Electronic Supplementary Material (ESI) for ChemComm.

Electrocatalytic reduction of CO_2 with CCC-NHC pincer nickel complexes

James D. Cope,[a] Nalaka P. Liyanage,[b] Paul J. Kelley,[b] Jason A. Denny,[a] Edward J. Valente,[c] Charles Edwin Webster,[a] Jared H. Delcamp,*[b] and T. Keith Hollis*[a]*

[a]Department of Chemistry and the Center for Computational Sciences, Mississippi State University, Mississippi State, MS, 39762.

[b]Department of Chemistry and Biochemistry, The University of Mississippi, University, MS, 38677.

[c]University of Portland Diffraction Facility, 112A Swindells Hall, Department of Chemistry, University of Portland, 5000 North Willamette Blvd, Portland, OR, 97203.

Electronic Supporting Information for *Chemical Communications*

Contents

I. Syntheses

Reagents for syntheses were purchased from commercial sources and used without further purification. All experiments took place under inert atmosphere argon atmosphere using a LC Technology Solutions glovebox unless otherwise noted ^{1}H NMR and ^{13}C NMR were obtained using Bruker AVANCE III 500 MHz. referenced against the residual solvent peak in $CDCl_3$, CD_2Cl_2, and d_6-acetone at 7.26 and 2.05 ppm, respectively. $CDCl_3$ and d_6-acetone were both degassed and dried prior to use in initial synthesis and NMR characterization. ESI-MS was obtained using Bruker UHPLC-Micro-Q-ToF MS/MS. 1,3-bis(1-N-butyl-imidizol-3-yl)benzene dichloride salts were prepared from a previously reported synthesis.[1]

Synthesis of 2-(1,3-bis(N-butyl-imidazol-2'-ylidene)phenylene)nickel(II) chloride, 2

In a 4 dram vial, 1,3-bis(1-N-butyl-imidizol-3-yl)benzene dichloride (0.307 g, 0.777 mmol) and $Zr(NMe_2)_4$ (0.301 g, 1.13 mmol) were combined in CH_2Cl_2 (10 mL) and stirred for 1 hour. $NiCl_2$(glyme) (0.168 g, 0.763 mmol) was added and stirred for 3 hours. Water (0.600 mL, 0.033 mmol) was added producing a precipitate that was removed and washed with CH_2Cl_2 (3 x 10 mL). The filtrate was concentrated, and the resulting orange-yellow solid was dried under reduced pressure. Isopropyl alcohol (2 mL) was added and the resulting suspension vigorously stirred for 2 minutes. Filtration afforded a glittering orange-yellow microcrystalline solid (0.182 g, 0.439 mmol, 59%). X-ray quality crystals were obtained by a vapor diffusion of diethyl ether with a CH_2Cl_2 solution of **2**. ^{1}H NMR ($CDCl_3$; 500 MHz): δ 7.23 (d, 2H, *J* = 1.7 Hz), 7.03 (t, 1H, *J* = 7.8 Hz), 6.79 (d, 2H, *J* = 1.7 Hz), 6.71 (d, 2H, *J* = 7.8 Hz), 4.65 (t, 4H, *J* = 7.4 Hz), 1.87 (quintet, 4H, *J* = 7.6 Hz), 1.45 (sextet, 4H, *J* = 7.6 Hz), 0.97 (t, 6H, *J* = 7.4 Hz). $^{13}C\{H\}$ NMR ($CDCl_3$; 125 MHz): δ 172.5, 146.9, 145.5, 124.7, 121.7, 112.8, 106.5, 49.0, 34.1, 19.8, 13.9. ESI-MS (m/z): observed, 379.1545 for $[M - Cl\cdot]^+$; calcd, 379.1433 for ($C_{20}H_{25}N_4Ni$). Elem. Anal. Calcd for $C_{20}H_{25}N_4NiCl$: C, 57.86; H, 6.06; N, 13.08. Found: C, 57.38; H, 6.12; N, 13.28.

Synthesis of 2-(1,3-bis(N-butyl-imidazol-2'-ylidene)phenylene)acetonitrile nickel(II) hexafluorophosphate, 3

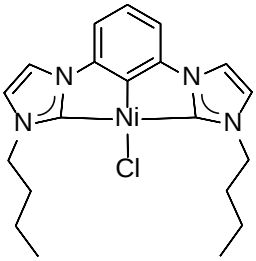
In a 4 dram vial, 2-(1,3-bis(N-butyl-imidazol-2'-ylidene)phenylene) nickel(II) chloride, **2**, (56.0 mg, 0.13 mmol), silver hexafluorophosphate (35.5 mg, 0.15 mmol) and acetonitrile (10 mL) were combined and covered with aluminum foil. The mixture was stirred for 1 h at room temperature to afford a yellow solution. The solution was passed through a plug of Celite, concentrated under reduced pressure, dissolved in CH_2Cl_2 (2 mL) and passed through a second plug of Celite, concentrated to dryness under reduced pressure affording a yellow solid (76.0 mg, 0.13 mmol, 82%). X-ray quality crystals were obtained by a vapor diffusion of diethyl ether with a CH_2Cl_2 solution of **3**. ^{1}H NMR (d_6-acetone; 500 MHz): δ 7.79 (s, 2H), 7.32 (s, 2H), 7.17 (t, 1H, *J* = 7.5 Hz), 7.05 (d, 2H, *J* = 7.8 Hz), 4.09 (t, 4H, *J* = 7.2 Hz), 2.61 (s, 3H), 1.88 (quintet, 4H, *J* = 7.2 Hz), 1.42 (sextet, 4H, *J* = 7.4 Hz), 0.99 (t, 6H, *J* = 7.4 Hz). $^{13}C\{H\}$ NMR (d_6- Acetone; 125 MHz): 147.9, 147.2, 143.3, 127.1, 123.1, 114.7, 108.0, 49.1, 33.5, 19.6, 13.1, 2.4. ESI-MS (m/z): observed, 379.1545 $[M - NCMe]^+$; calcd, 379.1433 for

($C_{20}H_{25}N_4Ni$). Elem. Anal. Calcd for $C_{22}H_{28}N_5F_6PNi$: C, 46.67; H, 4.99; N, 12.37. Found: C, 46.89; H, 5.00; N, 12.40.

References:

1) V.C. Vargas, R.J. Rubio, T.K. Hollis, M.E. Salcido, Org. Lett. 5(25) (2003) 4847-9.

II. Characterization



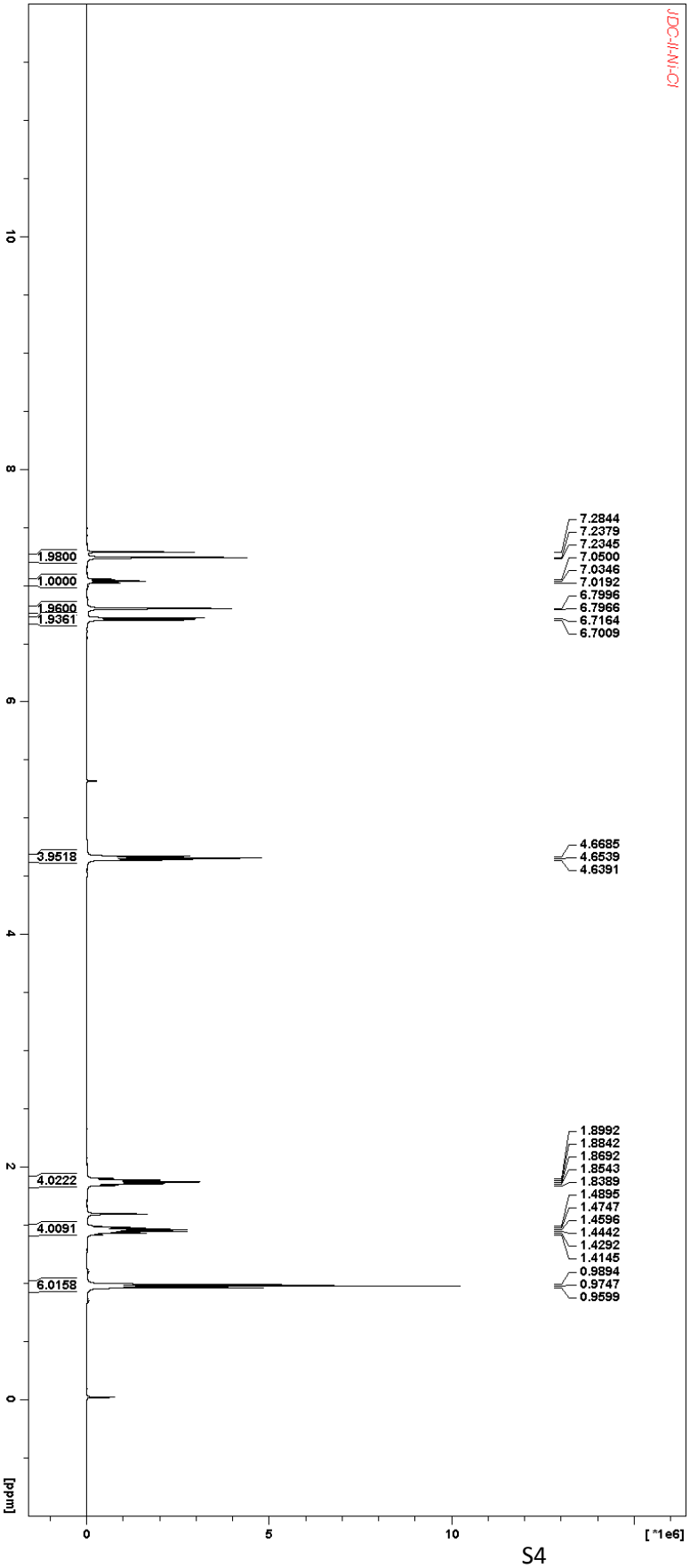
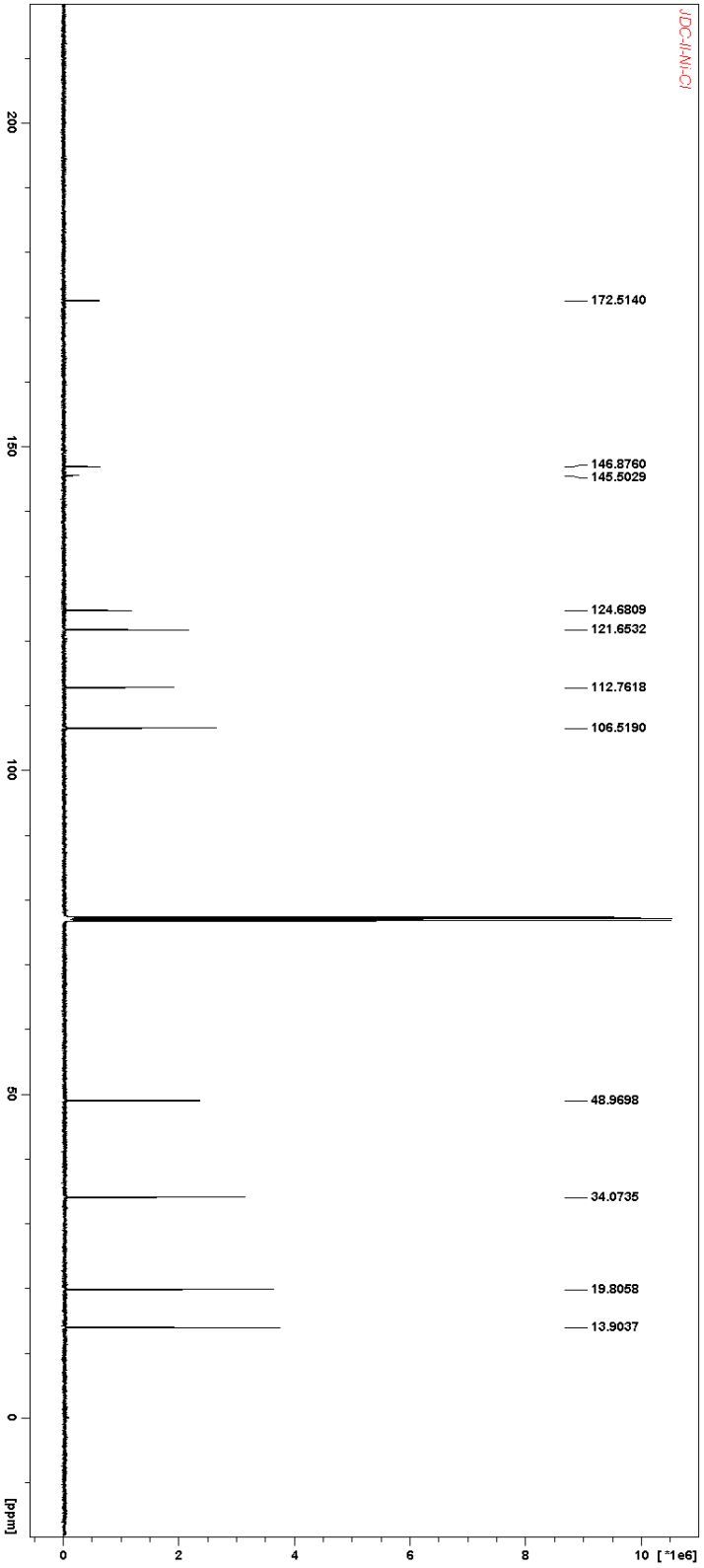


Figure S1. ^{1}H NMR of **2**.



