Carbene Formation and Transfer at a Dinickel Active Site

Arnab K. Maity, Matthias Zeller, and Christopher Uyeda

Department of Chemistry, Purdue University, West Lafayette, IN 47907, United States

Correspondence: cuyeda@purdue.edu

Supporting Information

1. General Information

Physical Methods. ^{1}H and ^{13}C{^{1}H} NMR spectra were collected at room temperature on a Bruker AV-111-400-HD, Bruker DRX 500-2 , Varian INOVA600, and Bruker Avance-III-800 NMR spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra are reported in parts per million relative to tetramethylsilane, using the residual solvent resonances as an internal standard. ATR-IR data were collected on a Thermo Nicolet Nexus spectrometer containing a MCT* detector and KBr beam splitter with a range of 350–7400 cm^{-1}. UV-vis measurements were acquired on a Cary 100 UV/vis spectrophotometer or Perkin Elmer Lambda 950 UV-VIS-NIR spectrophotometer using a 1-cm two-window quartz cuvette. Electrochemical measurements were performed using a Pine WaveNow Potentiostat. Cyclic voltammograms were acquired using glassy carbon working electrode (3 mm diameter disk) under an atmosphere of N2. The potentials were internally referenced to the reversible $Cp_2Fe/[Cp_2Fe]^+$ couple.

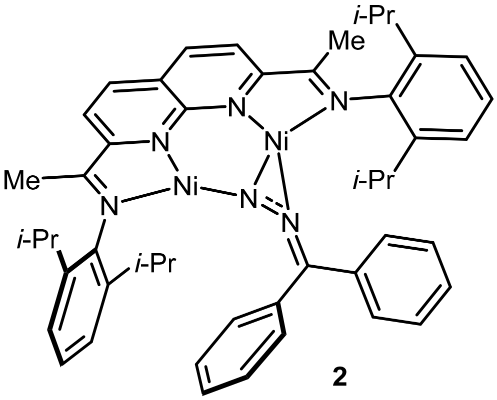
Single X-Ray Crystallography. Single crystal X-ray measurements for Complex **2** and **3** were conducted on a Rigaku Rapid II curved image plate diffractometer with a Cu-Kα X-ray microsource (λ = 1.54178 Å) with a laterally graded multilayer mirror for monochromatization. Single crystals were mounted on Mitegen micromesh mounts using a trace of mineral oil and cooled in-situ to 100 K for data collection. Data were collected using the dtrek option of CrystalClear-SM Expert 2.1 b32.[1] Data were processed using HKL3000 and data were corrected for absorption and scaled using Scalepack.[2]

Single crystals for Complex **4**, **5** and **6** compounds were coated with mineral oil and quickly transferred to the goniometer head of a Bruker Quest diffractometer with a fixed chi angle, a sealed tube fine focus X-ray tube, single crystal curved graphite incident beam monochromator, a Photon100 CMOS area detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Mo Kα radiation (λ = 0.71073 Å) at 100 or 150 K. Data were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX3[3] and Sadabs or Twinabs[4].

For all crystals, the space groups were assigned and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs[5] and refined by full matrix least squares against F2 with all reflections using Shelxl2016[6] using the graphical interface Shelxle[7]. If not specified otherwise H atoms attached to carbon and nitrogen atoms and hydroxyl hydrogens were positioned geometrically and constrained to ride on their parent atoms, with carbon hydrogen bond distances of 0.95 Å for and aromatic C-H, 1.00, 0.99 and 0.98 Å for aliphatic C-H, CH2 and CH3 moieties, respectively. Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. Uiso(H) values were set to a multiple of Ueq(C) with 1.5 for CH3, and 1.2 for C-H units, respectively. Additional data collection and refinement details, including description of disorder (where present) can be found in the sections below.

Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1839064–1839068 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2. Characterization of Complexes



2

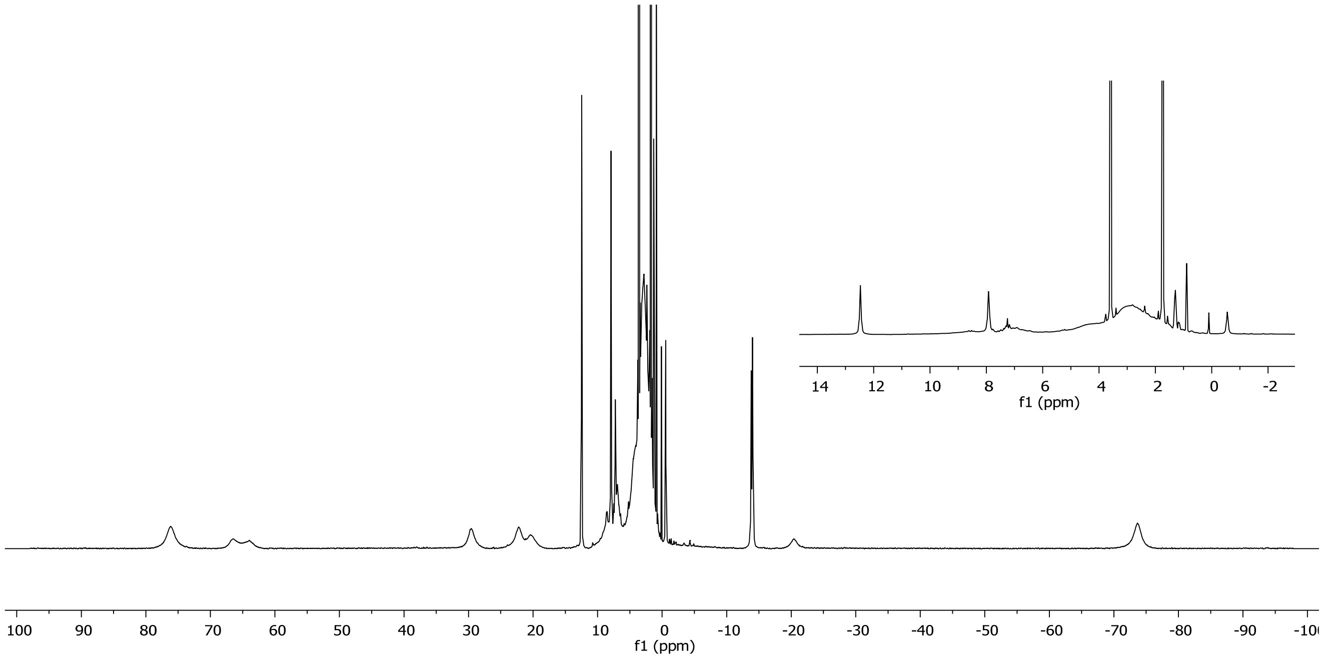


Figure S1. ^{1}H NMR spectrum for complex **2** (THF-d_8, room temperature).

