# Bimetallic C-C Bond Forming Reductive 

## Elimination from Nickel

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-SUPPORTING INFORMATION-

## Table of Contents

I. Experimental Details ..... S3
II. X-Ray Crystal Structures of Ni Compounds ..... S12
III. Assigning the cis- and trans- Isomers for 2 ..... S14
IV. Additional Data for Characterizing Intermediates 4 and 5 ..... S16
V. Determining the Ni Species after the Reactions ..... S31
VI. Crossover Experiments ..... S36
VII. Effect of Bidentate Donor Ligands on Biphenyl Coupling from 3 ..... S37
VIII. Spectra ..... S39
IX. References ..... S53

## I. Experimental Details

General Considerations. Ligands, including 3,5-dimethyl-2-(2-pyridyl)pyrrole and 3,5-diphenyl-2-(2-pyridyl)pyrrole, ${ }^{1}$ (TMEDA)Ni( $\left.\mathrm{CH}_{3}\right)_{2}$ and (TMEDA)Ni( $\left.\mathrm{CD}_{3}\right)_{2},{ }^{2}$ and 1,1,1,3,3,5,5,5-octadeuteriopentane-2,4-dione ${ }^{3}$ were prepared according to literature procedures. All air- and moisture- sensitive manipulations were carried out in a glove box or using standard Schlenk techniques. Volatiles and liquid chemicals were dried over $4 \AA$ molecular sieves and distilled prior to use. Solvents were dried and deoxygenated by passing through alumina in a solvent purification system. NaH was purchased as a $60 \%$ dispersion in mineral oil and was washed with hexane prior to use.
${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra were recorded on Bruker 600 , 500 , and 400 MHz Avance spectrometers. 2D NMR experiments were performed on Bruker 500 MHz Avance. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ chemical shifts are referenced to residual solvent signals. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer. X-ray crystallographic data were collected on a Bruker AXS SMART APEXII single crystal diffractometer. Continuous wave (CW) EPR spectra were recorded on a Bruker X-band EMXPlus spectrometer equipped with an EMX standard resonator and a Bruker PremiumX microwave bridge. The spectra were simulated using EasySpin for MATLAB. Elemental analyses were performed at Robertson Microlit Laboratories, Ledgewood, NJ. Cyclic voltammetry was performed on a BASi E2 epsilon workstation.

## Preparation of (py- $\left.{ }^{\mathrm{Me}} \mathbf{p y r r}\right) \mathrm{Ni}($ acac $)(1)$.



A 20 mL scintillation vial was charged with $\mathrm{Ni}(\mathrm{acac})_{2}(0.100 \mathrm{~g}, 0.389 \mathrm{mmol})$, $3,5-$ dimethyl-2-(2-pyridyl)pyrrole $(0.067 \mathrm{~g}, 0.389 \mathrm{mmol}), \mathrm{NaH}(0.011 \mathrm{~g}, 0.467 \mathrm{mmol})$ and 10 mL of toluene. The solution was stirred at ambient temperature for 10 min , resulting in a color change from green to dark red. The solvent was removed in vacuo and the residue was extracted with diethyl ether, filtered through filter paper, concentrated to 6 mL and recrystallized at $-35^{\circ} \mathrm{C}$ to afford 66 mg of (1) (52\% after first recrystallization) as a brick red solid. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}\right) \delta 7.33(\mathrm{dt}, 6.1 \mathrm{~Hz}, 1.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{py}-H), 6.71-6.72(\mathrm{~m}$, 2 H, py- $H), 5.94-5.96(\mathrm{~m}, 1 \mathrm{H}$, py-H), $5.94(\mathrm{~s}, 1 \mathrm{H}$, pyrr- $H), 5.03(\mathrm{~s}, 1 \mathrm{H}$, acac- $-H), 2.35(\mathrm{~s}$, 3 H , pyrr- $\left.\mathrm{CH}_{3}\right), 2.30\left(\mathrm{~s}, 3 \mathrm{H}\right.$, pyrr- $\left.\mathrm{CH}_{3}\right), 1.46\left(\mathrm{~s}, 6 \mathrm{H}\right.$, acac- $\left.-\mathrm{CH}_{3}\right) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}\right) \delta$ 186.68, 157.34, 144.62, 144.51 (ру-CH), 137.52 (py-CH), 134.28, 123.72, 116.26 (pyrr$C H), 115.34($ py -CH$), 113.50($ py- CH$), 101.77($ acac- -CH$), 24.60\left(\right.$ acac- $\left.-\mathrm{CH}_{3}, 2 \mathrm{C}\right), 15.32$ (pyrr- $\left.\mathrm{CH}_{3}\right), 13.66\left(\right.$ pyrr- $\left.\mathrm{CH}_{3}\right)$; IR $\left(\mathrm{KBr}, \mathrm{cm}^{-1}\right) 1610,1590,1526,1489,1351,764$. Anal. Calcd. For $\mathrm{C}_{16} \mathrm{H}_{18} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Ni}$ : C 58.41; H 5.51; N 8.51. Found: C 58.15; H 5.47; N 8.64. Preparation of (py- $\left.{ }^{\mathrm{Me}} \mathbf{p y r r}\right) \mathrm{Ni}(\mathrm{Me})(\mathrm{lut})(2)$.


A 20 ml scintillation vial was charged with (py- ${ }^{\text {Me }}$ pyrr) $\mathrm{Ni}($ acac $)(0.050 \mathrm{~g}, 0.152$ $\mathrm{mmol})(1), 2,4-l u t i d i n e(0.018 \mathrm{~g}, 0.168 \mathrm{mmol})$ and 5 mL toluene. The vial was then stored at $-35{ }^{\circ} \mathrm{C}$ for 20 min after all the (py- $\left.{ }^{\mathrm{Me}} \mathrm{pyrr}\right) \mathrm{Ni}(\mathrm{acac})$ (1) had dissolved. While cold, 1.1 equivalents ( $56 \mu \mathrm{~L}$ ) of methylmagnesium bromide ( 3 M in diethyl ether) were added slowly by microsyringe. An immediate color change from red/orange to yellow was observed. The solution was stirred for 5 min at ambient temperature followed by removing solvents in vacuo to afford (py- $\left.{ }^{\mathrm{Me}} \mathrm{pyrr}\right) \mathrm{Ni}(\mathrm{Me})(\mathrm{lut})$ (2) in $40 \%$ yield as a
yellow/orange powder. The material may be recrystallized from pentane at $-35{ }^{\circ} \mathrm{C} \cdot{ }^{1} \mathrm{H}$ NMR ( $\mathrm{C}_{6} \mathrm{D}_{6}$, major isomer) $\delta 8.69(\mathrm{~d}, 5.8 \mathrm{~Hz}, 1 \mathrm{H}$, lut- $H$ ), 7.85 (br d, $5.9 \mathrm{~Hz}, 1 \mathrm{H}$, py- $H$ ), 7.08 (br d, $8.3 \mathrm{~Hz}, 1 \mathrm{H}$, py- $H$ ), 6.85 (ddd, $8.5 \mathrm{~Hz}, 7.0 \mathrm{~Hz}, 1.5 \mathrm{~Hz}, 1 \mathrm{H}$, py-H), 6.12 (s, 1H, lut- $H$ ), $6.10(\mathrm{~s}, 1 \mathrm{H}$, pyrr-H), $6.06(\mathrm{ddd}, 7.0 \mathrm{~Hz}, 6.0 \mathrm{~Hz}, 1.4 \mathrm{~Hz}, 1 \mathrm{H}$, py- $H$ ), 6.01 (br d, 5.8 $\mathrm{Hz}, 1 \mathrm{H}$, lut- $H$ ), $3.28\left(\mathrm{~s}, 3 \mathrm{H}\right.$, lut- $\left.\mathrm{CH}_{3}\right), 2.45\left(\mathrm{~s}, 3 \mathrm{H}\right.$, pyrr- $\left.\mathrm{CH}_{3}\right), 1.49\left(\mathrm{~s}, 3 \mathrm{H}\right.$, lut- $\left.\mathrm{CH}_{3}\right), 1.18$ (s, 3 H, pyrr- $\left.\mathrm{CH}_{3}\right),-0.22\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Ni}-\mathrm{CH}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}\right.$, minor isomer, nonoverlapping peaks) $\delta 8.49(\mathrm{~d}, 5.8 \mathrm{~Hz}, 1 \mathrm{H}$, lut- $H$ ), $6.17(\mathrm{~s}, 1 \mathrm{H}) ,3.12(\mathrm{~s}, 3 \mathrm{H}),, 2.65(\mathrm{~s}, 3 \mathrm{H})$, $2.46(\mathrm{~s}, 3 \mathrm{H}), 1.51(\mathrm{~s}, 3 \mathrm{H}), 0.31\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Ni}-\mathrm{CH}_{3}\right) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}\right.$, major isomer) $\delta$ $160.23,159.78,151.02$ (lut- $C H$ ), 147.47 (py-CH), 147.22, 144.62, 141.28, 136.26 (py$C \mathrm{H}), 134.87,125.52($ lut- CH ), 122.72, $122.52($ lut- CH$), 116.07$ (pyrr- CH ), 115.98 (pyCH ), 114.56 (py- CH ), 26.19 (lut- $\mathrm{CH}_{3}$ ), $20.16\left(\right.$ lut- $\left.\mathrm{CH}_{3}\right), 14.56$ (pyrr- $\mathrm{CH}_{3}$ ), 13.60 (pyrr$\left.C \mathrm{H}_{3}\right),-4.34\left(\mathrm{Ni}-\mathrm{CH}_{3}\right)$. Anal. Calcd. For $\mathrm{C}_{19} \mathrm{H}_{23} \mathrm{~N}_{3} \mathrm{Ni}$ : C 64.81; H 6.58; N 11.93. Found: C 64.80; H 6.50; N 11.87.