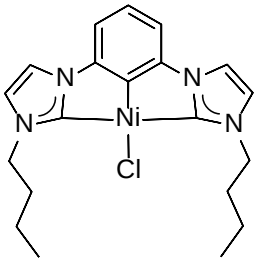
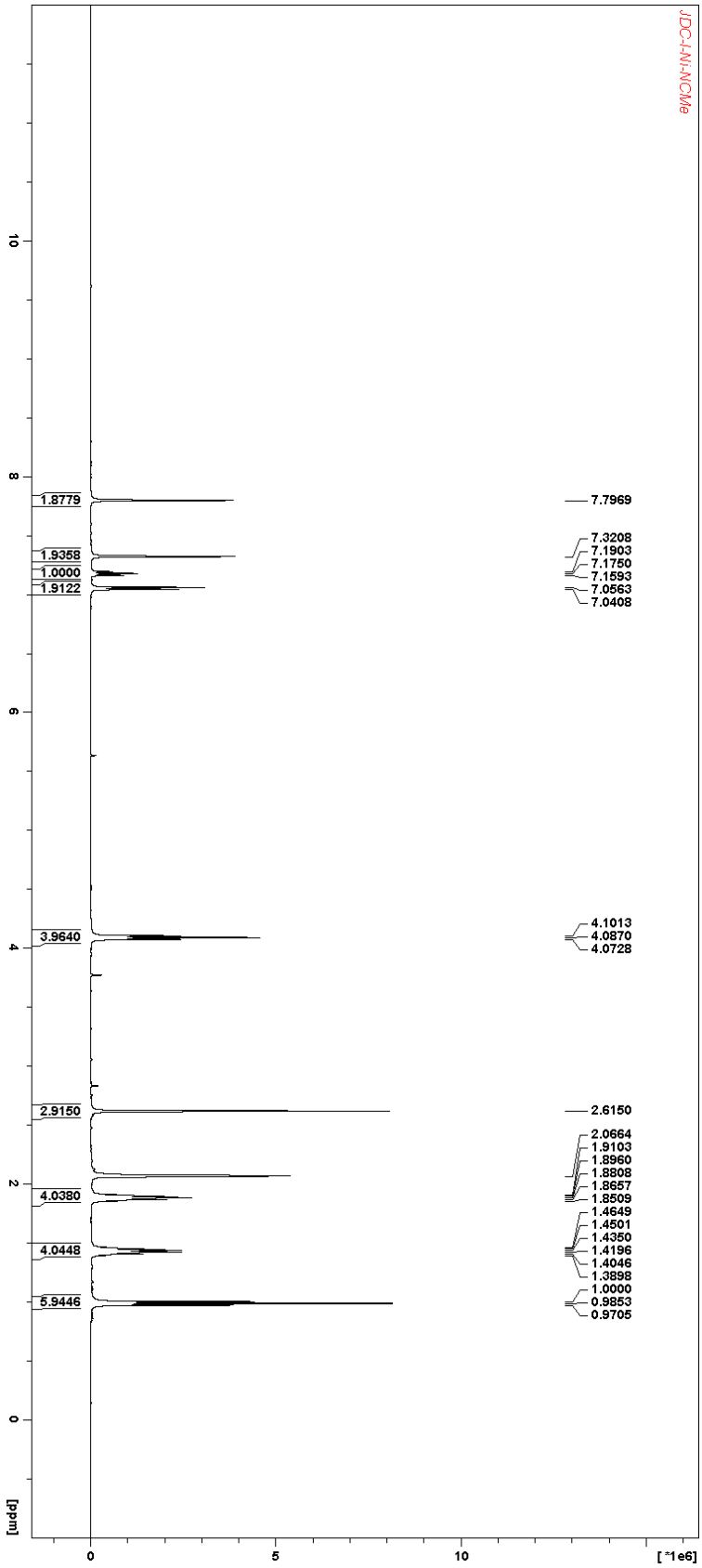


Figure S2. ^{13}C NMR of **2**.



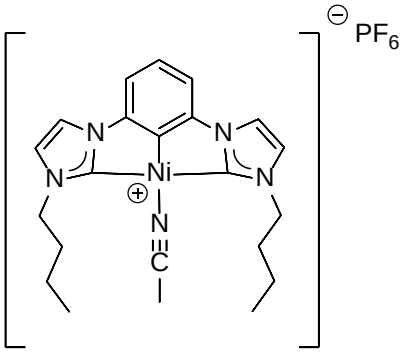
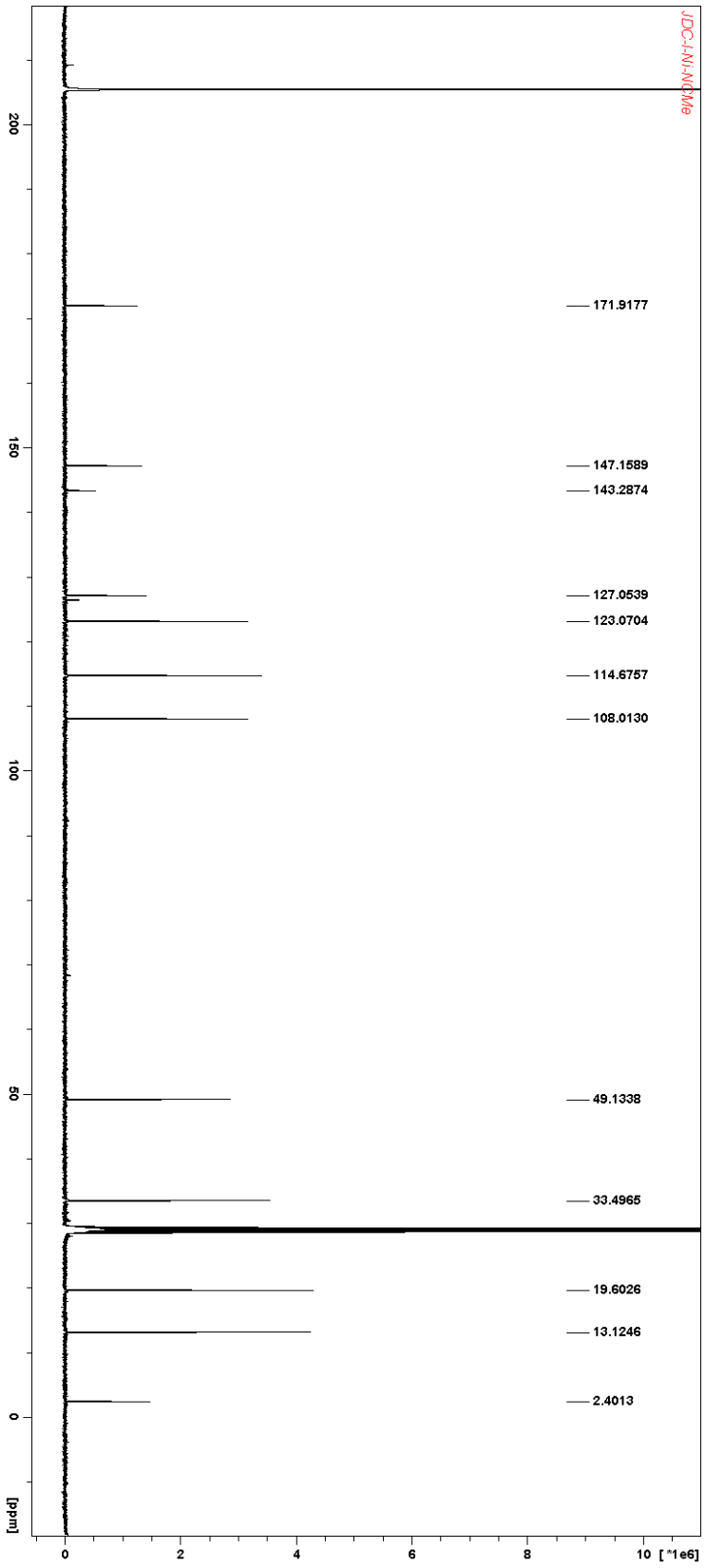


Figure S3. ^{1}H NMR of **3**.



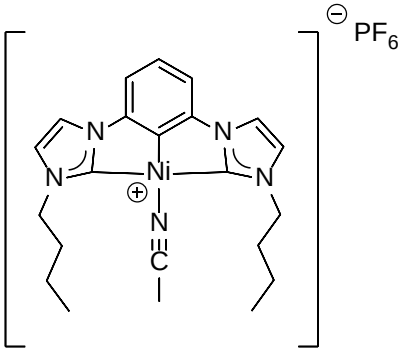


Figure S4. ^{13}C NMR of **3**.

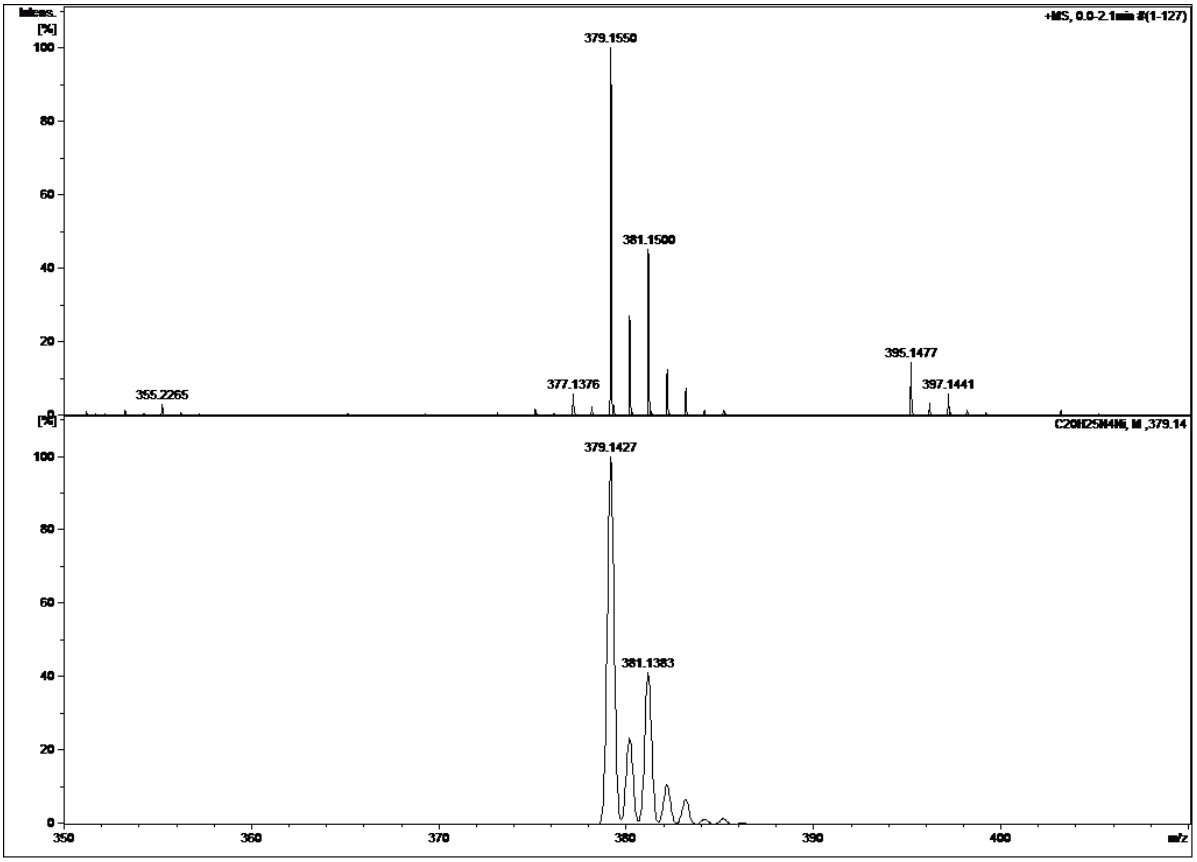


Figure S5. HRMS spectrum of **2**.

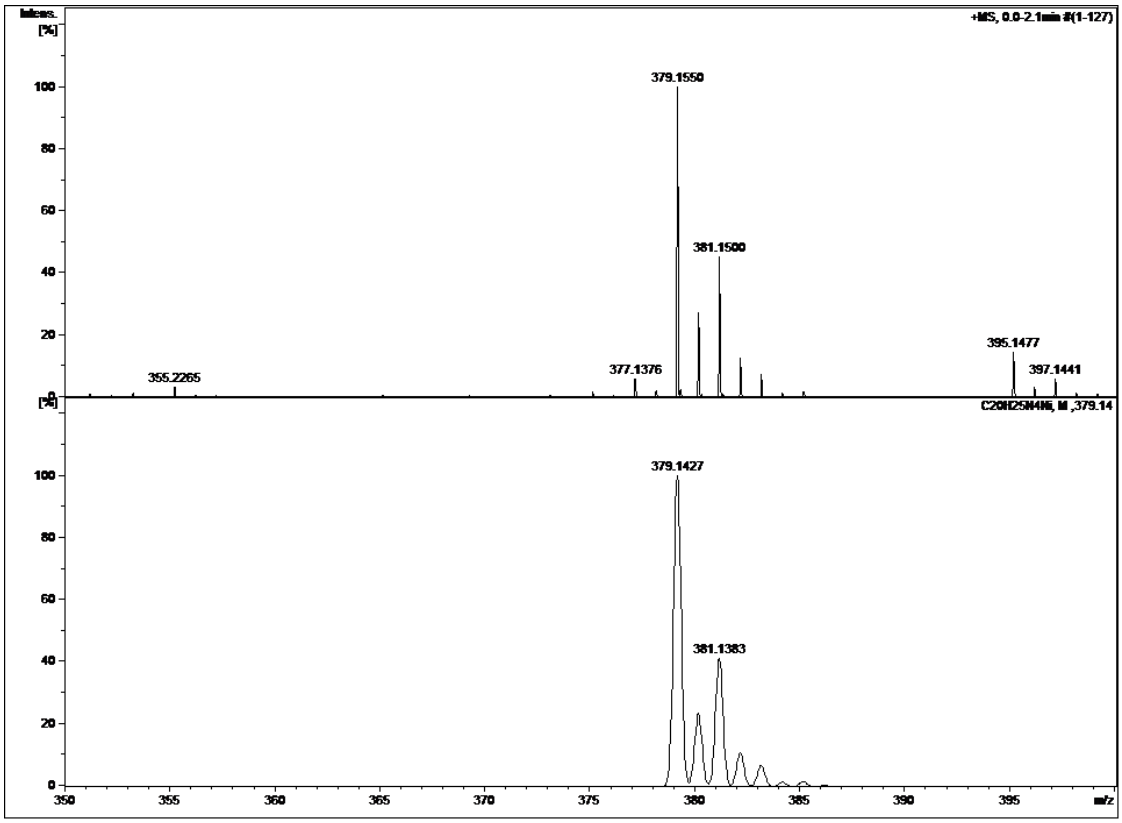


Figure S6. HRMS spectrum of **3**.

III. Details of Crystal Data Collection

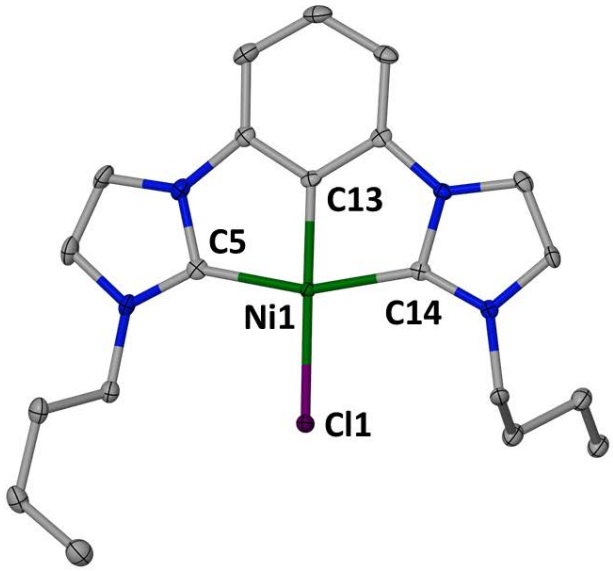


Figure S7. ORTEP diagram (50% thermal ellipsoids) of $^{Bu}C^{i}C^{i}C^{Bu}$ Ni^{II}-Cl, **2**.

Table S1. Crystal data and structure refinement for **2**.