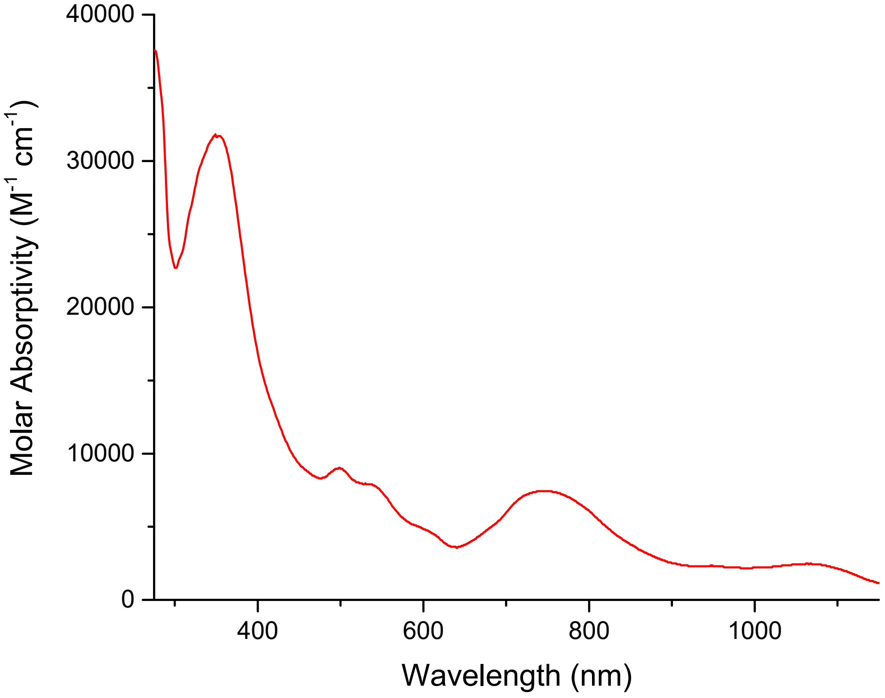


Figure S2. UV-Vis spectrum for complex **2** (THF, room temperature).

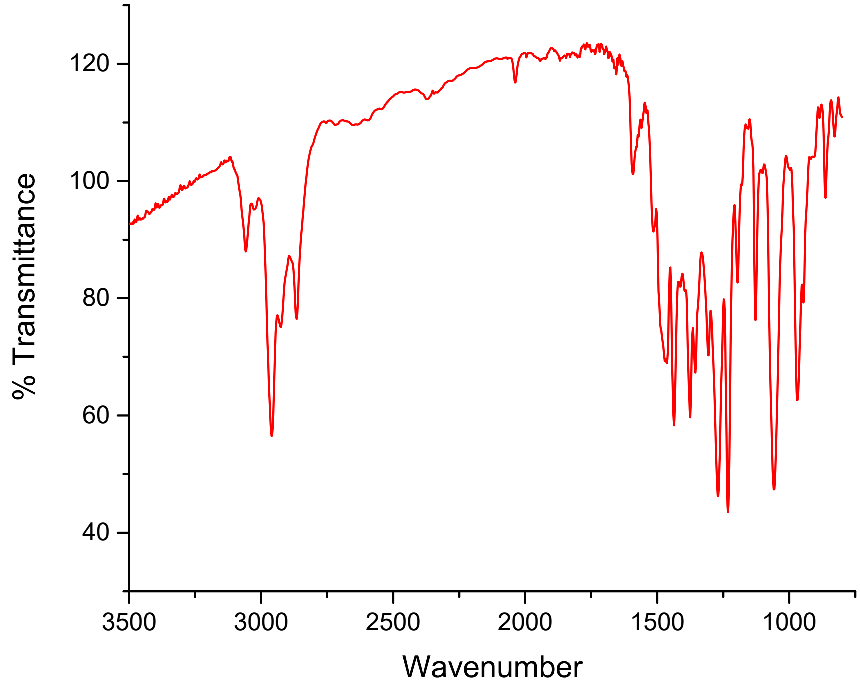
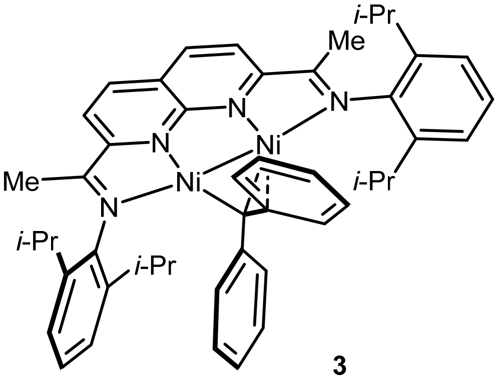


Figure S3. ATR-IR spectrum for complex **2**.



3

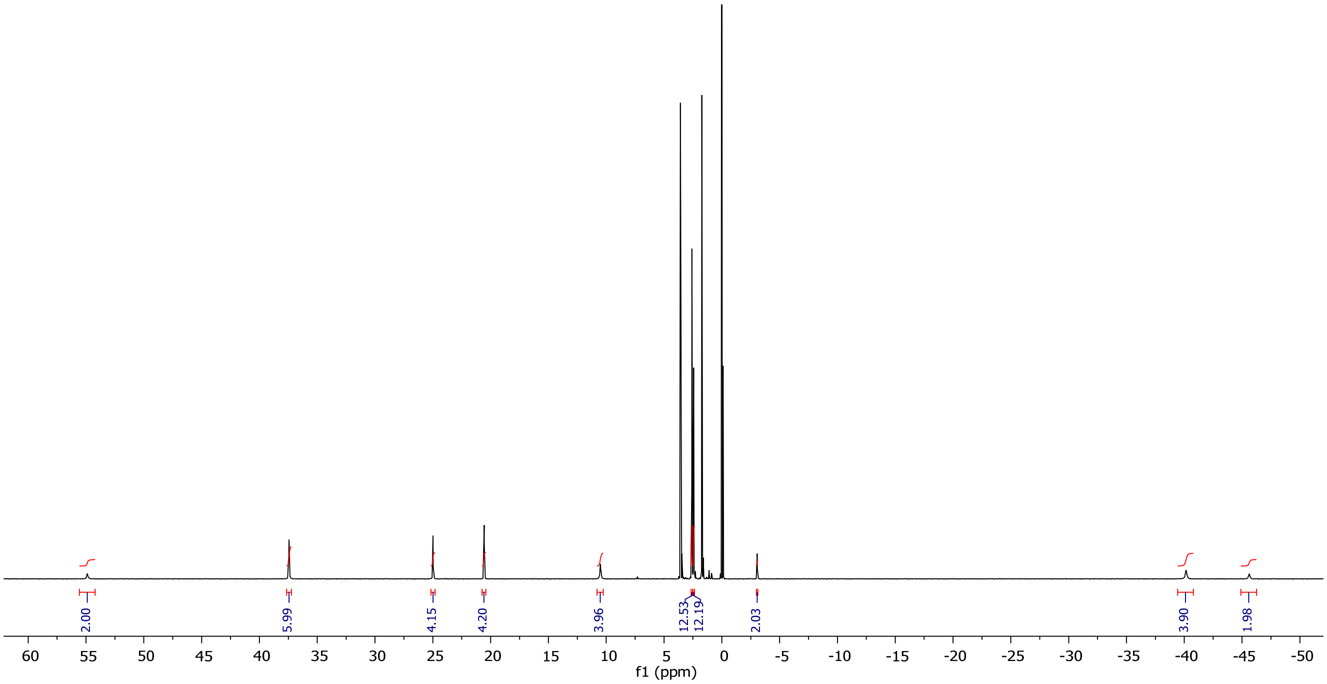


Figure S4. ^{1}H NMR spectrum for complex **3** (THF-d_8, room temperature).

