Supplementary Information

Synthesis, Structure, and Olefin Polymerization with Nickel(II) N-Heterocyclic Carbene Enolates

Benjamin E. Ketz, Xavier G. Ottenwaelder*, and Robert M. Waymouth**
Department of Chemistry, Stanford University, Stanford, California 94305

Experimental

General Considerations. All organometallic reactions were performed under an inert atmosphere of N_2 using standard Schlenk line techniques. Degassing of solvents was achieved via multiple freeze pump thaw cycles. Mesityl imidazole, 2,6-Diisopropyl-phenyl imidazole, and 3-Mesityl-1-(2-oxo-2-phenyl-ethyl)-imidazolium bromide are literature compounds.[1,2] 2,6-Diisopropyl-phenyl imidazole was purified via column chromatography (eluting with 9 hexane : 1 CH_2Cl_2 then 75 hexane : 15 CH_2Cl_2 : 10 acetone), filtering through activated charcoal, and recrystallizing from heptane. 2-Bromoacetophenone was used as received from Aldrich, and $NaN(TMS)_2$ was purchased from Aldrich and stored in an inert atmosphere. $Ni(COD)_2$ was purchased from Strem and stored in a glovebox freezer (-30 °C). Celite was baked out at 140 °C prior to use. Pyridine was purchased as an extra dry solvent from Acros, degassed, and stored over activated molecular sieves. PMAO-IP was purchased from Akzo Nobel and dried *in vacuo* prior to use; it is refered to as MAO in this report. Chlorobenzene was dried over calcium hydride, degassed, and vacuum transferred. Other reaction solvents were purified by passing through a column of either alumina or molecular sieves and degassing. Deuterated benzene was purchased from Acros, dried over sodium benzophenone, degassed, and vacuum transferred. Deuterated chloroform and bromobenzene were purchased from Acros and used as received. NMR spectra were taken on a Varian Unity Inova 500 MHz NMR, a Varian Unity Inova 600 MHz NMR (^{15}N NMR only), and a Varian Unity Inova 300 MHz NMR (polymer NMRs). Chemical shifts were referenced to residual solvent peak: chloroform (7.26 ppm, 77 ppm), benzene (7.15 ppm, 128 ppm), bromobenzene (at 100 °C, furthest upfield peak, 7 ppm, 123 ppm). Where applicable, peak assignments were made by gHSQC, gHMBC, gCOSY, and g^{15}NHMBC. NMR spectra of polymers were taken of saturated polymer solutions at 100 °C. For ^{13}C NMR spectra of polymers, 80% o-dichlorobenzene / 20% d-benzene with a minimal amount of $Cr(acac)_3$ was used as a solvent, and d-bromobenzene was used for ^1H spectra. ^{13}C spectra were taken with a 90° pulse and inverse gated decoupling. Elemental analyses were performed by Atlantic Microlab, Inc. in Norcross, GA 30091. High temp GPC analysis was performed on a Polymer Laboratories 220 GPC equipped with a refractometer detector; the polystyrene standard peak molecular weights were converted to polyethylene molecular weights.[3]

3-(2,6-Diisopropyl-phenyl)-1-(2-oxo-2-phenyl-ethyl)-imidazolium bromide, 1b.
2-Bromoacetophenone (1.84 g) was dissolved in THF (20 mL) and transferred to a solution of 2,6-Diisopropyl-phenyl imidazole (2.0 g) in THF (20 mL). THF (10 mL) was used to complete the transfer, and the rxn was stirred 4 hr under N_2, being concentrated to 25 mL. Ether (30 mL) was layered on top, and after 2 days the mixture was filtered to afford off-white powder and crystals. This was recrystallized from CH_2Cl_2 layered with THF and ether. The crystals were redissolved in CH_2Cl_2, mixed with activated charcoal, filtered, and recrystallized in the same manner to afford clear white crystals, which were dried *in vacuo* (3.4 g, 91%). ^1H NMR (500 MHz, $CDCl_3$): δ 1.16 (d, 6H, J = 7 Hz, CH_3), 1.22 (d, 6H, J = 7 Hz, CH_3), 2.40 (sept, 2H, J = 7 Hz, isopropyl C*H*), 6.77 (s, 2H, NCH_2C=O), 7.19 (t, 1H, J = 2 Hz, ArN–C*H*=C), 7.30 (d, 2H, J = 7.5 Hz, m-Ar), 7.49 (t, 2H, J = 7.3 Hz, m-Ph), 7.53 (t, 1H, J = 7.8 Hz, p-Ar), 7.61 (tt, 1H, J = 7.5 Hz, 1.5 Hz, p-Ph), 8.05 (t, 1H, J = 1 Hz, ArN–C=C*H*), 8.12 (dd, 2H, J = 7.5 Hz, 1.5 Hz, o-Ph), 9.91 (t, 1H, J = 1.5 Hz, N–C*H*=N). ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.16 (CH_3), 24.35 (CH_3), 28.57 (isopropyl *C*H), 56.37 (N–*C*–C=O), 123.08 (ArN–*C*=C), 124.62 (m-Ar), 124.87 (ArN–C=*C*), 128.71 (o-Ph), 129.10 (m-Ph), 130.03 (ipso-Ar), 131.89 (p-Ar), 133.48 (ipso-Ph), 134.64 (p-Ph), 139.14 (N–*C*=N), 145.50 (o-Ar), 190.68 (*C*=O).

General Procedures for (Phenyl)Ni(carbene)(pyridine) complexes. In a nitrogen glove box, the imidazolium salt, $Ni(COD)_2$, and a base were all added to one flask in a 1:1:2 ratio. Special care was used to ensure that no reagent was used in excess. Repeated experiments showed that highly pure imidazolium salt is important for the success of the reaction and the purity of the product. This flask was cooled in liquid nitrogen, and pyridine was added. The mixture was allowed to warm until half of the pyridine melted and stirring became possible; then, an excess (10-20 equiv) of chlorobenzene was added. The rxn was allowed to slowly warm to RT. As the rxn progressed, the solution quickly turned from pale yellow to deep red. After 30 min, the solution became deep yellow-orange. The rxn stirred an additional 30 min before removing the solvent *in vacuo*. The product was extracted with a less polar solvent, filtered through Celite, and dried in vacuo to yield a yellow solid.