Identification code	**2**	
Empirical formula	$C_{20}H_{25}ClN_4Ni$	
Formula weight	415.60	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.8944(11) Å	α = 90°.
	b = 11.3015(13) Å	β = 90°.
	c = 16.6259(19) Å	γ = 90°.
Volume	1859.1(4) $Å^3$	
Z	4	
Density (calculated)	1.485 Mg/m^3	
Absorption coefficient	1.199 mm^{-1}	
F(000)	872	
Crystal size	0.5 × 0.5 × 0.23 mm^3	
Theta range for data collection	2.179 to 28.405°.	
Index ranges	-13<=h<=13, -15<=k<=15, -22<=l<=22	
Reflections collected	57709	
Independent reflections	4645 [R(int) = 0.0839]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.5424	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4645 / 15 / 236	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R1 = 0.0307, wR2 = 0.0608	
R indices (all data)	R1 = 0.0382, wR2 = 0.0628	
Absolute structure parameter	0.034(6)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.420 and -0.478 $e.Å^{-3}$	

Table S2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	7603(1)	6705(1)	2761(1)	9(1)
Cl(1)	8470(1)	6104(1)	3931(1)	18(1)
N(2)	5638(2)	8482(2)	2558(1)	14(1)
N(1)	6042(2)	8560(2)	3817(2)	15(1)
N(3)	8073(2)	5680(2)	1239(1)	11(1)
N(4)	9312(2)	4640(2)	2020(1)	11(1)
C(13)	6823(3)	7159(2)	1796(2)	12(1)
C(12)	7127(3)	6588(2)	1085(2)	13(1)
C(11)	6510(3)	6872(3)	362(2)	17(1)
C(10)	5527(3)	7754(3)	371(2)	21(1)
C(9)	5163(3)	8340(3)	1075(2)	20(1)
C(8)	5836(3)	8026(2)	1774(2)	14(1)
C(5)	6434(3)	7979(2)	3146(2)	13(1)
C(4)	6531(3)	8371(3)	4641(2)	16(1)
C(3)	7069(3)	9500(3)	5020(2)	19(1)
C(2)	7479(3)	9311(3)	5888(2)	20(1)
C(1)	8739(3)	8550(3)	5984(2)	25(1)
C(6)	5033(3)	9376(3)	3653(2)	21(1)
C(7)	4777(3)	9330(3)	2858(2)	19(1)
C(15)	8647(3)	4821(3)	761(2)	14(1)
C(16)	9430(3)	4172(3)	1252(2)	14(1)
C(17)	9995(3)	4126(2)	2719(2)	14(1)
C(18A)	9109(3)	3255(3)	3165(2)	18(1)
C(19A)	8535(3)	2271(3)	2647(2)	18(1)
C(20A)	7797(4)	1346(3)	3139(2)	18(1)
C(14)	8457(3)	5575(2)	2031(2)	11(1)
C(18B)	9485(17)	2882(15)	2903(14)	18(1)
C(19B)	7971(17)	2813(16)	3022(12)	18(1)
C(20B)	7440(20)	1624(17)	3273(14)	18(1)

Table S3. Bond lengths [Å] and angles [°] for **2**.

Ni(1)-Cl(1)	2.2312(8)	C(16)-H(16)	0.9300
Ni(1)-C(13)	1.854(3)	C(17)-H(17A)	0.9700
Ni(1)-C(5)	1.954(3)	C(17)-H(17B)	0.9700
Ni(1)-C(14)	1.955(3)	C(17)-H(17C)	0.9700
N(2)-C(8)	1.416(4)	C(17)-H(17D)	0.9700
N(2)-C(5)	1.378(4)	C(17)-C(18A)	1.512(4)
N(2)-C(7)	1.376(4)	C(17)-C(18B)	1.525(15)
N(1)-C(5)	1.352(4)	C(18A)-H(18A)	0.9700
N(1)-C(4)	1.468(4)	C(18A)-H(18B)	0.9700
N(1)-C(6)	1.387(4)	C(18A)-C(19A)	1.517(5)
N(3)-C(12)	1.412(3)	C(19A)-H(19A)	0.9700
N(3)-C(15)	1.378(4)	C(19A)-H(19B)	0.9700
N(3)-C(14)	1.375(3)	C(19A)-C(20A)	1.515(5)
N(4)-C(16)	1.386(4)	C(20A)-H(20A)	0.9600
N(4)-C(17)	1.465(3)	C(20A)-H(20B)	0.9600
N(4)-C(14)	1.353(4)	C(20A)-H(20C)	0.9600
C(13)-C(12)	1.380(4)	C(18B)-H(18C)	0.9700
C(13)-C(8)	1.383(4)	C(18B)-H(18D)	0.9700
C(12)-C(11)	1.387(4)	C(18B)-C(19B)	1.513(17)
C(11)-H(11)	0.9300	C(19B)-H(19C)	0.9700
C(11)-C(10)	1.392(4)	C(19B)-H(19D)	0.9700
C(10)-H(10)	0.9300	C(19B)-C(20B)	1.503(17)
C(10)-C(9)	1.392(4)	C(20B)-H(20D)	0.9600
C(9)-H(9)	0.9300	C(20B)-H(20E)	0.9600
C(9)-C(8)	1.385(4)	C(20B)-H(20F)	0.9600
C(4)-H(4A)	0.9700		
C(4)-H(4B)	0.9700	C(13)-Ni(1)-Cl(1)	177.55(9)
C(4)-C(3)	1.518(4)	C(13)-Ni(1)-C(5)	80.38(12)
C(3)-H(3A)	0.9700	C(13)-Ni(1)-C(14)	79.80(12)
C(3)-H(3B)	0.9700	C(5)-Ni(1)-Cl(1)	99.62(9)
C(3)-C(2)	1.516(4)	C(5)-Ni(1)-C(14)	160.15(11)
C(2)-H(2A)	0.9700	C(14)-Ni(1)-Cl(1)	100.12(8)
C(2)-H(2B)	0.9700	C(5)-N(2)-C(8)	115.0(2)
C(2)-C(1)	1.523(4)	C(7)-N(2)-C(8)	132.4(3)
C(1)-H(1A)	0.9600	C(7)-N(2)-C(5)	112.5(3)
C(1)-H(1B)	0.9600	C(5)-N(1)-C(4)	127.3(2)
C(1)-H(1C)	0.9600	C(5)-N(1)-C(6)	111.5(2)
C(6)-H(6)	0.9300	C(6)-N(1)-C(4)	121.2(2)
C(6)-C(7)	1.346(5)	C(15)-N(3)-C(12)	132.8(2)
C(7)-H(7)	0.9300	C(14)-N(3)-C(12)	114.9(2)
C(15)-H(15)	0.9300	C(14)-N(3)-C(15)	112.2(2)
C(15)-C(16)	1.344(4)	C(16)-N(4)-C(17)	122.7(2)

C(14)-N(4)-C(16)	111.3(2)	H(1A)-C(1)-H(1B)	109.5
C(14)-N(4)-C(17)	126.0(2)	H(1A)-C(1)-H(1C)	109.5
C(12)-C(13)-Ni(1)	121.4(2)	H(1B)-C(1)-H(1C)	109.5
C(12)-C(13)-C(8)	117.6(3)	N(1)-C(6)-H(6)	126.2
C(8)-C(13)-Ni(1)	120.8(2)	C(7)-C(6)-N(1)	107.7(3)
C(13)-C(12)-N(3)	109.2(2)	C(7)-C(6)-H(6)	126.2
C(13)-C(12)-C(11)	122.6(3)	N(2)-C(7)-H(7)	127.3
C(11)-C(12)-N(3)	128.2(3)	C(6)-C(7)-N(2)	105.5(3)
C(12)-C(11)-H(11)	121.2	C(6)-C(7)-H(7)	127.3
C(12)-C(11)-C(10)	117.6(3)	N(3)-C(15)-H(15)	127.1
C(10)-C(11)-H(11)	121.2	C(16)-C(15)-N(3)	105.7(2)
C(11)-C(10)-H(10)	119.0	C(16)-C(15)-H(15)	127.1
C(9)-C(10)-C(11)	122.1(3)	N(4)-C(16)-H(16)	126.2
C(9)-C(10)-H(10)	119.0	C(15)-C(16)-N(4)	107.6(2)
C(10)-C(9)-H(9)	121.3	C(15)-C(16)-H(16)	126.2
C(8)-C(9)-C(10)	117.3(3)	N(4)-C(17)-H(17A)	109.1
C(8)-C(9)-H(9)	121.3	N(4)-C(17)-H(17B)	109.1
C(13)-C(8)-N(2)	109.4(3)	N(4)-C(17)-H(17C)	109.3
C(13)-C(8)-C(9)	122.9(3)	N(4)-C(17)-H(17D)	109.3
C(9)-C(8)-N(2)	127.7(3)	N(4)-C(17)-C(18A)	112.3(2)
N(2)-C(5)-Ni(1)	114.2(2)	N(4)-C(17)-C(18B)	111.8(8)
N(1)-C(5)-Ni(1)	142.9(2)	H(17A)-C(17)-H(17B)	107.9
N(1)-C(5)-N(2)	102.8(2)	H(17C)-C(17)-H(17D)	107.9
N(1)-C(4)-H(4A)	109.1	C(18A)-C(17)-H(17A)	109.1
N(1)-C(4)-H(4B)	109.1	C(18A)-C(17)-H(17B)	109.1
N(1)-C(4)-C(3)	112.3(2)	C(18B)-C(17)-H(17C)	109.3
H(4A)-C(4)-H(4B)	107.9	C(18B)-C(17)-H(17D)	109.3
C(3)-C(4)-H(4A)	109.1	C(17)-C(18A)-H(18A)	108.6
C(3)-C(4)-H(4B)	109.1	C(17)-C(18A)-H(18B)	108.6
C(4)-C(3)-H(3A)	109.3	C(17)-C(18A)-C(19A)	114.6(3)
C(4)-C(3)-H(3B)	109.3	H(18A)-C(18A)-H(18B)	107.6
H(3A)-C(3)-H(3B)	107.9	C(19A)-C(18A)-H(18A)	108.6
C(2)-C(3)-C(4)	111.7(2)	C(19A)-C(18A)-H(18B)	108.6
C(2)-C(3)-H(3A)	109.3	C(18A)-C(19A)-H(19A)	109.1
C(2)-C(3)-H(3B)	109.3	C(18A)-C(19A)-H(19B)	109.1
C(3)-C(2)-H(2A)	108.9	H(19A)-C(19A)-H(19B)	107.9
C(3)-C(2)-H(2B)	108.9	C(20A)-C(19A)-C(18A)	112.4(3)
C(3)-C(2)-C(1)	113.5(3)	C(20A)-C(19A)-H(19A)	109.1
H(2A)-C(2)-H(2B)	107.7	C(20A)-C(19A)-H(19B)	109.1
C(1)-C(2)-H(2A)	108.9	C(19A)-C(20A)-H(20A)	109.5
C(1)-C(2)-H(2B)	108.9	C(19A)-C(20A)-H(20B)	109.5
C(2)-C(1)-H(1A)	109.5	C(19A)-C(20A)-H(20C)	109.5
C(2)-C(1)-H(1B)	109.5	H(20A)-C(20A)-H(20B)	109.5
C(2)-C(1)-H(1C)	109.5	H(20A)-C(20A)-H(20C)	109.5

H(20B)-C(20A)-H(20C)	109.5	C(18B)-C(19B)-H(19D)	108.4
N(3)-C(14)-Ni(1)	114.71(19)	H(19C)-C(19B)-H(19D)	107.5
N(4)-C(14)-Ni(1)	142.1(2)	C(20B)-C(19B)-C(18B)	115.5(17)
N(4)-C(14)-N(3)	103.2(2)	C(20B)-C(19B)-H(19C)	108.4
C(17)-C(18B)-H(18C)	108.8	C(20B)-C(19B)-H(19D)	108.4
C(17)-C(18B)-H(18D)	108.8	C(19B)-C(20B)-H(20D)	109.5
H(18C)-C(18B)-H(18D)	107.7	C(19B)-C(20B)-H(20E)	109.5
C(19B)-C(18B)-C(17)	113.7(14)	C(19B)-C(20B)-H(20F)	109.5
C(19B)-C(18B)-H(18C)	108.8	H(20D)-C(20B)-H(20E)	109.5
C(19B)-C(18B)-H(18D)	108.8	H(20D)-C(20B)-H(20F)	109.5
C(18B)-C(19B)-H(19C)	108.4	H(20E)-C(20B)-H(20F)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	9(1)	9(1)	10(1)	0(1)	0(1)	1(1)
Cl(1)	23(1)	19(1)	12(1)	-3(1)	-3(1)	10(1)
N(2)	14(1)	11(1)	18(1)	1(1)	0(1)	1(1)
N(1)	14(1)	11(1)	18(1)	-1(1)	1(1)	3(1)
N(3)	13(1)	11(1)	9(1)	1(1)	0(1)	-2(1)
N(4)	11(1)	11(1)	12(1)	0(1)	1(1)	-1(1)
C(13)	12(1)	10(1)	13(1)	4(1)	-1(1)	-2(1)
C(12)	13(1)	11(1)	15(1)	4(1)	2(1)	-3(1)
C(11)	21(1)	18(2)	11(1)	3(1)	-1(1)	-4(1)
C(10)	24(2)	22(2)	16(2)	7(1)	-6(1)	-2(1)
C(9)	18(1)	17(1)	24(2)	6(1)	-4(1)	2(1)
C(8)	14(1)	11(1)	16(1)	1(1)	0(1)	-2(1)
C(5)	11(1)	13(1)	16(1)	2(1)	2(1)	-3(1)
C(4)	17(1)	14(1)	17(1)	-1(1)	1(1)	2(1)
C(3)	19(2)	14(1)	24(2)	-3(1)	1(1)	0(1)
C(2)	17(1)	22(1)	21(1)	-7(1)	1(1)	-1(1)
C(1)	20(2)	31(2)	24(2)	-3(1)	-1(1)	2(1)
C(6)	16(2)	17(2)	29(2)	-5(1)	3(1)	6(1)
C(7)	16(1)	15(2)	26(2)	1(1)	-2(1)	7(1)
C(15)	16(1)	16(1)	11(1)	-2(1)	4(1)	-4(1)
C(16)	17(1)	13(1)	12(1)	-4(1)	4(1)	0(1)
C(17)	13(1)	16(1)	14(1)	-2(1)	-4(1)	4(1)
C(18A)	20(1)	16(1)	18(1)	2(1)	3(1)	3(1)
C(19A)	20(1)	16(1)	18(1)	2(1)	3(1)	3(1)
C(20A)	20(1)	16(1)	18(1)	2(1)	3(1)	3(1)
C(14)	8(1)	12(1)	13(1)	1(1)	1(1)	-4(1)
C(18B)	20(1)	16(1)	18(1)	2(1)	3(1)	3(1)
C(19B)	20(1)	16(1)	18(1)	2(1)	3(1)	3(1)
C(20B)	20(1)	16(1)	18(1)	2(1)	3(1)	3(1)

Table S5. Hydrogen coordinates (× 10^4) and isotropic displacement parameters ($Å^2$ × 10^3) for **2**.

	x	y	z	U(eq)
H(11)	6743	6487	-113	20
H(10)	5101	7958	-108	25
H(9)	4495	8918	1077	24
H(4A)	7244	7782	4634	19
H(4B)	5798	8067	4969	19
H(3A)	7844	9775	4715	23
H(3B)	6378	10108	4994	23
H(2A)	6737	8938	6173	24
H(2B)	7641	10075	6136	24
H(1A)	8567	7773	5774	37
H(1B)	8970	8494	6544	37
H(1C)	9475	8904	5695	37
H(6)	4609	9867	4024	25
H(7)	4150	9777	2573	23
H(15)	8519	4713	211	17
H(16)	9956	3525	1105	17
H(17A)	10259	4755	3083	17
H(17B)	10811	3726	2542	17
H(17C)	9846	4628	3184	17
H(17D)	10960	4097	2618	17
H(18A)	8365	3685	3408	21
H(18B)	9633	2904	3596	21
H(19A)	7917	2608	2257	21
H(19B)	9266	1894	2354	21
H(20A)	7459	739	2789	27
H(20B)	7055	1710	3418	27
H(20C)	8407	1003	3523	27
H(18C)	9738	2362	2463	21
H(18D)	9929	2596	3385	21
H(19C)	7714	3390	3426	21
H(19D)	7534	3038	2522	21
H(20D)	7485	1086	2827	27
H(20E)	6515	1702	3444	27
H(20F)	7972	1323	3710	27

Table S6. Torsion angles [°] for **2**.