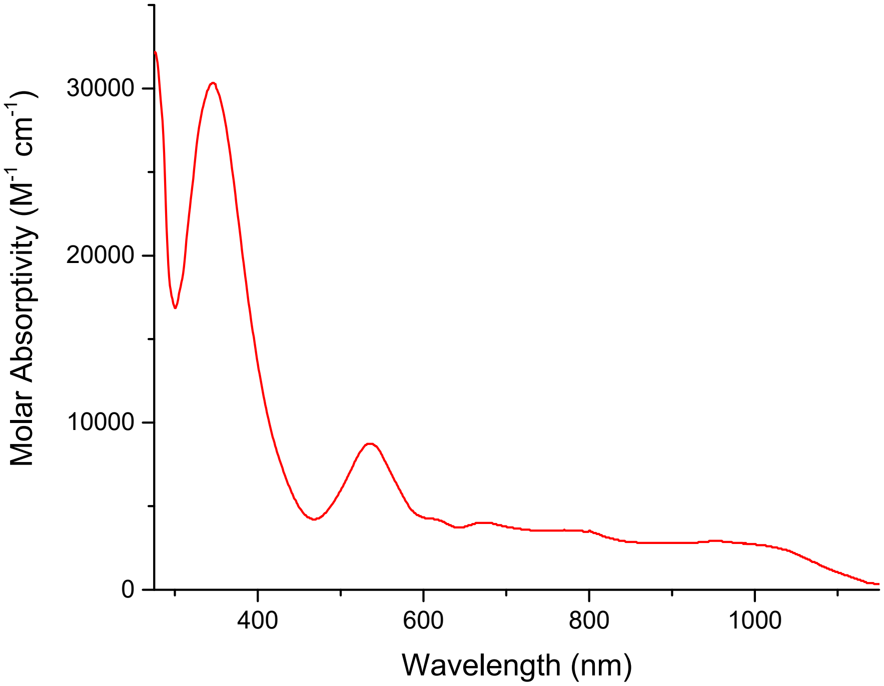
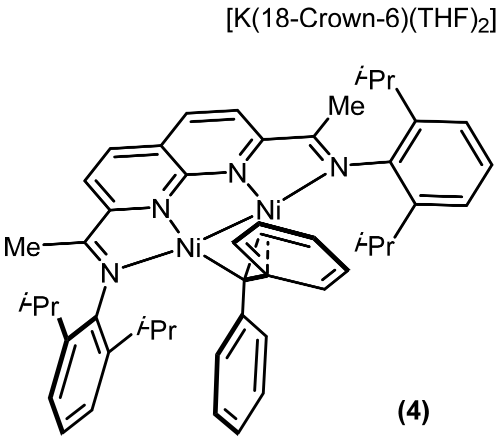


Figure S5. UV-Vis spectrum for complex **3** (THF, room temperature).



(4)

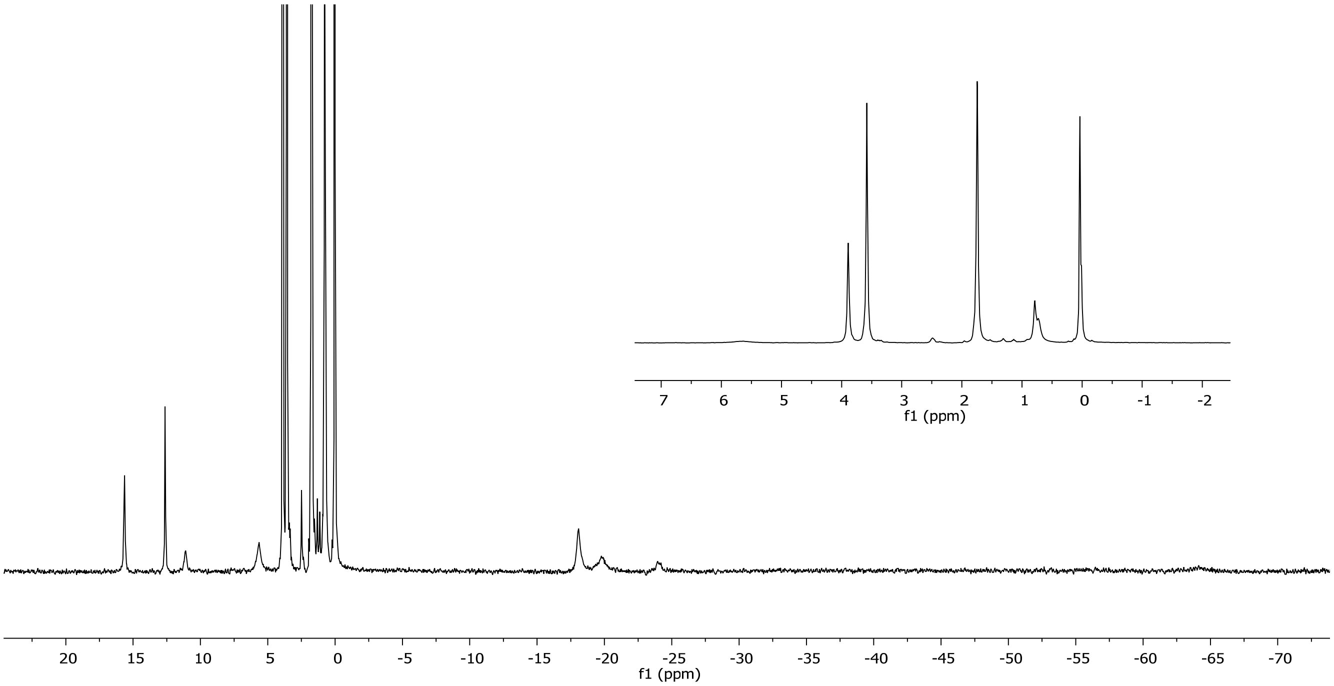


Figure S6. ^{1}H NMR spectrum for complex **4** (THF-d_8, room temperature).