(Phenyl)Ni(3-mesityl-1-(2-phenyl-1-ethen-2-olate)-imidazolin-2-ylidene)(pyridine), 2a. NHMDS (145 mg), 3-Mesityl-1-(2-oxo-2-phenyl-ethyl)-imidazolium bromide (147 mg), Ni(COD)$_2$ (105 mg), chlorobenzene (0.6 mL), and pyridine (20 mL) were used for the rxn. The product was extracted with 50/50 pentane/CH_2Cl_2, filtered through Celite, and dried *in vacuo* to give a deep yellow powder (151 mg, 76%). The product was dissolved in a concentrated solution of ether/CH_2Cl_2; a small amount of ether was layered on top, and pentane was layered on top of that. After 2.5 days, very large deep yellow crystals formed; the solvent was decanted, and the crystals were dried under N_2 and a slight vacuum. ^{1}H NMR (500 MHz, C_6D_6): δ 2.07 (s, 3H, p-CH_3), 2.24 (s, 6H, o-CH_3), 6.01 (d, 1H, J = 2 Hz, ArN–C*H*=C), 6.20 (m, 2H, J = 8 Hz, 6.5 Hz, 1.5 Hz, m-pyr), 6.44 (d, 1H, J = 2 Hz, ArN–C=C*H*), 6.49 (s, 2H, m-Ar), 6.55 (m, 3H, m-NiPh and p-pyr), 6.64 (tt, 1H, J = 7.3 Hz, 1.6 Hz, p-NiPh), 6.74 (s, 1H, NC*H*C–O), 7.12 (tt, 1H, 7.3 Hz, 1.5 Hz, p-enolPh), 7.22 (m, 4H, o-NiPh and m-enolPh), 7.85 (dd, 2H, J = 8.3 Hz, 1.3 Hz, o-enolPh), 8.45 (dd, 2H, J = 6.5 Hz, 2 Hz, o-pyr). ^{13}C NMR (125 MHz, C_6D_6): δ 19.08 (o-*C*H_3), 20.82 (p-CH_3), 98.93 (N–*C*=C–O), 118.12 (ArN–C=*C*), 120.98 (p-NiPh), 121.90 (ArN–*C*=C), 122.77 (m-pyr), 124.78 (m-NiPh), 125.65 (o-enolPh), 127.23 (p-enolPh), 128.29 (m-enolPh), 128.96 (m-Ar), 134.51 (o-Ar), 135.75 (p-pyr), 137.09 (p-Ar), 137.51 (ipso-Ar), 137.82 (o-NiPh), 141.05 (ipso-enolPh), 151.16 (o-pyr), 154.56 (*C*–O), 157.76 (ipso-NiPh), 161.96 (carbene). ^{15}N NMR (60 MHz, C_6D_6): δ 189 (Ar–*N*), 200 (ArN–C=C–*N*), 269 (pyr). Anal. Calcd for $C_{31}H_{29}N_3NiO$: C, 71.84; H, 5.64; N, 8.11. Found: C, 71.50; H, 5.66; N, 8.06.

(Phenyl)Ni(3-(2,6-Diisopropyl-phenyl)-1-(2-phenyl-1-ethen-2-olate)-imidazolin-2-ylidene)(pyridine), 2b. NHMDS (698 mg), 3-(2,6-Diisopropyl-phenyl)-1-(2-oxo-2-phenyl-ethyl)-imidazolium bromide (790 mg), Ni(COD)$_2$ (509 mg), chlorobenzene (3 mL), and pyridine (50 mL) were used for the rxn. The product was extracted with 50/50 pentane/ether (3 x 25 mL), filtered through Celite, and dried in vacuo to give a deep yellow powder (940 mg, 91%). ^{1}H NMR (500 MHz, C_6D_6): δ 0.99 (d, 6H, J = 7 Hz, CH_3), 1.47 (d, 6H, J = 6.5 Hz, CH_3), 3.06 (sept, 2 H, J = 6.8 Hz, isopropyl C*H*), 6.23 (m, 2H, J = 7.5 Hz, 6.5 Hz, 1.3 Hz, m-pyr), 6.45 (d, 1H, J = 1.5 Hz, ArN–C*H*=C), 6.52 (d, 1H, J = 2 Hz, ArN–C=C*H*), 6.54 (tt, 1H, J = 7.5 Hz, 1.5 Hz, p-pyr), 6.63 (m, 3H, m-NiPh and p-NiPh), 6.77 (s, 1H, NC*H*C–O), 6.94 (d, 2H, J = 7.5 Hz, m-Ar), 7.12 (m, 2H, p-Ar and p-enolPh), 7.20 (m, 4H, m-enolPh and o-NiPh), 7.83 (dd, 2H, J = 8 Hz, 1 Hz, o-enolPh), 8.27 (dd, 2H, J = 6.5 Hz, 1.5 Hz, o-pyr). ^{13}C NMR (125 MHz, C_6D_6): δ 23.47 (*C*H_3), 26.34 (*C*H_3), 28.75 (isopropyl *C*H), 98.90 (N–*C*=C–O), 118.02 (ArN–C=*C*), 121.08 (p-NiPh), 122.73 (m-pyr), 123.68 (m-Ar), 123.87 (ArN–*C*=C), 125.45 (m-NiPh), 125.70 (o-enolPh), 127.34 (p-enolPh), 128.29 (m-enolPh), 129.10 (p-Ar), 135.78 (p-pyr), 137.61 (o-NiPh), 137.64 (ipso-Ar), 140.78 (ipso-enolPh), 145.80 (o-Ar), 150.91 (o-pyr), 155.36 (*C*–O), 157.62 (ipso-NiPh), 162.95 (carbene). Anal. Calcd for $C_{34}H_{35}N_3NiO$: C, 72.88; H, 6.30; N, 7.50. Found: C, 72.62; H, 6.36; N, 7.37.

Ethylene Polymerizations. A 300 mL stainless steel reactor (Parr) equipped with a mechanical stirrer was evacuated and purged several times with nitrogen and three times with ethylene. To this, 80 mL of solvent (toluene or heptane) was added, and the reactor was equilibrated at the appropriate temperature and pressure for at least 20 min. The reactor was vented slightly, the catalyst was injected with ethylene, and the reactor was vented slightly for 10 sec. Polymerizations were terminated by venting the ethylene and cooling the reactor. The polymerization solution was immediately poured on a solution of methanol and HCl. The solution was concentrated, and the resultant polymer was washed with methanol, then dried *in vacuo* at 60 °C.

Propylene Polymerizations. The same reactor used for ethylene polymerizations was evacuated and purged several times with nitrogen and three times with propylene. To this, 100 mL liquid propylene was added, and the temperature was equilibrated at 40 °C. The precatalyst, **2b** (80 μmol), was dissolved in 10 mL toluene and loaded into a single-ended injection tube, which was pressurized with 20 bar argon and injected into the reactor. The polymerization was allowed to proceed 1 hour before venting and pouring the product on HCl in methanol. The solvent was removed *in vacuo*, and the polymer was washed with methanol to afford 326 mg of a viscous solid/liquid oligomer.

(1) Ketz, B. E.; Cole, A. P.; Waymouth, R. M. *Organometallics* **2004**, *23*, 2835-2837.
(2) Liu, J. P.; Chen, J. B.; Zhao, J. F.; Zhao, Y. H.; Li, L.; Zhang, H. B. *Synthesis* **2003**, 2661-2666.
(3) Williams, T.; Ward, I. *J. Poly. Sci. B* **1968**, *6*, 621.