Ni(1)-C(13)-C(12)-N(3)	-0.3(3)	C(4)-N(1)-C(5)-Ni(1)	2.4(5)
Ni(1)-C(13)-C(12)-C(11)	176.8(2)	C(4)-N(1)-C(5)-N(2)	178.5(3)
Ni(1)-C(13)-C(8)-N(2)	3.0(3)	C(4)-N(1)-C(6)-C(7)	-178.5(3)
Ni(1)-C(13)-C(8)-C(9)	-175.7(2)	C(4)-C(3)-C(2)-C(1)	70.0(3)
N(1)-C(4)-C(3)-C(2)	176.0(2)	C(6)-N(1)-C(5)-Ni(1)	-175.3(3)
N(1)-C(6)-C(7)-N(2)	0.1(3)	C(6)-N(1)-C(5)-N(2)	0.8(3)
N(3)-C(12)-C(11)-C(10)	175.2(3)	C(6)-N(1)-C(4)-C(3)	-57.8(3)
N(3)-C(15)-C(16)-N(4)	0.4(3)	C(7)-N(2)-C(8)-C(13)	-179.0(3)
N(4)-C(17)-C(18A)-C(19A)	54.4(4)	C(7)-N(2)-C(8)-C(9)	-0.4(5)
N(4)-C(17)-C(18B)-C(19B)	-55.5(19)	C(7)-N(2)-C(5)-Ni(1)	176.69(19)
C(13)-C(12)-C(11)-C(10)	-1.4(4)	C(7)-N(2)-C(5)-N(1)	-0.7(3)
C(12)-N(3)-C(15)-C(16)	-177.0(3)	C(15)-N(3)-C(12)-C(13)	175.9(3)
C(12)-N(3)-C(14)-Ni(1)	0.1(3)	C(15)-N(3)-C(12)-C(11)	-1.0(5)
C(12)-N(3)-C(14)-N(4)	178.1(2)	C(15)-N(3)-C(14)-Ni(1)	-176.59(18)
C(12)-C(13)-C(8)-N(2)	178.3(2)	C(15)-N(3)-C(14)-N(4)	1.5(3)
C(12)-C(13)-C(8)-C(9)	-0.4(4)	C(16)-N(4)-C(17)-C(18A)	-93.4(3)
C(12)-C(11)-C(10)-C(9)	0.0(4)	C(16)-N(4)-C(17)-C(18B)	-64.1(9)
C(11)-C(10)-C(9)-C(8)	1.1(4)	C(16)-N(4)-C(14)-Ni(1)	175.9(3)
C(10)-C(9)-C(8)-N(2)	-179.3(3)	C(16)-N(4)-C(14)-N(3)	-1.2(3)
C(10)-C(9)-C(8)-C(13)	-0.8(4)	C(17)-N(4)-C(16)-C(15)	177.9(2)
C(8)-N(2)-C(5)-Ni(1)	-2.3(3)	C(17)-N(4)-C(14)-Ni(1)	-1.3(5)
C(8)-N(2)-C(5)-N(1)	-179.7(2)	C(17)-N(4)-C(14)-N(3)	-178.4(2)
C(8)-N(2)-C(7)-C(6)	179.1(3)	C(17)-C(18A)-C(19A)-C(20A)	173.1(3)
C(8)-C(13)-C(12)-N(3)	-175.6(2)	C(17)-C(18B)-C(19B)-C(20B)	-175.0(16)
C(8)-C(13)-C(12)-C(11)	1.6(4)	C(14)-Ni(1)-C(13)-C(12)	0.3(2)
C(5)-Ni(1)-C(13)-C(12)	-178.5(2)	C(14)-Ni(1)-C(13)-C(8)	175.4(2)
C(5)-Ni(1)-C(13)-C(8)	-3.4(2)	C(14)-N(3)-C(12)-C(13)	0.2(3)
C(5)-N(2)-C(8)-C(13)	-0.3(3)	C(14)-N(3)-C(12)-C(11)	-176.8(3)
C(5)-N(2)-C(8)-C(9)	178.4(3)	C(14)-N(3)-C(15)-C(16)	-1.2(3)
C(5)-N(2)-C(7)-C(6)	0.4(3)	C(14)-N(4)-C(16)-C(15)	0.5(3)
C(5)-N(1)-C(4)-C(3)	124.7(3)	C(14)-N(4)-C(17)-C(18A)	83.5(3)
C(5)-N(1)-C(6)-C(7)	-0.6(3)	C(14)-N(4)-C(17)-C(18B)	112.8(9)

Symmetry transformations used to generate equivalent atoms:

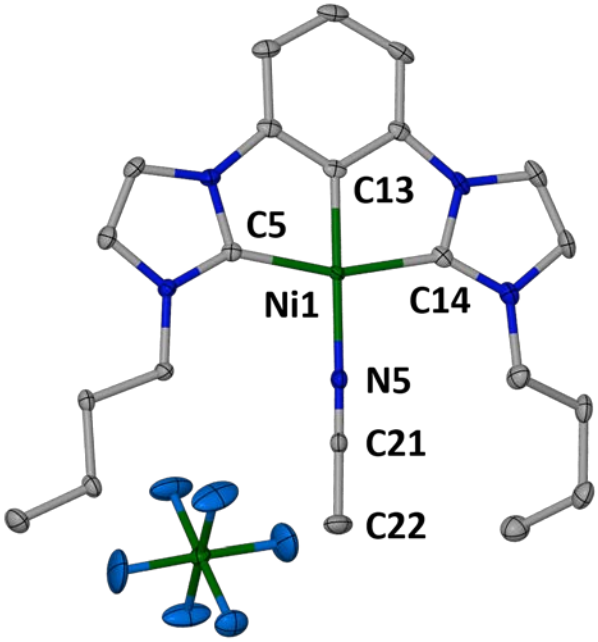


Figure S8. ORTEP diagram (50% thermal ellipsoids) of ($^{Bu}C^{i}C^{i}C^{Bu}$ Ni^{II}-NCMe)PF_6, **3**.

Table S7. Crystal data and structure refinement for **3**.

Identification code	**3**	
Empirical formula	$C_{22}H_{28}F_6N_5NiP$	
Formula weight	566.17	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 9.0649(8) Å	α = 90°.
	b = 11.8003(9) Å	β = 92.820(3)°.
	c = 22.1082(17) Å	γ = 90°.
Volume	2362.0(3) $Å^3$	
Z	4	
Density (calculated)	1.592 Mg/m^3	
Absorption coefficient	0.958 mm^{-1}	
F(000)	1168	
Crystal size	0.64 × 0.44 × 0.14 mm^3	
Theta range for data collection	2.249 to 28.392°.	
Index ranges	-11<=h<=12, -15<=k<=14, -26<=l<=29	
Reflections collected	14192	
Independent reflections	5426 [R(int) = 0.0438]	
Completeness to theta = 26.000°	95.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.5743	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5426 / 0 / 319	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0394, wR2 = 0.0854	
R indices (all data)	R1 = 0.0588, wR2 = 0.0931	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.415 and -0.592 $e.Å^{-3}$	

Table S8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$)for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	2329(1)	5068(1)	4721(1)	11(1)
N(1)	784(2)	6956(2)	5427(1)	14(1)
N(2)	2251(2)	5838(2)	5924(1)	15(1)
N(3)	4282(2)	3232(2)	4700(1)	17(1)
N(4)	3467(2)	3350(2)	3779(1)	18(1)
N(5)	1188(2)	5650(2)	4050(1)	15(1)
C(1)	-2919(3)	9890(2)	4684(1)	25(1)
C(2)	-1890(2)	8914(2)	4544(1)	18(1)
C(3)	-1028(2)	8475(2)	5103(1)	15(1)
C(4)	-100(2)	7478(2)	4924(1)	15(1)
C(5)	1674(2)	6053(2)	5353(1)	14(1)
C(6)	806(2)	7289(2)	6032(1)	18(1)
C(7)	1733(2)	6583(2)	6343(1)	18(1)
C(8)	3266(2)	4920(2)	5955(1)	16(1)
C(9)	4039(2)	4486(2)	6462(1)	20(1)
C(10)	4983(3)	3574(2)	6373(1)	22(1)
C(11)	5160(2)	3106(2)	5801(1)	22(1)
C(12)	4343(2)	3574(2)	5319(1)	16(1)
C(13)	3399(2)	4478(2)	5384(1)	15(1)
C(14)	3350(2)	3850(2)	4326(1)	15(1)
C(15)	4951(3)	2368(2)	4402(1)	23(1)
C(16)	4436(3)	2437(2)	3822(1)	22(1)
C(17)	2715(3)	3744(2)	3215(1)	22(1)
C(18)	3526(3)	3443(2)	2653(1)	22(1)
C(19)	2894(3)	4052(2)	2090(1)	25(1)
C(20)	3089(3)	5331(2)	2106(1)	29(1)
C(21)	502(2)	6022(2)	3652(1)	16(1)
C(22)	-372(3)	6503(2)	3146(1)	26(1)
P(1)	2187(1)	9476(1)	3262(1)	16(1)
F(1)	877(2)	9258(1)	2763(1)	33(1)
F(2)	3131(2)	8546(2)	2935(1)	56(1)
F(3)	1543(2)	8517(2)	3678(1)	52(1)
F(4)	2833(2)	10427(2)	2837(1)	47(1)
F(5)	1224(2)	10402(2)	3566(1)	65(1)
F(6)	3502(2)	9678(2)	3745(1)	46(1)

Table S9. Bond lengths [Å] and angles [°] for **3**.

Ni(1)-N(5)	1.8943(19)	C(15)-C(16)	1.344(4)
Ni(1)-C(5)	1.933(2)	C(16)-H(16)	0.9300
Ni(1)-C(13)	1.854(2)	C(17)-H(17A)	0.9700
Ni(1)-C(14)	1.940(2)	C(17)-H(17B)	0.9700
N(1)-C(4)	1.472(3)	C(17)-C(18)	1.517(3)
N(1)-C(5)	1.351(3)	C(18)-H(18A)	0.9700
N(1)-C(6)	1.392(3)	C(18)-H(18B)	0.9700
N(2)-C(5)	1.367(3)	C(18)-C(19)	1.524(3)
N(2)-C(7)	1.375(3)	C(19)-H(19A)	0.9700
N(2)-C(8)	1.420(3)	C(19)-H(19B)	0.9700
N(3)-C(12)	1.425(3)	C(19)-C(20)	1.519(4)
N(3)-C(14)	1.363(3)	C(20)-H(20A)	0.9600
N(3)-C(15)	1.371(3)	C(20)-H(20B)	0.9600
N(4)-C(14)	1.355(3)	C(20)-H(20C)	0.9600
N(4)-C(16)	1.391(3)	C(21)-C(22)	1.454(3)
N(4)-C(17)	1.467(3)	C(22)-H(22A)	0.9600
N(5)-C(21)	1.141(3)	C(22)-H(22B)	0.9600
C(1)-H(1A)	0.9600	C(22)-H(22C)	0.9600
C(1)-H(1B)	0.9600	P(1)-F(1)	1.6010(15)
C(1)-H(1C)	0.9600	P(1)-F(2)	1.5872(17)
C(1)-C(2)	1.523(3)	P(1)-F(3)	1.5879(17)
C(2)-H(2A)	0.9700	P(1)-F(4)	1.5937(16)
C(2)-H(2B)	0.9700	P(1)-F(5)	1.5703(18)
C(2)-C(3)	1.520(3)	P(1)-F(6)	1.5788(16)
C(3)-H(3A)	0.9700		
C(3)-H(3B)	0.9700	N(5)-Ni(1)-C(5)	99.96(8)
C(3)-C(4)	1.510(3)	N(5)-Ni(1)-C(14)	99.84(8)
C(4)-H(4A)	0.9700	C(5)-Ni(1)-C(14)	160.14(9)
C(4)-H(4B)	0.9700	C(13)-Ni(1)-N(5)	178.42(9)
C(6)-H(6)	0.9300	C(13)-Ni(1)-C(5)	79.70(9)
C(6)-C(7)	1.348(3)	C(13)-Ni(1)-C(14)	80.46(10)
C(7)-H(7)	0.9300	C(5)-N(1)-C(4)	122.96(18)
C(8)-C(9)	1.390(3)	C(5)-N(1)-C(6)	110.99(18)
C(8)-C(13)	1.377(3)	C(6)-N(1)-C(4)	126.04(18)
C(9)-H(9)	0.9300	C(5)-N(2)-C(7)	112.00(18)
C(9)-C(10)	1.395(3)	C(5)-N(2)-C(8)	113.83(18)
C(10)-H(10)	0.9300	C(7)-N(2)-C(8)	134.15(19)
C(10)-C(11)	1.396(4)	C(14)-N(3)-C(12)	115.11(18)
C(11)-H(11)	0.9300	C(14)-N(3)-C(15)	112.4(2)
C(11)-C(12)	1.382(3)	C(15)-N(3)-C(12)	132.5(2)
C(12)-C(13)	1.380(3)	C(14)-N(4)-C(16)	110.69(19)
C(15)-H(15)	0.9300	C(14)-N(4)-C(17)	124.58(18)

