Supplementary Information

Analysis of Key Steps in the Catalytic Cross-Coupling of Alkyl Electrophiles Under Negishi-like Conditions

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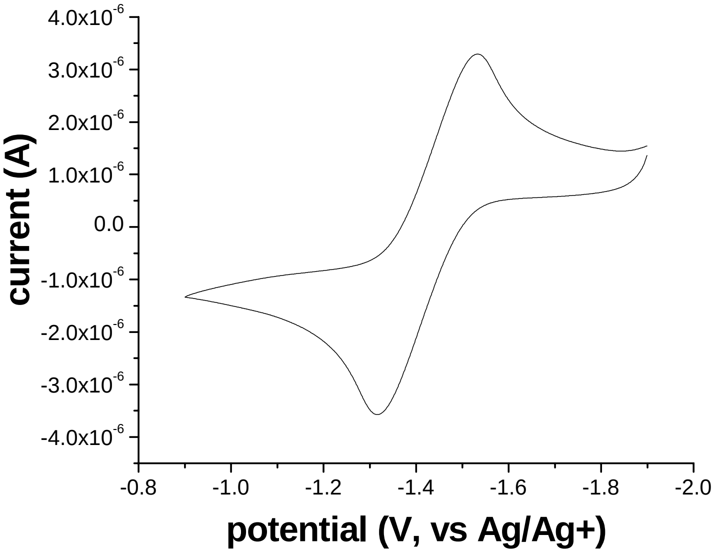
General Considerations. All manipulations were performed using standard Schlenk techniques or in a nitrogen-filled dry box, unless otherwise noted. Solvents were distilled from Na/benzophenone or CaH_2. All reagents were used as received from commercial vendors unless otherwise noted. Aluminum oxide (activated, neutral, Brockmann I, ~150 mesh) was dried at 200 °C under vacuum for two days prior to use. Elemental analyses were performed by Desert Analytics. ^{1}H NMR spectra were recorded at ambient temperature (unless otherwise noted) on a Bruker Avance 300 MHz spectrometer and referenced to residual proton solvent peaks. $^{31}P\{^1H\}$ spectra were recorded on the Bruker Avance spectrometer operating at 121.44 MHz and referenced to an 85 % phosphoric acid external standard set to 0 ppm. A Rigaku MSC Mercury/AFC8 diffractometer was used for X-ray structural determinations.

Cyclic Voltammetry Measurements. Cyclic voltammetry was performed in predried solutions of 3 mM Ni complex in 0.1 M $TBAPF_6$ in THF ($TBAPF_6$ = tetrabutylammonium hexafluorophosphate). The $TBAPF_6$ was recrystallized from THF/pentane and dried on high vacuum manifold overnight). Measurements were performed at a scan rate of 10 mV/sec under an argon atmosphere. A platinum disk (2.0 mm diameter, CH Instruments, Inc.) and a platinum flag were served as the working electrode and the counter electrode, respectively. A silver wire in a 0.01 M $AgNO_3$ solution of DMF (anhydrous) served as non-aqueous reference electrode which was separated from the test solution by a fine glass frit. A CH Instrument, Inc. model CHI650A potentiostat and CHI650A personal computer software controlled the electrochemical experiments. The non-aqueous reference electrode kit was purchased from Bioanalytical Systems, Inc. model #MF-2062.

The cyclic voltammogram of **1a** was previously reported as an Addition/Correction.[1]
Figure S1 (below): The cyclic voltammogram of **1b**:



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[1] Anderson, T. J.; Jones, G. D.; Vicic, D. A. *J. Amer. Chem. Soc.* **2004**, *126*, 11113.

Magnetic Properties:

Sample calculation of the diamagnetic susceptibility of tpy'NiI (3) in CD_2Cl_2:

15 x C(aromatic ring)	=	15(-6.24e-6)	=	-93.6 e-6 emu
35 x H	=	35(-2.93e-6)	=	-102.55 e-6 emu
3 x N (aromatic ring)	=	3(-4.6e-6)	=	-13.8 e-6 emu
12 x C (alkyl)	=	12(-6.0e-6)	=	-72.0 e-6 emu
1 x I	=	1(-50e-6)	=	-50 e-6 emu
1 x Ni*	=	1(-12.8e-6)	=	-12.8 e-6 emu
				-344.75 e-6 emu

(*) A diamagnetic correction for Ni(+1) is not reported.

Solution magnetic susceptibilities were then calculated using the Evans NMR method with a superconducting NMR spectrometer according to eq 1:[2] Diamagnetic correction for THF solvent: -0.735 e-6 cm^3g^{-1}. Diamagnetic correction for methylene chloride solvent: -0.549 e-6 cm^3g^{-1}.

