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Supporting Information for:

Ligand-Centered Electrochemical Processes Enable CO_2 Reduction with a Nickel Bis(triazapentadienyl) Complex

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Modified Syntheses of *N*-Thiobenzoylbenzamidine and HTAPPh·HCl

***N*-thiobenzoylbenzamidine.**[1] In a closed vessel under argon, thiobenzamide (4.040 g, 0.0294 mol) was dissolved in 30 mL of dry benzonitrile. $HCl_{(g)}$ was bubbled in while stirring until the solution turned red, after which stirring was continued overnight. The orange mixture was allowed to stand for 24 h, and 50 mL of Et_2O was added. The mixture was filtered in air and the filtrand washed with acetone (3 x 5 mL) to remove residual starting materials. The dry orange solid was shaken in a separatory funnel with Et_2O (200 mL) and 10% $KHCO_{3(aq)}$ (150 mL) until all solids dissolved. The red organic layer was dried with Na_2SO_4, and the solvent was removed in vacuo to yield the product (4.049 g, 57%) which was used without further purification.

HTAPPh·HCl.[1] In a closed vessel under argon, a solution of N-thiobenzoylbenzamidine (3.715 g, 0.0155 mol) in Et_2O (65 mL) was stirred with 4 Å molecular sieves for 1 h. Solid benzamidine (1.857 g, 0.0155 mol) was added and the mixture was stirred overnight. The next day, the yellow mixture was cooled to -78 °C for one hour and then filtered in air. A concentrated HCl solution (5 M) in EtOH (10 mL) (made from acetyl chloride in EtOH) was added dropwise to the filtrate until it became acidic (pH 3-4). The white precipitate was collected and washed with distilled H_2O (5 mL). The solid was then recrystallized from warm EtOH to yield HTAPPh·HCl (1.045 g, 29%).

X-Ray Crystallography

Table S1 – Selected bond distances from X-ray and calculated bond distances from DFT (italicized) for **$Ni(TAPPy)_2$** and **$[K(crypt)][Ni(TAPPy)_2]$**.

Bond	$Ni(TAPPy)_2$	$[K(crypt)][Ni(TAPPy)_2]$
Ni-N (Å)	1.841(2) 1.832(2) *1.851*	1.844(3) 1.844(3) 1.843(3) 1.842(3) *1.855*
C-N(H) (Å)	1.307(4) 1.309(3) *1.330*	1.305(5) 1.311(5) 1.320(5) 1.325(5) *1.345*
C-N (pentadiene core, Å)	1.340(4) 1.338(4) *1.353*	1.340(5) 1.341(5) 1.349(4) 1.362(5) *1.354*

NMR Spectra

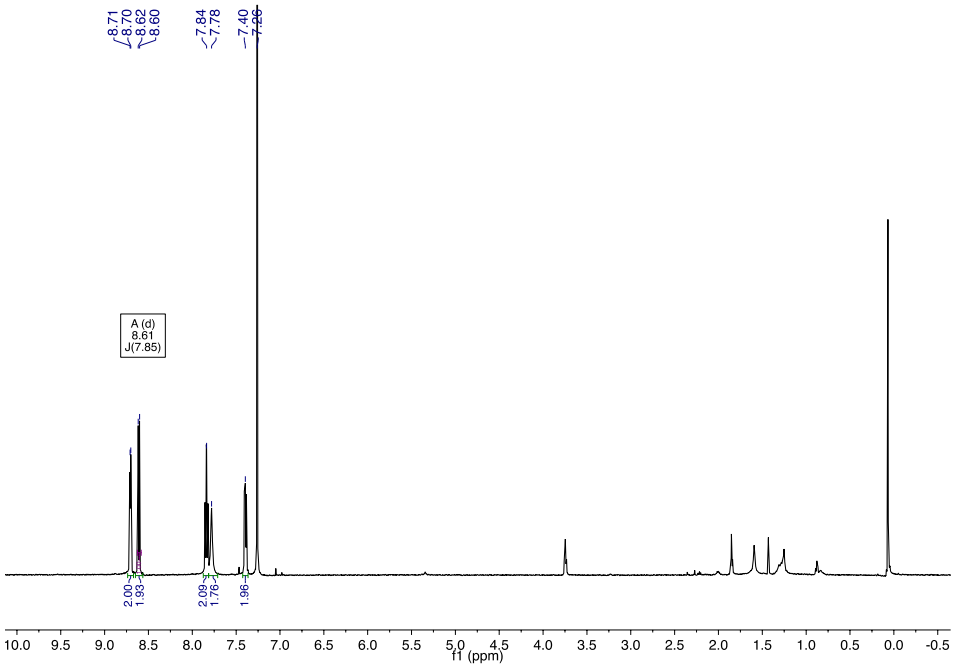

Figure S1 - ^{1}H NMR spectrum of **Ni(TAPPy)$_2$** (500 MHz, $CDCl_3$, 25 °C). Residual impurities (THF, pentane, silicone grease) are prominent due to the low solubility of **Ni(TAPPy)$_2$** in $CDCl_3$.

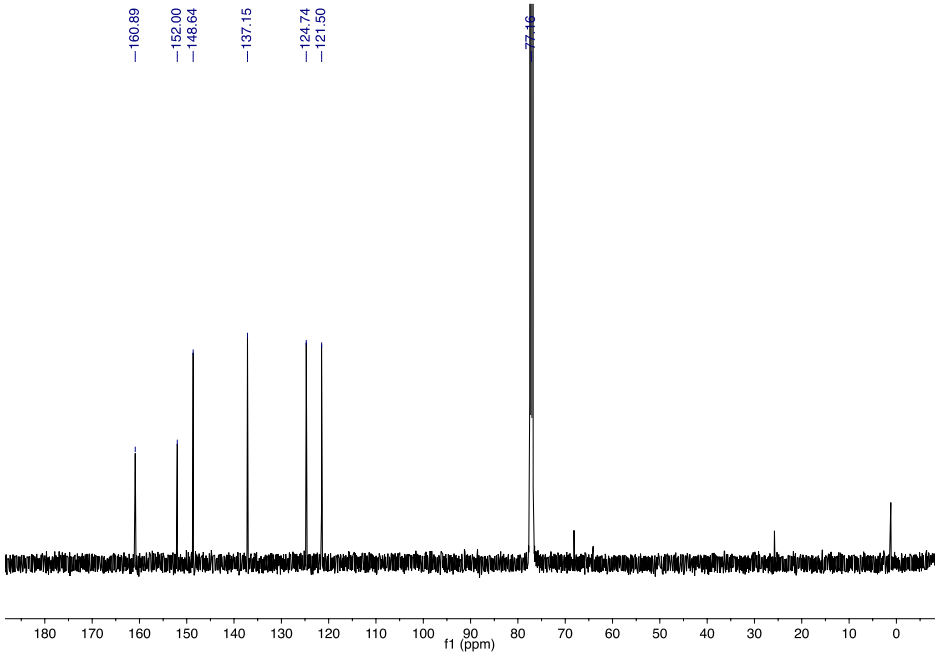

Figure S2 – ^{13}C{^{1}H} NMR spectrum of **Ni(TAPPy)$_2$** (126 MHz, $CDCl_3$, 25 °C). Residual impurities (THF, silicone grease) are prominent due to the poor solubility of **Ni(TAPPy)$_2$** in $CDCl_3$.

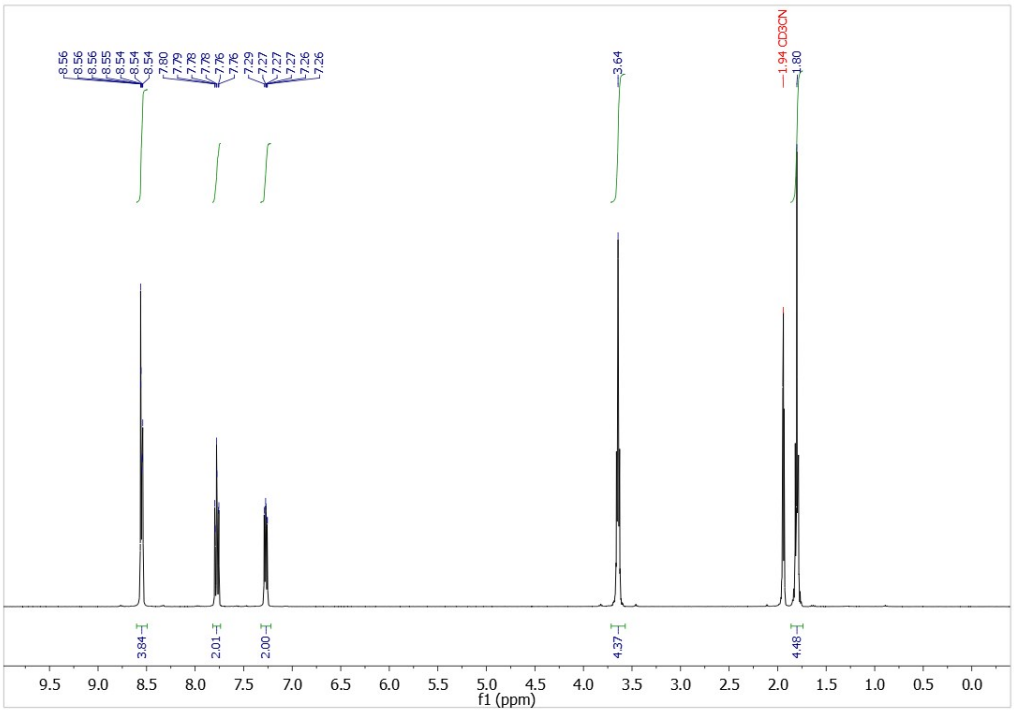

Figure S3 - ^{1}H NMR spectrum of freshly prepared **KTAPPy·THF** (400 MHz, CD_3CN, 25 °C).