C(16)-N(4)-C(17)	124.70(19)	C(10)-C(11)-H(11)	121.3
C(21)-N(5)-Ni(1)	178.59(19)	C(12)-C(11)-C(10)	117.3(2)
H(1A)-C(1)-H(1B)	109.5	C(12)-C(11)-H(11)	121.3
H(1A)-C(1)-H(1C)	109.5	C(11)-C(12)-N(3)	128.4(2)
H(1B)-C(1)-H(1C)	109.5	C(13)-C(12)-N(3)	108.90(19)
C(2)-C(1)-H(1A)	109.5	C(13)-C(12)-C(11)	122.7(2)
C(2)-C(1)-H(1B)	109.5	C(8)-C(13)-Ni(1)	121.16(17)
C(2)-C(1)-H(1C)	109.5	C(8)-C(13)-C(12)	118.1(2)
C(1)-C(2)-H(2A)	109.0	C(12)-C(13)-Ni(1)	120.74(17)
C(1)-C(2)-H(2B)	109.0	N(3)-C(14)-Ni(1)	114.78(16)
H(2A)-C(2)-H(2B)	107.8	N(4)-C(14)-Ni(1)	141.61(17)
C(3)-C(2)-C(1)	112.84(19)	N(4)-C(14)-N(3)	103.61(18)
C(3)-C(2)-H(2A)	109.0	N(3)-C(15)-H(15)	127.1
C(3)-C(2)-H(2B)	109.0	C(16)-C(15)-N(3)	105.9(2)
C(2)-C(3)-H(3A)	109.9	C(16)-C(15)-H(15)	127.1
C(2)-C(3)-H(3B)	109.9	N(4)-C(16)-H(16)	126.3
H(3A)-C(3)-H(3B)	108.3	C(15)-C(16)-N(4)	107.4(2)
C(4)-C(3)-C(2)	108.85(17)	C(15)-C(16)-H(16)	126.3
C(4)-C(3)-H(3A)	109.9	N(4)-C(17)-H(17A)	108.9
C(4)-C(3)-H(3B)	109.9	N(4)-C(17)-H(17B)	108.9
N(1)-C(4)-C(3)	114.70(17)	N(4)-C(17)-C(18)	113.47(19)
N(1)-C(4)-H(4A)	108.6	H(17A)-C(17)-H(17B)	107.7
N(1)-C(4)-H(4B)	108.6	C(18)-C(17)-H(17A)	108.9
C(3)-C(4)-H(4A)	108.6	C(18)-C(17)-H(17B)	108.9
C(3)-C(4)-H(4B)	108.6	C(17)-C(18)-H(18A)	109.1
H(4A)-C(4)-H(4B)	107.6	C(17)-C(18)-H(18B)	109.1
N(1)-C(5)-Ni(1)	140.19(16)	C(17)-C(18)-C(19)	112.3(2)
N(1)-C(5)-N(2)	103.78(18)	H(18A)-C(18)-H(18B)	107.9
N(2)-C(5)-Ni(1)	116.03(15)	C(19)-C(18)-H(18A)	109.1
N(1)-C(6)-H(6)	126.4	C(19)-C(18)-H(18B)	109.1
C(7)-C(6)-N(1)	107.1(2)	C(18)-C(19)-H(19A)	108.7
C(7)-C(6)-H(6)	126.4	C(18)-C(19)-H(19B)	108.7
N(2)-C(7)-H(7)	127.0	H(19A)-C(19)-H(19B)	107.6
C(6)-C(7)-N(2)	106.08(19)	C(20)-C(19)-C(18)	114.3(2)
C(6)-C(7)-H(7)	127.0	C(20)-C(19)-H(19A)	108.7
C(9)-C(8)-N(2)	128.3(2)	C(20)-C(19)-H(19B)	108.7
C(13)-C(8)-N(2)	109.28(19)	C(19)-C(20)-H(20A)	109.5
C(13)-C(8)-C(9)	122.5(2)	C(19)-C(20)-H(20B)	109.5
C(8)-C(9)-H(9)	121.4	C(19)-C(20)-H(20C)	109.5
C(8)-C(9)-C(10)	117.3(2)	H(20A)-C(20)-H(20B)	109.5
C(10)-C(9)-H(9)	121.4	H(20A)-C(20)-H(20C)	109.5
C(9)-C(10)-H(10)	118.9	H(20B)-C(20)-H(20C)	109.5
C(9)-C(10)-C(11)	122.2(2)	N(5)-C(21)-C(22)	179.6(2)
C(11)-C(10)-H(10)	118.9	C(21)-C(22)-H(22A)	109.5

C(21)-C(22)-H(22B)	109.5	F(4)-P(1)-F(1)	89.39(8)
C(21)-C(22)-H(22C)	109.5	F(5)-P(1)-F(1)	89.84(10)
H(22A)-C(22)-H(22B)	109.5	F(5)-P(1)-F(2)	178.20(11)
H(22A)-C(22)-H(22C)	109.5	F(5)-P(1)-F(3)	91.13(12)
H(22B)-C(22)-H(22C)	109.5	F(5)-P(1)-F(4)	89.45(12)
F(2)-P(1)-F(1)	88.51(10)	F(5)-P(1)-F(6)	91.28(11)
F(2)-P(1)-F(3)	89.59(12)	F(6)-P(1)-F(1)	178.83(10)
F(2)-P(1)-F(4)	89.82(11)	F(6)-P(1)-F(2)	90.37(11)
F(3)-P(1)-F(1)	90.17(9)	F(6)-P(1)-F(3)	90.16(9)
F(3)-P(1)-F(4)	179.27(11)	F(6)-P(1)-F(4)	90.28(9)

Symmetry transformations used to generate equivalent atoms:

Table S10. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	12(1)	10(1)	11(1)	1(1)	1(1)	2(1)
N(1)	14(1)	15(1)	11(1)	0(1)	2(1)	1(1)
N(2)	16(1)	16(1)	12(1)	2(1)	1(1)	0(1)
N(3)	15(1)	10(1)	25(1)	1(1)	2(1)	2(1)
N(4)	16(1)	14(1)	22(1)	0(1)	4(1)	1(1)
N(5)	17(1)	14(1)	14(1)	-2(1)	4(1)	2(1)
C(1)	22(1)	24(1)	28(1)	1(1)	1(1)	9(1)
C(2)	18(1)	15(1)	21(1)	0(1)	4(1)	4(1)
C(3)	16(1)	13(1)	17(1)	-2(1)	4(1)	2(1)
C(4)	16(1)	17(1)	12(1)	0(1)	1(1)	2(1)
C(5)	12(1)	14(1)	14(1)	2(1)	2(1)	-2(1)
C(6)	19(1)	21(1)	15(1)	-3(1)	5(1)	0(1)
C(7)	21(1)	23(1)	11(1)	-2(1)	2(1)	-2(1)
C(8)	15(1)	16(1)	18(1)	6(1)	1(1)	-3(1)
C(9)	20(1)	24(1)	16(1)	7(1)	-2(1)	-5(1)
C(10)	20(1)	22(1)	24(1)	12(1)	-6(1)	-4(1)
C(11)	16(1)	15(1)	33(1)	7(1)	-4(1)	2(1)
C(12)	15(1)	12(1)	20(1)	3(1)	0(1)	-3(1)
C(13)	13(1)	14(1)	18(1)	6(1)	1(1)	-4(1)
C(14)	12(1)	14(1)	20(1)	3(1)	3(1)	-2(1)
C(15)	18(1)	13(1)	39(2)	0(1)	4(1)	4(1)
C(16)	23(1)	15(1)	30(1)	-6(1)	6(1)	5(1)
C(17)	20(1)	28(1)	20(1)	-2(1)	4(1)	3(1)
C(18)	26(1)	18(1)	22(1)	-6(1)	9(1)	1(1)
C(19)	26(1)	31(1)	19(1)	-7(1)	6(1)	2(1)
C(20)	33(1)	30(1)	26(1)	4(1)	3(1)	-1(1)
C(21)	17(1)	13(1)	16(1)	-3(1)	1(1)	1(1)
C(22)	30(1)	25(1)	22(1)	4(1)	-10(1)	-1(1)
P(1)	19(1)	18(1)	13(1)	1(1)	3(1)	0(1)
F(1)	29(1)	37(1)	31(1)	2(1)	-8(1)	-7(1)
F(2)	57(1)	58(1)	55(1)	-14(1)	6(1)	36(1)
F(3)	66(1)	58(1)	31(1)	20(1)	-1(1)	-34(1)
F(4)	47(1)	56(1)	37(1)	29(1)	-11(1)	-27(1)
F(5)	79(1)	62(1)	54(1)	-32(1)	10(1)	35(1)
F(6)	52(1)	46(1)	36(1)	13(1)	-26(1)	-20(1)

Table S11. Hydrogen coordinates (× 10^4) and isotropic displacement parameters ($Å^2$ × 10^3) for **3**.

	x	y	z	U(eq)
H(1A)	-3492	10094	4323	37
H(1B)	-2345	10531	4824	37
H(1C)	-3568	9661	4991	37
H(2A)	-2467	8299	4363	22
H(2B)	-1199	9166	4250	22
H(3A)	-398	9070	5275	18
H(3B)	-1706	8244	5406	18
H(4A)	-747	6905	4741	18
H(4B)	562	7726	4619	18
H(6)	281	7887	6191	22
H(7)	1974	6596	6756	22
H(9)	3930	4790	6846	24
H(10)	5514	3269	6705	27
H(11)	5801	2503	5747	26
H(15)	5622	1844	4566	28
H(16)	4683	1960	3507	27
H(17A)	2605	4561	3234	27
H(17B)	1734	3416	3182	27
H(18A)	3465	2631	2587	26
H(18B)	4561	3640	2717	26
H(19A)	3365	3756	1739	30
H(19B)	1848	3882	2041	30
H(20A)	2691	5651	1733	44
H(20B)	4121	5510	2154	44
H(20C)	2580	5639	2439	44
H(22A)	-550	5934	2841	39
H(22B)	154	7126	2978	39
H(22C)	-1298	6768	3285	39

Table S12. Torsion angles [°] for **3**.

N(1)-C(6)-C(7)-N(2)	-0.1(2)	C(8)-C(9)-C(10)-C(11)	-0.1(3)
N(2)-C(8)-C(9)-C(10)	-179.7(2)	C(9)-C(8)-C(13)-Ni(1)	179.10(17)
N(2)-C(8)-C(13)-Ni(1)	-0.7(3)	C(9)-C(8)-C(13)-C(12)	-0.2(3)
N(2)-C(8)-C(13)-C(12)	179.94(18)	C(9)-C(10)-C(11)-C(12)	-0.6(4)
N(3)-C(12)-C(13)-Ni(1)	-1.0(2)	C(10)-C(11)-C(12)-N(3)	-177.6(2)
N(3)-C(12)-C(13)-C(8)	178.30(19)	C(10)-C(11)-C(12)-C(13)	0.9(3)
N(3)-C(15)-C(16)-N(4)	0.4(3)	C(11)-C(12)-C(13)-Ni(1)	-179.85(17)
N(4)-C(17)-C(18)-C(19)	-168.8(2)	C(11)-C(12)-C(13)-C(8)	-0.5(3)
C(1)-C(2)-C(3)-C(4)	177.31(19)	C(12)-N(3)-C(14)-Ni(1)	0.6(2)
C(2)-C(3)-C(4)-N(1)	-179.26(18)	C(12)-N(3)-C(14)-N(4)	-178.73(17)
C(4)-N(1)-C(5)-Ni(1)	1.9(4)	C(12)-N(3)-C(15)-C(16)	177.9(2)
C(4)-N(1)-C(5)-N(2)	-178.98(18)	C(13)-C(8)-C(9)-C(10)	0.5(3)
C(4)-N(1)-C(6)-C(7)	178.9(2)	C(14)-Ni(1)-C(13)-C(8)	-178.24(19)
C(5)-Ni(1)-C(13)-C(8)	0.90(18)	C(14)-Ni(1)-C(13)-C(12)	1.08(18)
C(5)-Ni(1)-C(13)-C(12)	-179.78(19)	C(14)-N(3)-C(12)-C(11)	179.0(2)
C(5)-N(1)-C(4)-C(3)	179.69(19)	C(14)-N(3)-C(12)-C(13)	0.2(3)
C(5)-N(1)-C(6)-C(7)	0.2(3)	C(14)-N(3)-C(15)-C(16)	0.1(3)
C(5)-N(2)-C(7)-C(6)	-0.1(3)	C(14)-N(4)-C(16)-C(15)	-0.8(3)
C(5)-N(2)-C(8)-C(9)	-179.9(2)	C(14)-N(4)-C(17)-C(18)	152.5(2)
C(5)-N(2)-C(8)-C(13)	-0.1(3)	C(15)-N(3)-C(12)-C(11)	1.2(4)
C(6)-N(1)-C(4)-C(3)	1.1(3)	C(15)-N(3)-C(12)-C(13)	-177.5(2)
C(6)-N(1)-C(5)-Ni(1)	-179.4(2)	C(15)-N(3)-C(14)-Ni(1)	178.74(15)
C(6)-N(1)-C(5)-N(2)	-0.2(2)	C(15)-N(3)-C(14)-N(4)	-0.5(2)
C(7)-N(2)-C(5)-Ni(1)	179.58(14)	C(16)-N(4)-C(14)-Ni(1)	-178.2(2)
C(7)-N(2)-C(5)-N(1)	0.2(2)	C(16)-N(4)-C(14)-N(3)	0.8(2)
C(7)-N(2)-C(8)-C(9)	1.7(4)	C(16)-N(4)-C(17)-C(18)	-25.1(3)
C(7)-N(2)-C(8)-C(13)	-178.5(2)	C(17)-N(4)-C(14)-Ni(1)	3.9(4)
C(8)-N(2)-C(5)-Ni(1)	0.8(2)	C(17)-N(4)-C(14)-N(3)	-177.2(2)
C(8)-N(2)-C(5)-N(1)	-178.65(17)	C(17)-N(4)-C(16)-C(15)	177.2(2)
C(8)-N(2)-C(7)-C(6)	178.4(2)	C(17)-C(18)-C(19)-C(20)	65.7(3)

Symmetry transformations used to generate equivalent atoms:

IV. Electrochemical

Experimental Procedure: CV studies and electrode surface area measurement.

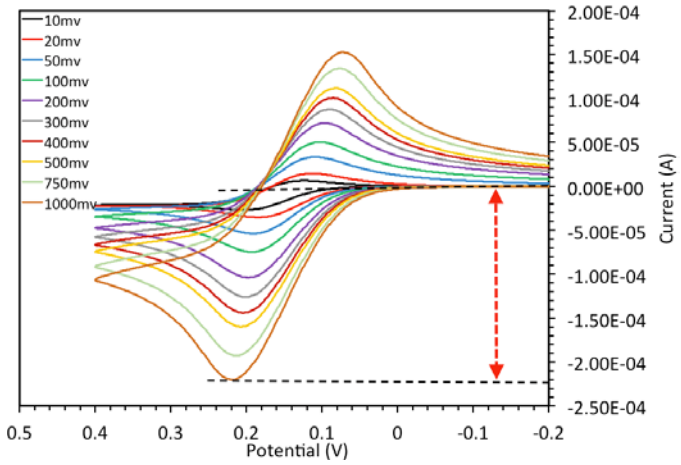
Cyclic voltammetry was measured using a CH Instruments electrochemical analyzer with ferrocene as an internal reference, platinum as a pseudo-reference electrode, platinum as a counter electrode, and glassy carbon as the working electrode. All electrochemical measurements were in acetonitrile using the scan rate of 100 mV/s. An acetonitrile 0.1 M tetrabutylammonium hexafluorophosphate electrolyte solution (3 mL) was used with a complex concentration of 1 mM. Before each measurement the solution was degassed with N_2 or CO_2 (for ~15 min). To avoid concentration changes for the electrolyte and catalyst, the desired experimental solvent volume and accurate concentrations were added to the electrolysis cell. The solvent height in the cell was marked and, the mixture was then diluted with pure acetonitrile (2-3 mL). The mixture was then degassed with N_2 or CO_2 until the solvent evaporated and level returned to the marked volume. For experiments with water, the catalyst concentration in water was adjusted prior to dilution with pure acetonitrile to yield a 2 *M* water concentration. Control experiments in the absence of nickel complex showed no response in this set-up in these potential windows. No additional water was added during evaporation. During cyclic voltammetry scans, the sweep width window was set to approximately 100 mV past the second reduction wave peak.