## Preparation of $N$-deuterio-4-deuterio-3,5-dimethyl-2-(2-pyridyl)pyrrole ( py - ${ }^{\mathrm{Me}} \mathbf{p y r r}$ -

 $\left.d_{2}\right)$.

A 50 mL bomb flask was charged with 3,5-dimethyl-2-(2-pyridyl)pyrrole ( 251 mg , 1.457 mmol ), $p$-toluenesulfonic acid ( $10 \mathrm{~mol} \%$ ), tetrabutylammonium bromide ( $10 \mathrm{~mol} \%$ ) and 3 mL of toluene and $\mathrm{D}_{2} \mathrm{O}$. The solution was stirred at $120^{\circ} \mathrm{C}$ overnight. After cooling to room temperature, the organic layer was extracted with diethyl ether and solvent was removed under vacuum to afford py- ${ }^{\mathrm{Me}}$ pyrr- $d_{2}$ in $40 \%$ yield with $99 \%$ deuterium incorporation to the 4-position of pyrrole. Py- ${ }^{\text {Me }}$ pyrr- $d_{2}$ was analyzed by ${ }^{1} \mathrm{H}$ NMR
spectroscopy and used without further purification. ${ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{CDCl}_{3}\right) \delta 8.45(\mathrm{~d}, 4.8 \mathrm{~Hz}$, 1H), 7.61 (t, $7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.45(\mathrm{~d}, 8.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.96(\mathrm{t}, 6 \mathrm{~Hz}, 1 \mathrm{H}), 2.35(\mathrm{~s}, 3 \mathrm{H}), 2.28(\mathrm{~s}$, $3 \mathrm{H})$.

Preparation of 4-deuterio-3,5-bis(trideuteriomethyl)-2-(2-pyridyl)pyrrole (py${ }^{\mathrm{Me}} \mathrm{pyrr}^{-} \boldsymbol{d}_{7}$ ).


A 100 mL round bottom flask was charge with $1,1,1,3,3,5,5,5$-octadeuteriopentane-2,4-dione ( $99 \%$ deuterium incorporation to all positions) ( $0.400 \mathrm{~g}, 3.7 \mathrm{mmol}$ ), 2(aminomethyl)pyridine ( $0.440 \mathrm{~g}, 4.07 \mathrm{mmol}$ ), approximate 40 mL xylenes and catalytic amount of $\mathrm{D}_{2} \mathrm{SO}_{4}$. The round bottom flask was fitted with a Dean-Stark trap and a reflux condenser. The reaction mixture was heated to reflux overnight. The crude product obtained after removal of solvent was purified by flash chromatography on silica gel (hexane:ethyl acetate $\left.=5: 1,3 \% \mathrm{Et}_{3} \mathrm{~N}\right)$. Following removal of solvents, py- ${ }^{\mathrm{Me}}$ pyrr- $d_{7}(345$ $\mathrm{mg}, 50 \%$ ) was obtained as a yellow solid. The proton NMR spectrum indicates that the resulting ligand is a mixture of isotopologues and isotopomers. The overall deuterium incorporation to all positions is $60 \% .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 9.18(\mathrm{br}, 1 \mathrm{H}), 8.45(\mathrm{~d}, 4.8 \mathrm{~Hz}$, $1 \mathrm{H}), 7.61(\mathrm{t}, 7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.45(\mathrm{~d}, 8.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.96(\mathrm{t}, 6 \mathrm{~Hz}, 1 \mathrm{H}), 5.82(\mathrm{~d}, 3.1 \mathrm{~Hz}, 0.4 \mathrm{H})$ 2.31-2.35 (m, 1.2H), 2.25-2.28 (m, 1.2H).

Preparation of (py- $\left.{ }^{\mathbf{M e}} \mathbf{p y r r}-d_{l}\right) \mathrm{Ni}\left(\mathrm{CH}_{3}\right)$ (lut) (2- $\left.\boldsymbol{d}_{1}\right)$.
(TMEDA)NiMe ${ }_{2}+$


A 20 mL scintillation vial was charged with py- ${ }^{\mathrm{Me}}{ }^{\mathrm{p}} \operatorname{prr}-d_{2}(0.020 \mathrm{~g}, 0.12 \mathrm{mmol}), 2,4-$ lutidine $(0.017 \mathrm{~g}, 0.16 \mathrm{mmol})$, and (TMEDA)Ni(CH3$)_{2}(0.024 \mathrm{~g}, 0.12 \mathrm{mmol})$ and 3 mL diethyl ether. The resulting solution was allowed to stir at room temperature for 2 hours followed by removing solvents in vacuo to afford (py- $\left.{ }^{\mathrm{Me}}{ }^{\mathrm{pyrr}}-\boldsymbol{d}_{1}\right) \mathrm{Ni}\left(\mathrm{CH}_{3}\right)(\mathrm{lut})\left(\mathbf{2}-\boldsymbol{d}_{1}\right)$ in $85 \%$ yield as a dark yellow-brown powder. The material may be recrystallized from pentane at $-35^{\circ} \mathrm{C}$. The level of deuterium incorporation to the 3-position of pyrrole remains $99 \%$. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}\right.$, major isomer) $\delta 8.69(\mathrm{~d}, 5.8 \mathrm{~Hz}, 1 \mathrm{H}$, lut- $H$ ), 7.85 (br d, $5.9 \mathrm{~Hz}, 1 \mathrm{H}$, pyH), 7.08 (br d, $8.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{py}-H), 6.85$ (ddd, $8.5 \mathrm{~Hz}, 7.0 \mathrm{~Hz}, 1.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{py}-H), 6.12$ (s, 1 H , lut- $H$ ), 6.06 (ddd, $7.0 \mathrm{~Hz}, 6.0 \mathrm{~Hz}, 1.4 \mathrm{~Hz}, 1 \mathrm{H}$, py- $H$ ), 6.01 (br d, $5.8 \mathrm{~Hz}, 1 \mathrm{H}$, lut- $H$ ), $3.28\left(\mathrm{~s}, 3 \mathrm{H}\right.$, lut- $\left.\mathrm{CH}_{3}\right), 2.45\left(\mathrm{~s}, 3 \mathrm{H}\right.$, pyrr- $\left.\mathrm{CH}_{3}\right), 1.49\left(\mathrm{~s}, 3 \mathrm{H}\right.$, lut- $\left.\mathrm{CH}_{3}\right), 1.18(\mathrm{~s}, 3 \mathrm{H}$, pyrr-$\left.\mathrm{CH}_{3}\right),-0.22\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Ni}-\mathrm{CH}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}\right.$, minor isomer, non-overlapping peaks) $\delta$ $8.49(\mathrm{~d}, 5.8 \mathrm{~Hz}, 1 \mathrm{H}$, lut-H), $3.12(\mathrm{~s}, 3 \mathrm{H}),, 2.65(\mathrm{~s}, 3 \mathrm{H}), 2.46(\mathrm{~s}, 3 \mathrm{H}), 1.51(\mathrm{~s}, 3 \mathrm{H}), 0.31(\mathrm{~s}$, $\left.3 \mathrm{H}, \mathrm{Ni}-\mathrm{CH}_{3}\right)$.
(py- $\left.{ }^{\mathrm{Me}} \mathbf{p y r r}-\boldsymbol{d}_{6}\right) \mathbf{N i}\left(\mathbf{C H}_{3}\right)($ lut $)\left(2-\boldsymbol{d}_{7}\right)$ was prepared with py- ${ }^{\mathrm{Me}}$ pyrr- $d_{7}$ using the method described above. The degree of deuterium incorporation is identical to the starting py-pyrr- $d_{7}$.


Preparation of (py- $\left.{ }^{\mathrm{Me}} \mathbf{p y r r}\right) \mathrm{Ni}\left(\mathrm{CD}_{3}\right)($ lut $)\left(2-\boldsymbol{d}_{3}\right)$.