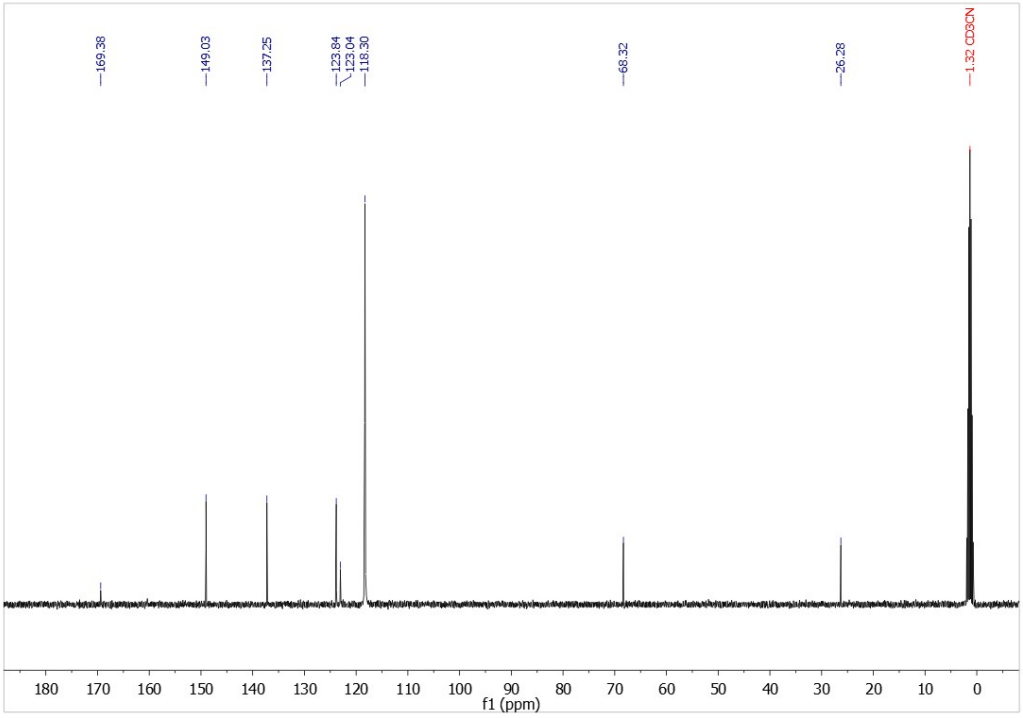

Figure S4 – ^{13}C{^{1}H} NMR spectrum of freshly prepared **KTAPPy·THF** (101 MHz, CD_3CN, 25 °C).

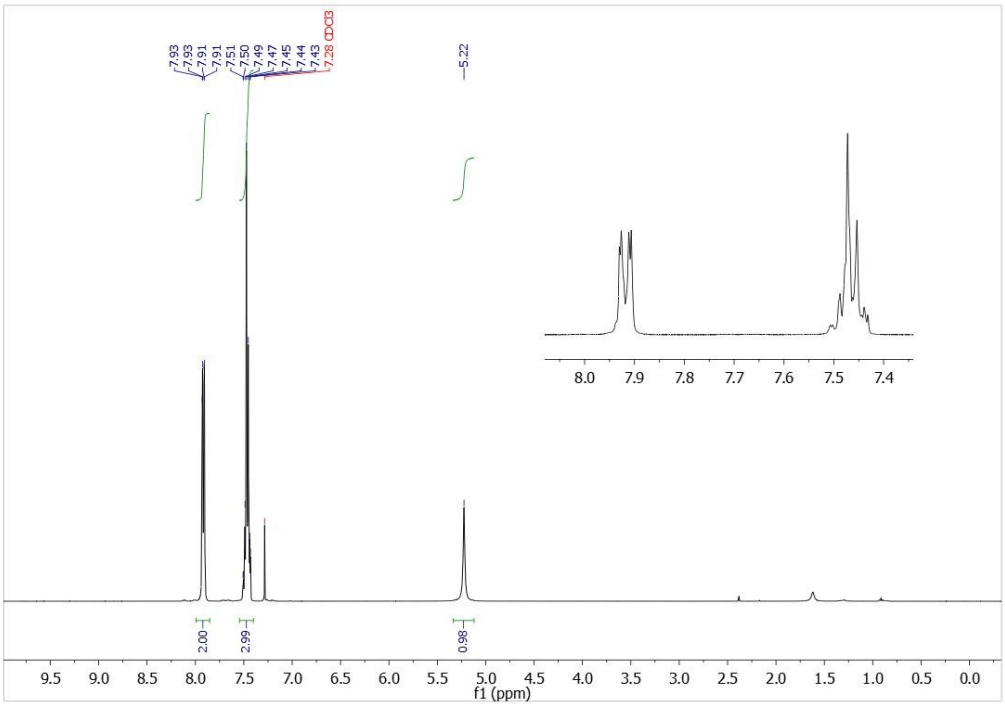

Figure S5 - ^{1}H NMR spectrum of **Ni(TAPPh)$_2$** (400 MHz, $CDCl_3$, 25 °C).

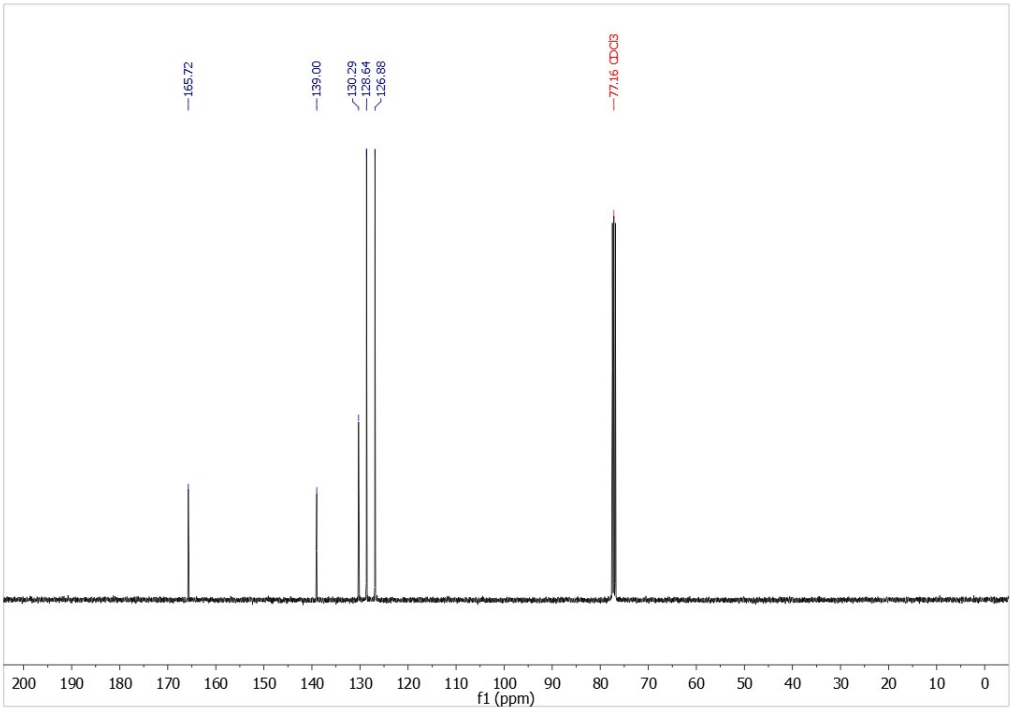

Figure S6 – ^{13}C{^{1}H} NMR spectrum of **Ni(TAPPh)$_2$** (101 MHz, $CDCl_3$, 25 °C).

