons we are confident in our assignment of monomolecular complex **5** based on NMR spectroscopy, in lieu of a solid-state molecular structure.

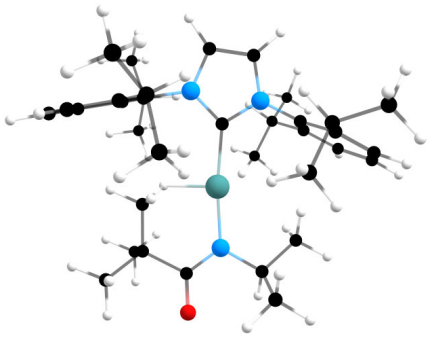


Nuclei	B (δ)	2 (δ)
Ni-C_{NHC}	178.9	181.9
Ni-C_{alkyl}	14.5	18.1
C=O	176.2	182.5
HC=CH	6.35	6.34

Supplementary Figure 27. Proposed synthesis of Ni(II)-3.12B via C-H activation by PCET from complex 5, and comparing chemical shifts of selected peaks in 1H and 13C NMR spectra of complex 5b(refs) and Complex 5.

Appendix – Calculation Coordinates

Complex 1

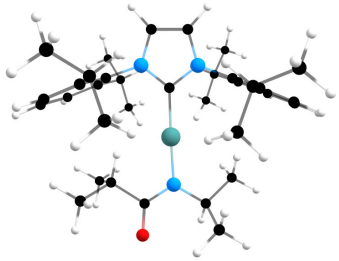


UKS PBE0 D3BJ def2-SVP def2/J RIJCOSX
newgto Ni def2-TZVP

Ni	3.727164	9.195253	13.992052	C	3.048276	5.077815	13.820574
O	7.277636	11.133025	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	-0.846913	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
H	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	8.787508	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	8.861713	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
H	-1.958639	12.098995	14.072418	H	6.011331	7.403608	16.964729
H	-1.974355	10.966329	12.692976	H	4.701467	7.442816	15.77185
C	2.005736	6.793992	15.391957	C	7.222318	7.966058	14.542647
C	1.797763	7.374149	16.652943	H	6.63708	7.314907	13.874752
C	2.399108	6.758125	17.754453	H	7.853659	7.32789	15.183626
H	2.271087	7.191711	18.748832	H	7.881541	8.594237	13.926362
C	3.16978	5.611918	17.59771	H	4.111212	10.256428	12.182393
H	3.644965	5.149678	18.466247	H	3.28743	11.08291	13.584987
C	3.353389	5.055277	16.335976	H	3.460204	11.883889	12.036857
H	3.971307	4.162518	16.226741	H	4.018704	8.216369	11.41333
C	2.774508	5.633234	15.203337	H	0.7	7.828949	8.634235