A 20 mL scintillation vial was charged with 3,5-dimethyl-2-(2-pyridyl)pyrrole (0.020
$\mathrm{g}, 0.11 \mathrm{mmol}), 2,4-\mathrm{lutidine}(0.015 \mathrm{~g}, 0.14 \mathrm{mmol})$, and (TMEDA)Ni( $\left.\mathrm{CD}_{3}\right)_{2}(0.024 \mathrm{~g}, 0.11$
mmol ). To the vial was added 5 mL of THF, and the yellow solution was allowed to stir at room temperature overnight. Solvent was removed under vacuum leaving a dark yellow-brown residue. The residue was extracted with $10 \times 2 \mathrm{~mL}$ pentane, discarding the first 6 mL . The yellow extracts were stored at $-35^{\circ} \mathrm{C}$ overnight, furnishing 12 mg of yellow crystals (30\%). ${ }^{1} \mathrm{H}$ NMR ( $\mathrm{C}_{6} \mathrm{D}_{6}$, major isomer) $\delta 8.69(\mathrm{~d}, 5.8 \mathrm{~Hz}, 1 \mathrm{H}$, lut- $H$ ), 7.85 (br d, $5.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{py}-H$ ), 7.08 (br d, $8.3 \mathrm{~Hz}, 1 \mathrm{H}$, py-H), 6.85 (ddd, $8.5 \mathrm{~Hz}, 7.0 \mathrm{~Hz}, 1.5 \mathrm{~Hz}$, 1 H, py-H), $6.12(\mathrm{~s}, 1 \mathrm{H}$, lut- $H$ ), $6.10(\mathrm{~s}, 1 \mathrm{H}$, pyrr- $H), 6.06(\mathrm{ddd}, 7.0 \mathrm{~Hz}, 6.0 \mathrm{~Hz}, 1.4 \mathrm{~Hz}$, $1 \mathrm{H}, \mathrm{py}-H), 6.01\left(\mathrm{brd}, 5.8 \mathrm{~Hz}, 1 \mathrm{H}\right.$, lut- $H$ ), $3.28\left(\mathrm{~s}, 3 \mathrm{H}\right.$, lut- $\left.\mathrm{CH}_{3}\right), 2.45(\mathrm{~s}, 3 \mathrm{H}$, pyrr-CH3$)$, $1.49\left(\mathrm{~s}, 3 \mathrm{H}\right.$, lut- $\left.\mathrm{CH}_{3}\right), 1.18\left(\mathrm{~s}, 3 \mathrm{H}\right.$, pyrr- $\left.\mathrm{CH}_{3}\right)$.

## Preparation of (py- $\left.{ }^{\mathrm{Me}} \mathbf{p y r r}\right) \mathrm{Ni}(\mathbf{P h})($ lut $)(3)$.



A 20 ml scintillation vial was charged with ( $\mathrm{py}-{ }^{\mathrm{Me}} \mathrm{pyrr}$ ) Ni(acac) $(0.050 \mathrm{~g}, 0.152 \mathrm{mmol})$ (1), 2,4-lutidine $(0.018 \mathrm{~g}, 0.168 \mathrm{mmol})$ and 5 mL toluene. The vial was then stored at $35{ }^{\circ} \mathrm{C}$ for 20 min after all the ( $\mathrm{py}-{ }^{\mathrm{Me}} \mathrm{pyrr}$ ) $\mathrm{Ni}(\mathrm{acac})(1)$ had dissolved. While cold, 1.1 equivalents ( $56 \mu \mathrm{~L}$ ) of phenylmagnesium bromide ( 3 M in diethyl ether) were added slowly by microsyringe. An immediate color change from red/orange to yellow was observed. The solution was stirred for 5 min at ambient temperature followed by removing solvents in vacuo to afford 25 mg (40\%) (py- ${ }^{\mathrm{Me}}$ pyrr) $\mathrm{Ni}(\mathrm{Ph})$ (lut) (3) as yellow/orange powder. The material may be recrystallized from pentane at $-35{ }^{\circ} \mathrm{C}$ to obtain material of analytical purity. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}\right.$, major isomer) $\delta 8.77(\mathrm{~d}, 5.9 \mathrm{~Hz}, 1 \mathrm{H}$, lut- $H$ ), 7.93 (br d, $7.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ph}-H$ ), 7.81 (br d, $7.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ph}-H$ ), $7.02-7.14$ (m, 2H, Ph-H), 7.12 (br d, $5.8 \mathrm{~Hz}, 1 \mathrm{H}$, py-H), 7.02 (br d, $8.3 \mathrm{~Hz}, 1 \mathrm{H}$, py- $H$ ), $6.91(\mathrm{tt}, 7.3 \mathrm{~Hz}, 1.2$

Hz, 1H, Ph-H), 6.75 (ddd, $8.3 \mathrm{~Hz}, 7.1 \mathrm{~Hz}, 1.6 \mathrm{~Hz}, 1 \mathrm{H}$, py-H), 6.08 (s, 1H, pyrr-H), 5.95 (s, 1 H , lut- $H$ ), 5.93 (br d, $6.0 \mathrm{~Hz}, 1 \mathrm{H}$, lut- $H$ ), 5.75 (ddd, $7.1 \mathrm{~Hz}, 6.0 \mathrm{~Hz}, 1.4 \mathrm{~Hz}, 1 \mathrm{H}$, py- $H$ ), $3.40\left(\mathrm{~s}, 3 \mathrm{H}\right.$, lut- $\left.\mathrm{CH}_{3}\right), 2.43\left(\mathrm{~s}, 3 \mathrm{H}\right.$, pyrr- $\left.\mathrm{CH}_{3}\right), 1.35\left(\mathrm{~s}, 3 \mathrm{H}\right.$, lut- $\left.\mathrm{CH}_{3}\right), 1.18(\mathrm{~s}, 3 \mathrm{H}$, pyrr$\left.\mathrm{CH}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR ( $\mathrm{C}_{6} \mathrm{D}_{6}$, minor isomer, non-overlapping peaks) $\delta 8.58(\mathrm{~d}, 5.8 \mathrm{~Hz}, 1 \mathrm{H}$, lutH), $6.05(\mathrm{~s}, 1 \mathrm{H}) ,3.18(\mathrm{~s}, 3 \mathrm{H}),, 2.41(\mathrm{~s}, 3 \mathrm{H}), 1.73(\mathrm{~s}, 3 \mathrm{H}), 1.39(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}\right.$, major isomer) $\delta 161.33,160.30,159.55,151.42(\mathrm{py}-\mathrm{CH}), 150.48$ (lut- CH$), 147.67$, 141.60, $137.09(\mathrm{Ph}-C), 136.56(\mathrm{py}-\mathrm{CH}), 135.77(\mathrm{Ph}-C), 134.92$ (q), $126.78(\mathrm{Ph}-C)$, 126.54 ( $\mathrm{Ph}-\mathrm{C}$ ), 125.61 (lut- CH ), 123.06 (q), 122.91 (Ph-C), 122.68 (lut- CH ), 116.09 (pyrr- CH ), $115.73($ py- CH$), 114.82$ (py- CH$), 26.06\left(\right.$ lut- $\left.\mathrm{CH}_{3}\right), 20.08$ (lut- $\mathrm{CH}_{3}$ ), 14.48 (pyrr- $\mathrm{CH}_{3}$ ), $13.45\left(\right.$ pyrr- $\left.-\mathrm{CH}_{3}\right)$. Anal. Calcd. For $\mathrm{C}_{24} \mathrm{H}_{25} \mathrm{~N}_{3} \mathrm{Ni}$ : C 69.60; H 6.08; N 10.15. Found: C 69.01; H 5.92; N 9.84.
(py- $\left.{ }^{\mathbf{M e}} \mathbf{p y r r}\right) \mathbf{N i}(\boldsymbol{p}$-Tol)(lut) was prepared using the same method as described above. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}\right.$, major isomer) $\delta 8.79(\mathrm{~d}, 5.9 \mathrm{~Hz}, 1 \mathrm{H}$, lut- $H$ ), 7.82 (br d, $7.5 \mathrm{~Hz}, 1 \mathrm{H}, p-$ tolyl-H), 7.71 (br d, $7.5 \mathrm{~Hz}, 1 \mathrm{H}, p$-tolyl-H), 7.20 (br d, $6.2 \mathrm{~Hz}, 1 \mathrm{H}$, py-H), 7.03 (br d, 8.3 Hz, 1H, py-H), 6.99 (br d, 7.2 Hz, 1H, p-tolyl-H), 6.91 (br d, 7.1 Hz, 1H, $p$-tolyl- $H$ ), 6.75 (ddd, $8.3 \mathrm{~Hz}, 7.1 \mathrm{~Hz}, 1.6 \mathrm{~Hz}, 1 \mathrm{H}$, py- $H$ ), 6.09 (s, 1H, pyrr-H), 5.96 (s, 1H, lut-H), 5.96 (br d, $6.0 \mathrm{~Hz}, 1 \mathrm{H}$, lut- $H$ ), 5.76 (ddd, $7.2 \mathrm{~Hz}, 6.2 \mathrm{~Hz}, 1.4 \mathrm{~Hz}, 1 \mathrm{H}$, py- $H$ ), $3.42(\mathrm{~s}, 3 \mathrm{H} \text {, lut-CH })_{3}$, $2.44\left(\mathrm{~s}, 3 \mathrm{H}\right.$, pyrr- $\left.\mathrm{CH}_{3}\right), 2.17\left(\mathrm{~s}, 3 \mathrm{H}\right.$, p-tolyl- $\left.\mathrm{CH}_{3}\right), 1.36(\mathrm{~s}, 3 \mathrm{H}$, lut-CH3$), 1.19(\mathrm{~s}, 3 \mathrm{H}$, pyrr$\left.\mathrm{CH}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR ( $\mathrm{C}_{6} \mathrm{D}_{6}$, minor isomer, non-overlapping peaks) $\delta 8.59(\mathrm{~d}, 5.9 \mathrm{~Hz}, 1 \mathrm{H}$, lutH), $6.06(\mathrm{~s}, 1 \mathrm{H}), 5.98(\mathrm{~s}, 1 \mathrm{H}) 3.20(\mathrm{~s}, 3 \mathrm{H}), 2.42(\mathrm{~s}, 3 \mathrm{H}), 1.78(\mathrm{~s}, 3 \mathrm{H}), 1.39(\mathrm{~s}, 3 \mathrm{H})$.