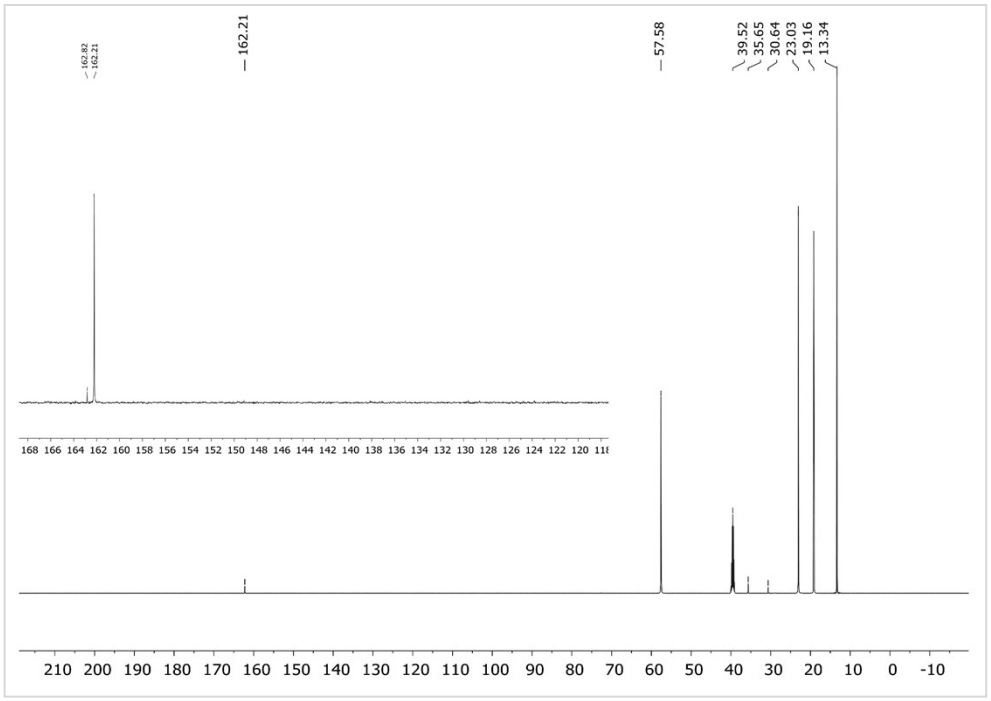

Figure S7 – $^{13}C\{^{1}H\}$ UDEFT NMR spectrum (151 MHz, d_6-DMSO, 25 °C) under natural abundance CO_2 after CPE (-2.5 V vs. $Fc^{+/0}$, glassy carbon working electrode, Pt mesh counter electrode). Inset shows expansion of region between 164-124 ppm. Peaks at 162.21, 35.65, and 30.64 ppm are from residual DMF.

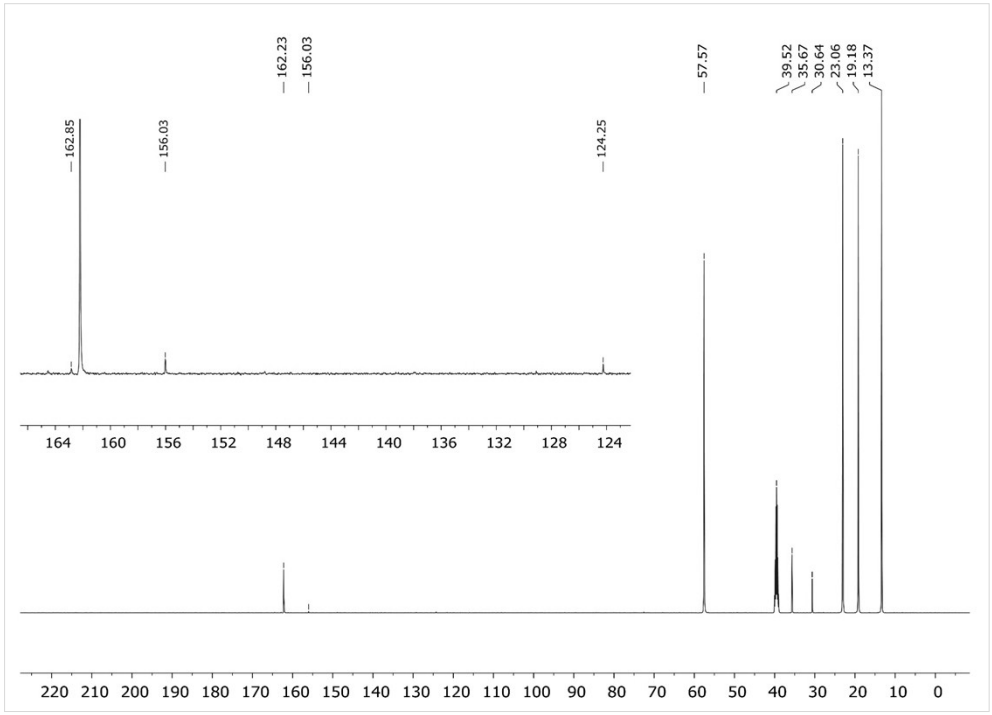

Figure S8 – $^{13}C\{^{1}H\}$ UDEFT NMR spectrum (151 MHz, d_6-DMSO, 25 °C) under $^{13}CO_2$ after CPE (-2.5 V vs. $Fc^{+/0}$, glassy carbon working electrode, Pt mesh counter electrode). Inset shows expansion of region between 164-124 ppm. Peaks at 162.21, 35.65, and 30.64 ppm are from residual DMF.

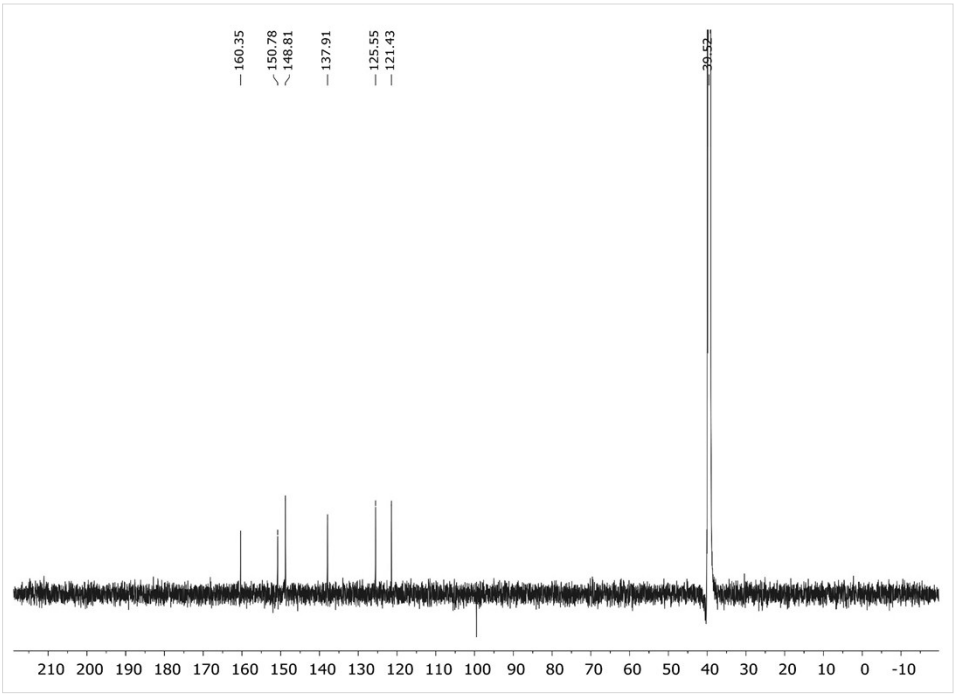

Figure S9 – $^{13}C\{^{1}H\}$ UDEFT NMR spectrum of **Ni(TAPPy)$_2$** (151 MHz, d6-DMSO, 25 °C).

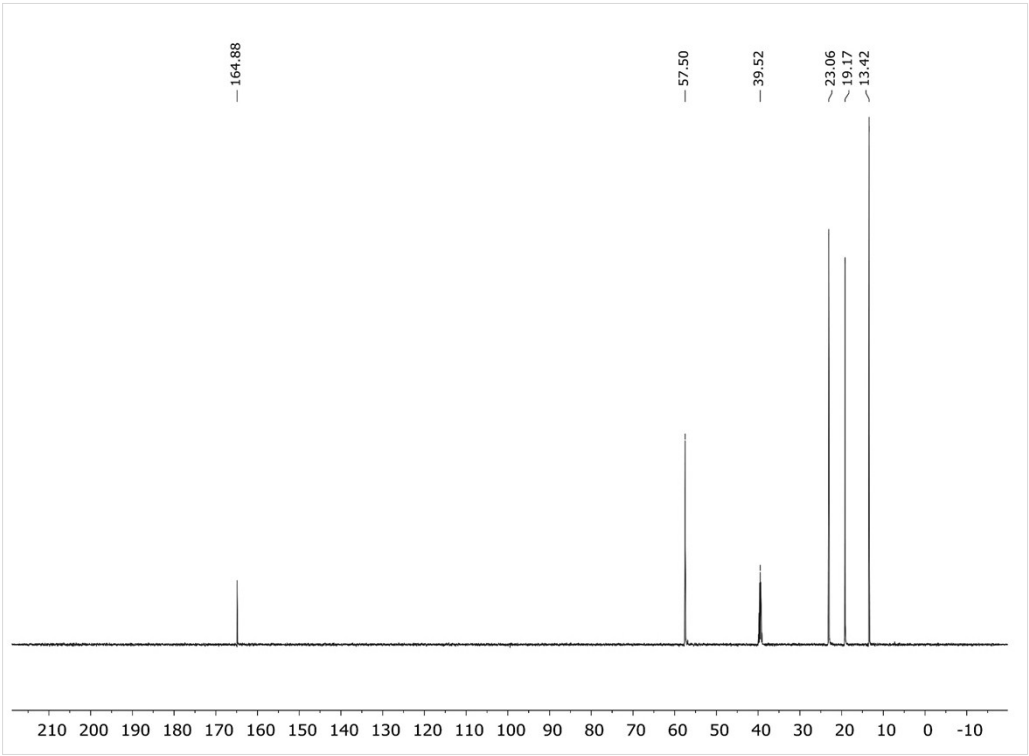

Figure S10: $^{13}C\{^{1}H\}$ UDEFT NMR spectrum of ($^{n}Bu_4N$)(HCOO) (151 MHz, d6-DMSO, 25 °C).[2]