Complex 2

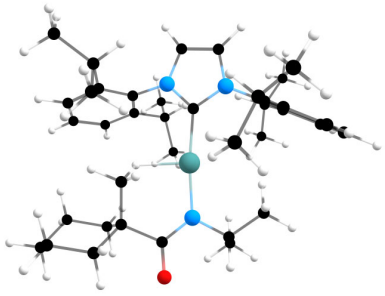


UKS PBE0 D3BJ def2-SVP def2/J RIJCOSX
newgto Ni def2-TZVP

Ni	3.690679	9.16424	14.067807	C	3.274872	5.173653	13.9291
O	7.109055	11.163317	13.724263	H	2.505998	5.484733	13.204303
N	5.428067	9.771155	14.432316	C	3.366929	3.650834	13.894492
N	1.064325	8.837973	12.745623	H	4.171245	3.278598	14.546695
N	1.397654	7.378369	14.271233	H	3.60323	3.305449	12.876464
C	1.982772	8.450174	13.669492	H	2.42877	3.175425	14.218982
C	-0.07221	8.049643	12.786859	C	4.597966	5.810382	13.498654
H	-0.915966	8.220989	12.124929	H	4.528113	6.910574	13.472513
C	0.138763	7.123686	13.758239	H	4.894475	5.466277	12.495519
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
H	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	10.428375	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
C	1.934373	8.091287	8.722163	H	4.138897	12.793526	13.989536
H	2.201068	7.058245	8.450696	H	3.998126	13.236058	12.2674
H	2.484317	8.753891	8.037205	C	5.644889	11.293869	11.237461
C	0.291978	11.448153	13.725956	H	5.891183	10.266259	10.931331
H	0.153061	10.459903	14.188685	H	6.586998	11.860925	11.269658
C	1.223232	12.242113	14.640449	H	4.981587	11.737032	10.478305
H	2.184338	11.721213	14.771188	C	6.297482	9.191487	15.442907
H	0.767909	12.373538	15.633767	H	6.863346	10.009772	15.926663
H	1.437276	13.241616	14.231412	C	5.441156	8.48441	16.483152
C	-1.088828	12.091351	13.6129	H	4.776826	9.193281	17.000662
H	-1.040206	13.088302	13.146676	H	6.054098	7.972556	17.240813
H	-1.540684	12.211001	14.609923	H	4.807343	7.714297	16.007375
H	-1.767259	11.476114	13.003339	C	7.320522	8.251074	14.811179
C	1.960924	6.766445	15.431769	H	6.808526	7.447867	14.259159
C	1.615894	7.3138	16.678382	H	7.974132	7.790367	15.570012
C	2.186224	6.738772	17.817315	H	7.944998	8.81882	14.107355
H	1.940383	7.143998	18.801992	H	4.05785	10.735133	12.584088
C	3.072875	5.672171	17.708117	H	4.049395	8.311755	11.486274
H	3.520287	5.237791	18.605525	H	0.859157	8.232179	8.533612
C	3.407082	5.15958	16.458538				
H	4.113991	4.330679	16.387803				
C	2.857536	5.69461	15.289721				

Complex 3



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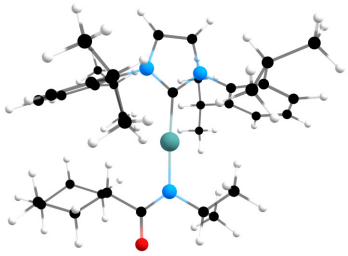
newgto Ni def2-TZVP

Ni	3.421346	11.730938	15.321682	H	1.902363	9.531025	17.83243
O	1.233	15.139252	15.725736	H	1.354945	7.840258	17.720681
N	5.147348	9.368427	15.670737	H	2.056365	8.438351	19.235497
N	4.276215	9.355061	13.715053	C	0.522941	13.708932	13.24463
N	2.511318	13.265513	16.004271	H	0.274301	12.684804	13.57338
C	5.38889	9.6879	17.04335	H	-0.171699	14.387663	13.765593
C	4.32319	10.095646	14.863808	C	0.960475	13.020045	17.897575

C	5.029969	8.19884	13.817708	H	0.816505	11.940404	17.719865
H	5.0961	7.480126	13.006056	H	0.809589	13.224642	18.970304
C	1.877913	14.194095	15.263299	H	0.202488	13.578926	17.333088
C	3.383767	9.647453	12.636888	C	3.450037	12.735337	18.194804
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	17.647959	H	3.415592	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	11.457984	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	9.800697
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	19.23353
H	4.266684	8.879867	20.14355	H	3.06475	5.932131	17.765777
C	6.577981	10.924835	18.713833	H	4.806755	6.294261	17.784462
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 4