Representative NMR Spectra

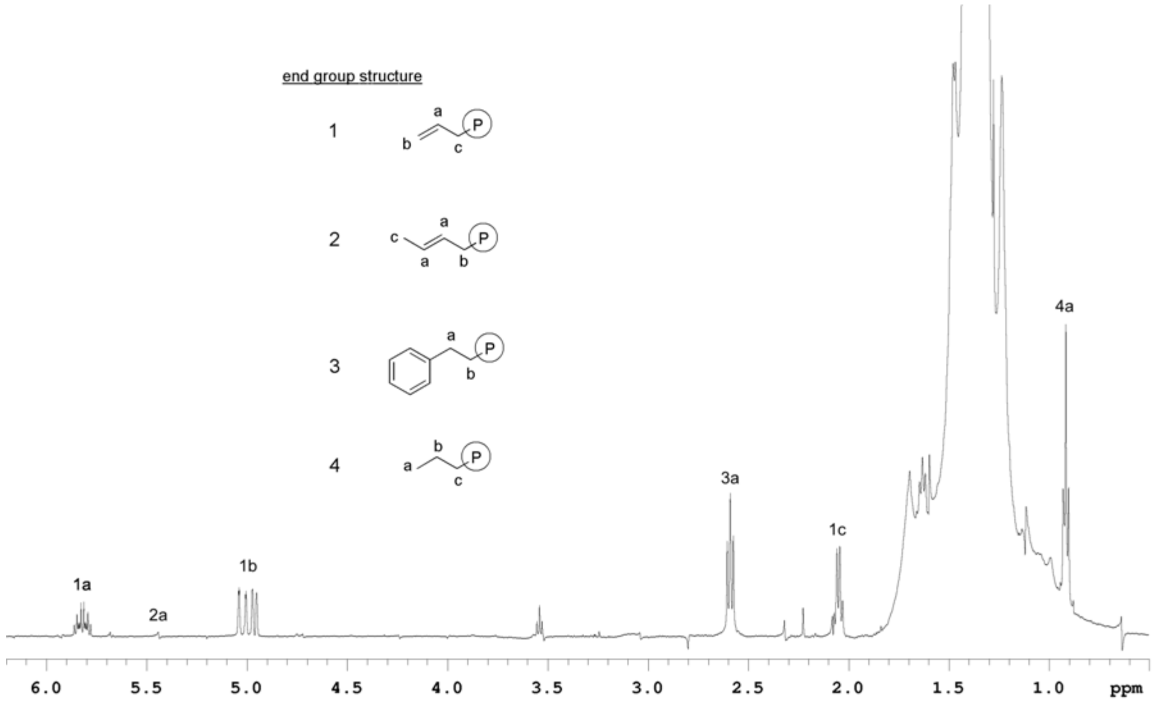

Figure S1. ^{1}H NMR of PE from run 2 (**2b**, 15 bar ethylene, 20 °C, toluene, 1 hour) in d$_5$-bromobenzene at 100 °C, 500 MHz.

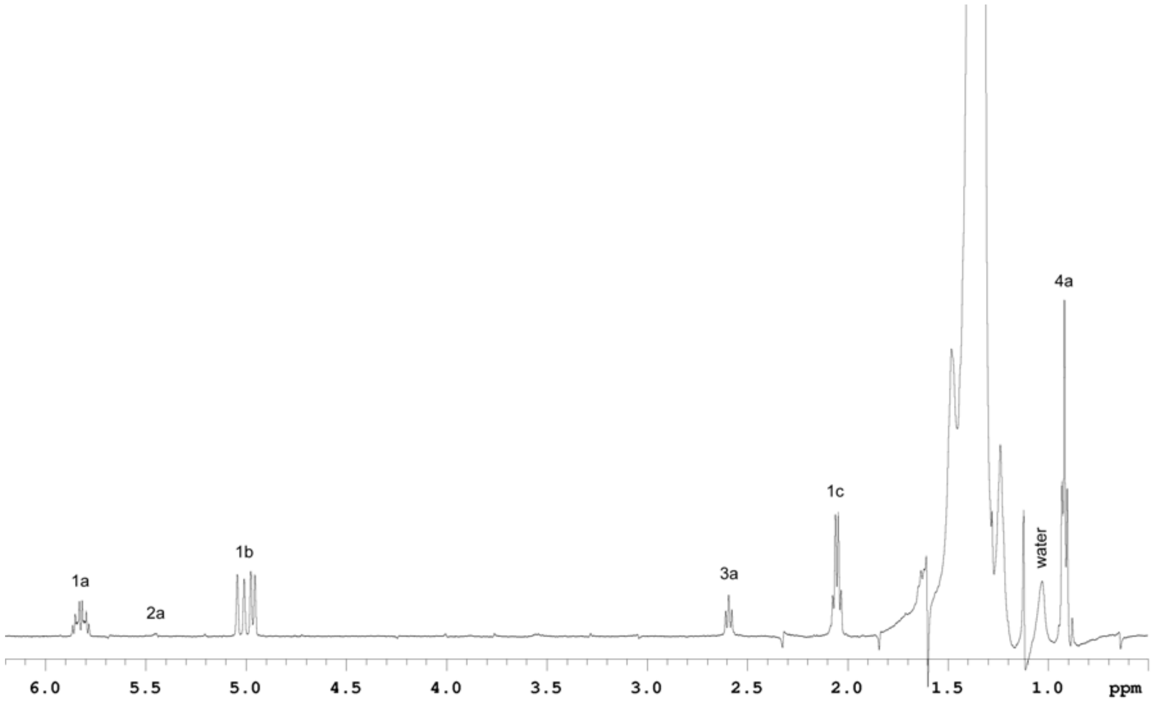

Figure S2. ^{1}H NMR of PE from run 7 (**2b**, 15 bar ethylene, 60 °C, toluene, 1 hour) in d_5-bromobenzene at 100 °C, 500 MHz.

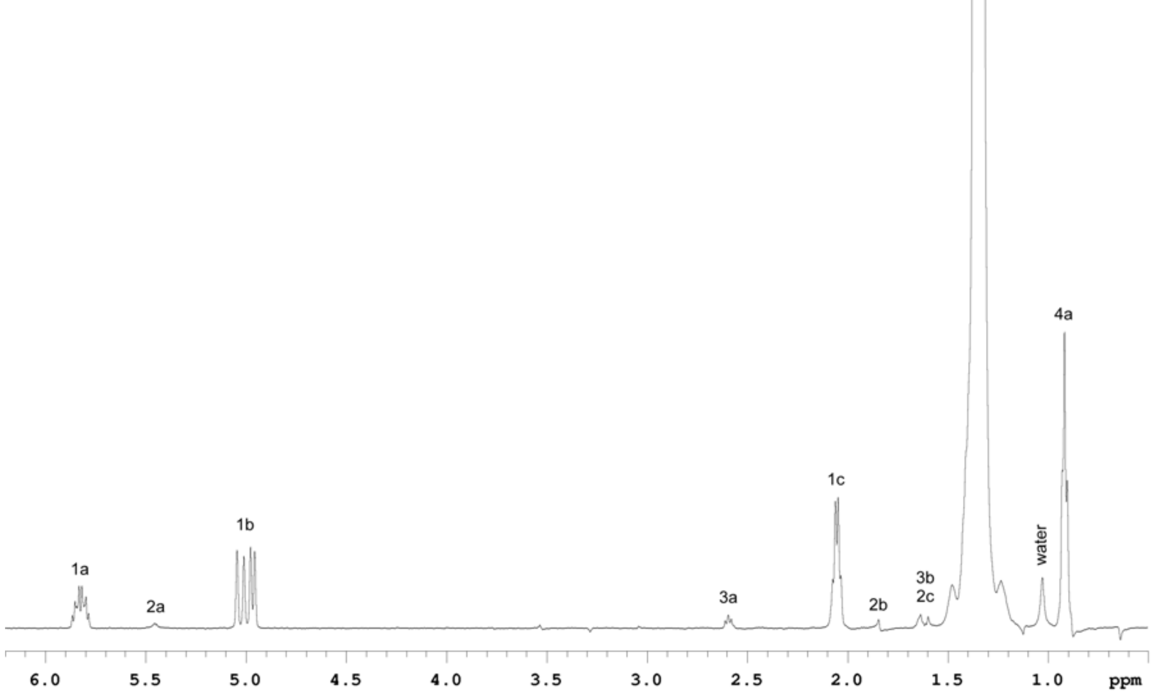

Figure S3. ^{1}H NMR of PE from run 13 (**2b**, 1 bar ethylene, 60 °C, toluene, 20 min) in d_5-bromobenzene at 100 °C, 500 MHz.