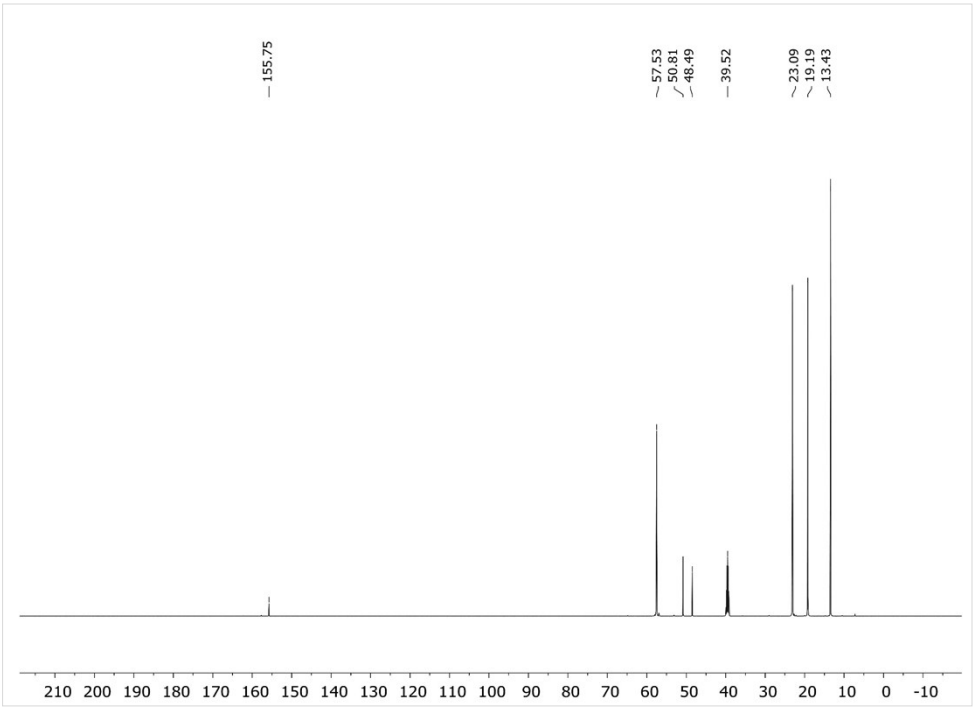

Figure S11: $^{13}C\{^{1}H\}$ UDEFT NMR spectrum of $(^{n}Bu_4N)(HCO_3)$ (151 MHz, d6-DMSO, 25 °C).[3]

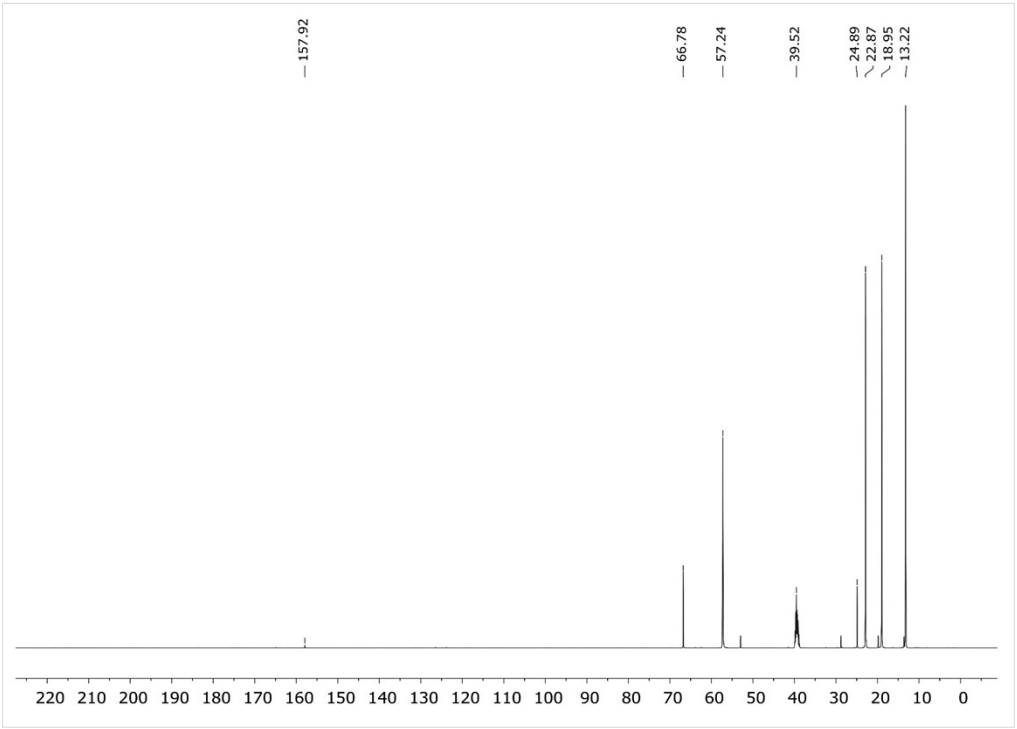

Figure S12: $^{13}C\{^{1}H\}$ UDEFT NMR spectrum of $(^{n}Bu_4N)_2(CO_3)$ (151 MHz, d6-DMSO, 25 °C).[3]

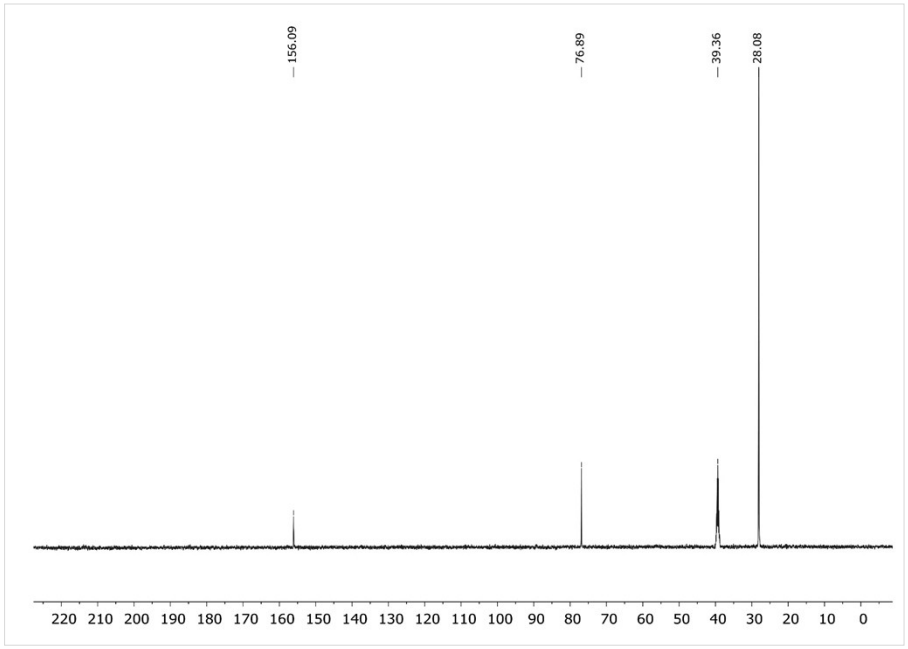

Figure S13: $^{13}C\{^{1}H\}$ UDEFT NMR spectrum of commercially available *tert*-butyl carbamate (151 MHz, d6-DMSO, 25 °C).