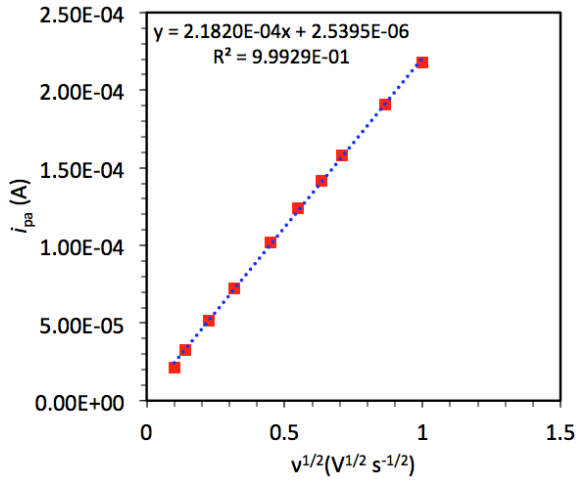
The glassy carbon working electrode surface area was measured using the Randles-Sevcik equation:

$i_p = 0.4463\ nFA_{eff}C(nFvD/RT)^{1/2}$ where at room temperature the equation is simplified to:

$i_p = 269{,}000\ n^{3/2}A_{eff}D^{1/2}Cv^{1/2}$

Where i_p is the current maximum in amps, n is number of electrons transferred, A_{eff} is the effective electrode surface area in cm^2, D is the diffusion coefficient in cm^2/s, C is the concentration in mol/cm^3, and v is the scan rate in V/s. The simplified term definitions are as follows: F is Farraday's constant in C/mol, R is the gas constant in VC/Kmol, and T is temperature in K. Experimental data was collected via CV with a glassy carbon working electrode, a platinum reference and platinum counter electrode in acetonitrile with a 0.1 M tetrabutylammonium hexafluorophosphate electrolyte solution. Ferrocene was used as a reversible redox standard with a concentration of 1 mM. The diffusion coefficient of ferrocene in acetonitrile was taken as 2.60×10^{-5} cm^2/s as reported in: Wang, Y.; Rogers, E. I.; Compton, R. G. *Journal of Electroanalytical Chemistry* **2010**, *648*, 15-19. The scan rates were varied from 10 mV to 1000 mV, and the square root of the scan rate was potted versus the absolute value of the anodic peak current. The slope of the linear fit was used in the Randles-Sevcik equation and A_{eff} found.





Experimental Procedure: Controlled Potential Electrolysis (CPE)

All the measurements were taken with a CH Instruments electrochemical analyzer and using a three-neck flask (50 mL) as the cell with rubber septum sealed electrode ports. The electrodes used are a platinum cylindrical plate as the counter electrode inside of a fine fritted isolation chamber, Ag/AgCl as the reference electrode and a glassy carbon 3 mm diameter carbon type 2 rod as the working electrode (see image below). Ferrocene (saturated in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate) was used as a sacrificial oxidant in the isolation chamber to avoid complete consumption of electrolyte during electrolysis. The height of solution in the isolation chamber (~2 mL) was even with the larger glassy carbon chamber solution level when the isolation chamber was fully submerged. To the glassy carbon chamber was added 6 mL of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile solution. Two additional milliliters of pure acetonitrile was then added to the glassy carbon chamber with 6 μmol of catalyst, then the solution was degassed with CO_2 (~ 15 min) until 2 mL of acetonitrile had evaporated from the glassy carbon chamber and a slow scan (0.01 mV/s CV scan was taken of the solution) to find the fixed potential to be used during CPE. The fixed CPE potential was set 200 mV more negative than the peak current potential obtained via CV with the CPE electrodes with the charge passed being monitored over time. During electrolysis headspace samples (300 μL) were taken with a VICI valved syringe. The gas in the syringe was compressed to 250 μL,

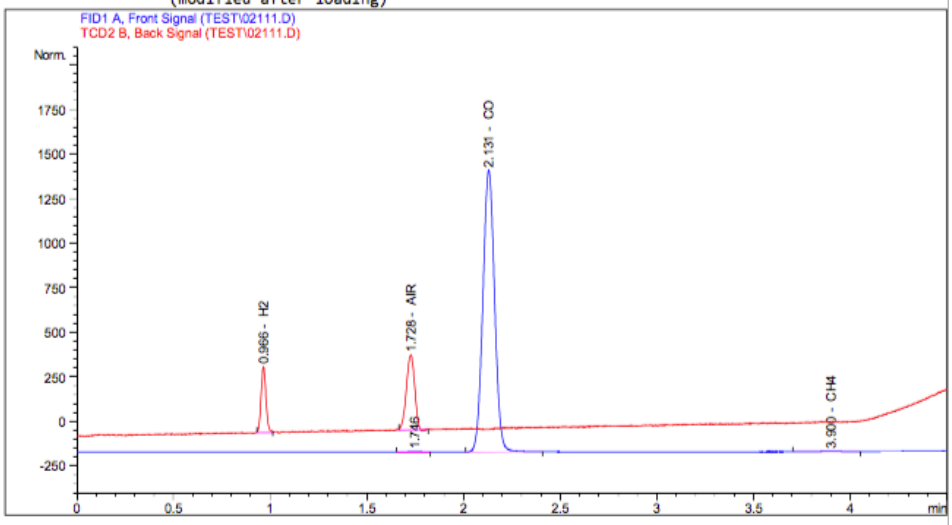
then with the tip of the syringe submerged in a vial of diethyl ether, the valve was opened to allow the pressure to equalize to atmospheric pressure. The entire 250 μL sample was then injected into a custom Agilent 7890B Gas Chromatograph (column, Agilent PorapakQ 6 ft, 1/8 OD) with a dual detector system (TCD and FID), a methanizer before the FID detector, and a backflush system to maintain good spectrum in the presence of CO_2. Quantification of CO and methane was made using the FID detector and H_2 was quantified on the TCD detector (all calibrated using standards purchased from BuyCalGas.com). Formate detection is outlined below. Note that the formate analysis method requires sacrificing the reaction mixture which precludes detection method from continuous monitoring. As such, the formate analysis results as time varies were conducted as separate experiments. TON (max.) in Table 2 refers to the maximum product/catalyst ratio for a 2-electron reduced product.

Controlled Potential Electrolysis Setup (CPE/Bulk Electrolysis/BE)

Left electrode is a platinum cylindrical plate counter electrode inside of an isolation chamber with the glass frit visible just below the bottom red line. The isolation chamber has an exchangeable atmosphere with the larger chamber. The central electrode is the glassy carbon type 2 working electrode. The right electrode is an Ag/AgCl reference electrode.

Data File C:\CHEM32\2\DATA\TEST\02111.D
Sample Name: Agilent_Standard_valve_syringe

```
    ================================================================
    Acq. Operator   : SYSTEM
    Sample Operator : SYSTEM
    Acq. Instrument : Agilent                       Location : Vial 1
    Injection Date  : 12/8/2015 3:58:49 PM
                                                    Inj Volume : Manually
    Acq. Method     : C:\CHEM32\2\METHODS\START.M
    Last changed    : 7/21/2014 11:28:33 AM by SYSTEM
    Analysis Method : C:\CHEM32\2\METHODS\START.M
    Last changed    : 7/29/2016 2:45:58 PM by SYSTEM
                      (modified after loading)
```



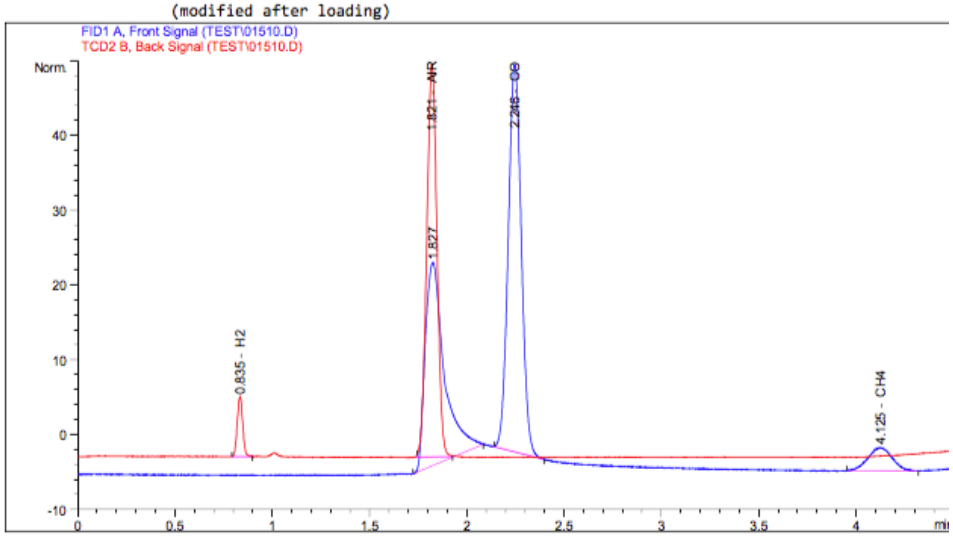

```
    ================================================================
                        External Standard Report
    ================================================================

    Sorted By             :      Signal
    Calib. Data Modified  :      7/29/2016 2:09:59 PM
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

    Signal 1: FID1 A, Front Signal

    RetTime  Type     Area     Amt/Area    Amount   Grp   Name
     [min]          [pA*s]                [ng/ul]
    -------|------|----------|----------|----------|--|-----------------
      2.131 BB     5194.17480 1.15369e-1  599.24849    CO
      3.900 BB       19.61243 1.40742e-1    2.76028    CH4

    Totals :                               602.00877
```

Agilent 7/29/2016 2:46:02 PM SYSTEM Page 1 of 2

Figure S9. Example GC trace from CPE analysis (2 hours CPE with H_2O) for **2**.

Data File C:\CHEM32\2\DATA\TEST\01510.D
Sample Name: Agilent_Standard_valve_syringe

```
    ================================================================
    Acq. Operator   : SYSTEM
    Sample Operator : SYSTEM
    Acq. Instrument : Agilent                       Location : Vial 1
    Injection Date  : 3/26/2015 2:59:30 PM
                                                    Inj Volume : Manually
    Acq. Method     : C:\CHEM32\2\METHODS\START.M
    Last changed    : 7/21/2014 11:28:33 AM by SYSTEM
    Analysis Method : C:\CHEM32\2\METHODS\START.M
    Last changed    : 7/29/2016 2:11:06 PM by SYSTEM
                      (modified after loading)
```




```
    ================================================================
                        External Standard Report
    ================================================================

    Sorted By             :      Signal
    Calib. Data Modified  :      7/29/2016 2:09:59 PM
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

    Signal 1: FID1 A, Front Signal

    RetTime  Type     Area     Amt/Area    Amount   Grp   Name
     [min]          [pA*s]                [ng/ul]
    -------|------|----------|----------|----------|--|-----------------
      2.246 BB      145.91183 1.15369e-1   16.83375    CO
      4.125 BB       16.13622 1.40742e-1    2.27104    CH4

    Totals :                               19.10479
```

Agilent 7/29/2016 2:11:12 PM SYSTEM Page 1 of 2

Figure S10. GC calibration trace (50 ppm CO standard, 2.5% CH_4, balance air [20.9% O_2, 79.1% N_2).

^{1}H NMR Formate Detection

Previously described here: Fei, H.; Sampson, M. D.; Lee, Y.; Kubiak, C. P.; Cohen, S. M. *Inorg. Chem.* **2015**, *54*, 6821.

Our slightly modified procedure is as follows: Upon reaction completion, 0.8 mL of the reaction solution was taken into a syringe and added to a 4 mL vial. To this 36 uL of Verkade's Triisobutyl Superbase (CAS# 331465-71-5; 2,8,9-Triisobutyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane) was added to the solution. The mixture was sonicated for 10 minutes at room temperature. 1.16 mL of a d_3-MeCN ferrocene solution (1.19 mM concentration) was added to the mixture. The vial was thoroughly mixed, then an NMR spectrum was taken on a 500 MHz NMR with an extended D_1-delay of 10 seconds and a minimum of 200 scans. The ratio of the formate peak (~8.7 ppm) and the ferrocene peak (~4.2 ppm, see below) were then compared to a calibration curve generated through the analysis of known concentrations of formate (0.0 mM, 0.1 mM, 1.0 mM, and 10.0 mM solutions). Through this method the concentration of formate could be evaluated accurately through a trendline having an R^2 value of 0.997 (see below). All NMR spectra were evaluated with MestReNova software to ensure level baselines in the analyte region prior to integrating peaks.

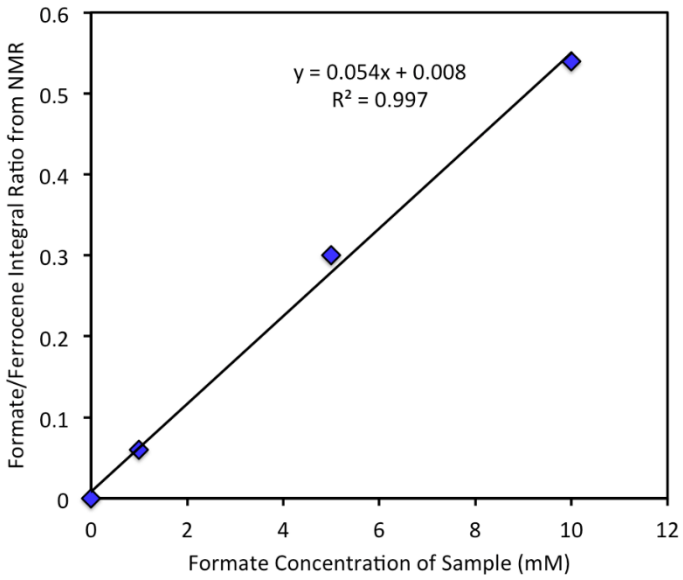


Figure S11. Formate calibration curve of NMR samples of formate in d_3-MeCN with ferrocene as an internal standard.