Preparation of (py- $\left.{ }^{\text {Ph }} \mathbf{p y r r}\right) \mathbf{N i}(\mathbf{a c a c})$ (7). A 20 mL scintillation vial was charged with $\mathrm{Ni}(\mathrm{acac})_{2}(0.150 \mathrm{~g}, 0.583 \mathrm{mmol}), 3,5-$ diphenyl-2-(2-pyridyl)pyrrole ( $0.180 \mathrm{~g}, 0.607$ $\mathrm{mmol}), \mathrm{NaH}(0.020 \mathrm{~g}, 0.833 \mathrm{mmol})$, and 12 mL of toluene. The solution was stirred at
ambient temperature for 20 min resulting in a color change from green to red/orange. The solvent was removed in vacuo and the residue was extracted with toluene, filtered through filter paper, concentrated to approximately 5 mL and then 2 ml pentane was layered on the top of toluene extracts. Dark red crystals of (py- $\left.{ }^{\mathrm{Ph}} \mathrm{pyrr}\right) \mathrm{Ni}(\mathrm{acac})(120 \mathrm{mg}$, $45 \%$ after first recrystallization) were obtained by storing this toluene/pentane solution in the freezer at $-35{ }^{\circ} \mathrm{C}$ overnight. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}\right) \delta 7.85(\mathrm{~m}, 2 \mathrm{H}, \mathrm{Ph}-H), 7.58(\mathrm{~m}, 2 \mathrm{H}, \mathrm{Ph}-$ $H$ ), 7.35 (br d, $6.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{py}-H), 7.25$ (m, 2H, Ph-H), $7.14-7.18$ (m, 3H, Ph-H), 7.08 (br d, $8.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{py}-H), 7.05(\mathrm{~m}, 1 \mathrm{H}, \mathrm{Ph}-H), 6.48(\mathrm{ddd}, 8.3 \mathrm{~Hz}, 7.2 \mathrm{~Hz}, 1.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{py}-H)$, $6.43(\mathrm{~s}, 1 \mathrm{H}$, pyrr- $H$ ), 5.94 (ddd, $7.3 \mathrm{~Hz}, 6.6 \mathrm{~Hz}, 1.3 \mathrm{~Hz}, 1 \mathrm{H}$, py- $H$ ), 4.94 (s, 1H, acacH), $1.19\left(\mathrm{~s}, 6 \mathrm{H}\right.$, acac- $\left.\mathrm{CH}_{3}\right) ;{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}\right) \delta$ 186.36, 157.60, 148.09, 144.88 (py$C \mathrm{H}), 137.82$ (ру-CH), 135.09, 130.47, 129.68 (Ph-C, 2C), 129.22 (Ph-C, 2C), 128.72 (Ph-C, 2C), 127.30 (Ph-C, 2C), 126.52 (q), 125.64 (Ph-C), 116.79 (pyrr-CH), 116.59 (py$C H), 116.01($ py -CH$), 101.67(\operatorname{acac}-\mathrm{CH}), 24.60\left(\right.$ acac- $\left.\mathrm{CH}_{3}, 2 \mathrm{C}\right)$; IR $\left(\mathrm{KBr}, \mathrm{cm}^{-1}\right) 1608$, 1577, 1522, 1489, 1464, 1383, 759, 698. Anal. Calcd. For $\mathrm{C}_{26} \mathrm{H}_{22} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Ni}: \mathrm{C} 68.91 ; \mathrm{H}$ 4.89; N 6.18. Found: C 68.76; H 4.80; N 6.08 .

Preparation of (py- $\left.{ }^{\mathbf{P h}} \mathbf{p y r r}\right) \mathbf{N i}(\mathbf{P h})(\mathbf{l u t})$ (8). A 20 ml scintillation vial was charged with (py- ${ }^{\text {Ph }}$ pyrr) $\mathrm{Ni}($ acac $)(0.060 \mathrm{~g}, 0.132 \mathrm{mmol}), 2,4-l u t i d i n e(0.015 \mathrm{~g}, 0.140 \mathrm{mmol})$ and 5 mL toluene. The vial was then kept at $-35^{\circ} \mathrm{C}$ for 20 min after all the (py- ${ }^{\mathrm{Ph}}$ pyrr) $\mathrm{Ni}(\mathrm{acac}$ ) had dissolved. While cold, 1.1 equivalents $(49 \mu \mathrm{~L})$ of phenylmagnesium bromide ( 3 M in diethyl ether) were added slowly by microsyringe. An immediate color change from red/orange to yellow was observed. The solution was stirred for 5 min at ambient temperature followed by removing solvents in vacuo to afford 25 mg (42\%) (py${ }^{\mathrm{Ph}}$ pyrr) $\mathrm{Ni}(\mathrm{Ph})($ lut ) as yellow/orange powder. The material may be recrystallized from
pentane at $-35{ }^{\circ} \mathrm{C}$ to obtain material of analytical purity. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}\right) \delta 8.59(\mathrm{~d}, 5.9$ $\mathrm{Hz}, 1 \mathrm{H}$, lut- $H$ ), $7.87(\mathrm{~m}, 2 \mathrm{H}, \mathrm{Ph}-H), 7.73(\mathrm{~m}, 2 \mathrm{H}, \mathrm{Ph}-H), 7.31(\mathrm{br} \mathrm{d}, 8.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{py}-H)$, 7.20-7.27 (m, 5H, Ph-H), 7.13 (m, 1H, Ph-H), 7.06 (m, 2H, Ph-H), 6.89 (tt, $7.3 \mathrm{~Hz}, 1.2$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{Ph}-H), 6.75$ (ddd, $8.4 \mathrm{~Hz}, 7.3 \mathrm{~Hz}, 1.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{py}-H), 6.69(\mathrm{~m}, 2 \mathrm{H}, \mathrm{Ph}-H), 6.63$ (m, 1H, Ph-H), $6.59(\mathrm{~s}, 1 \mathrm{H}$, pyrr- $H), 5.74(\mathrm{ddd}, 7.3 \mathrm{~Hz}, 6.0 \mathrm{~Hz}, 1.4 \mathrm{~Hz}, 1 \mathrm{H}$, py- $H$ ), 5.71 (br d, $6.0 \mathrm{~Hz}, 1 \mathrm{H}$, lut- $H$ ), $5.48\left(\mathrm{~s}, 1 \mathrm{H}\right.$, lut- $H$ ), $3.14\left(\mathrm{~s}, 3 \mathrm{H}\right.$, lut- $\left.\mathrm{CH}_{3}\right), 1.29(\mathrm{~s}, 3 \mathrm{H} \text {, lut-CH })_{3}$ ). ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}\right): \delta 159.85,159.8,159.48,151.31$ (py-CH), 150.78 (lut- CH$), 147.45$, $147.05,139.57,138.39,136.51$ (py-CH), 129.86 (Ph-C, 2C), 129.57, 128.71 (Ph-C, 2C), 127.21 (Ph-C, 2C), 126.22 (Ph-C, 2C), 126.21 (Ph-C, 2C), 125.47 (lut- $C \mathrm{H}$ ), 124.07 (PhC), $123.02(\mathrm{Ph}-C), 122.11($ lut- $C \mathrm{H}), 117.36($ pyrr- CH$), 117.12($ py- CH$), 116.58$ (pyrrCH ), 26.06 (lut- $\mathrm{CH}_{3}$ ), 19.94 (lut- $\mathrm{CH}_{3}$ ). Anal. Calcd. For $\mathrm{C}_{34} \mathrm{H}_{29} \mathrm{~N}_{3} \mathrm{Ni}$ : C 75.86; H 5.43; N 7.81. Found: C 76.73; H 5.32; N 7.83.

Procedure for the Reaction of 2 and 3 with Oxygen. A J. Young NMR tube was charged with a stock solution of $\mathbf{2}$ or $\mathbf{3}$ in benzene- $d_{6}$ followed by a stock solution of hexamethyldisiloxane (NMR internal standard) in benzene- $d_{6}$. On a high vacuum line, 5 equivalents of oxygen were condensed via a calibrated gas bulb with a liquid nitrogen bath. The tube was allowed to warm to room temperature. The reaction was monitored by ${ }^{1} \mathrm{H}$ NMR spectroscopy at 2 h intervals. The delay between scans was set at 40 s in order to obtain accurate integration against the hexamethyldisiloxane standard.

Procedure for the Reaction of $\mathbf{2}$ and $\mathbf{3}$ with $\mathbf{I}_{\mathbf{2}}$. A J. Young NMR tube was charged with a stock solution of $\mathbf{2}$ or $\mathbf{3}$ in benzene- $d_{6}$, then a stock solution of hexamethyldisiloxane (NMR internal standard) in benzene- $d_{6}$, followed by the addition of a solution of iodine in benzene- $d_{6}$ via microsyringe. An immediate color change was
observed. A proton spectrum was taken right after the addition of $\mathrm{I}_{2}$ and the delay between scans was set at 40 s to obtain accurate integration against the hexamethyldisiloxane standard.