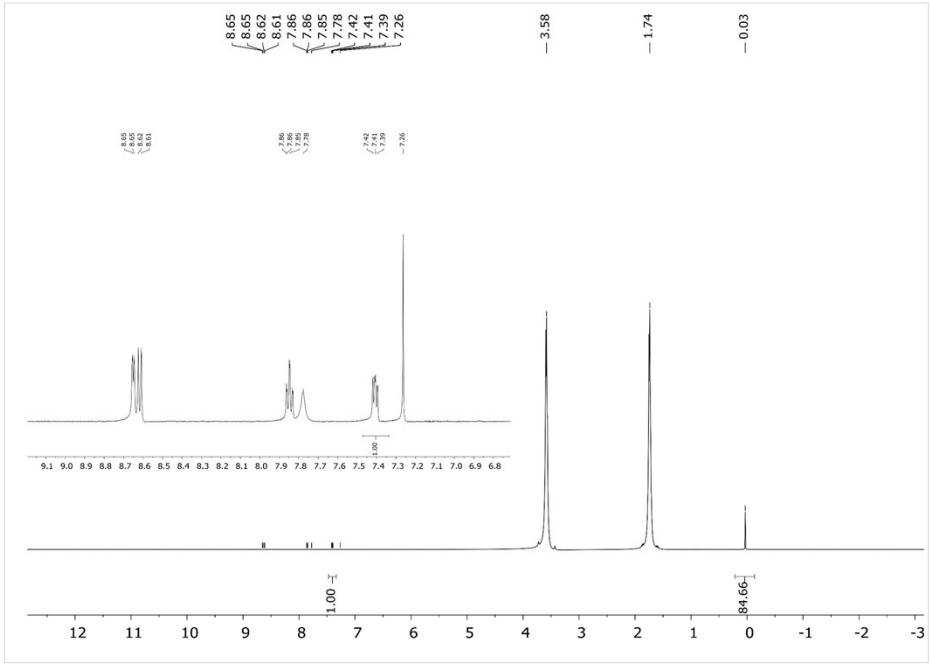

Figure S14: ^{1}H NMR after reacting **[K(crypt)][Ni(TAPPy)$_2$]** and CO_2 (1 atm) in THF with 1% HMDSO as an internal standard (500 MHz, h_8-THF, 25 ˚C). yielding ca. 60% **Ni(TAPPy)$_2$**. See main text for discussion.

Electrochemistry

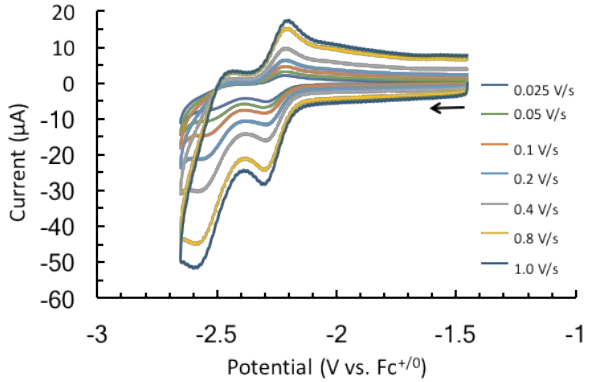

Figure S15 – CV traces of **Ni(TAPPy)$_2$** (0.50 mM) at various scan rates. Conditions: 0.1 M ^{n}Bu$_4$NPF$_6$, DMF, glassy carbon WE, Pt wire CE, Ag/AgCl pseudoreference.

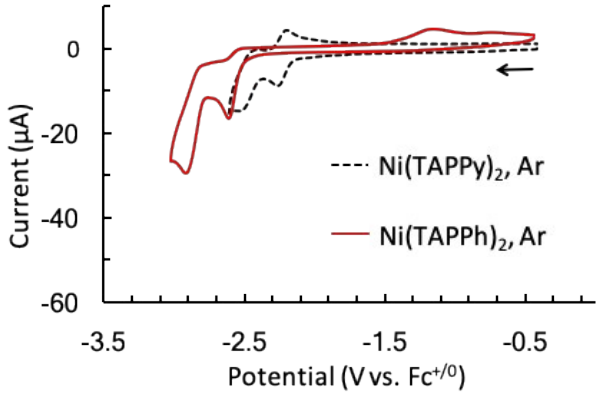

Figure S16 – CV traces of **Ni(TAPPh)$_2$** (0.50 mM, red) and **Ni(TAPPy)$_2$** (0.50 mM, dashed black). Conditions: 0.1 V/s, 0.1 M ^{n}Bu$_4$NPF$_6$, DMF, glassy carbon WE, Pt wire CE, Ag/AgCl pseudoreference.

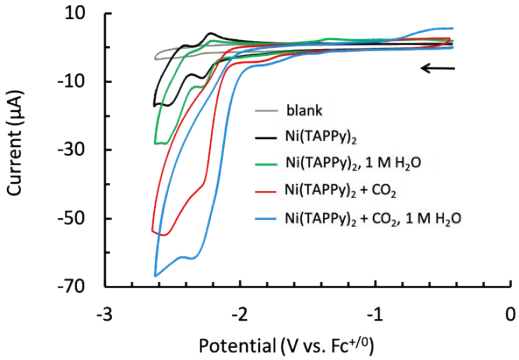

Figure S17 – CV traces of **Ni(TAPPy)$_2$** (0.50 mM) under Ar (black), with 1 M H_2O under Ar (green), under CO_2 (red), and with 1 M H_2O under CO_2 (blue). Conditions: 0.1 V/s, 0.1 M ^{n}Bu$_4$NPF$_6$, DMF, glassy carbon WE, Pt wire CE, Ag/AgCl pseudoreference.

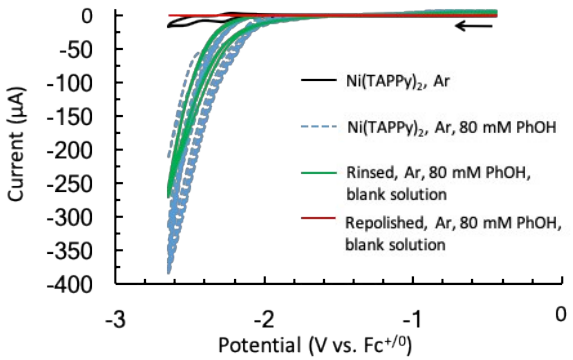

Figure S18 – CV traces (6 consecutive scans) under various conditions: **Ni(TAPPy)$_2$** (0.50 mM) under Ar (black); **Ni(TAPPy)$_2$** (0.50 mM) and 80 mM PhOH under Ar (blue); rinsed electrode in blank solution containing 80 mM PhOH under Ar (green); repolished electrode in blank solution containing 80 mM PhOH under Ar (red). Conditions: 0.1 V/s, 0.1 M $^{n}Bu_4NPF_6$, DMF, glassy carbon WE, Pt wire CE, Ag/AgCl pseudoreference.

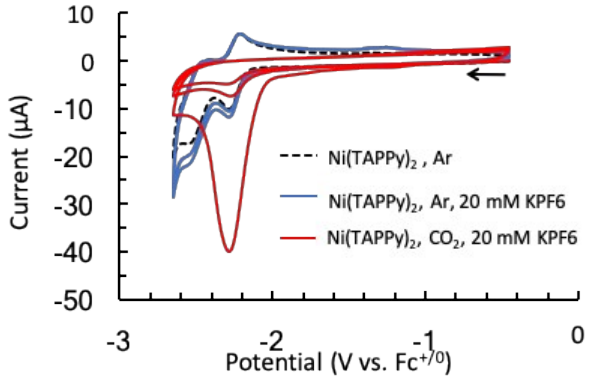

Figure S19 – Representative CV trace of **Ni(TAPPy)$_2$** (0.50 mM) with Lewis acids: **Ni(TAPPy)$_2$** under Ar (dashed black), **Ni(TAPPy)$_2$** with 20 mM KPF_6 under Ar (blue, 3 consecutive scans), and **Ni(TAPPy)$_2$** with 20 mM KPF_6 under CO_2 (red, 3 consecutive scans). Conditions: 0.1 V/s, 0.1 M $^{n}Bu_4NPF_6$, DMF, glassy carbon WE, Pt wire CE, Ag/AgCl pseudoreference.

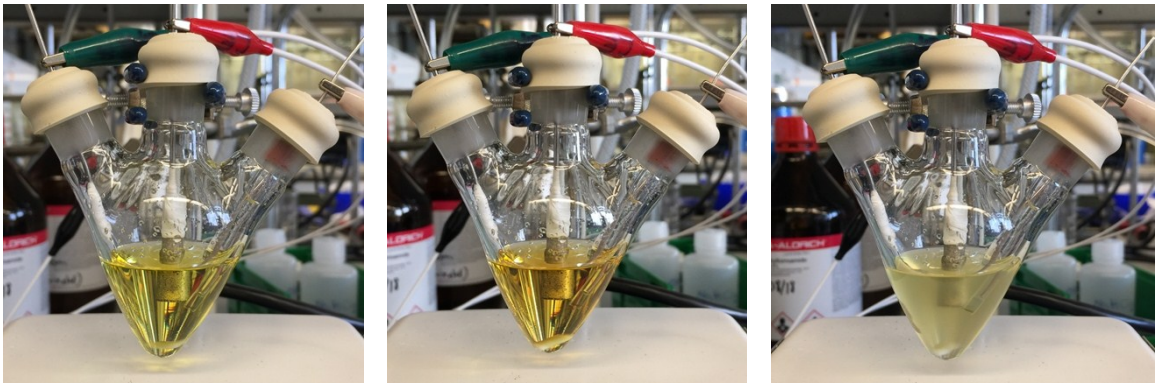

Figure S20 – Photos of a CPE experiment containing **Ni(TAPPy)$_2$** (0.50 mM) and 0.1 M $^{n}Bu_4NPF_6$ in DMF at 0 h (left), 2 h (middle), and 6 h (right). Conditions: Pt mesh WE, Mg rod CE, Ag/AgCl pseudoreference, -2.5 V applied potential vs. $Fc^{+/0}$.