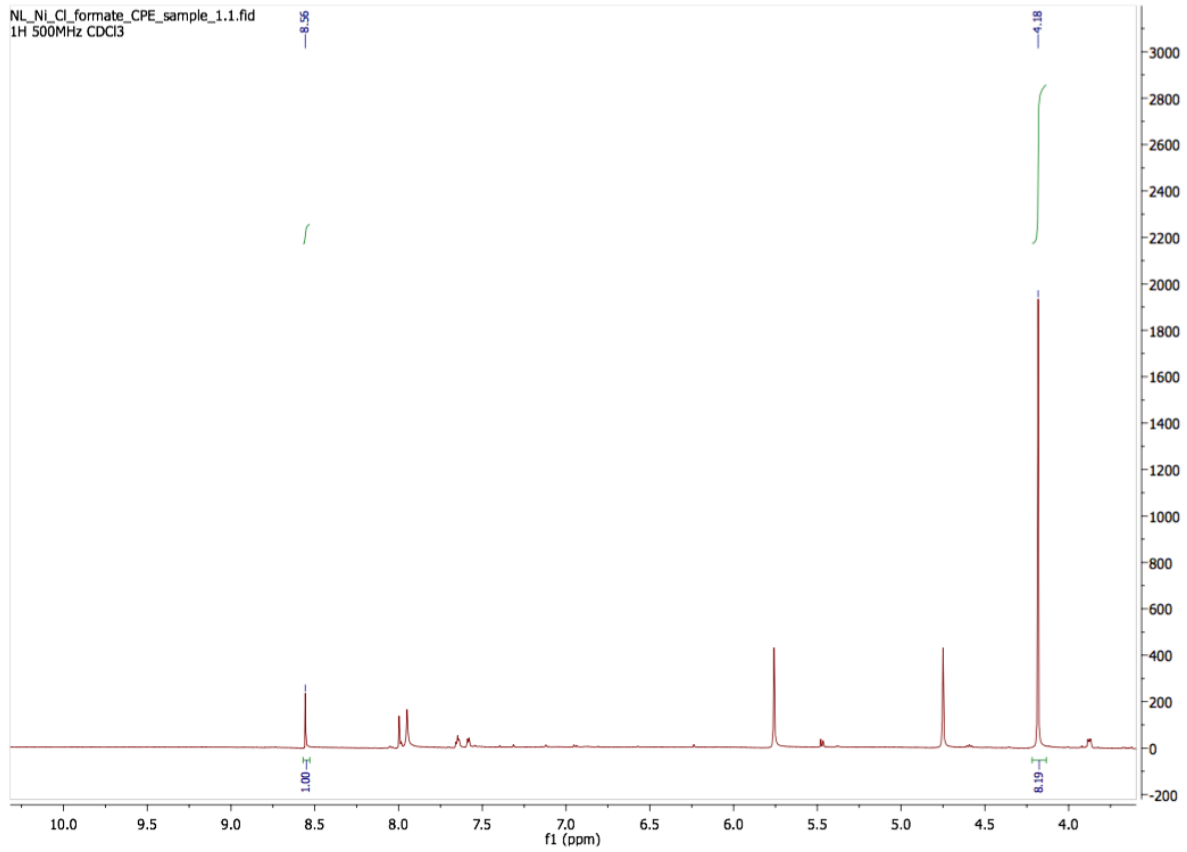


Figure S12. ^{1}H NMR for CPE formate analysis (8.6 ppm = formate; 4.2 ppm = ferrocene). *p*-Xylene was also used as an internal standard in separate experiments to confirm ferrocene was not leaking from the isolation chamber.

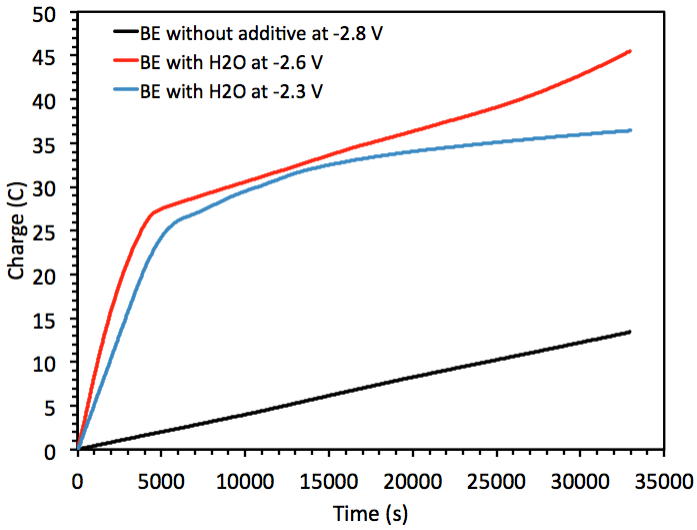


Figure S13. Controlled potential electrolysis for 550 minutes at -2.6 V versus ferrocene with water (red curve), -2.3 V versus ferrocene with water (blue) and -2.8 V versus ferrocene without water (black curve).

For the experiments with H_2O, it is important to note that a dramatic change in catalyst charge passing rate occurs between 1 and 2 hours of electrolysis (after roughly 27 C have passed). Additionally, the Faradaic Efficiency has decreased dramatically for this reaction with extended electrolysis time. The origin of this change is not well understood at this time and could be related to a change in the catalyst, or a change in the presence of a reagent in the reaction. Our experiments are setup on a small scale (5 mL total volume or less) to allow for the testing of small amounts of catalyst at a common molarity (1 mM). In our experience, catalysis is found to occur at seemingly faster and more reproducible rate if the counter electrode compartment has a solution of a sacrificial electron source (ferrocene in our case). This also provides a visual indicator of how fast the reaction is going as ferrocene turns from orange to dark green over time as ferrocene turns to ferrocenium salts and in many cases allows visual inspection to ensure the isolation chamber is not leaking during electrolysis. This dramatic change in charge passing rate may be related to the amount of reagent remaining in the isolation chamber. After 27 C, the ferrocene may have been completely consumed, and catalysis slowed. Finally, the water in the reaction may have been consumed or the pH may have dropped substantially after consumption of water leading to substantial change in the catalytic environment.

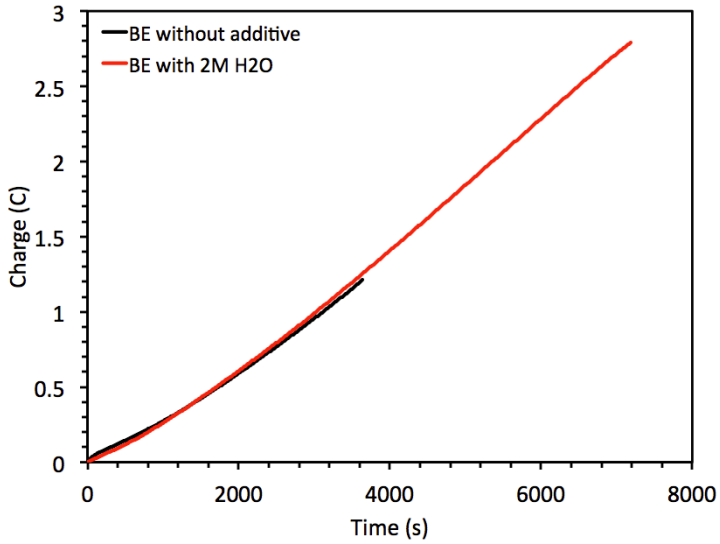


Figure S14. Controlled potential electrolysis for 120 minutes at -2.3 V versus ferrocene with water (red curve) and 60 minutes at -2.7 V versus ferrocene without water (black curve). Note that rates seems similar with and without water, however this is the effect of the working electrode being positioned somewhat higher (less surface area submerged) in the solution for the red curve.

Equation S1. Equation for estimating TOF from electrochemical cyclic voltammetry studies.

$$\text{TOF} = k_{\text{cat}}[\text{S}] = \frac{Fvn_{\text{p}}^3}{RT}\left(\frac{0.4463}{n_{\text{cat}}}\right)^2\left(\frac{i_{\text{cat}}}{i_{\text{p}}}\right)^2$$

$i_{cat} = n_{\text{cat}}FA[C_{\text{cat}}](D_{\text{c}}k_{\text{cat}}[S]^{y})^{1/2}$

$i_{\text{p}} = 0.4463(F/RT)^{1/2}n_{\text{p}}^{3/2}AD_{\text{c}}[C_{\text{p}}]v^{1/2}$

Concentration of carbon dioxide substrate [S] in MeCN is 0.28 M. See *Inorg. Chem.* **2013**, *52*, 2484 for more discussion of this equation.

V. Computational

For computational convenience, the n-butyl groups were trimmed to methyl groups, except in the case of the computation of the Raman spectra, where the full CCC-NHC ligand was utilized. Geometries were optimized using the Gaussian09[1] implementation of B3LYP (the B3 exchange functional[2] and LYP correlation functional[3]) density functional theory.[4] All other computations utilized the default pruned fine grids for energies (75, 302) and default pruned coarse grids for gradients and Hessians (35, 110) [neither grid is pruned for nickel]. All computations utilized non-default SCF convergence for geometry optimizations (10-6). The LANL2DZ basis set and effective core potential (ECP),[5,6] as modified by Couty and Hall,[7] was utilized for nickel. The basis set for chlorine was the LANL2DZ(d,p)[8,9] BS/ECP combinations. The 6-31G(d') basis sets[10] were utilized for carbon, nitrogen, and oxygen, and the 6-31G basis set[11] was utilized for hydrogen. All computations were conducted with the same basis set combination.

For trimmed models each geometry was optimized in acetonitrile solution phase and determined to be a minimum energy conformation using an analytical frequency calculation. Solvent effects were modelled implicitly by utilizing the self-consistent reaction field (SCRF) keyword with the default Integral Equation Formalism[12,13] variant of the Polarizable Continuum Model[14] (IEFPCM) method. The solvent cavity was built using non-default United Atom Kohn Sham (UAKS) radii. Default solvent parameters consistent with acetonitrile were used to model implicit solvation by the solvent. All energies are Gibbs free energies and have been calculated using standard conditions (298.15 K and 1 atm).

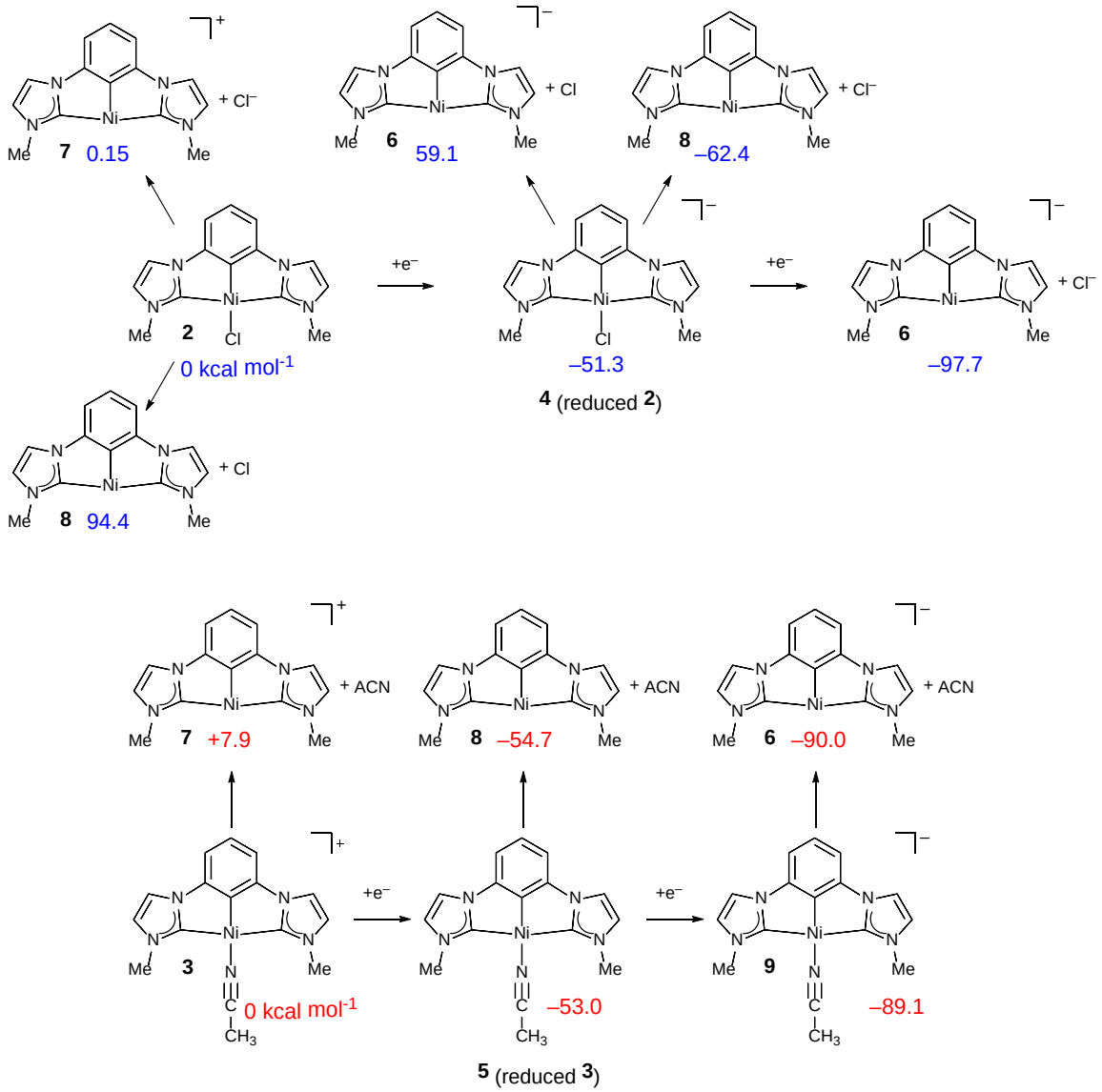


Figure S15. Calculated free energies (kcal mol^{-1}) of possible intermediates in the reduction processes of **2** and **3**.