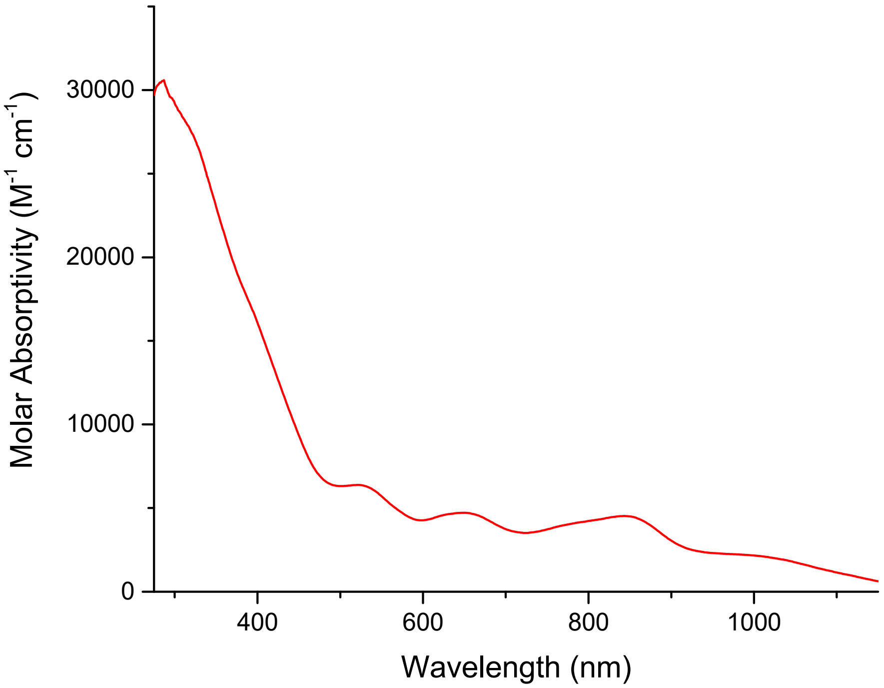
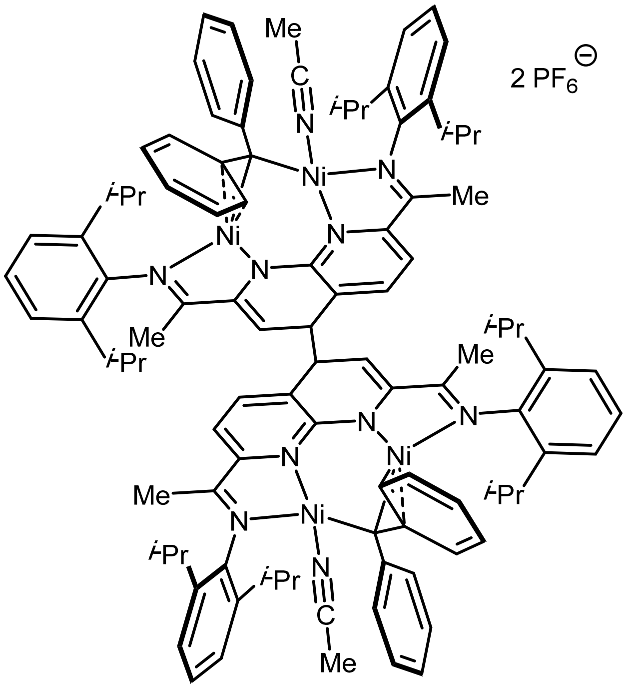


Figure S7. UV-Vis spectrum for complex **4** (THF, room temperature).



(5)

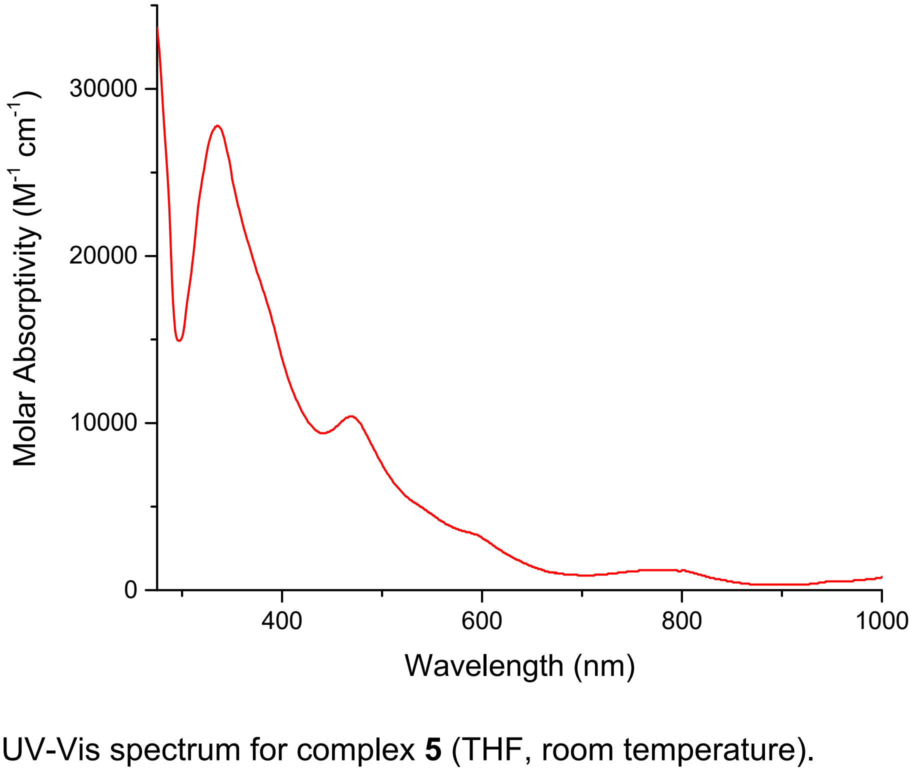
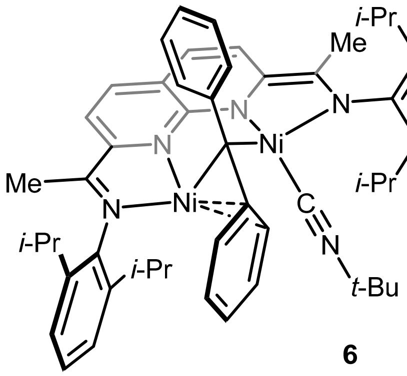


Figure S8. UV-Vis spectrum for complex **5** (THF, room temperature).