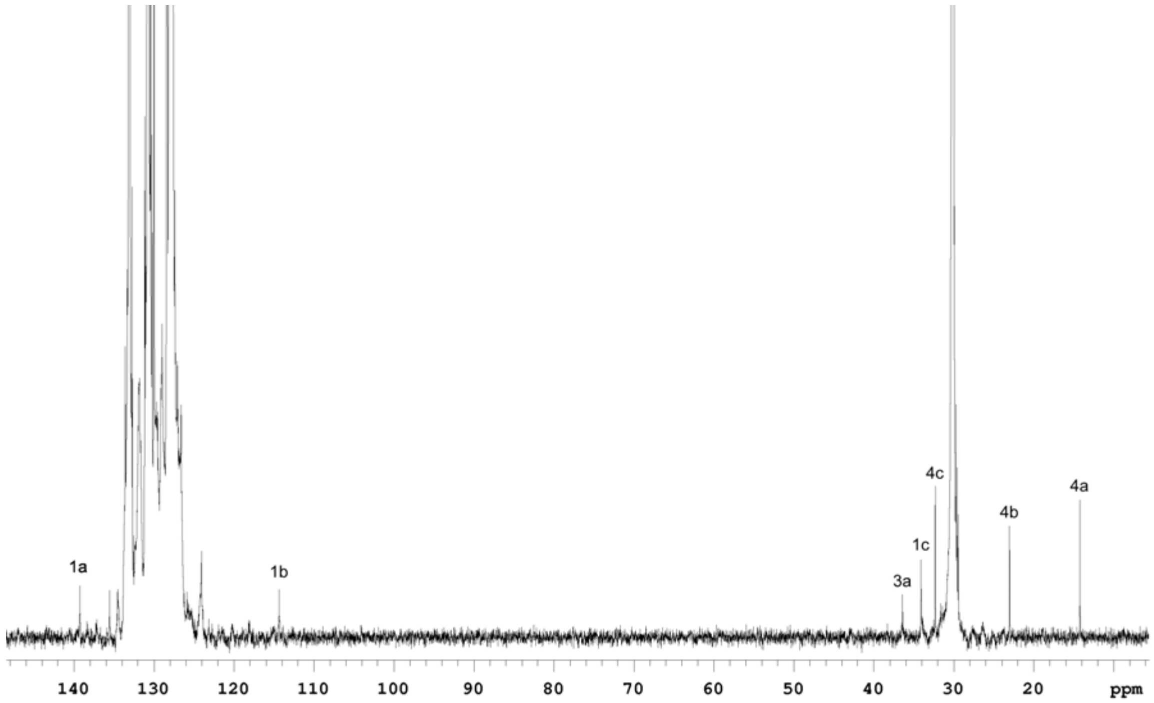

Figure S4. ^{13}C NMR of PE from run 6 (**2b**, 15 bar ethylene, 60 °C, toluene, 20 min) in chlorobenzene/d$_6$-benzene at 100 °C, 75 MHz.

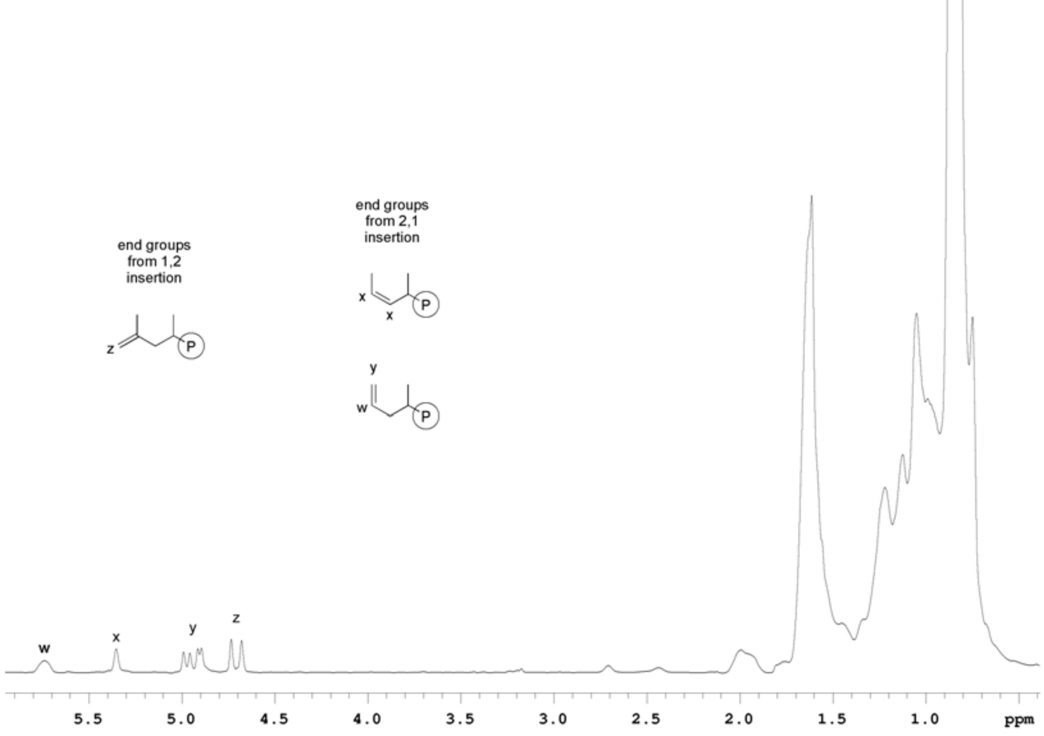

Figure S5. ^{1}H NMR of propylene oligomers in chlorobenzene/d$_6$-benzene at 80 °C, 500 MHz.