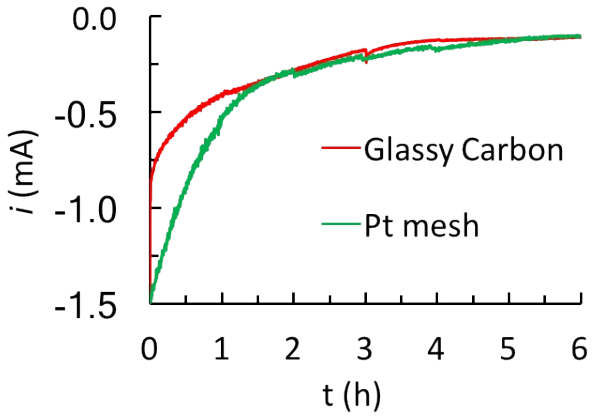

Figure S21 – CPE experiments (-2.5 V) of **Ni(TAPPy)2** (0.50 mM) with Mg counter electrode and either glassy carbon rod (red) or Pt mesh (green) working electrode. Conditions: 0.1 V/s, 0.1 M $^{n}Bu_4NPF_6$, DMF, glassy carbon WE, Pt wire CE, Ag/AgCl pseudoreference.

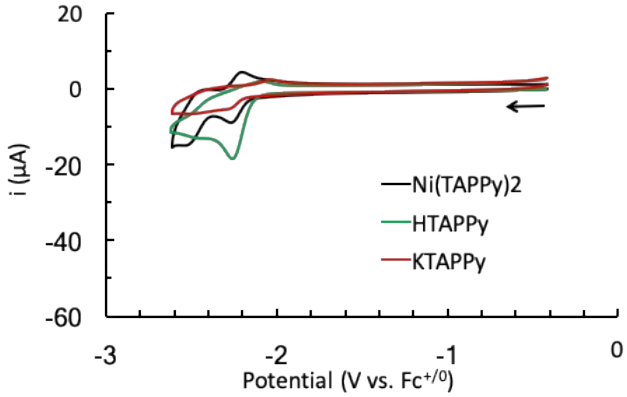

Figure S22 – CV traces of **Ni(TAPPy)$_2$** (0.50 mM, black), **HTAPPy** (0.50 mM, green), and **KTAPPy·THF** (0.50 mM, red) under Ar. Conditions: 0.1 V/s, 0.1 M $^{n}Bu_4NPF_6$, DMF, glassy carbon WE, Pt wire CE, Ag/AgCl pseudoreference.

UV-vis Spectra

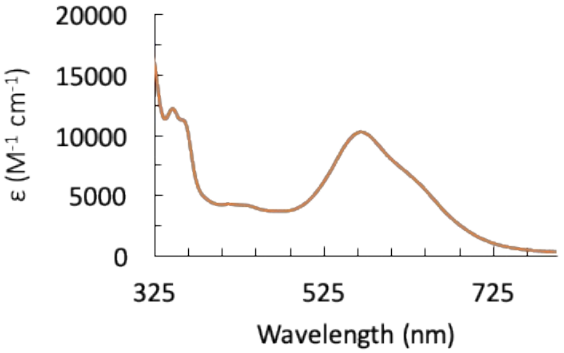

Figure S23 – UV-vis spectrum of **[K(crypt)][Ni(TAPPy)$_2$]** in THF (76.8 µM, 298 K).

GC-MS Data

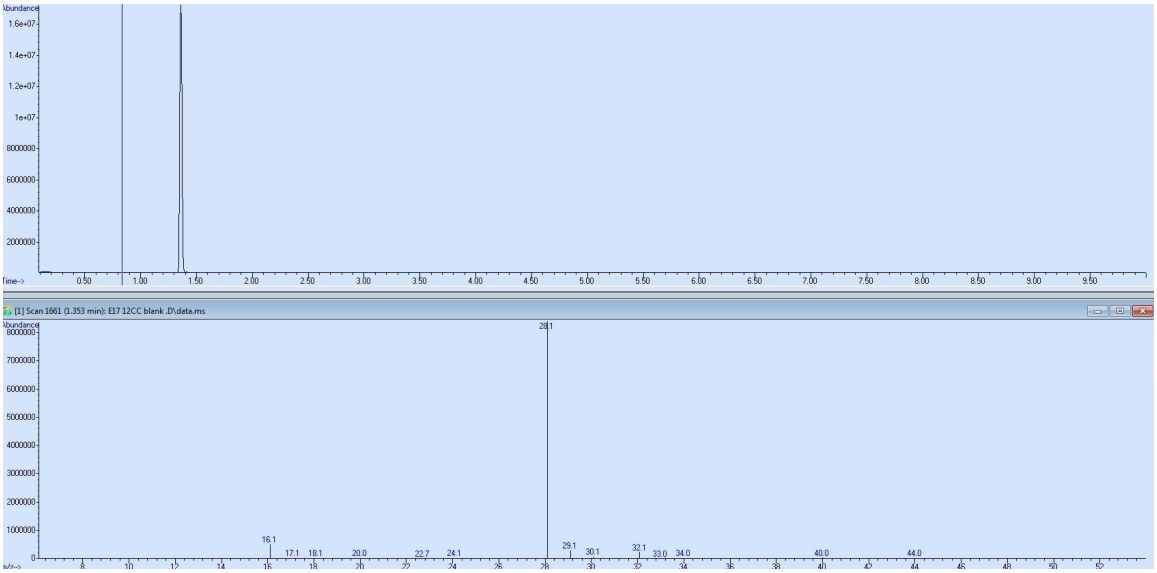

Figure S24 – Gas chromatograph (top) and mass spectrum (bottom) for natural abundance CO (t_R = 1.38 min).

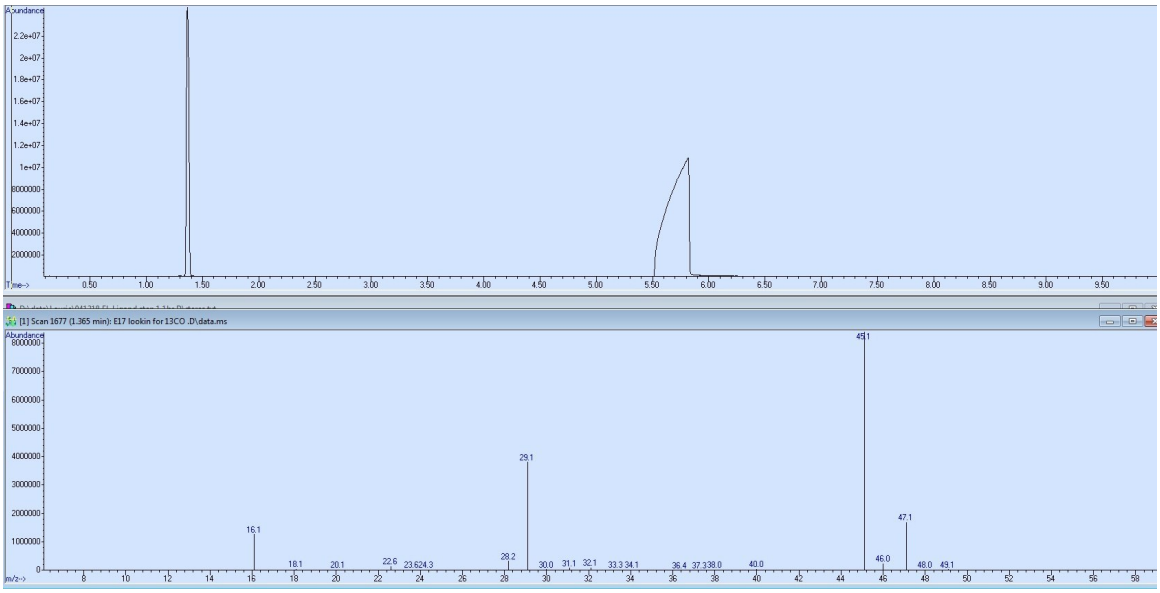

Figure S25 – Gas chromatograph (top) and mass spectrum (bottom) of headspace after electrolysis under $^{13}CO_2$. The gas chromatograph shows ^{13}CO (t_R = 1.38 min) and the mass spectrum shows ^{13}CO at m/z = 29.1 from the reduction of $^{13}CO_2$ (m/z = 45.1). Solvent vapor (DMF) appears at t_R = 5.58 min in the GC.

IR Spectra

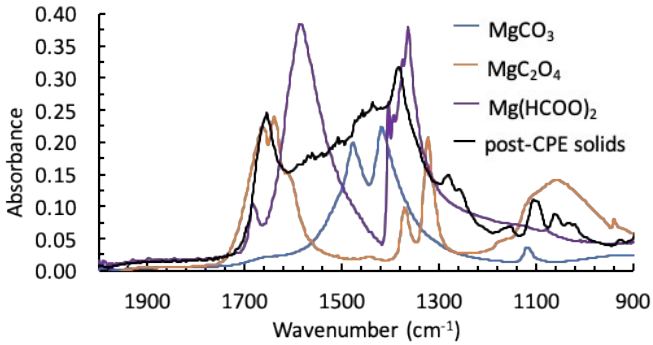

Figure S26 – ATR-IR spectra of $MgCO_3$, MgC_2O_4, $Mg(HCOO)_2$, and precipitated solids after CPE of **Ni(TAPPy)$_2$**.