Sample calculation of μ_{eff} for tpy'NiI (3) in CD_2Cl_2:

$$\chi_g = 3\Delta\upsilon/4\pi\upsilon c \quad + \chi_o \qquad (1)$$

where:
χ_g = gram susceptibility
c = concentration in g/mL
$\Delta\upsilon$ = observed shift difference in Hz
υ = spectrometer frequency in Hz
χ_o = mass susceptibility of solvent

$\chi_g = [3(33.193\ \text{Hz})/4\pi(300e^6\ \text{Hz})(0.0104\text{g/mL})] - 0.549\text{e-}6\ cm^3g^{-1}$
$\chi_g = 1.991\text{e-}6\ cm^3g^{-1}$
$\chi_m = (\chi_g)(\text{formula weight}) = (1.991\text{e-}6\ cm^3g^{-1})(587.18\ \text{g/mol}) = 1.169\text{e-}3$ emu
$\chi_{corrected} = (\chi_m)$ - diamagnetic correction = 1.169e-3 + 344.75e-6 = 1.513e-3 emu
$\mu_{eff} = 2.828[(\chi_{corrected})(T)]^{1/2}$
$\mu_{eff} = 2.828[(1.513\text{e-}3)(295\ K)]^{1/2} = 1.89\ \mu_B$

Experimental:

Preparation of (tpy')NiMe (1b): (TMEDA)Ni$(CH_3)_2$ (718 mg, 3.5 mmol) was dissolved in 100 mL diethyl ether. This solution was cooled to -78 °C, and tpy' (1.409 g, 3.5 mmol) in 25 mL ether was added dropwise to the slurry. After addition was complete, the solution was allowed to warm to room temperature. The solution changed from yellow-green color to a dark violet/black color

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[2] (a) Sur, S. K. J. Magnetic Resonance **1989**, *82*, 169-173. (b) Schubert, E. M. *J. Chem. Ed*. **1992**, *68*, p.62.

within 1 hour. The resulting suspension was then allowed to stir overnight. The product was filtered and washed with ether leaving 1.464 g (3.08 mmol) of (tpy')Ni(Me) (88% yield). Compound is paramagnetic, ($\mu_{eff} = 1.4\ \mu_B$ in THF-d_8). UV-Vis (THF, 25˚C): $\varepsilon_{583\ nm} = 4113$ L mol^{-1} cm^{-1}. Anal. Calcd for $C_{28}H_{38}N_3Ni$: 70.75 (69.06) %C; 8.06 (8.21) %H.

Preparation of [(tpy')NiMe]I (2): A 1000 mL round bottom flask (RBF) was charged with $Ni(COD)_2$ (802 mg, 2.9 mmol), tpy' (1.17 g, 2.9 mmol), and THF (250 mL). The dark green solution was stirred for 50 minutes at room temperature at which point methyl iodide (415 mg, 2.9 mmol) in THF (20 mL) was added dropwise via a pipette. The resulting solution was stirred at room temperature for 20 minutes. Diethyl ether (200 mL) was added, and the suspension was immediately filtered. The solid was discarded and the filtrate was stirred for an additional 40 min, at which point an orange/red solid precipitated. The solids were filtered, washed with benzene and ether, and dried under vacuum. Yield: 810 mg (46 %). Layering of **2** in cold CH_2Cl_2 with cold toluene cooled to -35 ºC for 2 days afforded X-ray quality crystals. Compound **2** decomposes rapidly in warm CD_2Cl_2 but is more stable (>1 day) in dry DMF-d_7 when kept in the dark. ^{1}H NMR (CD_2Cl_2, 22 ºC): δ 8.27 (d, J = 6.1 Hz, 2H), 8.22 (s, 2H), 8.17 (d, J = 1.9 Hz, 2H), 7.55 (dd, J = 6.2, 2.1 Hz, 2H), 1.57 (s, 9H), 1.46 (s, 18H), 0.20 (s, 3H). Anal. Calcd for $C_{28}H_{38}N_3INi$: 55.84 (55.30) %C; 6.36 (6.08) %H.

Preparation of [(tpy')NiMe]PF_6 (2b): A solution (tpy')NiMe (**1b**) (262 mg, 0.55 mmol) in 80 mL of THF was cannulated into a slurry of ferrocenium hexafluorophosphate (183 mg, 0.55 mmol) at -40 °C in 20 mL THF. The reaction was stirred at -40 °C for 1 hr resulting in an orange solution. The THF was removed via high-vacuum manifold yielding a dark orange solid. The orange solid is washed with excess Et_2O to remove the ferrocene. The resulting dark orange solid is collected and washed with pentane yielding 281 mg (82 %) of product, which can be recrystallized from THF/pentane. ^{1}H-NMR (22 °C, THF-d_8) δ: 8.40 (s, 2H), 8.37 (d, J = 2.0 Hz, 2H), 8.31 (d, J = 6.1 Hz, 2H), 7.67 (dd, J = 6.1, 2.1 Hz, 2H), 1.52 (s, 9H), 1.44 (s, 18H), 0.16 (s, 3H). $^{31}P\{^1H\}$ NMR (22 °C, THF-d_8) δ: -143.43 (sept, J_{P-F} = 710.3 Hz). The full ^{1}H NMR spectrum is provided at the end of the experimental section.