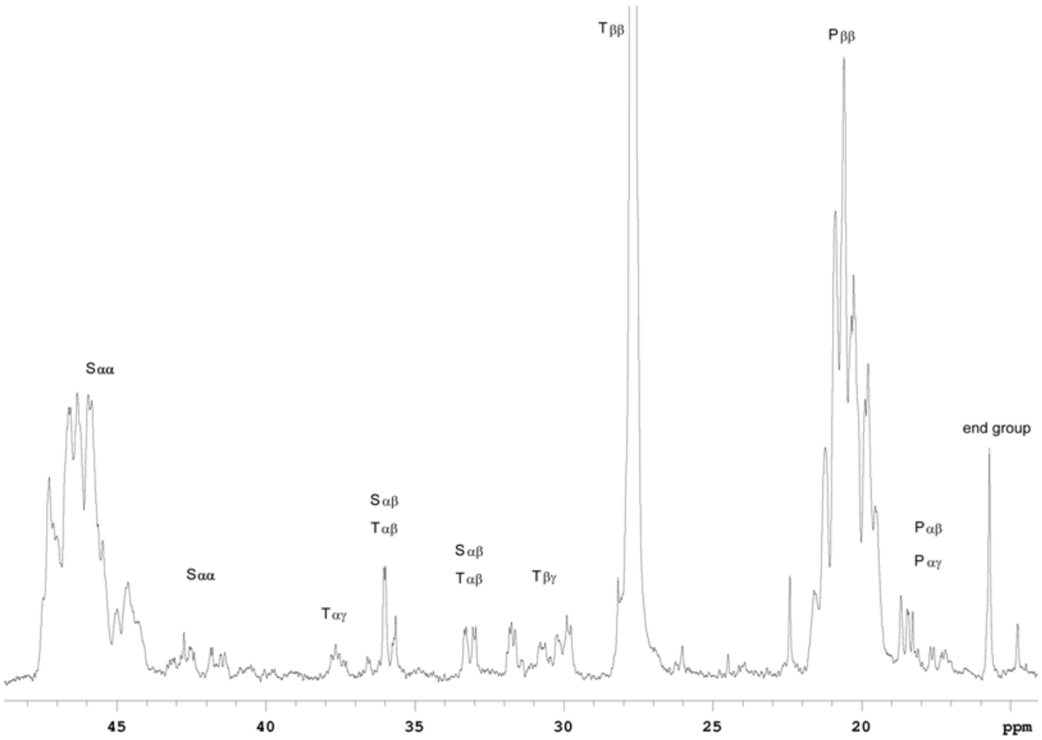

Figure S6. ^{13}C NMR of propylene oligomers in chlorobenzene/d$_6$-benzene at 80 °C, 125 MHz.

Crystal Structure Determination (Solved by X. Ottenwaelder, 2/1/2005)

Data Collection

A(n) yellow rhombic crystal of C31 H29 N3 Ni O having approximate dimensions of 0.43 x 0.19 x 0.14 mm was mounted on a quartz fiber using Paratone N hydrocarbon oil. All measurements were made on a Bruker-Siemens SMART[1] CCD area detector with monochromatic radiation of wavelength 0.71073 Å.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the measured positions of 2392 centered reflections with $I > 10\sigma(I)$ in the range $4.15^o < \theta < 24.39^o$, corresponded to a primitive triclinic cell with dimensions:

a = 9.742(1) Å	α = 81.520(2)°
b = 9.913(1) Å	β = 85.137(2)°
c = 13.653(2) Å	γ = 88.411(2)°
V = 1299.1(3) Å^3	

For $Z = 2$ and $F.W.$ = 518.28, the calculated density is 1.325 g/cm^3.

Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

P -1

The data were collected at a temperature of 150 K. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3° counted for a total of 10 seconds per frame.

Data Reduction

Data were integrated by the program SAINT[2] with box parameters of 1.6 x 1.6 x 1.0° to a maximum θ value of 24.74°. The data were corrected for Lorentz and polarization effects. The linear absorption coefficient, μ, for 0.71073 Å radiation is 0.775 mm^{-1}. Data were analyzed for agreement and possible absorption using XPREP[3]. A semi-empirical absorption correction based on 1841 reflections with $I > 10\sigma(I)$ was applied that resulted in normalized transmission factors ranging from 0.71 to 0.9. Of the 6591 reflections that were collected, 4231 were unique ($R_{\text{int}} = 0.0582$); equivalent reflections were merged. No decay correction was deemed necessary.

Structure Solution and Refinement

The structure was solved by direct methods (SIR-97)[4] and expanded using Fourier techniques[5]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located on the difference Fourier map, but were positioned using the HFIX command (idealized positions via a riding refinement). A single torsional parameter about the C-C bond was refined in the case of methyl groups. The aromatic ring C21-C26 presents severe disorder, as can be seen by the very oblong thermal ellipsoids for C22-C25. Attempts to resolve this positional disorder by a 50:50 mixture of two isotropic ideal rings did not significantly improve R_1 and wR_2 values. Using the P1 space group did not improve the solution. This ring has been modeled as an ideal hexagon with fixed C-C distances of 1.39 Å and anisotropic carbon atoms, which long ellipsoids likely denote librational movement. Hydrogen atoms on this ring have been positioned (ideal positions via riding) because some of them could be seen in the difference Fourier map. N3 is clearly a nitrogen, as evidenced by a peak of ca. 7.8 e$^-$/Å^3 in the difference Fourier map when removed from the model. Also, replacing this atom by a carbon, in the hypothesis of this ring being a Ph, yielded a very small ellipsoid compared to those of neighboring atoms. The final cycle of full-matrix least-squares refinement[6] was based on 4231 reflections (all data) and 316 variable parameters and converged (largest parameter shift was 0.000 times its esd) with conventional unweighted and weighted agreement factors of:

$$R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o| = 0.0440 \text{ for 2942 data with } F_o > 4\sigma(F_o)$$

$$wR_2 = [(\Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w |F_o|^2)]^{1/2} = 0.1027$$

The standard deviation of an observation of unit weight (S)[7] was 0.926. Sheldrick weights[6] were used; where applicable, weights were refined to convergence. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.63 and -0.59 e$^-$/Å^3, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[8]. Anomalous dispersion effects were included in Fcalc[9]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[10]. The values for the mass attenuation coefficients were those of Creagh and Hubbel[11]. All calculations were performed using the Crystal Structure[12] crystallographic software package.

References

(1) SMART: Area-Detector Software Package, Siemens Industrial Automation, Inc.: Madison, WI (1995).

(2) SAINT: SAX Area-Dectector Integration Program, V5.04; Siemens Industrial Automation, Inc.: Madison, WI, (1995)

(3) XPREP: (v 5.03) Part of the SHELXTL Crystal Structure Determination, Siemens Industrial Automation, Inc.: Madison, WI (1995).

(4) SIR97: a new tool for crystal structure determination and refinement.: A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna. J. Appl. Cryst., (1999). 32, 115-119.

(5) DIRDIF99: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M. (1999). The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(6) Least-Squares:

Function minimized: $\Sigma w\,(|F_o|^2 - |F_c|^2)^2$

$w = 1/[\sigma^2(F_o^2) + (0.0500P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

Sheldrick weights: G. M. Sheldrick (1997)

(7) Standard deviation of an observation of unit weight:

$S = [\Sigma w\,(|F_o|^2 - |F_c|^2)^2/(N_o - N_v)]^{1/2}$

where: N_o = number of observations

N_v = number of variables

(8) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(9) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(10) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(11) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(12) CrystalStructure 3.51: Crystal Structure Analysis Package, Rigaku and MSC (2000-3).

(13) CRYSTALS Issue 10: Watkin, D.J.; Prout, C.K.; Carruthers, J.R.; Betteridge, P.W. Chemical Crystallography Laboratory, Oxford, UK.