DFT Calculations

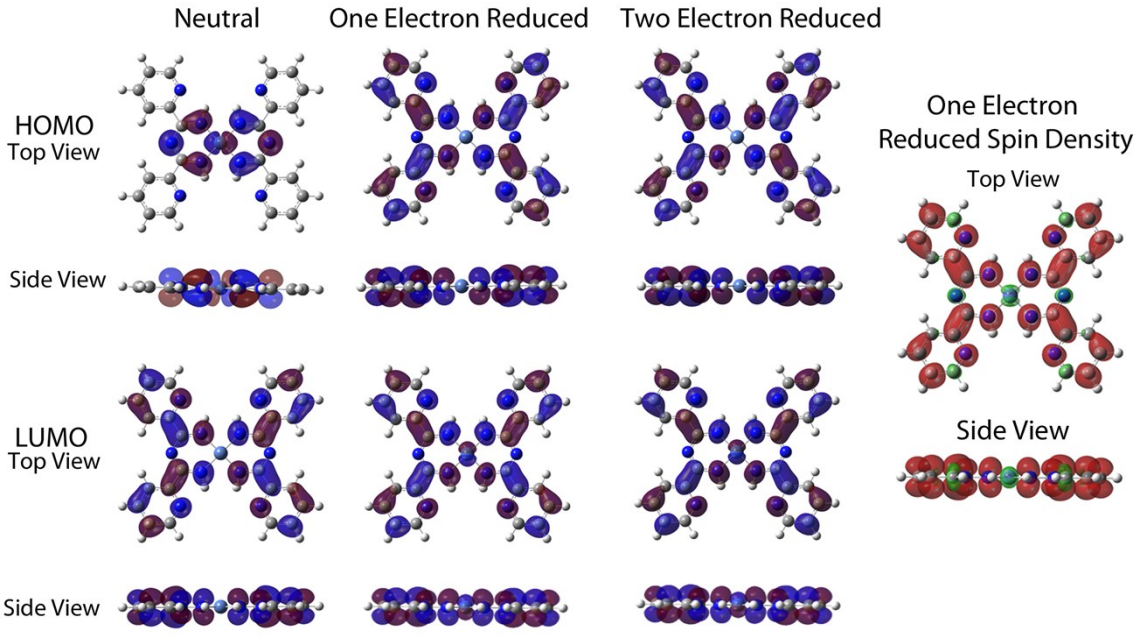

Figure S27 – Frontier Kohn-Sham orbitals for neutral, singly, and doubly reduced **Ni(TAPPy)$_2$** in gas phase (isovalue = 0.02) and Mulliken spin density plots (right) for the one electron reduced **Ni(TAPPy)$_2^-$** species (isovalue = 0.004).

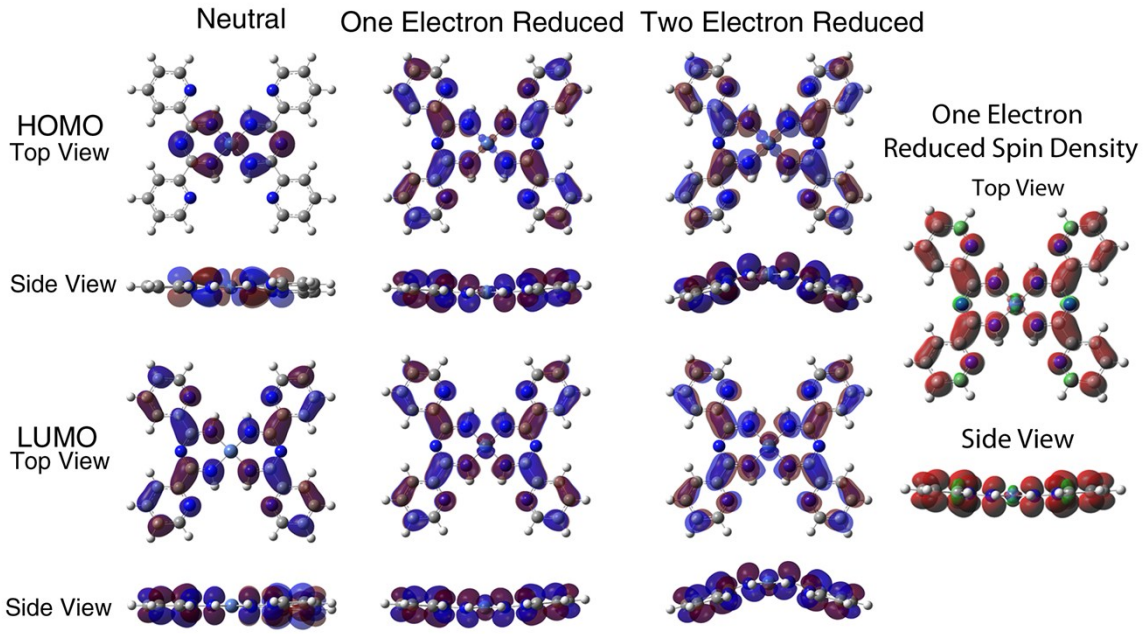

Figure S28 – Frontier Kohn-Sham orbitals for neutral, singly, and doubly reduced **Ni(TAPPy)$_2$**, DMF solvent continuum (isovalue = 0.02) and Mulliken spin density plots (right) for the one electron reduced **Ni(TAPPy)$_2^-$** species (isovalue = 0.004).

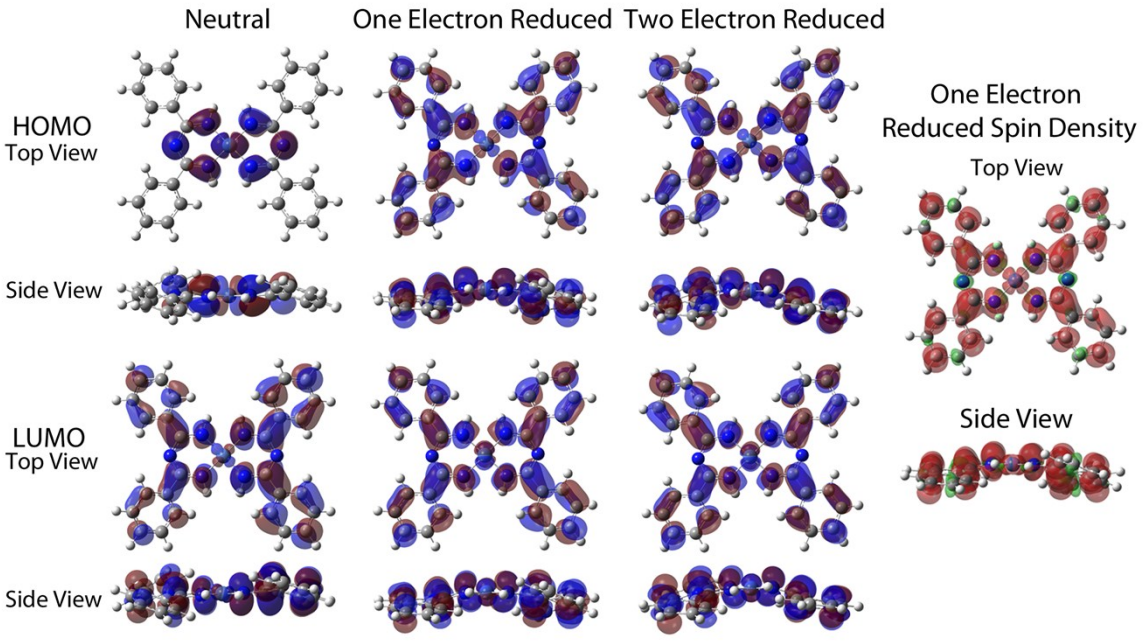

Figure S29 – Frontier Kohn-Sham orbitals for neutral, singly, and doubly reduced **Ni(TAPPy)$_2$** in the gas phase (isovalue = 0.02) and Mulliken spin density plots (right) for the one electron reduced **Ni(TAPPy)$_2^-$** species (isovalue = 0.004).

Table S2: Optimized geometry of **Ni(TAPPy)$_2$** in the gas phase and with DMF solvent continuum.