Procedure for Crossover Experiments. A J. Young NMR tube was charged with 2 $(1.8 \mathrm{mg}, 0.006 \mathrm{mmol}), \mathbf{2}-\boldsymbol{d}_{\mathbf{3}}(1.8 \mathrm{mg}, 0.006 \mathrm{mmol})$, and $300 \mu \mathrm{~L} \mathrm{C}_{6} \mathrm{D}_{6}$. The solution was frozen in the cold well filled with liquid nitrogen. An additional $225 \mu \mathrm{~L} \mathrm{C}_{6} \mathrm{D}_{6}$ were added to the tube and frozen, followed by the addition of a stock solution of $\mathrm{I}_{2}(0.16 \mathrm{M}, 75 \mu \mathrm{~L}$, $0.012 \mathrm{mmol})$. The tube was capped and thawed. The ratio of ethane to ethane- $d_{3}$ was determined by integration of the ${ }^{1} \mathrm{H}$ NMR spectrum with the relaxation time set to 15 seconds. The crossover experiment between complex $\mathbf{3}$ and (py- $\left.{ }^{\mathrm{Me}} \mathrm{pyrr}\right) \mathrm{Ni}(p-\mathrm{Tol})(\mathrm{lut})$ was carried out using an analogous procedure.

## II. X-Ray Crystal Structures of Ni Compounds

Procedure for Single Crystal Structure Determination. The X-ray data were collected with a Bruker SMART APEXII CCD area detector on a D8 goniometer at 100 K. The temperature during the data collection was controlled with an Oxford Cryosystems Series 700+ instrument. Preliminary lattice parameters and orientation matrices were obtained from three sets of frames. Data were collected using graphitemonochromated and $0.5 \mathrm{~mm}-$ MonoCap-collimated $\operatorname{Mo} K \alpha$ radiation $(\lambda=0.71073 \AA)$ with the $\omega$ scan method. Data were processed with the INTEGRATE program of the APEX2 software (version 2014.5) for reduction and cell refinement. Multi-scan absorption corrections were applied by using the SCALE program for the area detector. The structure was solved by the direct method and refined on $F^{2}$ (SHELX, version 2014/7). Non-hydrogen atoms were refined with anisotropic displacement parameters, and
hydrogen atoms on carbons were placed in idealized positions $(\mathrm{C}-\mathrm{H}=0.95-0.98 \AA)$ and included as riding with $U_{\text {iso }}(\mathrm{H})=1.2$ or $1.5 U_{\mathrm{eq}}($ non -H$)$.

(A)



Figure S1. (A) X-ray crystal structure of 1 with $50 \%$ probability ellipsoids. (B) X-ray crystal structures of cis- and trans-2 with $30 \%$ probability ellipsoids. Hydrogen atoms have been omitted for clarity.
(A)

(B)


Figure S2. X-ray crystal structures of (py- $\left.{ }^{\text {Ph }} \mathrm{pyrr}\right) \mathrm{Ni}(\mathrm{acac}) 7$ (A) and (py- $\left.{ }^{\text {Ph }} \mathrm{pyrr}\right) \mathrm{Ni}(\mathrm{Ph})$ (lut)
8 (B) with $50 \%$ probability ellipsoids. Hydrogen atoms have been omitted for clarity.
Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for $\left(\right.$ py- ${ }^{\text {Ph }}$ pyrr $) \mathrm{Ni}(\mathrm{Ph})(\mathrm{lut}): \mathrm{Ni}(1)-\mathrm{N}(1)=$
$1.967(4), \mathrm{Ni}(1)-\mathrm{N}(2)=1.909(4), \mathrm{Ni}(1)-\mathrm{C}(29)=1.885(5), \mathrm{N}(3)-\mathrm{Ni}(1)-\mathrm{N}(2)=176.77(15)$.
(A)

(B)


Figure S3. X-ray crystal structures of (py- ${ }^{\mathrm{Me}} \mathrm{pyrr}_{2}{ }_{2} \mathrm{Ni}(\mathrm{bpy}) 9$ (A) and (py$\left.{ }^{\mathrm{Me}} \mathrm{pyrr}\right) \mathrm{Ni}(\mathrm{Ph})($ phen $) \mathbf{1 0}$ (B) with $50 \%$ probability ellipsoids. Hydrogen atoms have been omitted for clarity.

## III. Assigning the cis- and trans- Isomers for 2

DFT Calculations. Density functional calculations were performed using the Gaussian $09^{4}$ quantum chemistry package. The energy difference between the geometry optimized cis and trans isomers of 2 was calculated using the lc-uolyp ${ }^{5} / \mathrm{m}^{2}-31 \mathrm{G}^{* 6}$ method with the zero-point and thermodynamic corrections. The trans-isomer is more stable by $1.93 \mathrm{kcal} / \mathrm{mol}$ relative to the cis-geometry, in gas phase.
(A)

(B)


Figure S4. ${ }^{1} \mathrm{H}-{ }^{1} \mathrm{H} \operatorname{COSY}(\mathrm{A})$ and ${ }^{1} \mathrm{H}-{ }^{1} \mathrm{H} \operatorname{NOESY}(\mathrm{B})$ spectra of $\mathbf{2}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.

## IV. Additional Data for Characterizing Intermediate 4 and 5

Cyclic Voltammetry. Cyclic voltammetry was carried out in an Mbraun glovebox under nitrogen atmosphere. Tetrabutylammonium hexafluorophosphate was used as the electrolyte. A glassy carbon electrode (GCE) was used as the working electrode, whereas Pt and Ag wires were employed as the counter and reference electrodes, respectively. Ferrocene was added at the end of the experiment as the internal standard.

The CV of $\mathbf{2}$ exhibits two irreversible oxidation waves at 12 and 411 mV (vs. $\mathrm{Fc} / \mathrm{Fc}^{+}$) (Figure S5). The potentials were determined by measuring $\mathrm{E}_{1 / 2}$ relative to the $\mathrm{E}_{1 / 2}$ of the oxidation wave of $\mathrm{Fc} / \mathrm{Fc}^{+} .7$ The irreversible waves underline the unstable nature of highvalent Ni species. The second oxidation potential, therefore, could only serve as an estimation for the $\mathrm{Ni}(\mathrm{III}) / \mathrm{Ni}(\mathrm{IV})$ transition, rather than a direct measurement.


Figure S5. Cyclic voltammetry of $2(0.1 \mathrm{mM})$ in THF with $\mathrm{Bu}_{4} \mathrm{NPF}_{6}(0.1 \mathrm{M})$, scan rate $=$ $100 \mathrm{mV} / \mathrm{s}$.

DFT Calculations of Intermediate 4. All density functional calculations were performed using the Gaussian $09^{4}$ quantum chemistry package. The structure of $\mathbf{4}$ was optimized using the LC-UOLYP method with the m6-31G* basis set for the nickel center and 6-31G* for main-group atoms. A second single-point calculation was performed using the optimized conformations in order to obtain more accurate energies. The singlepoint calculations utilized the LC-UOLYP method with the Def2-TZVP basis set for the nickel and 6-311G** for the main-chain atoms. The LC-UOLYP and the m6-31G* have been used previously in DFT calculations of nickel complexes ${ }^{8}$ and performed well in
geometry optimization calculations. Both the high $(S=3 / 2)$ and low $(S=1 / 2)$ spin states were optimized, with the low spin state being the more stable spin isomer. The pentacoordinated $\mathrm{Ni}($ III ) complexes optimized to a square-pyramidal structure, 4.

| $\mathbf{4}$ |  |  |  |
| :--- | ---: | ---: | ---: |
| C | 1.72894400 | -1.89221800 | 1.50512200 |
| C | 2.54022700 | 0.05872500 | 0.54784700 |
| C | 2.85861700 | -2.06070400 | 2.26575400 |
| H | 0.90352900 | -2.59581600 | 1.53716000 |
| C | 3.71683600 | -0.05675200 | 1.28826500 |
| C | 3.86802400 | -1.11552800 | 2.14652500 |
| H | 2.94878000 | -2.91173600 | 2.92861500 |
| H | 4.49586900 | 0.68430600 | 1.17554300 |
| H | 4.77966800 | -1.21423500 | 2.72667400 |
| N | 1.03229800 | 1.01182000 | -1.02020500 |
| C | 2.23444400 | 1.10887500 | -0.37929100 |
| C | 0.91197700 | 2.05486900 | -1.84227700 |
| C | 2.89471300 | 2.25624000 | -0.79767600 |
| C | 2.04197500 | 2.85258800 | -1.72864400 |
| H | 2.22739000 | 3.77137900 | -2.27018700 |
| C | -0.28060600 | 2.24938200 | -2.70711200 |
| H | -0.51603500 | 1.34369200 | -3.27338800 |
| H | -1.16581600 | 2.51255700 | -2.12125600 |
| H | -0.10609900 | 3.05298200 | -3.42371100 |
| C | 4.22225100 | 2.77973300 | -0.36904900 |
| H | 4.26463200 | 2.97485400 | 0.70657400 |
| H | 5.03621600 | 2.09002700 | -0.61090600 |
| H | 4.43638400 | 3.72174100 | -0.87677600 |
| N | 1.57168400 | -0.86134200 | 0.68307200 |
| Ni | 0.03327100 | -0.53701300 | -0.57651600 |
| C | -1.29524900 | 1.43440700 | 1.44839000 |
| C | -2.53964400 | 0.73302000 | -0.3336600 |
| C | -2.31855400 | 2.28869500 | 1.82841400 |
| C | -3.58163000 | 1.56620400 | -0.02121300 |
| H | -2.61409100 | 0.07169600 | -1.18913600 |
| C | -3.48452700 | 2.37543100 | 1.09905200 |
| H | -2.18631700 | 2.89560500 | 2.71692300 |
| H | -4.46830000 | 1.57290100 | -0.64502000 |
| N | -1.41112000 | 0.65706000 | 0.37263200 |
| C | -0.04036100 | 1.37973700 | 2.24464600 |
| H | 0.19791500 | 0.35356500 | 2.52270100 |
| H | 0.79269200 | 1.76895000 | 1.65679700 |
| H | -0.1339990 | 1.97620400 | 3.15191800 |
| C | -4.59762200 | 3.28555700 | 1.49561400 |
|  |  |  |  |
| H |  |  |  |
| H |  |  |  |


| H | -4.33232400 | 3.89026100 | 2.36329600 |
| :--- | ---: | ---: | ---: |
| H | -4.85895200 | 3.95905600 | 0.67661000 |
| H | -5.49327900 | 2.71104200 | 1.74302200 |
| C | 1.02713200 | -1.42894100 | -1.96424300 |
| H | 1.96011200 | -0.88910800 | -2.09046100 |
| H | 1.18117800 | -2.47065200 | -1.70366500 |
| H | 0.39225800 | -1.34108000 | -2.84644900 |
| I | -1.44273000 | -2.59925500 | -0.40225900 |