A. Crystal Data

Empirical Formula	C31 H29 N3 Ni O
Formula Weight	518.28
Crystal Color, Habit	yellow, rhombic
Crystal Dimensions	0.43 x 0.19 x 0.14 mm
Crystal System	triclinic
Lattice Type	primitive
Lattice Parameters	a = 9.742(1) Å b = 9.913(1) Å c = 13.653(2) Å α = 81.520(2)° β = 85.137(2)° γ = 88.411(2)° V = 1299.1(3) Å^3
Space Group	P -1
Z value	2
d_{calc}	1.325 g/cm^3
F_{000}	544
μ(0.71073 Å radiation)	0.77 cm^{-1}

B. Intensity Measurements

Diffractometer	Bruker-Siemens SMART CCD
Radiation	λ = 0.71073 Å graphite monochromated
Exposure Time	10 seconds per frame.
Scan Type	ω (0.3 degrees per frame)
θ_{max}	24.74°
Data Collection Temperature	150 K
No. of Reflections Measured	Total: 6591 Unique: 4231 (R_{int} = 0.0582)
Corrections	Lorentz-polarization Absorption: T_{max} = 0.9 T_{min} = 0.71

C. Structure Solution and Refinement

Structure Solution	Direct (SIR-97)
Refinement	Full-matrix least-squares (SHELXL-97)
Function Minimized	$\Sigma w(\lvert F_o\rvert^2 - \lvert F_c\rvert^2)^2$
Least Squares Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0500P)^2]$ where $P=(F_o^2+2F_c^2)/3$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($F_o > 4\sigma(F_o)$)	2942
No. Variables	316
Reflection/Parameter Ratio	13.39
Residuals: R_1; wR_2	0.0440; 0.1027
Goodness of Fit Indicator (S)	0.926

Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.63 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.59 $e^-/Å^3$

Table 1. Atomic coordinates, $U_{\mathrm{iso}}/U_{\mathrm{eq}}$, and occupancy for **2a**

atom	x	y	z	U_{eq}	occ
Ni1	0.1599(1)	0.0448(1)	0.2779(1)	0.026(1)	1
O1	0.0207(2)	-0.0794(2)	0.3339(2)	0.037(1)	1
N1	-0.0402(3)	0.0364(3)	0.1401(2)	0.031(1)	1
N2	0.0596(2)	0.2307(3)	0.1061(2)	0.029(1)	1
N3	0.2577(2)	-0.0270(3)	0.3923(2)	0.026(1)	1
C1	0.0601(3)	0.1113(3)	0.1713(2)	0.025(1)	1
C2	-0.0350(3)	0.2277(4)	0.0355(2)	0.037(1)	1
C3	-0.0951(3)	0.1074(4)	0.0563(2)	0.038(1)	1
C4	-0.0945(3)	-0.0866(4)	0.1912(3)	0.037(1)	1
C5	-0.0699(3)	-0.1344(4)	0.2862(3)	0.034(1)	1
C6	-0.1465(3)	-0.2508(4)	0.3440(3)	0.038(1)	1
C7	-0.1002(4)	-0.3129(4)	0.4329(3)	0.046(1)	1
C8	-0.1713(4)	-0.4195(4)	0.4905(3)	0.058(1)	1
C9	-0.2891(5)	-0.4677(4)	0.4599(4)	0.062(1)	1
C10	-0.3355(4)	-0.4080(5)	0.3713(4)	0.061(1)	1
C11	-0.2667(4)	-0.3002(4)	0.3140(3)	0.050(1)	1
C12	0.1220(3)	0.3566(3)	0.1194(2)	0.030(1)	1
C13	0.0673(4)	0.4223(3)	0.1980(2)	0.034(1)	1
C14	0.1288(4)	0.5432(4)	0.2103(3)	0.042(1)	1
C15	0.2393(4)	0.5977(4)	0.1484(3)	0.040(1)	1
C16	0.2870(3)	0.5310(3)	0.0700(2)	0.035(1)	1
C17	0.2282(3)	0.4108(3)	0.0531(2)	0.028(1)	1
C18	-0.0503(4)	0.3640(4)	0.2692(3)	0.051(1)	1
C19	0.3051(5)	0.7260(4)	0.1661(3)	0.064(1)	1
C20	0.2802(4)	0.3445(4)	-0.0360(2)	0.040(1)	1
C21	0.3162(2)	0.1491(2)	0.2263(2)	0.035(1)	1
C22	0.3527(3)	0.2613(2)	0.2681(2)	0.069(2)	1
C23	0.4771(4)	0.3255(3)	0.2366(3)	0.136(4)	1
C24	0.5651(3)	0.2774(4)	0.1634(3)	0.163(5)	1
C25	0.5286(3)	0.1652(4)	0.1217(2)	0.119(3)	1
C26	0.4041(3)	0.1010(3)	0.1531(2)	0.062(1)	1
C27	0.1977(3)	-0.0190(3)	0.4834(2)	0.034(1)	1
C28	0.2539(4)	-0.0763(4)	0.5696(3)	0.042(1)	1
C29	0.3763(4)	-0.1447(4)	0.5631(3)	0.045(1)	1
C30	0.4409(4)	-0.1542(4)	0.4703(3)	0.040(1)	1
C31	0.3804(3)	-0.0937(3)	0.3881(3)	0.031(1)	1
H2	-0.0525	0.2966	-0.0162	0.044	1
H3	-0.1622	0.0759	0.0211	0.045	1
H4	-0.1497	-0.1372	0.1583	0.044	1
H7	-0.0200	-0.2825	0.4544	0.055	1

H8	-0.1390	-0.4590	0.5504	0.069	1
H9	-0.3366	-0.5394	0.4987	0.074	1
H10	-0.4144	-0.4406	0.3496	0.073	1
H11	-0.3008	-0.2600	0.2548	0.060	1
H14	0.0941	0.5890	0.2620	0.051	1
H16	0.3606	0.5672	0.0273	0.042	1
H18A	-0.1193	0.3313	0.2327	0.077	1
H18B	-0.0897	0.4337	0.3054	0.077	1
H18C	-0.0168	0.2899	0.3149	0.077	1
H19A	0.2348	0.7898	0.1841	0.096	1
H19B	0.3576	0.7653	0.1065	0.096	1
H19C	0.3649	0.7052	0.2188	0.096	1
H20A	0.2880	0.2477	-0.0166	0.060	1
H20B	0.3689	0.3801	-0.0614	0.060	1
H20C	0.2168	0.3636	-0.0866	0.060	1
H22	0.2938	0.2935	0.3170	0.083	1
H23	0.5015	0.4006	0.2646	0.163	1
H24	0.6483	0.3203	0.1424	0.195	1
H25	0.5874	0.1330	0.0727	0.143	1
H26	0.3797	0.0260	0.1252	0.074	1
H27	0.1139	0.0277	0.4888	0.041	1
H28	0.2086	-0.0681	0.6313	0.051	1
H29	0.4159	-0.1846	0.6202	0.054	1
H30	0.5244	-0.2010	0.4640	0.048	1
H31	0.4259	-0.0986	0.3260	0.038	1