Reaction of $Ni(COD)_2$, tpy', and 1-iodo-3-phenylpropane (equation 5): A 100 mL RBF was charged with with $Ni(COD)_2$ (128 mg, 0.465 mmol), tpy' (187 mg, 0.465 mmol), hexamethylbenzene (105 mg, 0.647 mmol) and benzene (50 mL). The dark green solution was stirred for 5 minutes at which point 1-iodo-3-phenylpropane (75 µL, 0.466 mmol) was added via syringe and stirred for 1 hour. Filtered off a yellow solid that was found to be $[(tpy')_2Ni]I_2$ (123 mgs, 47 % (based on tpy')) and washed with ether and dried. An aliquot of the "organics" was analyzed by GC and was found to contain 1,6-diphenylhexane (70 %). Compound **4**: Anal. Calcd for $C_{54}H_{70}N_6I_2Ni$: 58.13 (58.56) %C; 6.32 (6.02) %H. A preliminary X-ray structure has been obtained for **4**, but because of disorder in the counter-ions, the structure has not been included. Compound **4**, due to its octahedral geometry, is paramagnetic.

Reaction of [(tpy')NiMe]I with heptylZnBr (equation 3) : HeptylZnBr (0.5 M, 0.98 mL, 0.49 mmol) was added via syringe to a screw cap scintillation vial containing a magnetic stir bar, THF (2 mL), and *n*-undecane (50 µL, 0.237 mmol, internal standard). Freshly recrystallized [(tpy')NiMe]I (59 mg, 0.10 mmol) was slurried in THF (3 mL). The Ni slurry was pipeted into the HeptylZnBr solution and adjusted the total volume to 10 mL. The reaction was stirred for 23 h in the dry box at which time a 50 µL aliquot was removed and worked-up by quenching with ethanol and filtering through a pipette packed with silica gel under aerobic conditions. The catalyst is not recovered. The resulting solution was then analyzed by GC. Yield: 8 %.

Reaction of (tpy')NiMe with iodoheptane (equation 4): 1-iodoheptane (0.080 mL, 0.52 mmol) was added via syringe to a screw cap scintillation vial containing a magnetic stir bar, THF (2 mL), and *n*-undecane (50 µL, 0.237 mmol, internal standard). (tpy')NiMe (49 mg, 0.10 mmol) was slurried in THF (3 mL). The Ni slurry was pipeted into the 1-iodoheptane solution and adjusted the total volume to 10 mL. The reaction was stirred for 23 h in the dry box at which time a 50 µL aliquot was removed and worked-up by quenching with ethanol and filtering through a pipette packed with silica gel. The resulting solution was then analyzed by GC. Yield: 90 %.

Reaction of [(tpy')NiMe]PF_6 with heptylZnBr : HeptylZnBr (0.5 M, 0.30 mL, 0.15 mmol) was added via syringe to a screw cap scintillation vial containing a magnetic stir bar, THF (1 mL), and *n*-undecane (50 µL, 0.237 mmol, internal standard). Freshly recrystallized [(tpy')NiMe]PF_6 (17 mg, 0.03 mmol) was slurried in THF (2 mL). The Ni slurry was pipeted into the HeptylZnBr solution and adjusted the total volume to 5 mL. The reaction was stirred for 23 h in the dry box at which time a 50 µL aliquot was removed and worked-up by quenching with ethanol and filtering through a pipette packed with silica gel. The resulting solution was then analyzed by GC. Yield: 29 % of tetradecane.

General Method for Catalytic Preparation of Phenyloctane (Table 1): A small screw capped vial equipped with a magnetic stir bar was charged with 1-halo-3-phenylpropane (0.72 mmol) and internal standard (undecane, 76 µL, 0.36 mmol) in THF (6.56 mL). Ni(COD)$_2$ (10mg, 0.036 mmol) and tpy' (12 mg, 0.036 mmol) were dissolved in THF (2 mL) and pipetted into the vial. To the stirring vial, *n*-pentylzinc bromide (1.44 mL, 0.72 mmol) was syringed into the vial. The vial was capped and stirred in the glove box for 23 hrs and worked-up by quenching with ethanol and filtering through a pipette packed with silica gel. The resulting solution was then analyzed by GC. Representative GC trace after reaction with nickel:

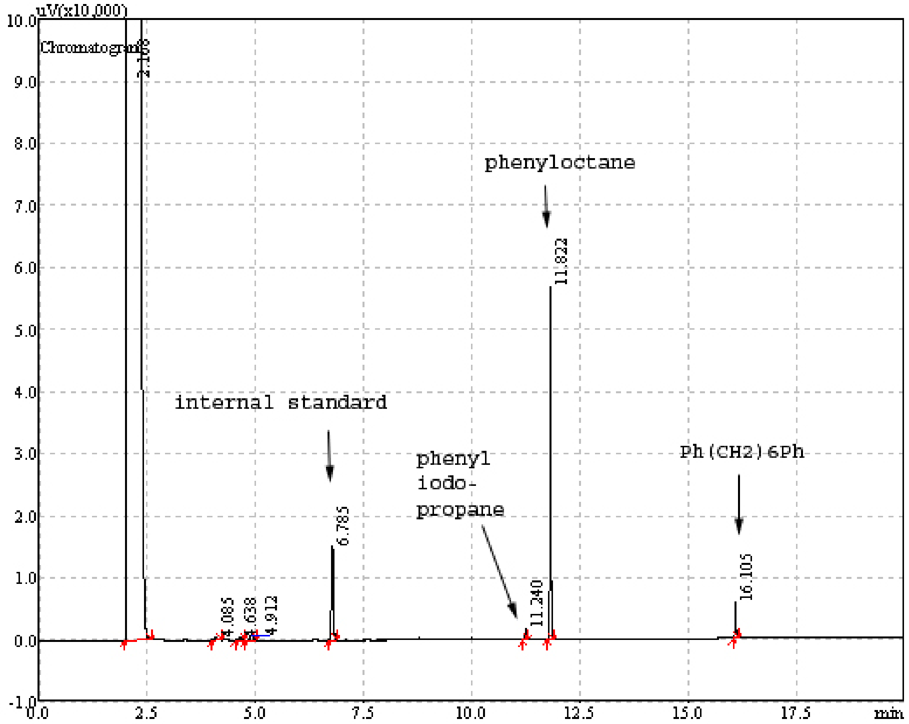
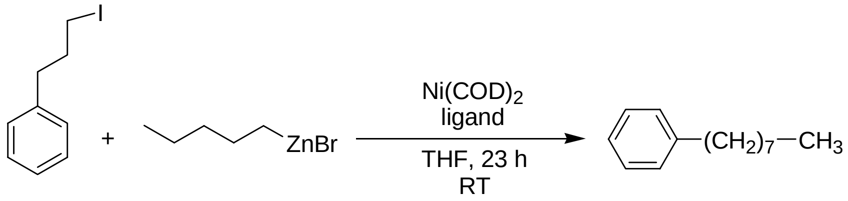

uV(x10,000)
Chromatogram
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
min
2.106
4.085
4.638
4.912
internal standard
6.785
phenyl
iodo-
propane
11.240
phenyloctane
11.822
Ph(CH2)6Ph
16.105

Figure S2 (below): Effect of catalyst loading on the cross-coupling of alkyl-iodides:



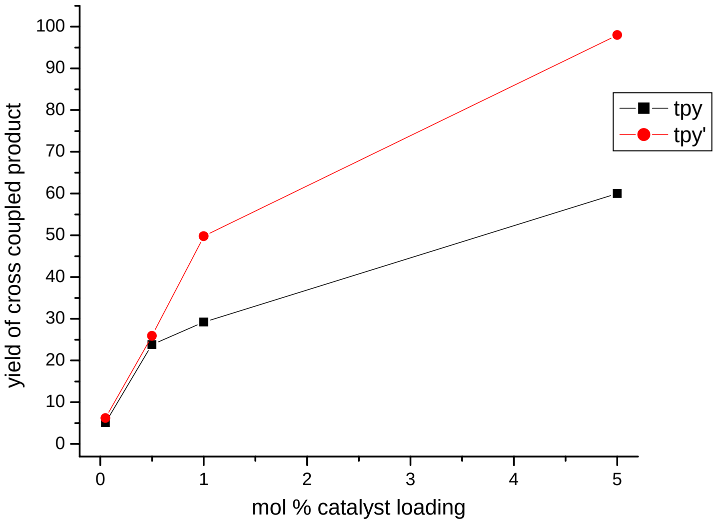
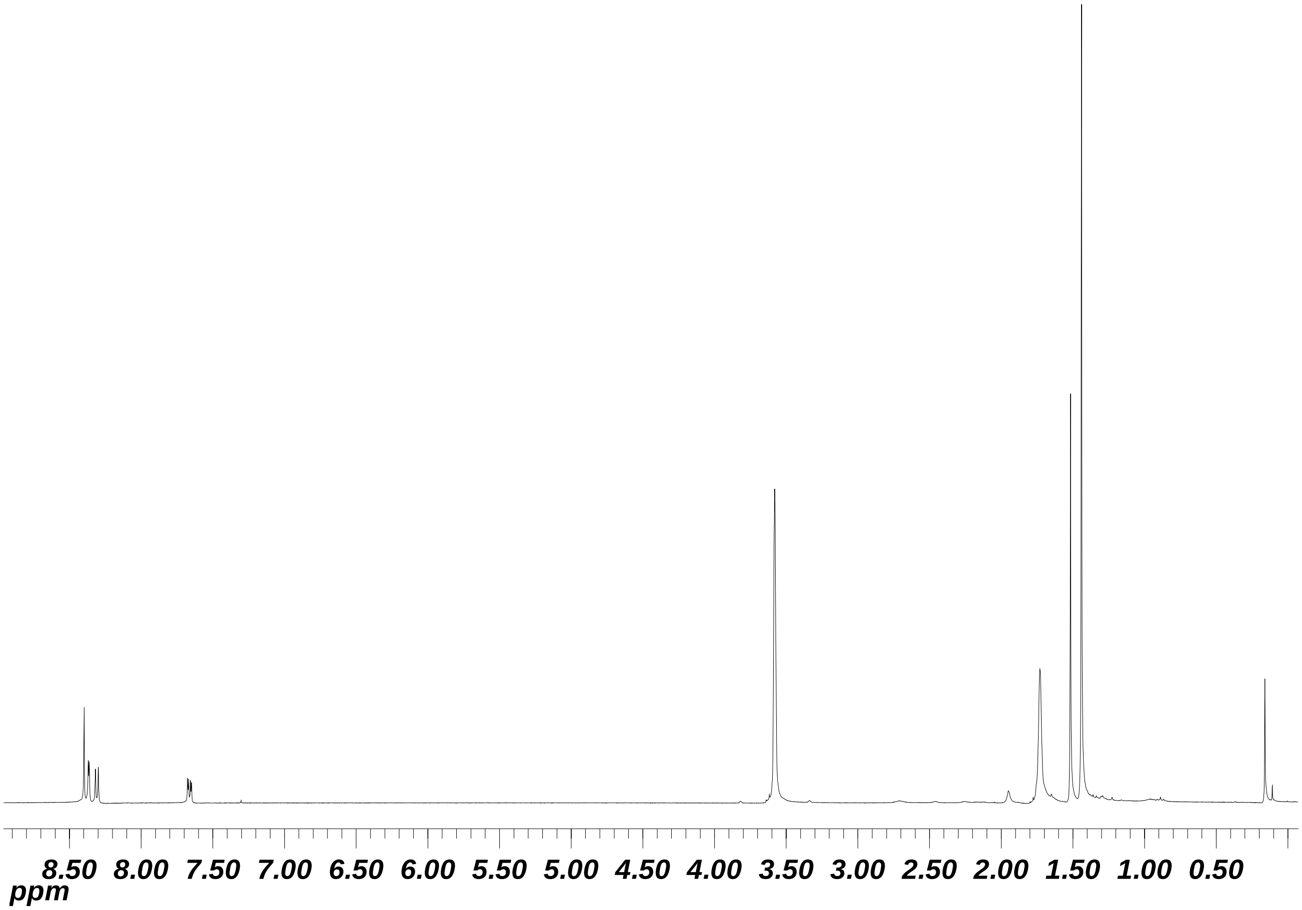


Figure S3 (below): ^{1}H NMR spectrum of [(tpy')NiMe]PF$_6$ (**2b**) in THF-d$_8$:



X-ray data for Compound **1b**: (tpy’)NiMe

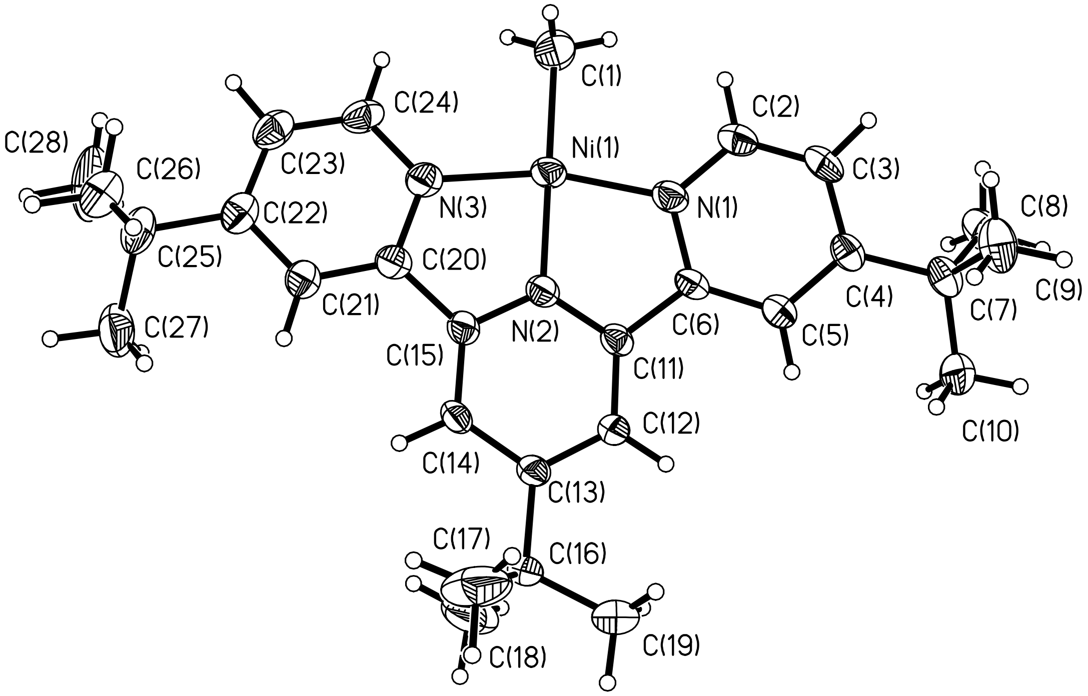


Table s1. Bond lengths [A] and angles [deg] for Compound 1b.