DFT Calculations of the EPR parameters of 4. The Mulliken spin-density plot (Figure 3) reveals that the unpaired alpha electron is primarily localized on the Ni center with some ligand contributions primarily arising from the pyridine ligand and minor contributions from lutidine and pyrrole. The spin density also shows some beta spin contribution on the methyl group. In order to obtain more evidence for the proposed $\mathrm{Ni}(\mathrm{III})$ intermediate, we carried out a calculation on the EPR parameters of intermediate 4 using the ORCA package. ${ }^{9}$ The DFT optimized structures from above were used as the input coordinates with the B3LYP method and EPR-III basis set for the main-group atoms, the def2-TZVP basis set for nickel and iodide for the calculation of the coupledperturbed SCF equations. The g-tensor parameter was calculated from the converged CPSCF wavefunction (Table S1). The isotropic and dipolar contributions of the hyperfine coupling constants were obtained with the second-order spin-orbit correction. The rhombic g values are in good agreement with the experimental values. The difference of $\mathrm{A}_{\text {iso }}$ between the experimental and computational is within the range of systematic error. For instance, when the EPR spectrum was conducted in THF glass, $\mathrm{A}_{\text {iso }}$ was varied to 49.7 MHz (Figure S6).

Table S1. Comparison of Experimental and Calculated EPR Parameters for 4

|  | $\mathrm{g}_{\mathrm{x}}$ | $\mathrm{g}_{\mathrm{y}}$ | $\mathrm{g}_{\mathrm{z}}$ | $\mathrm{A}_{\text {iso }}(\mathrm{MHz})$ |
| :--- | :--- | :--- | :--- | :---: |
| 4 (DFT) | 2.189 | 2.163 | 2.026 | 46.1 |
| Expt. | 2.21 | 2.14 | 2.03 | 41.9 |



Figure S6. X-band EPR spectrum of 4 recorded in THF glass at 10 K . Microwave frequency $=9.380 \mathrm{GHz}$, power $=0.25 \mathrm{~mW}$, modulation amplitude $=1 \mathrm{mT} / 100 \mathrm{kHz}$. Spectroscopic parameters for 4: $\mathrm{g}_{\mathrm{x}}=2.21, \mathrm{~g}_{\mathrm{y}}=2.14, \mathrm{~g}_{\mathrm{z}}=2.03, \mathrm{~A}_{\mathrm{xx}}=19 \mathrm{MHz}, \mathrm{A}_{\mathrm{yy}}=67$ $\mathrm{MHz}, \mathrm{A}_{z z}=63 \mathrm{MHz}$.

DFT Calculations of Intermediate 5. The structure of $\mathbf{5}$ was optimized using the B3LYP method with the Def2-TZVP basis set for the nickel center and 6-31G* for maingroup atoms. Magnetic shielding tensor calculations were performed using the gaugeindependent atomic orbital method with the B3LYP functional and the same basis sets for the nickel and main chain elements used in the geometric optimization. The proton NMR chemical shifts were obtained by subtracting proton chemical shielding constants from the TMS reference shielding constant obtained at the same level as the calculation of the
nickel dimers. $\mathbf{5 a}$ and $\mathbf{5 b}$ were converged as the lowest energy conformations, whereas $\mathbf{5 c}$ has a significantly higher energy. The different stereoisomers are determined to be the kinetic products. We calculated the $\mathrm{C}_{2}$ symmetric conformation, $\mathbf{5 g}$, which could interconvert with $\mathbf{5 c} . \mathbf{5 g}$ has a comparable energy relative to $\mathbf{5 c}$ (within the calculation error), and our NMR experiments favor the $\mathrm{C}_{1}$ symmetric structure $\mathbf{5 c}$.


5a

| C | -2.58437200 | -2.76836800 | -0.24447700 |
| :--- | ---: | ---: | ---: |
| C | -4.18649200 | -1.08162200 | 0.09283600 |
| C | -3.45129600 | -3.76383300 | 0.17106600 |
| H | -1.57093100 | -2.99159400 | -0.55902500 |
| C | -5.11251000 | -2.05539200 | 0.52522300 |
| C | -4.74129800 | -3.38501200 | 0.56219600 |
| H | -3.12956300 | -4.79652900 | 0.18946000 |
| H | -6.10485400 | -1.75278200 | 0.82589300 |
| H | -5.45167800 | -4.13367700 | 0.89521200 |
| N | -3.37195300 | 1.11089200 | -0.43575100 |
| C | -4.42857500 | 0.32812100 | -0.00191400 |
| C | -3.77593300 | 2.39958800 | -0.47404100 |
| C | -5.53409800 | 1.16049800 | 0.26560700 |
| C | -5.10522300 | 2.46494500 | -0.03532300 |
| H | -5.69242000 | 3.36760000 | 0.06121300 |
| C | -2.88010200 | 3.51068000 | -0.92094200 |
| H | -1.92683200 | 3.49153700 | -0.38272600 |
| H | -2.65439900 | 3.44875500 | -1.99167400 |
| H | -3.35133300 | 4.47792500 | -0.73836000 |
| C | -6.89005800 | 0.78328500 | 0.78632000 |
| H | -7.41071200 | 0.08569500 | 0.12081800 |
| H | -6.83818300 | 0.31399000 | 1.77510700 |
| H | -7.51837800 | 1.67129900 | 0.88172800 |
| N | -2.93325400 | -1.47672900 | -0.28252600 |
| Ni | -1.78533900 | 0.11360900 | -0.87839400 |
| C | -2.41393200 | 0.06199200 | -2.75583800 |
| H | -3.49743700 | 0.09745300 | -2.72411400 |


| H | -1.97915700 | 0.94923300 | -3.21506000 |
| :--- | ---: | :---: | :---: |
| H | -2.02806400 | -0.85676000 | -3.18788800 |
| I | 0.61478400 | -0.66869100 | -1.63753500 |
| C | 2.58417800 | 2.76828300 | 0.24410800 |
| C | 4.18642100 | 1.08162100 | -0.09303400 |
| C | 3.45103300 | 3.76377500 | -0.17151200 |
| H | 1.57071700 | 2.99145800 | 0.55862800 |
| C | 5.11235600 | 2.05541700 | -0.52556400 |
| C | 4.74105300 | 3.38500400 | -0.56264300 |
| H | 3.12923200 | 4.79644800 | -0.18998600 |
| H | 6.10469100 | 1.75284200 | -0.82629400 |
| H | 5.45137000 | 4.13368600 | -0.89575800 |
| N | 3.37199400 | -1.11094000 | 0.43562500 |
| C | 4.42859600 | -0.32808700 | 0.00185700 |
| C | 3.77607000 | -2.39959000 | 0.47391700 |
| C | 5.53423000 | -1.16038000 | -0.26553100 |
| C | 5.10542300 | -2.46484800 | 0.03534000 |
| H | 5.69271400 | -3.36745600 | -0.06105900 |
| C | 2.88026000 | -3.51077900 | 0.92062600 |
| H | 2.65356700 | -3.44834100 | 1.9911600 |
| H | 1.92745700 | -3.49230100 | 0.38155400 |
| H | 3.35202500 | -4.47794100 | 0.73899700 |
| C | 6.89024600 | -0.78305700 | -0.78601800 |
| H | 6.83858400 | -0.31460000 | -1.77522100 |
| H | 7.41036100 | -0.08471900 | -0.12088900 |
| H | 7.51895600 | -1.67090200 | -0.88044500 |
| N | 2.93315500 | 1.47667400 | 0.28227400 |
| Ni | 1.78524900 | -0.11365200 | 0.87823100 |
| C | 2.41413800 | -0.06172800 | 2.75565900 |
| H | 3.49763400 | -0.09714400 | 2.72368400 |
| H | 2.02833400 | 0.85712100 | 3.18755300 |
| H | 1.97949100 | -0.94887200 | 3.21517800 |
| I | -0.61476400 | 0.66864200 | 1.63795100 |