U_{eq} is defined as one third of the orthogonalized U_{ij} tensor

Table 2. Anisotropic Displacement Parameters for **2a**

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni1	0.023(1)	0.031(1)	0.025(1)	-0.004(1)	-0.003(1)	0.000(1)
O1	0.028(1)	0.052(2)	0.032(1)	-0.008(1)	-0.003(1)	-0.014(1)
N1	0.023(1)	0.044(2)	0.027(2)	-0.011(1)	-0.003(1)	-0.001(1)
N2	0.025(2)	0.038(2)	0.026(2)	-0.007(1)	-0.006(1)	0.005(1)
N3	0.025(2)	0.022(2)	0.030(2)	-0.003(1)	-0.002(1)	-0.002(1)
C1	0.021(2)	0.027(2)	0.028(2)	-0.009(2)	0.002(1)	0.003(1)
C2	0.030(2)	0.055(3)	0.026(2)	-0.007(2)	-0.011(2)	0.011(2)
C3	0.030(2)	0.060(3)	0.026(2)	-0.014(2)	-0.009(2)	0.003(2)
C4	0.029(2)	0.047(2)	0.038(2)	-0.018(2)	-0.001(2)	-0.009(2)
C5	0.022(2)	0.045(2)	0.036(2)	-0.016(2)	0.007(2)	-0.002(2)
C6	0.033(2)	0.045(2)	0.037(2)	-0.020(2)	0.013(2)	-0.011(2)
C7	0.045(2)	0.048(2)	0.044(2)	-0.010(2)	0.011(2)	-0.008(2)
C8	0.066(3)	0.050(3)	0.054(3)	-0.009(2)	0.024(2)	-0.010(2)
C9	0.069(3)	0.047(3)	0.069(3)	-0.027(2)	0.040(3)	-0.022(2)
C10	0.050(3)	0.066(3)	0.073(3)	-0.040(3)	0.025(2)	-0.030(2)
C11	0.042(2)	0.062(3)	0.048(2)	-0.027(2)	0.015(2)	-0.018(2)
C12	0.035(2)	0.031(2)	0.024(2)	-0.001(2)	-0.010(2)	0.009(2)
C13	0.043(2)	0.034(2)	0.026(2)	-0.004(2)	-0.007(2)	0.015(2)
C14	0.066(3)	0.033(2)	0.028(2)	-0.007(2)	-0.007(2)	0.020(2)
C15	0.059(3)	0.029(2)	0.033(2)	-0.003(2)	-0.014(2)	0.008(2)
C16	0.042(2)	0.030(2)	0.030(2)	0.006(2)	-0.010(2)	0.007(2)
C17	0.035(2)	0.028(2)	0.021(2)	0.000(1)	-0.010(2)	0.010(2)
C18	0.051(2)	0.054(3)	0.050(3)	-0.018(2)	0.007(2)	0.013(2)
C19	0.103(4)	0.034(2)	0.056(3)	-0.008(2)	-0.015(3)	-0.004(2)
C20	0.046(2)	0.042(2)	0.032(2)	-0.008(2)	0.001(2)	0.003(2)
C21	0.031(2)	0.024(2)	0.047(2)	0.012(2)	-0.021(2)	0.000(2)
C22	0.093(3)	0.032(2)	0.085(3)	0.024(2)	-0.071(3)	-0.022(2)
C23	0.186(7)	0.081(4)	0.136(6)	0.089(4)	-0.139(6)	-0.093(5)
C24	0.110(5)	0.208(9)	0.139(7)	0.150(6)	-0.105(5)	-0.113(6)
C25	0.034(3)	0.189(7)	0.099(5)	0.096(5)	-0.003(3)	-0.009(3)
C26	0.033(2)	0.075(3)	0.062(3)	0.033(2)	0.009(2)	0.001(2)
C27	0.030(2)	0.041(2)	0.029(2)	-0.003(2)	0.004(2)	-0.002(2)
C28	0.049(2)	0.047(2)	0.028(2)	0.000(2)	0.000(2)	-0.003(2)
C29	0.057(3)	0.043(2)	0.031(2)	0.009(2)	-0.016(2)	0.000(2)
C30	0.039(2)	0.037(2)	0.045(2)	-0.003(2)	-0.013(2)	0.011(2)
C31	0.030(2)	0.030(2)	0.034(2)	-0.007(2)	-0.001(2)	0.001(2)

The general temperature factor expression:
$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^* U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 3. Bond Lengths (Å) for **2a**

atom	atom	distance	atom	atom	distance
Ni1	C1	1.848(3)	Ni1	C21	1.891(2)
Ni1	O1	1.891(2)	Ni1	N3	1.934(2)
O1	C5	1.315(4)	N1	C1	1.375(4)
N1	C3	1.392(4)	N1	C4	1.406(4)
N2	C1	1.373(4)	N2	C2	1.393(4)
N2	C12	1.446(4)	N3	C27	1.341(4)
N3	C31	1.351(4)	C2	C3	1.325(5)
C2	H2	0.9300	C3	H3	0.9300
C4	C5	1.353(5)	C4	H4	0.9300
C5	C6	1.480(5)	C6	C7	1.383(5)
C6	C11	1.397(5)	C7	C8	1.385(5)
C7	H7	0.9300	C8	C9	1.374(6)
C8	H8	0.9300	C9	C10	1.373(6)
C9	H9	0.9300	C10	C11	1.381(6)
C10	H10	0.9300	C11	H11	0.9300
C12	C17	1.381(5)	C12	C13	1.396(4)
C13	C14	1.392(5)	C13	C18	1.508(5)
C14	C15	1.381(5)	C14	H14	0.9300
C15	C16	1.381(5)	C15	C19	1.500(5)
C16	C17	1.394(4)	C16	H16	0.9300
C17	C20	1.510(4)	C18	H18A	0.9600
C18	H18B	0.9600	C18	H18C	0.9600
C19	H19A	0.9600	C19	H19B	0.9600
C19	H19C	0.9600	C20	H20A	0.9600
C20	H20B	0.9600	C20	H20C	0.9600
C21	C22	1.3900	C21	C26	1.3900
C22	C23	1.3900	C22	H22	0.9300
C23	C24	1.3900	C23	H23	0.9300
C24	C25	1.3900	C24	H24	0.9300
C25	C26	1.3900	C25	H25	0.9300
C26	H26	0.9300	C27	C28	1.378(5)
C27	H27	0.9300	C28	C29	1.358(5)
C28	H28	0.9300	C29	C30	1.380(5)
C29	H29	0.9300	C30	C31	1.364(4)
C30	H30	0.9300	C31	H31	0.9300

Symmetry transformations used to generate equivalent atoms:

Table 4. Bond Angles (°) for **2a**

atom	atom	atom	angle	atom	atom	atom	angle
C1	Ni1	C21	93.17(12)	C1	Ni1	O1	92.56(12)
C21	Ni1	O1	172.19(10)	C1	Ni1	N3	177.79(13)
C21	Ni1	N3	88.91(10)	O1	Ni1	N3	85.43(10)
C5	O1	Ni1	126.9(2)	C1	N1	C3	110.7(3)
C1	N1	C4	125.8(3)	C3	N1	C4	123.1(3)
C1	N2	C2	111.6(3)	C1	N2	C12	125.5(2)
C2	N2	C12	121.4(3)	C27	N3	C31	116.2(3)
C27	N3	Ni1	119.0(2)	C31	N3	Ni1	124.7(2)
N2	C1	N1	103.1(2)	N2	C1	Ni1	134.6(2)
N1	C1	Ni1	122.2(2)	C3	C2	N2	106.6(3)
C3	C2	H2	126.7	N2	C2	H2	126.7
C2	C3	N1	108.0(3)	C2	C3	H3	126.0
N1	C3	H3	126.0	C5	C4	N1	122.7(3)
C5	C4	H4	118.6	N1	C4	H4	118.6
O1	C5	C4	122.7(3)	O1	C5	C6	115.7(3)
C4	C5	C6	121.6(3)	C7	C6	C11	117.7(4)
C7	C6	C5	119.4(3)	C11	C6	C5	122.9(4)
C6	C7	C8	121.1(4)	C6	C7	H7	119.5
C8	C7	H7	119.5	C9	C8	C7	120.7(4)
C9	C8	H8	119.6	C7	C8	H8	119.6
C10	C9	C8	118.9(4)	C10	C9	H9	120.6
C8	C9	H9	120.6	C9	C10	C11	121.0(4)
C9	C10	H10	119.5	C11	C10	H10	119.5
C10	C11	C6	120.7(4)	C10	C11	H11	119.6
C6	C11	H11	119.6	C17	C12	C13	122.3(3)
C17	C12	N2	119.9(3)	C13	C12	N2	117.7(3)
C14	C13	C12	117.1(3)	C14	C13	C18	120.7(3)
C12	C13	C18	122.1(3)	C15	C14	C13	122.5(3)
C15	C14	H14	118.8	C13	C14	H14	118.8
C14	C15	C16	118.2(3)	C14	C15	C19	120.8(3)
C16	C15	C19	121.1(4)	C15	C16	C17	121.9(3)
C15	C16	H16	119.0	C17	C16	H16	119.0
C12	C17	C16	117.9(3)	C12	C17	C20	122.1(3)
C16	C17	C20	120.0(3)	C13	C18	H18A	109.5
C13	C18	H18B	109.5	H18A	C18	H18B	109.5
C13	C18	H18C	109.5	H18A	C18	H18C	109.5
H18B	C18	H18C	109.5	C15	C19	H19A	109.5
C15	C19	H19B	109.5	H19A	C19	H19B	109.5
C15	C19	H19C	109.5	H19A	C19	H19C	109.5