Ni(1)-N(2)	1.845(3)
Ni(1)-N(1)	1.903(3)
Ni(1)-N(3)	1.914(3)
Ni(1)-C(1)	1.944(4)
N(1)-C(2)	1.356(4)
N(1)-C(6)	1.385(4)
N(2)-C(15)	1.355(4)
N(2)-C(11)	1.358(4)
N(3)-C(24)	1.350(4)
N(3)-C(20)	1.377(4)
C(2)-C(3)	1.364(5)
C(3)-C(4)	1.403(5)
C(4)-C(5)	1.384(4)
C(4)-C(7)	1.526(4)
C(5)-C(6)	1.403(4)
C(6)-C(11)	1.450(4)
C(7)-C(10)	1.518(5)
C(7)-C(8)	1.537(4)
C(7)-C(9)	1.544(5)
C(11)-C(12)	1.390(4)
C(12)-C(13)	1.393(4)
C(13)-C(14)	1.413(4)
C(13)-C(16)	1.533(4)
C(14)-C(15)	1.378(4)
C(15)-C(20)	1.455(4)
C(16)-C(19)	1.503(5)
C(16)-C(17)	1.518(5)
C(16)-C(18)	1.536(5)
C(20)-C(21)	1.396(4)
C(21)-C(22)	1.384(4)
C(22)-C(23)	1.399(5)
C(22)-C(25)	1.530(4)
C(23)-C(24)	1.375(5)
C(25)-C(28)	1.518(5)
C(25)-C(27)	1.529(5)
C(25)-C(26)	1.530(4)

N(2)-Ni(1)-N(1)	81.58(12)
N(2)-Ni(1)-N(3)	82.62(11)
N(1)-Ni(1)-N(3)	163.44(10)
N(2)-Ni(1)-C(1)	177.99(15)
N(1)-Ni(1)-C(1)	98.42(14)
N(3)-Ni(1)-C(1)	97.55(13)
C(2)-N(1)-C(6)	116.2(3)
C(2)-N(1)-Ni(1)	128.4(2)
C(6)-N(1)-Ni(1)	115.23(19)
C(15)-N(2)-C(11)	120.8(2)
C(15)-N(2)-Ni(1)	118.78(19)
C(11)-N(2)-Ni(1)	120.2(2)
C(24)-N(3)-C(20)	115.9(3)
C(24)-N(3)-Ni(1)	129.8(2)
C(20)-N(3)-Ni(1)	114.22(19)
N(1)-C(2)-C(3)	123.7(3)
C(2)-C(3)-C(4)	121.3(3)

C(5)-C(4)-C(3)	115.8(3)
C(5)-C(4)-C(7)	124.5(3)
C(3)-C(4)-C(7)	119.6(3)
C(4)-C(5)-C(6)	121.4(3)
N(1)-C(6)-C(5)	121.4(2)
N(1)-C(6)-C(11)	112.8(2)
C(5)-C(6)-C(11)	125.7(3)
C(10)-C(7)-C(4)	112.4(3)
C(10)-C(7)-C(8)	109.2(3)
C(4)-C(7)-C(8)	109.2(3)
C(10)-C(7)-C(9)	109.0(3)
C(4)-C(7)-C(9)	108.9(3)
C(8)-C(7)-C(9)	108.1(3)
N(2)-C(11)-C(12)	120.3(3)
N(2)-C(11)-C(6)	109.9(2)
C(12)-C(11)-C(6)	129.4(3)
C(11)-C(12)-C(13)	120.3(3)
C(12)-C(13)-C(14)	117.7(3)
C(12)-C(13)-C(16)	123.3(2)
C(14)-C(13)-C(16)	118.9(2)
C(15)-C(14)-C(13)	120.2(3)
N(2)-C(15)-C(14)	120.7(3)
N(2)-C(15)-C(20)	111.0(3)
C(14)-C(15)-C(20)	128.2(3)
C(19)-C(16)-C(17)	109.3(3)
C(19)-C(16)-C(13)	112.2(3)
C(17)-C(16)-C(13)	110.1(3)
C(19)-C(16)-C(18)	107.7(3)
C(17)-C(16)-C(18)	108.2(3)
C(13)-C(16)-C(18)	109.2(3)
N(3)-C(20)-C(21)	122.3(3)
N(3)-C(20)-C(15)	113.1(3)
C(21)-C(20)-C(15)	124.6(3)
C(22)-C(21)-C(20)	121.2(3)
C(21)-C(22)-C(23)	115.7(3)
C(21)-C(22)-C(25)	121.8(3)
C(23)-C(22)-C(25)	122.4(3)
C(24)-C(23)-C(22)	121.2(3)
N(3)-C(24)-C(23)	123.6(3)
C(28)-C(25)-C(27)	109.4(3)
C(28)-C(25)-C(22)	110.1(3)
C(27)-C(25)-C(22)	112.3(3)
C(28)-C(25)-C(26)	109.6(3)
C(27)-C(25)-C(26)	107.3(3)
C(22)-C(25)-C(26)	108.0(3)