## 5b

| C | -2.94055100 | -2.37642400 | -0.95480600 |
| :--- | ---: | ---: | ---: |
| C | -4.10947000 | -0.92056400 | 0.47302600 |
| C | -3.80221600 | -3.42741700 | -0.69528400 |
| H | -2.09894000 | -2.48869500 | -1.62926000 |
| C | -5.01999300 | -1.95730700 | 0.77319700 |
| C | -4.86242500 | -3.19886100 | 0.19068400 |
| H | -3.64922500 | -4.38902800 | -1.16665400 |
| H | -5.83338500 | -1.77101400 | 1.45903100 |
| H | -5.56090200 | -3.99540000 | 0.42223600 |


| N | -3.14777500 | 1.27316100 | 0.58852700 |
| :---: | :---: | :---: | :---: |
| C | -4.15115900 | 0.41190600 | 0.99773100 |
| C | -3.34588700 | 2.47815100 | 1.16389700 |
| C | -5.00281600 | 1.09710700 | 1.88873800 |
| C | -4.48043100 | 2.39767400 | 1.98412000 |
| H | -4.87391100 | 3.20025700 | 2.59233600 |
| C | -2.44994900 | 3.64975900 | 0.91683500 |
| H | -1.40129400 | 3.39281200 | 1.09721500 |
| H | -2.52877800 | 4.01420700 | -0.11402200 |
| H | -2.71350400 | 4.47617000 | 1.57905500 |
| C | -6.20521200 | 0.58101900 | 2.62338300 |
| H | -6.98610400 | 0.22412400 | 1.94265300 |
| H | -5.95529300 | -0.24621900 | 3.29700300 |
| H | -6.64348100 | 1.37411800 | 3.23277800 |
| N | -3.08308000 | -1.16900200 | -0.39516000 |
| Ni | -1.91943600 | 0.49424200 | -0.66462700 |
| C | -3.07702200 | 1.21238700 | -2.10662500 |
| H | -4.09139400 | 1.25906100 | $-1.72614400$ |
| H | -2.66991800 | 2.20238800 | -2.31469800 |
| H | -2.97854900 | 0.54061300 | -2.95584800 |
| I | -0.00015400 | -0.00088300 | -2.45715800 |
| C | 2.94094700 | 2.37590100 | -0.95636600 |
| C | 4.10935700 | 0.92086700 | 0.47271600 |
| C | 3.80258700 | 3.42700700 | -0.69721900 |
| H | 2.09957200 | 2.48779600 | $-1.63117700$ |
| C | 5.01984400 | 1.95773900 | 0.77252800 |
| C | 4.86250900 | 3.19894800 | 0.18922000 |
| H | 3.64977600 | 4.38833800 | -1.16921700 |
| H | 5.83302100 | 1.77182000 | 1.45871900 |
| H | 5.56093500 | 3.99560500 | 0.42051900 |
| N | 3.14727500 | -1.27263200 | 0.58959200 |
| C | 4.15082200 | -0.41128400 | 0.99824400 |
| C | 3.34553100 | -2.47745000 | 1.16535200 |
| C | 5.00253400 | -1.09611400 | 1.88947000 |
| C | 4.48012500 | -2.39663600 | 1.98543400 |
| H | 4.87368200 | -3.19900700 | 2.59388100 |
| C | 2.44959500 | -3.64919800 | 0.91892800 |
| H | 1.40113300 | -3.39289800 | 1.10134700 |
| H | 2.52675300 | -4.01274100 | -0.11236800 |
| H | 2.71469600 | -4.47603700 | 1.57999500 |
| C | 6.20513700 | -0.57985900 | 2.62365600 |
| H | 6.98595300 | -0.22340900 | 1.94260100 |
| H | 5.95552000 | 0.24772400 | 3.29696400 |
| H | 6.64339300 | -1.37274600 | 3.23333900 |
| N | 3.08323600 | 1.16881100 | -0.39593000 |
| Ni | 1.91972300 | -0.49454600 | -0.66481700 |


| C | 3.07749300 | -1.21377700 | -2.10607100 |
| :--- | :--- | :--- | :--- |
| H | 2.67070900 | -2.20404800 | -2.31341200 |
| H | 2.97889000 | -0.54262000 | -2.95576100 |
| H | 4.09179000 | -1.25977700 | -1.72530200 |
| I | 0.00010000 | 0.00056800 | 1.24988700 |

5c

| C | 1.77526000 | 2.48753100 | 1.31743900 |
| :--- | ---: | ---: | ---: |
| C | 3.68816800 | 1.50218100 | 0.37220500 |
| C | 2.36089500 | 3.74231000 | 1.34782300 |
| H | 0.76281100 | 2.32680800 | 1.66856500 |
| C | 4.33444600 | 2.75772900 | 0.38278800 |
| C | 3.66884500 | 3.86726300 | 0.86506500 |
| H | 1.80707400 | 4.59217000 | 1.72424300 |
| H | 5.35070000 | 2.83764000 | 0.02541500 |
| H | 4.16384000 | 4.83205600 | 0.87320200 |
| N | 3.49040100 | -0.86785700 | 0.09586400 |
| C | 4.26324300 | 0.26624700 | -0.06462800 |
| C | 4.20541800 | -1.94081800 | -0.31409600 |
| C | 5.51427600 | -0.10409000 | -0.61015900 |
| C | 5.46059100 | -1.49672300 | -0.76042000 |
| H | 6.24046000 | -2.12599400 | -1.16608200 |
| C | 3.68978500 | -3.34212600 | -0.24316500 |
| H | 3.73395500 | -3.73371100 | 0.77978800 |
| H | 2.64935500 | -3.40252200 | -0.57128600 |
| H | 4.28816900 | -4.00114500 | -0.87500300 |
| C | 6.67656000 | 0.77255700 | -0.97108700 |
| H | 6.40230900 | 1.54352000 | -1.69919800 |
| H | 7.09774800 | 1.28334500 | -0.09752400 |
| H | 7.47636000 | 0.17514200 | -1.41345200 |
| N | 2.40572000 | 1.40968500 | 0.83483900 |
| Ni | 1.75888200 | -0.55773700 | 0.82452700 |
| C | 2.46756600 | -1.02017400 | 2.59163800 |
| H | 1.92884700 | -0.42680100 | 3.32755100 |
| H | 2.27213600 | -2.08582000 | 2.71555100 |
| H | 3.53219400 | -0.80438300 | 2.59596500 |
| I | 0.64875500 | -0.78618500 | -1.677933000 |
| C | -3.85544300 | -2.38771200 | 0.23654500 |
| C | -4.37835400 | -0.09273900 | 0.12804000 |
| C | -5.08215200 | -2.70658600 | 0.78791200 |
| H | -3.11084000 | -3.15011300 | 0.03928400 |
| C | -5.64241000 | -0.36523800 | 0.69965800 |
| C | -5.98634500 | -1.66107700 | 1.02242300 |
| H | -5.32124900 | -3.73390600 | 1.02748800 |
| H | -6.32801800 | 0.44909700 | 0.88201600 |
|  |  |  |  |
| H |  |  |  |


| H | -6.95652900 | -1.86858300 | 1.45987900 |
| :--- | ---: | ---: | :---: |
| N | -2.60351100 | 1.22778800 | -0.78226300 |
| C | -3.89121700 | 1.18685700 | -0.27279400 |
| C | -2.31558000 | 2.49872800 | -1.12498000 |
| C | -4.42716000 | 2.49399800 | -0.27082600 |
| C | -3.42041000 | 3.30891300 | -0.80454800 |
| H | -3.48132000 | 4.37610700 | -0.96860800 |
| C | -1.03250300 | 2.91395900 | -1.77014900 |
| H | -0.16471100 | 2.60285200 | -1.18208200 |
| H | -0.91960900 | 2.47295400 | -2.76561100 |
| H | -0.99969100 | 3.99952500 | -1.87862600 |
| C | -5.77015600 | 2.95811800 | 0.21110100 |
| H | -6.59382100 | 2.47010800 | -0.32164100 |
| H | -5.91490700 | 2.76909600 | 1.28076600 |
| H | -5.87457600 | 4.03396900 | 0.05567600 |
| N | -3.51443200 | -1.13195100 | -0.08475000 |
| Ni | -1.75999000 | -0.53475300 | -0.83356200 |
| C | -2.45655000 | -0.86804400 | -2.62725900 |
| H | -1.89707300 | -0.27136200 | -3.34243200 |
| H | -2.31102100 | -1.93704400 | -2.79032700 |
| H | -3.50783600 | -0.59484000 | -2.61371500 |
| I | -0.68312600 | -0.63133400 | 1.72068800 |

NMR Experiments for Characterizing 5. A J. Young NMR tube was charged with a stock solution of 2 in toluene- $d_{8}$ and a solution of 1,3,5-trimethoxybenzene (NMR internal standard) in toluene- $d_{8}$. This NMR sample was frozen in a liquid nitrogen bath and added with a solution of iodine in toluene- $d_{8}$. The mixture was allowed to thaw at $78^{\circ} \mathrm{C}$ in a dry ice/acetone bath and immediately injected into the probe, pre-cooled to -40 ${ }^{\circ} \mathrm{C}$ (Figure S 7 A ). Figure S 8 shows a sample of 5 being stable at $-20^{\circ} \mathrm{C}$. The integrations have facilitated the assignments of peaks.

(B)


Figure S7. ${ }^{1} \mathrm{H}$ NMR spectra of intermediate 5 at $-40^{\circ} \mathrm{C}(\mathrm{A})$ and the resulting spectrum of the reaction after full conversion of 5 at $22{ }^{\circ} \mathrm{C}(\mathrm{B})$. Solvent $=$ toluene $-d_{8}$, internal standard = 1,3,5-trimethoxybenzene.


Figure S8. ${ }^{1} \mathrm{H}$ NMR spectrum of intermediate 5 at $-20^{\circ} \mathrm{C}$. Solvent $=$ toluene $-d_{8}$, internal standard $=1,3,5$-trimethoxybenzene.