6

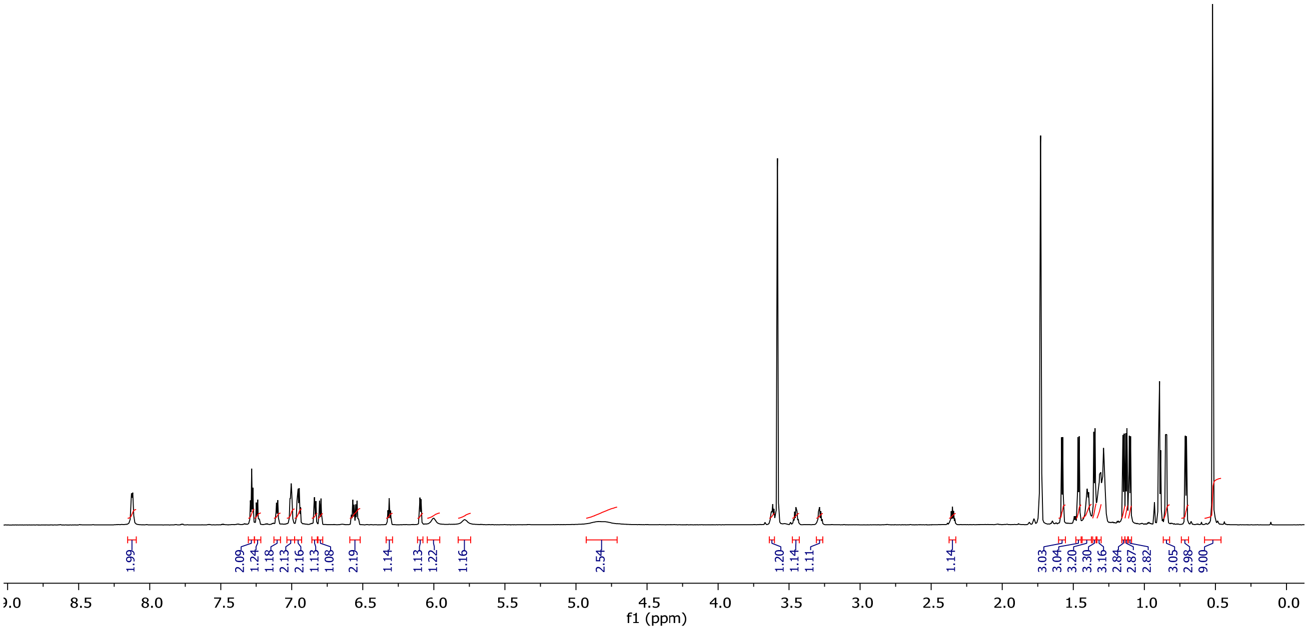


Figure S9. ^{1}H NMR spectrum for complex **6** (THF-d_8, room temperature)

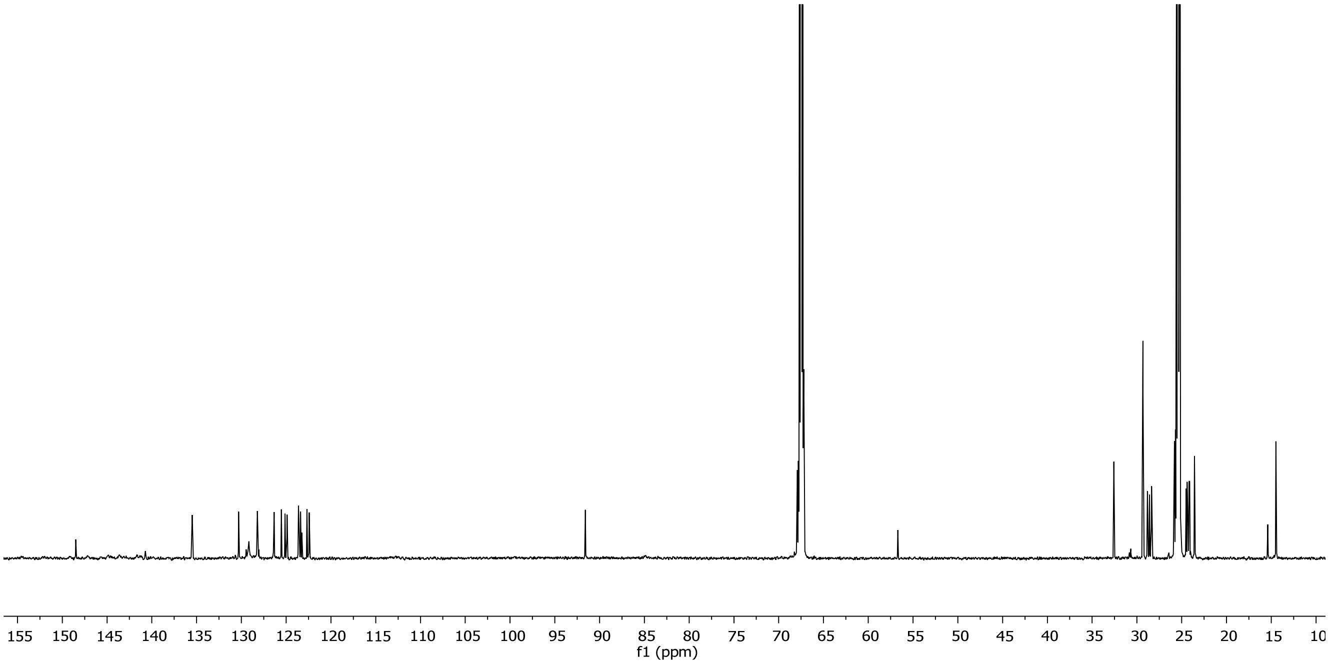


Figure S10. ^{13}C NMR spectrum for complex **6** (THF-d_8, room temperature)