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

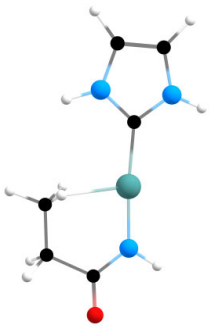
Ni	5.211446	14.467763	5.093242	C	6.333001	14.161152	2.446539
O	6.86513	14.525438	1.395932	C	5.943511	12.686254	2.571654
N	6.046977	14.969117	3.484282	H	5.58645	12.459754	3.599623
N	4.247448	12.847108	7.333257	C	4.810088	12.415853	1.576613
N	3.692253	14.896849	7.582335	H	5.129486	12.843341	0.611029
C	4.349013	14.061421	6.733738	H	3.910682	12.974588	1.884537
C	3.547649	12.918012	8.524708	C	4.508813	10.934633	1.397331
H	3.357389	12.041876	9.137355	H	4.146669	10.503153	2.349096
C	3.19389	14.219736	8.682622	H	3.698325	10.791743	0.66349
H	2.630881	14.723819	9.463608	C	5.762092	10.184305	0.968393
C	4.676482	11.648681	6.686996	H	5.539438	9.116862	0.802328
C	3.743409	10.972794	5.882016	H	6.112862	10.587216	0.000857
C	4.172975	9.812559	5.234606	C	6.861247	10.357509	2.00859
H	3.47792	9.263065	4.596232	H	7.776361	9.832001	1.688021
C	5.48274	9.362464	5.37321	H	6.537391	9.88009	2.949881
H	5.804162	8.457125	4.852966	C	7.171981	11.828537	2.253467
C	6.391328	10.068869	6.153324	H	7.625718	12.269492	1.350875
H	7.422022	9.715487	6.231037	H	7.914255	11.941105	3.061289
C	6.008029	11.230251	6.830539	C	6.424601	16.364136	3.293426
C	2.362604	11.54429	5.629402	H	7.369051	16.383959	2.721831
H	2.152921	12.290973	6.410881	C	6.643296	17.025002	4.645008
C	1.247051	10.507363	5.68717	H	5.703374	17.054398	5.230311
H	1.347219	9.752869	4.891668	H	6.983775	18.066698	4.532862
H	0.275999	11.00651	5.540965	H	7.395664	16.477347	5.232536
H	1.224922	9.977533	6.651539	C	5.384856	17.11135	2.464611
C	2.360459	12.270872	4.283883	H	5.208454	16.573848	1.522974
H	3.113302	13.075705	4.25987	H	5.725292	18.130516	2.217023
H	1.375522	12.719815	4.08137	H	4.432183	17.190038	3.01606
H	2.59397	11.575097	3.464569	C	1.351368	16.002889	4.188804
C	3.49759	16.284885	7.309081	H	2.248447	16.263878	3.608477
C	2.547022	16.648134	6.337173	H	0.654375	16.854907	4.150339
C	3.114402	18.962136	6.789865	H	0.854888	15.162203	3.681791
H	2.956507	20.023496	6.582868	C	7.013127	12.033281	7.628169
C	4.050138	18.571888	7.745567	H	6.451206	12.77898	8.211726
H	4.618781	19.33187	8.283339	C	7.945114	12.795065	6.683371
C	4.270068	17.219956	8.021698	H	8.53833	12.103184	6.064185

C	5.318213	16.754019	9.018367	H	8.642925	13.429331	7.251898
H	4.894644	15.887624	9.551661	H	7.374436	13.446303	5.9986
C	5.669581	17.796879	10.071972	C	7.789868	11.16945	8.619177
H	6.217321	18.64559	9.632774	H	7.112807	10.618315	9.290115
H	6.324671	17.348159	10.834296	H	8.44919	11.797762	9.238399
H	4.777466	18.194188	10.580272	H	8.426747	10.433725	8.104318
C	6.587031	16.271672	8.305298	C	0.458132	15.253185	6.426085
H	6.371865	15.506774	7.545003	H	-0.128487	14.478077	5.908359
H	7.293854	15.839606	9.030436	H	-0.188753	16.135263	6.555248
H	7.08619	17.110964	7.797602	H	0.709494	14.868779	7.426318
C	1.709833	15.606617	5.617387	C	2.376926	18.013474	6.090531
H	2.326956	14.700291	5.5432	H	1.65171	18.337685	5.34243

Complex 1*

UKS PBE0 D3BJ def2-SVP def2/J RIJCOSX

newgto Ni def2-TZVP



O	7.450600555	11.08700078	14.48790103	N	1.290800092	8.788000642	12.91580094
N	5.659100401	9.664400718	14.63760104	N	1.561400112	7.347500529	14.44130105
C	6.307200447	10.75800075	14.19120103	C	2.195200159	8.393900595	13.85000098
C	5.520800403	11.65210085	13.22550097	C	0.14140001	8.02600059	12.92540096
C	4.092500292	11.24220079	12.91880095	H	-0.694200052	8.205400568	12.2553009
H	6.280800429	9.147200655	15.25650109	C	0.315200022	7.100100534	13.90370099
H	4.064200295	10.24980072	12.41680087	H	-0.335600024	6.305700441	14.25720102
H	3.478500248	11.20670083	13.84290101	H	1.466300107	9.564800669	12.29250089
H	3.583100259	11.94160087	12.23720086	H	1.97840014	6.820000507	15.19590109
H	6.115100427	11.70690086	12.29930087	Ni	3.92060028	9.108000633	14.20870103
H	5.549700413	12.6659009	13.65510098				

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