X-ray data for Compound **2**: [(tpy’)NiMe]I·(toluene)(CH$_2$Cl$_2$)$_2$. The large thermal parameters on the co-crystallized solvent molecules may contribute to the size of the R factors.

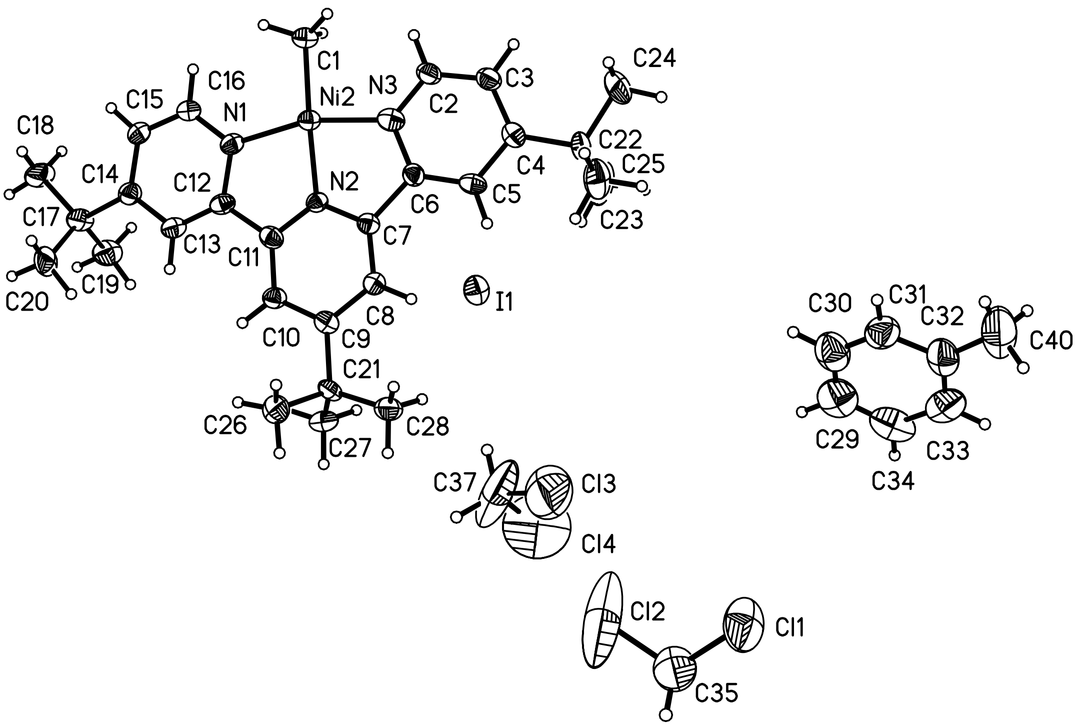


Table S2. Bond lengths [A] and angles [deg] for [(tpy’)NiMe]I.(toluene)(CH2Cl2)2.

Ni(2)-N(2)	1.880(7)
Ni(2)-C(1)	1.921(9)
Ni(2)-N(1)	1.923(8)
Ni(2)-N(3)	1.927(9)
Cl(1)-C(35)	1.741(17)
Cl(2)-C(35)	1.665(19)
Cl(3)-C(37)	2.03(3)
Cl(4)-C(37)	1.53(3)
N(1)-C(16)	1.346(11)
N(1)-C(12)	1.384(10)
N(2)-C(11)	1.328(11)
N(2)-C(7)	1.349(10)
N(3)-C(2)	1.336(11)
N(3)-C(6)	1.370(11)
C(2)-C(3)	1.370(13)
C(3)-C(4)	1.385(13)
C(4)-C(5)	1.416(12)
C(4)-C(22)	1.520(13)
C(5)-C(6)	1.364(13)
C(6)-C(7)	1.489(11)
C(7)-C(8)	1.371(11)
C(8)-C(9)	1.402(12)
C(9)-C(10)	1.401(12)
C(9)-C(21)	1.542(11)
C(10)-C(11)	1.387(12)
C(11)-C(12)	1.465(12)
C(12)-C(13)	1.370(13)
C(13)-C(14)	1.405(12)
C(14)-C(15)	1.410(12)
C(14)-C(17)	1.516(13)
C(15)-C(16)	1.379(13)
C(17)-C(18)	1.525(13)
C(17)-C(20)	1.529(15)
C(17)-C(19)	1.565(16)
C(21)-C(28)	1.508(13)
C(21)-C(27)	1.544(13)
C(21)-C(26)	1.546(13)
C(22)-C(23)	1.514(16)
C(22)-C(25)	1.537(14)
C(22)-C(24)	1.537(15)
C(29)-C(30)	1.35(2)
C(29)-C(34)	1.35(2)
C(30)-C(31)	1.32(2)
C(31)-C(32)	1.40(2)
C(32)-C(33)	1.43(2)
C(32)-C(40)	1.47(2)
C(33)-C(34)	1.38(2)