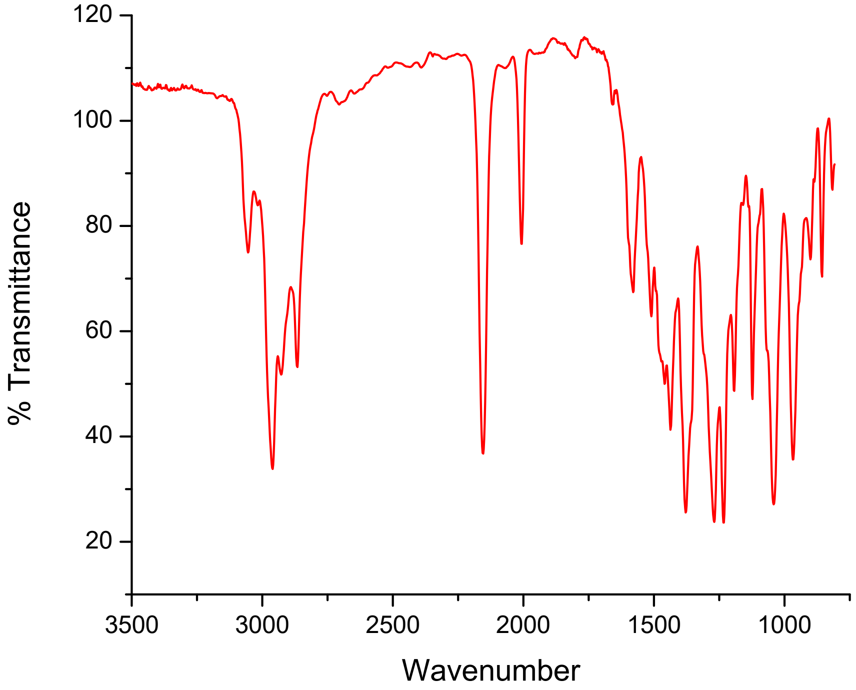


Figure S11. ATR-IR spectrum for complex **6**

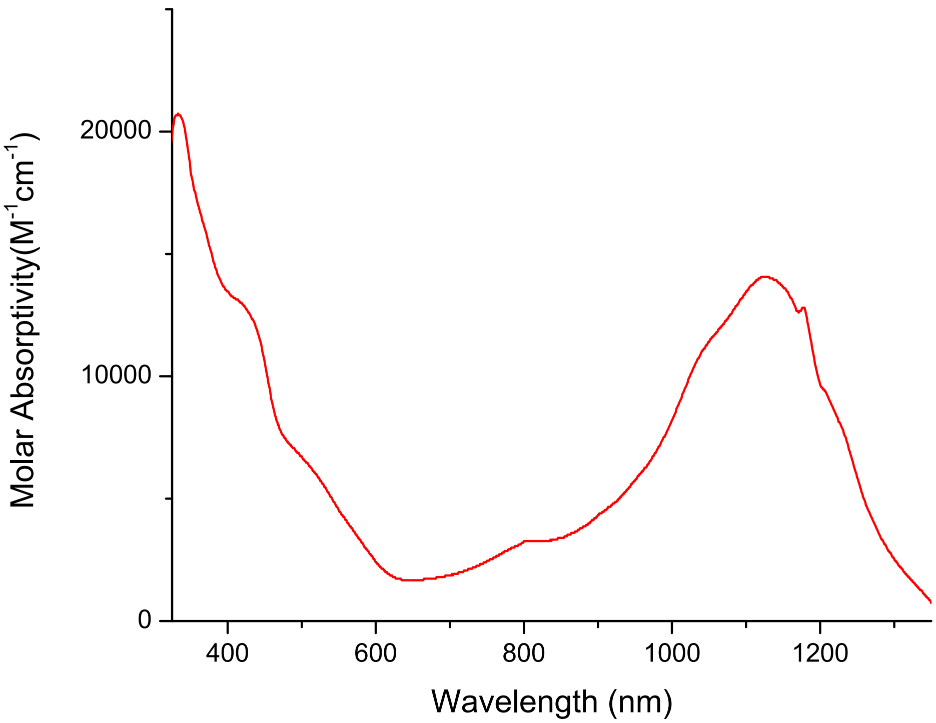


Figure S12. UV-Vis spectrum for complex **6** (THF, room temperature)

3. XRD Data

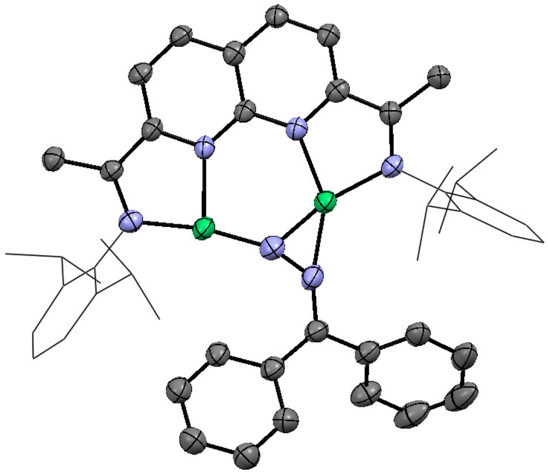


Figure S13. Crystal structure ORTEP diagram of complex **2**. Ellipsoids are shown at 30% probability level.

Table S1. Crystal, Data Collection and Refinement Parameters for Complex **2**

Crystal data	
Chemical formula	$C_{49}H_{54}N_6Ni_2$
M_r	844.40
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	19.4742 (15), 9.1303 (6), 23.6598 (17)
β (°)	103.812 (5)
V (Å^3)	4085.2 (5)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	1.47
Crystal size (mm)	0.21 × 0.11 × 0.03
Data collection	
Diffractometer	Rigaku Rapid II curved image plate
Absorption correction	Multi-scan
T_{min}, T_{max}	0.694, 0.957
No. of measured, independent and	55325, 7579, 4414
R_{int}	0.126
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.079, 0.233, 1.08
No. of reflections	7579

No. of parameters	525
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.54, −0.61

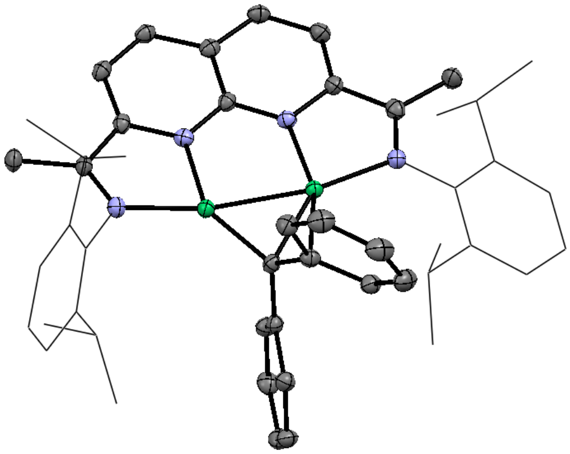


Figure S14. Crystal structure ORTEP diagram of complex **3**. Ellipsoids are shown at 30% probability level.

Table S2. Crystal, Data Collection and Refinement Parameters for Complex **3**

Crystal data	
Chemical formula	$C_{49}H_{54}N_4Ni_2$
M_r	816.38
Crystal system, space group	Orthorhombic, *Pca*2$_1$
Temperature (K)	100
a, *b*, *c* (Å)	11.4269 (1), 14.2146 (1), 51.4699 (3)
V (Å^3)	8360.19 (11)
Z	8
Radiation type	Cu *K*α
μ (mm^{-1})	1.40
Crystal size (mm)	0.25 × 0.21 × 0.15
Data collection	
Diffractometer	Rigaku Rapid II curved image plate
Absorption correction	Multi-scan
T_{min}, T_{max}	0.474, 0.817
No. of measured, independent and	50429, 15118, 14582
R_{int}	0.059
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.120, 1.09
No. of reflections	15118
No. of parameters	1011
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.55, −0.55

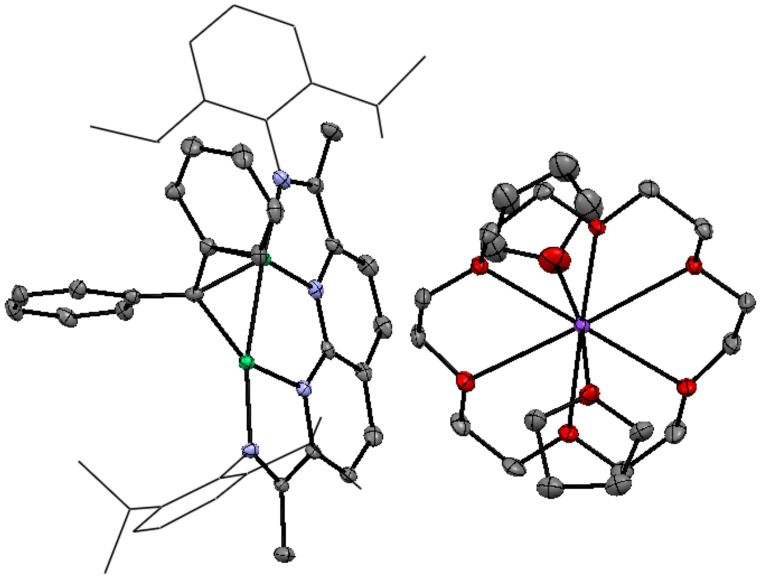


Figure S15. Crystal structure ORTEP diagram of complex **4**. Ellipsoids are shown at 30% probability level.