Computed Coordinates

```
2
Ni    0.000041  0.706458  0.000000
Cl    0.000659  3.035913  0.000000
C    -0.000038  0.369288  1.972975
C    -0.000038  0.369288 -1.972975
C    -0.000081 -1.160290  0.000000
C    -0.000147 -1.179065  3.658499
C    -0.000123  0.061271  4.220100
C    -0.000123  0.061271 -4.220100
C    -0.000147 -1.179065 -3.658499
C    -0.000077 -1.867114 -1.194118
C    -0.000077 -3.264280 -1.228027
C    -0.000078 -3.945797  0.000000
C    -0.000077 -3.264280  1.228027
C    -0.000077 -1.867114  1.194118
C    -0.000146  2.428604  3.430747
C    -0.000146  2.428604 -3.430747
N    -0.000073 -0.970383  2.293792
N    -0.000084  0.986501  3.180717
N    -0.000073 -0.970383 -2.293792
N    -0.000084  0.986501 -3.180717
H    -0.000186 -2.167677  4.105041
H    -0.000150  0.373394  5.259303
H    -0.000150  0.373394 -5.259303
H    -0.000186 -2.167677 -4.105041
H    -0.000072 -3.816489 -2.168590
H    -0.000074 -5.036161  0.000000
H    -0.000072 -3.816489  2.168590
H     0.896599  2.699043  4.006785
H    -0.897217  2.699069  4.006270
H     0.000133  2.948273  2.472707
H     0.000133  2.948273 -2.472707
H    -0.897217  2.699069 -4.006270
H     0.896599  2.699043 -4.006785
    el energy= -944.652170562
          zpe= -944.402784
    th energy= -944.385566
  th enthalpy= -944.384622
  free energy= -944.448046

4
Ni   -0.775859  0.007023  0.000000
Cl   -3.171156 -0.922762  0.000000
C    -0.368353  0.250354  2.030610
C    -0.368353  0.250354 -2.030610
C     1.135928 -0.331587  0.000000
C     1.218053 -0.079861  3.662168
C     0.028204  0.155069  4.281481
C     0.028204  0.155069 -4.281481
C     1.218053 -0.079861 -3.662168
C     1.851105 -0.185099 -1.188264
C     3.245848 -0.078440 -1.227312
C     3.934015 -0.066595  0.000000
C     3.245848 -0.078440  1.227312
C     1.851105 -0.185099  1.188264
C    -2.312368  0.679082  3.548243
C    -2.312368  0.679082 -3.548243
N     0.965268 -0.027194  2.301756
N    -0.915853  0.351546  3.278605
N     0.965268 -0.027194 -2.301756
N    -0.915853  0.351546 -3.278605
H     2.201529 -0.288824  4.069923
H    -0.228497  0.201479  5.335294
H    -0.228497  0.201479 -5.335294
H     2.201529 -0.288824 -4.069923
H     3.796830  0.020419 -2.164997
H     5.022396  0.006650  0.000000
H     3.796830  0.020419  2.164997
H    -2.373812  1.594664  4.155739
H    -2.799803 -0.146009  4.089521
H    -2.821261  0.837567  2.591211
H    -2.821261  0.837567 -2.591211
H    -2.799803 -0.146009 -4.089521
H    -2.373812  1.594664 -4.155739
    el energy= -944.725983911
          zpe= -944.480666
    th energy= -944.461702
  th enthalpy= -944.460758
  free energy= -944.529837

6
Ni    0.000010 -0.954421 -0.012665
C    -1.895783 -0.702674 -0.105309
C     1.895816 -0.702629 -0.105712
C     0.000097  0.880332  0.510524
C    -3.644374  0.785260  0.156057
C    -4.167092 -0.471652  0.114680
C     4.167069 -0.471613  0.115049
C     3.644381  0.785320  0.155866
C     1.196808  1.562548  0.162522
C     1.225792  2.919065 -0.170112
C    -0.000085  3.608118 -0.266997
C    -1.225931  2.919037 -0.169598
C    -1.196767  1.562520  0.162968
C    -3.246801 -2.804320 -0.132129
C     3.246826 -2.804309 -0.131747
N    -2.267866  0.643441  0.039283
N    -3.106639 -1.360372 -0.041428
N     2.267905  0.643532  0.038566
N     3.106635 -1.360353 -0.041204
H    -4.128312  1.750077  0.265543
H    -5.196763 -0.809862  0.173719
H     5.196712 -0.809845  0.174493
H     4.128314  1.750155  0.265208
H     2.162719  3.435078 -0.392634
H    -0.000152  4.670972 -0.511732
H    -2.162951  3.435043 -0.391745
H    -4.197102 -3.053813 -0.626425
H    -3.228999 -3.273791  0.864502
H    -2.408190 -3.198180 -0.724268
H     2.408795 -3.198189 -0.724698
H     3.228043 -3.273769  0.864873
H     4.197610 -3.053832 -0.625096
    el energy= -929.635723182
          zpe= -929.391987
    th energy= -929.375634
  th enthalpy= -929.374689
  free energy= -929.435486

7
Ni    0.000000 -0.969146  0.000022
C     1.931453 -0.686233 -0.000007
C    -1.931453 -0.686233 -0.000005
C     0.000000  0.867387 -0.000029
C     3.668136  0.786591  0.000011
C     4.178549 -0.478420  0.000002
C    -4.178549 -0.478420 -0.000016
C    -3.668136  0.786591  0.000024
C    -1.205377  1.554478 -0.000012
C    -1.231992  2.951370  0.000003
C     0.000000  3.627906 -0.000002
C     1.231992  2.951370 -0.000004
C     1.205377  1.554478 -0.000018
C     3.223897 -2.816305 -0.000018
```

```
C    -3.223897 -2.816305 -0.000018
N     2.293398  0.638393 -0.000004
N     3.099410 -1.358807  0.000000
N    -2.293398  0.638393  0.000003
N    -3.099410 -1.358807  0.000001
H     4.158971  1.754347 -0.000012
H     5.205018 -0.830763  0.000026
H    -5.205018 -0.830763 -0.000010
H    -4.158971  1.754347  0.000010
H    -2.170507  3.507018  0.000004
H     0.000000  4.718242 -0.000006
H     2.170507  3.507018 -0.000008
H     3.767973 -3.142470  0.897854
H     3.767307 -3.142528 -0.898275
H     2.215908 -3.248550  0.000372
H    -2.215908 -3.248550  0.000388
H    -3.767293 -3.142528 -0.898282
H    -3.767987 -3.142469  0.897847
    el energy= -929.483894829
          zpe= -929.235957
    th energy= -929.219857
  th enthalpy= -929.218913
  free energy= -929.279600

8
Ni   -0.000005 -1.031439  0.052663
C    -1.974998 -0.730203 -0.018463
C     1.975000 -0.730207 -0.018468
C     0.000000  0.877598  0.306177
C    -3.655886  0.827725  0.070900
C    -4.231399 -0.406447  0.008031
C     4.231401 -0.406440  0.007992
C     3.655884  0.827728  0.070876
C     1.193930  1.554269  0.111738
C     1.234021  2.934529 -0.117242
C     0.000001  3.610508 -0.193038
C    -1.234021  2.934531 -0.117236
C    -1.193930  1.554271  0.111739
C    -3.397964 -2.775390 -0.129282
C     3.397974 -2.775391 -0.129220
N    -2.288839  0.621593  0.063696
N    -3.194672 -1.332251 -0.044230
N     2.288838  0.621591  0.063688
N     3.194677 -1.332250 -0.044220
H    -4.100794  1.815493  0.128511
H    -5.274544 -0.705275 -0.002202
H     5.274547 -0.705264 -0.002258
H     4.100788  1.815499  0.128477
H     2.167392  3.482949 -0.258346
H     0.000001  4.688056 -0.361879
H    -2.167391  3.482953 -0.258331
H    -4.019545 -3.016232 -1.003995
H    -3.894786 -3.143199  0.780601
H    -2.417072 -3.254260 -0.230760
H     2.417093 -3.254260 -0.230799
H     3.894696 -3.143190  0.780723
H     4.019652 -3.016246 -1.003860
    el energy= -929.579480769
          zpe= -929.334062
    th energy= -929.317468
  th enthalpy= -929.316523
  free energy= -929.379268

Cl-
Cl    0.000000  0.000000  0.000000
    el energy= -15.1531849552
          zpe= -15.153185
    th energy= -15.151769
  th enthalpy= -15.150824
  free energy= -15.168208

Cl
Cl    0.000000  0.000000  0.000000
    el energy= -14.9026725713
          zpe= -14.902673
    th energy= -14.901256
  th enthalpy= -14.900312
  free energy= -14.918350

3
Ni   -0.000575  0.466237 -0.002286
C     1.946371  0.139211 -0.003139
C    -1.946538  0.133382 -0.003163
C     0.002216 -1.398546  0.000176
C     3.662698 -1.363973 -0.000362
C     4.193825 -0.108026 -0.004553
C    -4.193221 -0.120533 -0.004511
C    -3.658367 -1.374902 -0.000210
C    -1.193111 -2.103068  0.002484
C    -1.224442 -3.499735  0.006404
C     0.006345 -4.177589  0.008172
C     1.235115 -3.496069  0.006331
C     1.199637 -2.099501  0.002418
C     3.305573  2.245829 -0.010546
C    -3.312030  2.235943 -0.010792
N     2.292978 -1.190074  0.000332
N     3.132103  0.790989 -0.006435
N    -2.289168 -1.196917  0.000436
N    -3.134184  0.781636 -0.006489
H     4.135351 -2.340435  0.001779
H     5.225235  0.228739 -0.006635
H    -5.225636  0.213148 -0.006558
H    -4.128090 -2.352775  0.002061
H    -2.163204 -4.054961  0.008150
H     0.007982 -5.267951  0.011200
H     2.175507 -4.048529  0.008014
H     4.380570  2.463860 -0.026024
H     2.857152  2.679608  0.892617
H     2.832041  2.676674 -0.902089
H    -2.839716  2.668141 -0.902341
H    -2.865004  2.671207  0.892367
H    -4.387674  2.450737 -0.026396
C    -0.008926  5.022932  0.020078
C    -0.006044  3.566963  0.010090
N    -0.003825  2.409566  0.002638
H    -0.938690  5.394884 -0.430847
H     0.061183  5.383759  1.055124
H     0.849150  5.398964 -0.553053
    el energy= -1062.27526691
          zpe= -1061.979828
    th energy= -1061.958962
  th enthalpy= -1061.958017
  free energy= -1062.031522

5
Ni   -0.000448  0.566544 -0.044054
C     2.041806  0.139100 -0.278192
C    -2.041763  0.135143 -0.278244
C     0.001435 -1.337360  0.313973
C     3.668384 -1.426091  0.143441
C     4.287957 -0.236826 -0.095382
C    -4.287184 -0.245093 -0.095648
C    -3.665377 -1.433201  0.143145
C    -1.186581 -2.061363  0.203741
C    -1.223029 -3.458965  0.157433
C     0.004194 -4.145840  0.171606
```

```
C     1.230053 -3.456542  0.157532
C     1.190864 -2.059030  0.203829
C     3.551401  2.091572 -0.679580
C    -3.554951  2.084785 -0.679462
N     2.309086 -1.183639  0.036746
N     3.286361  0.695593 -0.347308
N    -2.306514 -1.188137  0.036594
N    -3.287350  0.689249 -0.347420
H     4.074874 -2.401447  0.388236
H     5.340874  0.025853 -0.111147
H    -5.340597  0.015567 -0.111494
H    -4.070026 -2.409361  0.387801
H    -2.160756 -4.013600  0.088469
H     0.005271 -5.235980  0.143231
H     2.168865 -4.009345  0.088640
H     4.207244  2.151399 -1.560574
H     4.038024  2.599256  0.166667
H     2.597257  2.582151 -0.900456
H    -2.601793  2.576982 -0.901037
H    -4.041849  2.591645  0.167126
H    -4.211511  2.143537 -1.559994
C    -0.006664  5.109466  0.808755
C    -0.004582  3.676219  0.538573
N    -0.002719  2.534498  0.321346
H    -0.969297  5.545305  0.509612
H     0.149077  5.288167  1.881286
H     0.799056  5.597864  0.244335
    el energy= -1062.35144317
          zpe= -1062.060136
    th energy= -1062.038054
  th enthalpy= -1062.037110
  free energy= -1062.115996
9
Ni   -0.000041  0.501788 -0.023861
C     1.905463  0.116285 -0.321362
C    -1.905464  0.115994 -0.321360
C     0.000090 -1.339107  0.420339
C     3.649664 -1.348984  0.105088
C     4.185769 -0.120530 -0.131152
C    -4.185732 -0.121103 -0.131192
C    -3.649467 -1.349492  0.105047
C    -1.197707 -2.080613  0.235757
C    -1.225191 -3.475056  0.169658
C     0.000295 -4.171286  0.194412
C     1.225683 -3.474885  0.169672
C     1.198000 -2.080439  0.235771
C     3.297778  2.166430 -0.684008
C    -3.298026  2.165988 -0.683943
N     2.271281 -1.205377 -0.010098
N     3.135306  0.753935 -0.392676
N    -2.271107 -1.205700 -0.010115
N    -3.135376  0.753497 -0.392698
H     4.124088 -2.294654  0.342268
H     5.221107  0.203837 -0.152820
H    -5.221114  0.203126 -0.152874
H    -4.123778 -2.295224  0.342206
H    -2.164001 -4.023102  0.063838
H     0.000374 -5.260939  0.154930
H     2.164575 -4.022792  0.063861
H     2.598601  2.458451 -1.480499
H     4.326844  2.352190 -1.020191
H     3.094651  2.785540  0.204687
H    -3.095276  2.785064  0.204863
H    -4.327029  2.351589 -1.020415
H    -2.598671  2.458201 -1.480205
C    -0.000452  5.006278  0.849123
C    -0.000289  3.571167  0.586468
N    -0.000157  2.420646  0.383240
H    -0.005115  5.577505 -0.090577
H    -0.890076  5.283372  1.431752
H     0.893844  5.284901  1.423796
    el energy= -1062.41247422
          zpe= -1062.122041
    th energy= -1062.100591
  th enthalpy= -1062.099646
  free energy= -1062.173450

acetonitrile
C     0.000000  0.000000 -1.181450
C     0.000000  0.000000  0.279339
N     0.000000  0.000000  1.439936
H     0.000000  1.032087 -1.555628
H     0.893814 -0.516044 -1.555628
H    -0.893814 -0.516044 -1.555628
    el energy= -132.761587428
          zpe= -132.716428
    th energy= -132.712864
  th enthalpy= -132.711920
  free energy= -132.73938
```

References

(1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; O.; Nakai, H.; Vreven, T.; Montgomery, J., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Revision D. 01; Gaussian, Inc.: Wallingford, CT, 2009.

(2) Becke, A. D. J. Chem. Phys. 1993, 98, 5648-5652.

(3) Lee, C.; Yang, W.; Parr, R. G. Physical Review B 1988, 37, 785.

(4) Parr, R. G.; Yang, W. Density-functional theory of atoms and molecules; Oxford University Press, Clarendon Press: New York and Oxford, England, 1989.

(5) Hay, P. J.; Wadt, W. R. J. Chem. Phys. 1985, 82, 270-283.

(6) Wadt, W. R.; Hay, P. J. J. Chem. Phys. 1985, 82, 284-298.

(7) Couty, M.; Hall, M. B. J. Comput. Chem. 1996, 17, 1359-1370.

(8) Check, C. E.; Faust, T. O.; Bailey, J. M.; Wright, B. J.; Gilbert, T. M.; Sunderlin, L. S. Journal of Physical Chemistry A 2001, 105, 8111-8116.

(9) Hay, P. J.; Wadt, W. R. J. Chem. Phys. 1985, 82, 299-310.

(10) Hariharan, P. C.; Pople, J. A. Theor. Chim. Acta 1973, 28, 213-222.

(11) Hehre, W. J.; Ditchfield, R.; Pople, J. A. J. Chem. Phys. 1972, 56, 2257-2262.

(12) Cancès, E.; Mennucci, B.; Tomasi, J. J. Chem. Phys. 1997, 107, 3032-3041.

(13) Mennucci, B.; Cammi, R.; Tomasi, J. J. Chem. Phys. 1998, 109, 2798.

(14) Miertuš, S.; Scrocco, E.; Tomasi, J. Chem. Phys. 1981, 55, 117−129