Figure S9. COSY spectra of intermediate 5 at $-40^{\circ} \mathrm{C}$. Solvent $=$ toluene $-d_{8}$. The zoomedin region shows aromatic resonances hidden underneath toluene- $d_{8}$.


Figure S10. HSQC spectra of intermediate 5 at $-40{ }^{\circ} \mathrm{C}$. Solvent $=$ toluene $-d_{8}$. The zoomed-in region shows the ${ }^{13} \mathrm{C}$ chemical shifts of $\mathrm{Ni}-\mathrm{CH}_{3}$ are 26.16, 27.94, 26.71, 28.42 ppm.

## V. Determining the Ni Species after the Reactions

Reaction between 2 and $\mathbf{I}_{2}$. To elucidate the identity of the resulting Ni species, we made efforts to independently synthesize the possible $\mathrm{Ni}(\mathrm{II})$ products, (py$\left.{ }^{\mathrm{Me}} \mathrm{pyrr}\right) \mathrm{Ni}^{\mathrm{II}}(\mathrm{lut})(\mathrm{I})$ or $\left[\left(\mathrm{py}-{ }^{\mathrm{Me}}\right.\right.$ pyrr) $\mathrm{Ni}^{\mathrm{II}}(\mu \text {-I) }]_{2}$ (Scheme 3$)$. Metalation of the py-pyrr ligand with $\mathrm{NiCl}_{2}$ precursors, such as $\mathrm{Ni}(\mathrm{DME}) \mathrm{Cl}_{2}$, in the presence of a variety of bases led to unidentifiable mixtures. Other methods, including transmetalation with Tl and Ag reagents and halogenation of (py-pyrr)Ni(acac) 1 and (py-pyrr)Ni(Me)(lut) 2 with HCl failed to afford any identifiable species corresponding to (py- ${ }^{\mathrm{Me}} \mathrm{pyrrr}^{\prime} \mathrm{Ni}^{\mathrm{II}}(\mathrm{lut})(\mathrm{X})$.

The stereoisomers of (py- ${ }^{\mathrm{Me}} \mathrm{pyrr}_{2}{ }_{2} \mathrm{Ni}^{\mathrm{IV}} \mathrm{Me}_{2}$ are possible structures of 5 . The reductive elimination from (py- $\left.{ }^{\mathrm{Me}} \mathrm{pyrr}_{2}\right)_{2} \mathrm{Ni}^{\mathrm{IV}} \mathrm{Me}_{2}$ is expected to generate (py- ${ }^{\mathrm{Me}}$ pyrr) $)_{2} \mathrm{Ni}^{\mathrm{II}}$. To verify this hypothesis, we independently prepared ( $\mathrm{py}-{ }^{\mathrm{Me}} \mathrm{pyrr}_{2} \mathrm{Ni}^{\mathrm{II}}$ by reacting two equiv. of pypyrr ligand with (TMEDA)NiMe 2 (eq S1, Figure S11). Addition of 2,4-lutidine to (py${ }^{\mathrm{Me}}$ pyrr) ${ }_{2} \mathrm{Ni}^{\mathrm{II}}$ leads to shift of the resonances (Figure S12). Neither of the species is present in the reaction mixture of 2 with $\mathrm{I}_{2}$, suggesting that (py- $\left.{ }^{\mathrm{Me}} \mathrm{pyrr}\right)_{2} \mathrm{Ni}^{\mathrm{IV}} \mathrm{Me}_{2}$ is not the structure of 5 .



Figure S11. ${ }^{1} \mathrm{H}$ NMR spectrum of $\left(\mathrm{py}-{ }^{\mathrm{Me}}{ }^{\mathrm{p}} \mathrm{prrr}\right)_{2} \mathrm{Ni}$ synthesized from eq S1.
(A)

(B)


Figure S12. Diamagnetic (A) and paramagnetic (B) regions of the ${ }^{1} \mathrm{H}$ NMR spectrum of (py- ${ }^{\mathrm{Me}} \mathrm{pyrr}_{2}{ }_{2} \mathrm{Ni}$ with 2 equivalents of 2,4-lutidine.

Reaction between 3 and bpy. The ${ }^{1} \mathrm{H}$ NMR spectrum of the resulting reaction mixture between $\mathbf{3}$ and bpy revealed that (py- ${ }^{\mathrm{Me}}$ pyrr) $)_{2} \mathrm{Ni}^{\mathrm{II}}(\mathrm{bpy})$ and $\mathrm{Ni}^{0}(\text { bpy })_{2}$ are present as minor products (Figure S13). The EPR spectrum of the reaction, conducted in toluene, established the same $S=1 / 2 \mathrm{Ni}$ species as observed in the comproportionation reaction, assigned as (py- ${ }^{\mathrm{Me}}$ pyrr) $\mathrm{Ni}^{\mathrm{I}}$ (bpy) (Figure 7). We speculate that (py- $\left.{ }^{\mathrm{Me}} \mathrm{pyrr}\right) \mathrm{Ni}^{\mathrm{I}}$ (bpy), once generated from the reaction, can undergo disproportionation to form (py- $-{ }^{\mathrm{Me}} \mathrm{pyrr}_{2}{ }_{2} \mathrm{Ni}^{\mathrm{II}}$ (bpy) and $\mathrm{Ni}^{0}(\text { bpy })_{2}$. The thermodynamic driving force is the formation of the stable octahedral (py-pyrr) ${ }_{2} \mathrm{Ni}^{\mathrm{II}}$ (bpy) that precipitates out from the solution.



Figure S13. Paramagentic (A) and diamagentic (B) region of the ${ }^{1} \mathrm{H}$ NMR spectrum of the reaction between $\mathbf{3}$ and bpy. Internal standard = hexamethyldisiloxane.

## VI. Cross-over Experiments



Figure S14. ${ }^{1} \mathrm{H}$ NMR spectrum of the crossover experiment between $\mathbf{2}$ and $\mathbf{2}-\boldsymbol{d}_{\mathbf{3}}$.


Figure S15. Crossover experiment between $\mathbf{3}$ and (py- $\left.{ }^{\text {Me }} \mathbf{p y r r}\right) \mathrm{Ni}(p$-Tol)(lut).

Crossover Experiments between 2 and 3. The 1:1 mixture of 2 and $\mathbf{3}$ in the presence of $\mathrm{O}_{2}$ and bpy did not afford toluene as the cross-coupling product (eqs S 2 and S3). Under both conditions, 2 reacted more rapidly than 3. Introduction of $\mathrm{O}_{2}$ led to reductive elimination from $\mathbf{2}$ to form ethane, whereas bpy induced the decomposition of $\mathbf{2}$ to methane. The lack of crossover product highlights the different reaction pathways of $\mathbf{2}$ and 3.

$$
\begin{array}{lll}
2+3 \\
1: 1
\end{array} \xrightarrow[22^{\circ} \mathrm{C}, 0.1 \mathrm{~h}, \mathrm{C}_{6} \mathrm{D}_{6}]{\mathrm{O}_{2} \text { (5 equiv) }} \begin{gathered}
\mathrm{CH}_{3} \mathrm{CH}_{3}+3 \\
35 \%>90 \% \\
\text { toluene (not observed) }
\end{gathered} \quad \text { (eq S2) }
$$

## VII. Effect of Bidentate Donor Ligands on Biphenyl Coupling from 3

We carried out additional experiments to evaluate the effect of bidentate donor ligands on biphenyl formation from 3. The association of phenanthroline and neocuproine to $\mathbf{3}$ was favorable (Table S2, entries 2-3). The rate for biphenyl formation, however, was dramatically decreased. The coordination of neocuproine also led to unidentifiable paramagnetic species. Bisphosphine ligands, such as dppe (bis(diphenylphsophino)ethane), resulted in decomposition of 3, but no biphenyl was detected.

The slow biphenyl formation with phenanthroline and neocuproine relative to bpy can be explained by the lack of free $\mathbf{3}$ to accept the phenyl group ejected from the pentacoordinate complex, due to the large equilibrium constant favoring the bident ligand association. However, the capability of bpy bridging between two molecules of $\mathbf{3}$ could also contribute to its role in promoting biphenyl formation. To fully understand the
precise effect of bpy, our ongoing efforts engage in evaluating a broader range of ligands and comparing the experimental results with DFT calculations.

Table S2. Effect of Bidentate Donor Ligands on Biphenyl Coupling from 3

| Entry | Ligand | $K_{\mathrm{eq}}\left(22^{\circ} \mathrm{C}\right)$ | Yield of $\mathrm{Ph}-\mathrm{Ph}(\%)\left(\right.$ after $\left.50{ }^{\circ} \mathrm{C}, 4 \mathrm{~h}\right)$ |
| :--- | :--- | :--- | :--- |
| 1 | $2,2^{\prime}$-Bipyridine | $0.019(2)$ | 99 |
| 2 | Phenanthroline | $10.2(5)$ | Trace $(90 \%$ after 2 days $)$ |
| 3 | Neocuproine | $\sim 13$ | Trace |
| 4 | dppe | $\mathrm{N} / \mathrm{A}$ | 0 |

## VIII. Spectra



















$\begin{array}{lllllllllllllllllllllll}210 & 200 & 190 & 180 & 170 & 160 & 150 & 140 & 130 & 120 & 110 & 100 & 90 & 80 & 70 & 60 & 50 & 40 & 30 & 20 & 10 & 0 & \mathrm{ppm}\end{array}$




- Free phenanthroline







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