Table S3. Crystal, Data Collection and Refinement Parameters for Complex **4**

Crystal data	
Chemical formula	$C_{49}H_{54}N_4Ni_2 \cdot C_{20}H_{40}KO_8 \cdot 1.532(C_4H_8O)$
M_r	1374.43
Crystal system, space	Orthorhombic, $Pna2_1$
Temperature (K)	100
a, *b*, *c* (Å)	22.1000 (13), 16.7571 (10), 19.9304 (11)
V (Å^3)	7380.9 (7)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.62
Crystal size (mm)	0.66 × 0.16 × 0.10
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS
Absorption correction	Multi-scan
T_{min}, T_{max}	0.579, 0.746
No. of measured,	129846, 18380, 14810
R_{int}	0.075
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.670
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.056, 0.124, 1.13
No. of reflections	18380
No. of parameters	1021

No. of restraints	845
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + 15.8447P]$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.81, −0.54

A THF molecule is partially occupied and several are disordered in response. The THF molecule of O9 is disordered over two orientations, and the sum of the moieties refines to only about 50%. In response two neighboring THF molecules, one potassium coordinated and one interstitial, show whole molecule disorder with one moiety each being moved slightly towards the void left by the absent THF molecule, and the other moiety moved the opposite way. The second potassium coordinated THF molecule also shows disorder, but limited to mostly just one methylene group.

All THF moieties were restrained to have similar geometries. U_{ij} components of all disordered atoms were restrained to be similar for atoms closer to each other than 1.7 Å. Occupancies refined to roughly complimentary values for neighboring THF molecules, but no attempts were made to constrain occupancies between neighboring THF molecules. Subject to these conditions the occupancy ratios refined to 0.599(16) to 0.401(16) for the molecule of O7, to 0.520(14) to 0.480)14) for that of O8, to 0.422(15) to 0.110(12) for that of O9 (total occupancy 0.533, and to 0.761(9) to 0.239(9) for that of O10

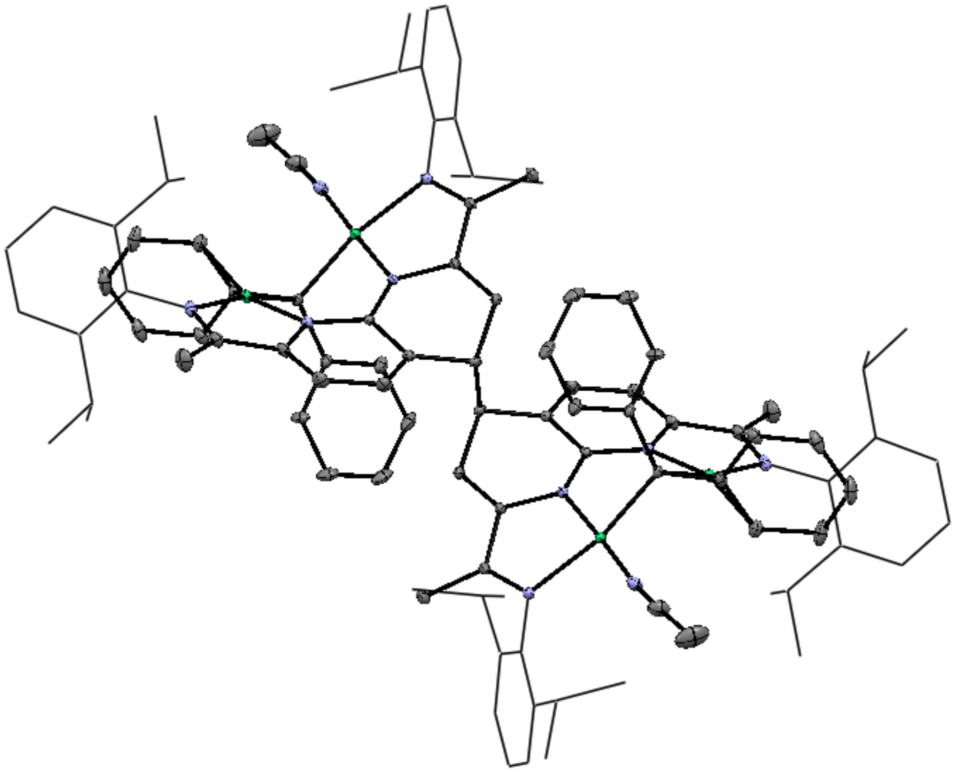


Figure S16. Crystal structure ORTEP diagram of complex **5**. Ellipsoids are shown at 30% probability level. Hexafluorophosphate and dimethoxyethane molecules are omitted for clarity.

Table S4. Crystal, Data Collection and Refinement Parameters for Complex **5**

Crystal data	
Chemical formula	$C_{102}H_{114}N_{10}Ni_4 \cdot 2(F_6P) \cdot 2.698(C_4H_{10}O_2)$
M_r	2247.90
Crystal system, space	Triclinic, *P*1
Temperature (K)	100
a, *b*, *c* (Å)	12.8603 (5), 15.1836 (7), 15.5346 (7)
α, β, γ (°)	108.6498 (15), 100.3676 (16), 100.8468 (15)
V (Å^3)	2727.1 (2)
Z	1
Radiation type	Mo *K*α
μ (mm^{-1})	0.79
Crystal size (mm)	0.45 × 0.26 × 0.07
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS
Absorption correction	Multi-scan
T_{min}, T_{max}	0.638, 0.747
No. of measured,	88813, 26363, 19711
R_{int}	0.036

$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.835
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.064, 0.149, 1.09
No. of reflections	26363
No. of parameters	1173
No. of restraints	1813
H-atom treatment	H atoms treated by a mixture of independent and constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.09, −1.17

Hexafluoro phosphate anions and dimethoxy ethylene solvate molecules are extensively disordered with each other. The disorder extends to parts of the cation's ligands. Three partially occupied PF_6 anions were located and refined embedded in disordered solvate molecules. The solvate molecules were tentatively refined as extensively disordered dimethoxy ethylene, but admixture of some disordered pentane cannot be positively excluded. Of the PF_6 molecules, one (the least occupied) is located on an inversion center. The others in general positions. The two major moiety PF_6 were refined to have similar geometries. The minor one had its P-F and F...F distances restrained to be each similar. Some DME molecules extend towards the next set of PF_6/DME units and are mutually exclusive. Each two DME moieties are disordered with every PF_6 anion, thus leading to six DME moieties. Of the DME molecules, one is located on an inversion center, another slightly offset an inversion center 1:1 disordered.