N(2)-Ni(2)-C(1)	175.8(4)
N(2)-Ni(2)-N(1)	82.1(3)
C(1)-Ni(2)-N(1)	99.3(4)

N(2)-Ni(2)-N(3)	82.1(3)
C(1)-Ni(2)-N(3)	96.4(4)
N(1)-Ni(2)-N(3)	164.0(3)
C(16)-N(1)-C(12)	117.1(7)
C(16)-N(1)-Ni(2)	128.8(6)
C(12)-N(1)-Ni(2)	114.0(6)
C(11)-N(2)-C(7)	121.4(7)
C(11)-N(2)-Ni(2)	119.2(6)
C(7)-N(2)-Ni(2)	119.3(5)
C(2)-N(3)-C(6)	116.9(8)
C(2)-N(3)-Ni(2)	128.3(7)
C(6)-N(3)-Ni(2)	114.8(6)
N(3)-C(2)-C(3)	123.3(9)
C(2)-C(3)-C(4)	120.8(8)
C(3)-C(4)-C(5)	116.1(8)
C(3)-C(4)-C(22)	124.1(8)
C(5)-C(4)-C(22)	119.7(8)
C(6)-C(5)-C(4)	120.1(8)
C(5)-C(6)-N(3)	122.6(8)
C(5)-C(6)-C(7)	123.8(8)
N(3)-C(6)-C(7)	113.5(7)
N(2)-C(7)-C(8)	120.7(7)
N(2)-C(7)-C(6)	110.0(7)
C(8)-C(7)-C(6)	129.3(8)
C(7)-C(8)-C(9)	119.6(8)
C(10)-C(9)-C(8)	118.2(8)
C(10)-C(9)-C(21)	120.1(7)
C(8)-C(9)-C(21)	121.7(7)
C(11)-C(10)-C(9)	119.2(8)
N(2)-C(11)-C(10)	120.8(8)
N(2)-C(11)-C(12)	111.2(7)
C(10)-C(11)-C(12)	128.0(8)
C(13)-C(12)-N(1)	120.9(7)
C(13)-C(12)-C(11)	125.6(7)
N(1)-C(12)-C(11)	113.4(7)
C(12)-C(13)-C(14)	122.5(8)
C(13)-C(14)-C(15)	115.3(8)
C(13)-C(14)-C(17)	122.2(8)
C(15)-C(14)-C(17)	122.4(8)
C(16)-C(15)-C(14)	120.2(8)
N(1)-C(16)-C(15)	123.7(8)
C(14)-C(17)-C(18)	112.8(8)
C(14)-C(17)-C(20)	109.2(8)
C(18)-C(17)-C(20)	110.3(9)
C(14)-C(17)-C(19)	106.9(9)
C(18)-C(17)-C(19)	107.1(9)
C(20)-C(17)-C(19)	110.5(9)
C(28)-C(21)-C(9)	112.8(7)
C(28)-C(21)-C(27)	110.6(9)
C(9)-C(21)-C(27)	107.4(7)
C(28)-C(21)-C(26)	108.3(8)
C(9)-C(21)-C(26)	108.9(8)
C(27)-C(21)-C(26)	108.9(8)
C(23)-C(22)-C(4)	110.2(8)
C(23)-C(22)-C(25)	109.8(10)
C(4)-C(22)-C(25)	111.1(8)
C(23)-C(22)-C(24)	107.4(11)

C(4)-C(22)-C(24)	112.3(9)
C(25)-C(22)-C(24)	106.0(10)
C(30)-C(29)-C(34)	121.7(18)
C(31)-C(30)-C(29)	120.6(18)
C(30)-C(31)-C(32)	122.5(16)
C(31)-C(32)-C(33)	115.7(15)
C(31)-C(32)-C(40)	119.8(17)
C(33)-C(32)-C(40)	124.5(16)
C(34)-C(33)-C(32)	120.2(15)
C(29)-C(34)-C(33)	119.2(16)
Cl(2)-C(35)-Cl(1)	110.1(10)
Cl(4)-C(37)-Cl(3)	108.3(12)