H19B	C19	H19C	109.5	C17	C20	H20A	109.5
C17	C20	H20B	109.5	H20A	C20	H20B	109.5
C17	C20	H20C	109.5	H20A	C20	H20C	109.5
H20B	C20	H20C	109.5	C22	C21	C26	120.0
C22	C21	Ni1	121.46(16)	C26	C21	Ni1	118.07(16)
C21	C22	C23	120.0	C21	C22	H22	120.0
C23	C22	H22	120.0	C22	C23	C24	120.0
C22	C23	H23	120.0	C24	C23	H23	120.0
C25	C24	C23	120.0	C25	C24	H24	120.0
C23	C24	H24	120.0	C24	C25	C26	120.0
C24	C25	H25	120.0	C26	C25	H25	120.0
C25	C26	C21	120.0	C25	C26	H26	120.0
C21	C26	H26	120.0	N3	C27	C28	123.4(3)
N3	C27	H27	118.3	C28	C27	H27	118.3
C29	C28	C27	119.0(3)	C29	C28	H28	120.5
C27	C28	H28	120.5	C28	C29	C30	118.9(3)
C28	C29	H29	120.5	C30	C29	H29	120.5
C31	C30	C29	119.0(3)	C31	C30	H30	120.5
C29	C30	H30	120.5	N3	C31	C30	123.3(3)
N3	C31	H31	118.3	C30	C31	H31	118.3

Symmetry transformations used to generate equivalent atoms:

Table 5. Torsion Angles (°) for **2a**

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
C1	Ni1	O1	C5	27.3(3)	C21	Ni1	O1	C5	-109.9(8)
N3	Ni1	O1	C5	-153.6(3)	C1	Ni1	N3	C27	-33(3)
C21	Ni1	N3	C27	127.3(2)	O1	Ni1	N3	C27	-58.1(2)
C1	Ni1	N3	C31	142(3)	C21	Ni1	N3	C31	-57.3(3)
O1	Ni1	N3	C31	117.3(3)	C2	N2	C1	N1	-1.7(3)
C12	N2	C1	N1	164.5(3)	C2	N2	C1	Ni1	177.9(2)
C12	N2	C1	Ni1	-15.9(5)	C3	N1	C1	N2	2.2(3)
C4	N1	C1	N2	-170.1(3)	C3	N1	C1	Ni1	-177.5(2)
C4	N1	C1	Ni1	10.3(4)	C21	Ni1	C1	N2	-28.4(3)
O1	Ni1	C1	N2	156.9(3)	N3	Ni1	C1	N2	132(3)
C21	Ni1	C1	N1	151.1(2)	O1	Ni1	C1	N1	-23.6(2)
N3	Ni1	C1	N1	-48(3)	C1	N2	C2	C3	0.5(4)
C12	N2	C2	C3	-166.3(3)	N2	C2	C3	N1	0.9(4)
C1	N1	C3	C2	-2.0(4)	C4	N1	C3	C2	170.5(3)
C1	N1	C4	C5	11.4(5)	C3	N1	C4	C5	-160.0(3)
Ni1	O1	C5	C4	-14.7(4)	Ni1	O1	C5	C6	166.8(2)
N1	C4	C5	O1	-9.1(5)	N1	C4	C5	C6	169.4(3)
O1	C5	C6	C7	-14.0(5)	C4	C5	C6	C7	167.5(3)
O1	C5	C6	C11	164.5(3)	C4	C5	C6	C11	-14.0(5)
C11	C6	C7	C8	-0.5(5)	C5	C6	C7	C8	178.1(3)
C6	C7	C8	C9	0.8(6)	C7	C8	C9	C10	-0.1(6)
C8	C9	C10	C11	-0.9(6)	C9	C10	C11	C6	1.2(6)
C7	C6	C11	C10	-0.5(5)	C5	C6	C11	C10	-179.1(3)
C1	N2	C12	C17	117.4(3)	C2	N2	C12	C17	-77.7(4)
C1	N2	C12	C13	-65.3(4)	C2	N2	C12	C13	99.6(4)
C17	C12	C13	C14	-3.0(5)	N2	C12	C13	C14	179.8(3)
C17	C12	C13	C18	178.9(3)	N2	C12	C13	C18	1.6(5)
C12	C13	C14	C15	-0.1(5)	C18	C13	C14	C15	178.1(3)
C13	C14	C15	C16	2.0(5)	C13	C14	C15	C19	-178.2(3)
C14	C15	C16	C17	-0.8(5)	C19	C15	C16	C17	179.3(3)
C13	C12	C17	C16	4.1(5)	N2	C12	C17	C16	-178.7(3)
C13	C12	C17	C20	-175.6(3)	N2	C12	C17	C20	1.6(4)
C15	C16	C17	C12	-2.1(5)	C15	C16	C17	C20	177.6(3)
C1	Ni1	C21	C22	107.67(16)	O1	Ni1	C21	C22	-115.1(8)
N3	Ni1	C21	C22	-71.60(15)	C1	Ni1	C21	C26	-80.24(15)
O1	Ni1	C21	C26	57.0(8)	N3	Ni1	C21	C26	100.49(14)
C26	C21	C22	C23	0.0	Ni1	C21	C22	C23	171.93(17)
C21	C22	C23	C24	0.0	C22	C23	C24	C25	0.0
C23	C24	C25	C26	0.0	C24	C25	C26	C21	0.0
C22	C21	C26	C25	0.0	Ni1	C21	C26	C25	-172.20(16)
C31	N3	C27	C28	-1.1(5)	Ni1	N3	C27	C28	174.8(3)
N3	C27	C28	C29	0.0(5)	C27	C28	C29	C30	0.3(5)

C28	C29	C30	C31	0.4(5)	C27	N3	C31	C30	1.9(5)
Ni1	N3	C31	C30	-173.7(2)	C29	C30	C31	N3	-1.6(5)