Geometries of all DME molecules were restrained to be similar. Occupancies were constrained to unity for the cluster around the inversion center, but not restrained for the other two sites. Total occupancies for these sites refined to around 90%, indicating some possible admixture of lighter pentane, but this was ignored in the refinement model. The total occupancy for the PF_6 anions was constrained to unity. Disorder extends to one phenyl ring in the proximity of the solvate region, and one diisopropyl benzene unit. They were refined as two fold disordered, ignoring correlation with the three fold disordered PF_6/DME units, and occupancy ratios were refined independently. For all disordered moieties, U^{ij} components of ADPs were restrained to be similar for atoms closer to each other than 1.7 Å. For the least occupied PF_6 anion atoms were also restrained to be close to isotropic. The two ipso C atoms of the diisopropyl benzene unit were constrained to be identical. Subject to these conditions occupancies refined to the values given in the atom coordinate table, below.

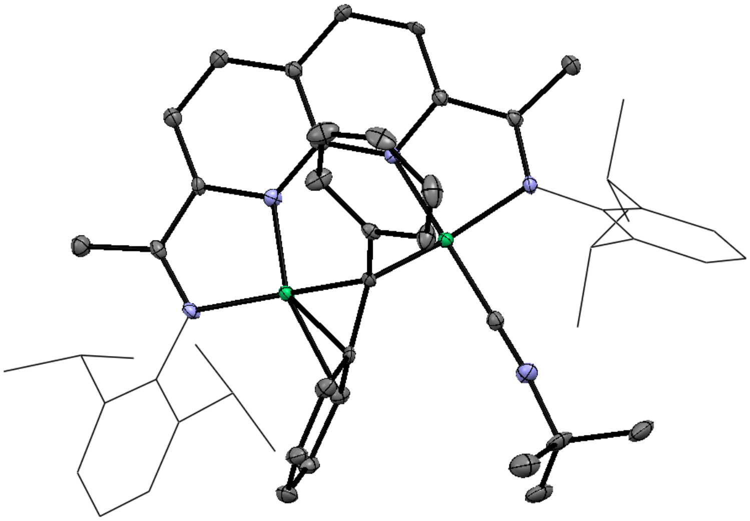


Figure S17. Crystal structure ORTEP diagram of complex **6**. Ellipsoids are shown at 30% probability level.

Table S5. Crystal, Data Collection and Refinement Parameters for Complex **6**

Crystal data	
Chemical formula	$C_{54}H_{63}N_5Ni_2 \cdot C_4H_{10}O$
M_r	973.63
Crystal system, space	Triclinic, *P*1
Temperature (K)	150
a, *b*, *c* (Å)	15.5210 (18), 19.523 (3), 19.994 (3)
α, β, γ (°)	64.063 (4), 75.841 (4), 88.178 (4)
V ($Å^3$)	5263.1 (12)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.76
Crystal size (mm)	0.51 × 0.20 × 0.06
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS
Absorption correction	Multi-scan
T_{min}, T_{max}	0.595, 0.746
No. of measured,	161760, 31409, 25284
R_{int}	0.079
$(\sin \theta/\lambda)_{max}$ ($Å^{-1}$)	0.641
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.067, 0.214, 1.12
No. of reflections	31409
No. of parameters	1415
No. of restraints	600

H-atom treatment	H atoms treated by a mixture of independent and constrained
	$w = 1/[\sigma^2(F_o^2) + (0.1036P)^2 + 16.7076P]$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.73, −0.77

The crystal under investigation was found to be non-merohedrally twinned. The orientation matrices for the two components were identified using the program Cell_Now, with the two components being related by a 180 degree rotation around the real a-axis. The two components were integrated using Saint and corrected for absorption using twinabs, resulting in the following statistics:

30885 data (6838 unique) involve domain 1 only, mean I/sigma 29.8

30987 data (6850 unique) involve domain 2 only, mean I/sigma 21.8

103710 data (19305 unique) involve 2 domains, mean I/sigma 30.6

205 data (164 unique) involve 3 domains, mean I/sigma 37.3

20 data (20 unique) involve 4 domains, mean I/sigma 94.7

6 data (6 unique) involve 6 domains, mean I/sigma 62.9

4 data (4 unique) involve 8 domains, mean I/sigma 64.9

The exact twin matrix identified by the integration program was found to be:

1.00182 -0.00733 -0.00518

0.06001 -1.00016 -0.00029

0.61895 -0.00213 -1.00166

The structure was solved using direct methods with only the non-overlapping reflections of component 1. The structure was refined using the hklf 5 routine with all reflections of component 1 (including the overlapping ones), resulting in a BASF value of 0.356(9).

The R_{int} value given is for all reflections and is based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twin fractions (TWINABS (Krause et al., 2015)).

Two ether molecules two tert-butyl groups and one isopropyl group were refined as disordered with each two alternative orientations. For all disordered sections chemically equivalent moieties were restrained to have similar geometries, and U^{ij} components of ADPs were restrained to be similar for atoms closer to each other than 1.7 Å. Subject to these conditions the occupancy ratios refined to 0.695(12) to 0.305(12) and 0.687(10) to 0.313(10) for the ether molecules. To 0.62(4) to 0.38(4) for the isopropyl group, and to 0.822(14) to 0.178(14) and 0.70(4) to 0.30(4) for the tert butyl groups. The H atom positions of H39A and H39B, bonded to Ni coordinated carbon atoms, were refined. C-H distances were restrained to 0.95(2) Å.

4. References

(1) Rigaku Corp., **2011**, The Woodlands, Texas, USA

(2) Otwinowski, Z.; Minor, W. Processing of X-ray diffraction data collected in oscillation mode. *Methods Enzymol.* **1997**, *276*, 307–326.

(3) Apex3 v2016.9-0, Saint V8.34A, *SAINT* V8.37A, Bruker AXS Inc.: Madison (WI), USA, **2013**–**2014**.

(4) Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. *J. Appl. Cryst.* **2015**, *48*, 3–10.

(5) (a) SHELXTL suite of programs, Version 6.14, **2003**, Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin: USA) (b) Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr A.* **2008**, *64*, 112–122.

(6) (a) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr Sect C Struct Chem.* **2015**, *71*, 3–8. (b) Sheldrick, G. M. University of Göttingen, Germany, **2016**.

(7) Hübschle, C. B.; Sheldrick, G. M.; Dittrich, B. ShelXle: a Qt graphical user interface for SHELXL. *J. Appl. Crystallogr.* **2011**, *44*, 1281–1284.