	Gas Phase			DMF		
Atom	X	Y	Z	X	Y	Z
C	-5.566790	-3.592730	-0.002340	2.635307	-1.162372	0.025736
C	-4.845770	-4.798630	-0.001470	3.453953	-2.425600	0.064516
C	-3.440520	-4.733520	-0.000100	4.862834	-2.394523	0.072380
C	-3.452600	-2.420880	-0.000480	5.560164	-3.611895	0.111334
C	-4.862010	-2.380880	-0.001820	4.831591	-4.812074	0.140759
C	-2.634010	-1.158970	0.000100	3.426203	-4.740734	0.129546
C	-2.634090	1.158990	0.000240	2.635310	1.162370	-0.025638
C	2.634120	1.159000	-0.000350	3.453960	2.425596	-0.064362
C	2.634100	-1.158940	0.000420	4.862842	2.394518	-0.072094
C	5.566900	3.592690	-0.000470	5.560177	3.611889	-0.110997
C	4.845920	4.798600	-0.001540	4.831608	4.812068	-0.140506
C	3.440660	4.733510	-0.002140	3.426219	4.740730	-0.129428
C	3.452700	2.420880	-0.000730	-2.635309	1.162374	0.025596
C	4.862100	2.380860	-0.000080	-3.453957	2.425601	0.064324
C	5.566810	-3.592730	0.000460	-4.862838	2.394524	0.072120
C	4.862060	-2.380870	0.000350	-5.560170	3.611896	0.111028
C	3.452650	-2.420850	0.000390	-4.831600	4.812075	0.140477
C	3.440520	-4.733480	0.000500	-3.426211	4.740736	0.129338
C	4.845770	-4.798620	0.000550	-2.635309	-1.162370	-0.025711
C	-5.567000	3.592550	0.000140	-3.453956	-2.425597	-0.064472
C	-4.862150	2.380750	-0.000190	-4.862838	-2.394519	-0.072341
C	-3.452750	2.420840	0.000510	-5.560169	-3.611891	-0.111280
C	-3.440790	4.733470	0.001860	-4.831598	-4.812071	-0.140685
C	-4.846050	4.798500	0.001210	-3.426209	-4.740733	-0.129470
H	-6.667720	-3.597350	-0.003410	2.818516	-5.661092	0.151376
H	-5.356890	-5.772790	-0.001840	5.336387	-5.788832	0.171807
H	-2.836390	-5.656950	0.000600	6.660754	-3.622113	0.118674
H	-5.362930	-1.404360	-0.002430	5.385272	-1.429296	0.048580
H	-1.079790	-2.314870	0.002070	2.818535	5.661088	-0.151329
H	-1.079960	2.314990	0.001690	5.336408	5.788826	-0.171516
H	1.079900	2.314900	-0.001300	6.660767	3.622106	-0.118232
H	1.079860	-2.314810	0.000340	5.385276	1.429291	-0.048234
H	6.667840	3.597280	0.000090	1.069847	2.314104	-0.044433
H	5.357060	5.772740	-0.001970	1.069841	-2.314104	0.044382
H	2.836550	5.656950	-0.003020	-2.818526	5.661094	0.151191
H	5.363000	1.404330	0.000660	-5.336398	5.788834	0.171489
H	6.667750	-3.597380	0.000510	-6.660761	3.622114	0.118312
H	5.362990	-1.404360	0.000200	-5.385275	1.429296	0.048305
H	2.836370	-5.656890	0.000490	-2.818524	-5.661092	-0.151285

H	5.356890	-5.772780	0.000630	-5.336395	-5.788829	-0.171720
H	-6.667930	3.597110	-0.000420	-6.660759	-3.622107	-0.118622
H	-5.363010	1.404200	-0.000950	-5.385274	-1.429291	-0.048557
H	-2.836720	5.656930	0.002720	-1.069844	-2.314105	-0.044339
H	-5.357220	5.772630	0.001520	-1.069844	2.314107	0.044303
N	-2.749140	-3.579690	0.000370	1.313084	-1.304376	0.020110
N	-3.329720	-0.000020	-0.000650	2.743139	-3.580903	0.092521
N	-1.313020	-1.303510	0.001630	3.326770	-0.000001	0.000082
N	-1.313110	1.303600	0.000680	2.743150	3.580900	-0.092451
N	1.313120	1.303550	-0.000550	1.313086	1.304375	-0.020123
N	1.313110	-1.303460	0.000680	-1.313086	1.304378	0.020023
N	3.329830	0.000020	0.000160	-2.743145	3.580905	0.092356
N	2.749260	3.579700	-0.001710	-3.326771	0.000002	-0.000075
N	2.749170	-3.579640	0.000460	-2.743144	-3.580902	-0.092459
N	-2.749350	3.579680	0.001510	-1.313087	-1.304376	-0.020078
Ni	0.000020	0.000060	0.000570	0.000000	0.000000	-0.000019

Table S3: Optimized geometry of the **Ni(TAPPy)$_2$**$^-$ in the gas phase and with DMF solvent continuum.

	Gas Phase			DMF		
Atom	X	Y	Z	X	Y	Z
C	5.600540	-3.564290	0.000720	2.653311	-1.166685	-0.066601
C	4.890610	-4.787620	0.000900	3.460830	-2.418143	0.003948
C	3.486230	-4.729390	0.000770	4.874299	-2.396318	0.094961
C	3.465600	-2.408880	0.000300	5.570560	-3.608312	0.157481
C	4.882030	-2.365840	0.000410	4.843274	-4.817955	0.128187
C	2.650100	-1.162640	-0.000040	3.442628	-4.743219	0.036040
C	2.650100	1.162630	-0.000320	2.653235	1.166832	-0.066305
C	-2.650080	1.162640	-0.000060	3.460662	2.418324	0.004693
C	-2.650080	-1.162640	-0.000200	4.874122	2.396578	0.095870
C	-5.600530	3.564280	0.001030	5.570285	3.608606	0.158828
C	-4.890600	4.787610	0.001020	4.842914	4.818204	0.129800
C	-3.486230	4.729380	0.000650	3.442284	4.743391	0.037469
C	-3.465580	2.408880	0.000330	-2.653319	1.166687	-0.066711
C	-4.882010	2.365830	0.000670	-3.460835	2.418142	0.003860
C	-5.600570	-3.564240	-0.000550	-4.874298	2.396319	0.094986
C	-4.882030	-2.365800	-0.000460	-5.570555	3.608312	0.157540
C	-3.465610	-2.408870	-0.000260	-4.843274	4.817957	0.128161
C	-3.486290	-4.729380	-0.000230	-3.442636	4.743221	0.035900
C	-4.890670	-4.787580	-0.000430	-2.653241	-1.166831	-0.066449
C	5.600530	3.564290	0.000040	-3.460659	-2.418324	0.004573
C	4.882020	2.365830	0.000040	-4.874111	-2.396585	0.095886

C	3.465580	2.408880	-0.000320	-5.570266	-3.608614	0.158881
C	3.486220	4.729380	-0.000660	-4.842897	-4.818212	0.129746
C	4.890590	4.787620	-0.000330	-3.442276	-4.743394	0.037275
H	6.702540	-3.554270	0.000800	2.837509	-5.666633	0.010520
H	5.410710	-5.757840	0.001150	5.347479	-5.794497	0.175098
H	2.892690	-5.662270	0.000890	6.669287	-3.615426	0.229853
H	5.369680	-1.381900	0.000250	5.396291	-1.430281	0.116180
H	1.077510	-2.310470	-0.000010	2.837098	5.666767	0.012149
H	1.077500	2.310450	-0.000800	5.347041	5.794769	0.177059
H	-1.077480	2.310460	-0.000160	6.669002	3.615780	0.231336
H	-1.077520	-2.310490	-0.000070	5.396189	1.430577	0.116879
H	-6.702530	3.554250	0.001320	1.074117	2.311853	-0.150293
H	-5.410710	5.757830	0.001300	1.074255	-2.311785	-0.150762
H	-2.892690	5.662270	0.000640	-2.837520	5.666636	0.010309
H	-5.369650	1.381890	0.000670	-5.347477	5.794499	0.175095
H	-6.702570	-3.554190	-0.000710	-6.669276	3.615426	0.230004
H	-5.369670	-1.381850	-0.000540	-5.396288	1.430282	0.116267
H	-2.892770	-5.662270	-0.000120	-2.837092	-5.666768	0.011866
H	-5.410780	-5.757790	-0.000500	-5.347017	-5.794779	0.177031
H	6.702530	3.554270	0.000320	-6.668976	-3.615791	0.231501
H	5.369670	1.381900	0.000310	-5.396179	-1.430586	0.116975
H	2.892670	5.662260	-0.000960	-1.074128	-2.311847	-0.150643
H	5.410690	5.757830	-0.000360	-1.074269	2.311787	-0.151037
N	2.773480	-3.588720	0.000460	1.318762	-1.304284	-0.161539
N	3.342740	0.000000	-0.000060	2.752644	-3.587324	-0.026197
N	1.316870	-1.302990	-0.000320	3.339131	0.000090	-0.026253
N	1.316870	1.302970	-0.000580	2.752393	3.587463	-0.025188
N	-1.316860	1.302980	-0.000320	1.318686	1.304370	-0.161337
N	-1.316870	-1.303010	-0.000210	-1.318772	1.304285	-0.161738
N	-3.342720	0.000000	-0.000130	-2.752653	3.587327	-0.026367
N	-2.773470	3.588720	0.000310	-3.339132	-0.000090	-0.026291
N	-2.773510	-3.588710	-0.000150	-2.752392	-3.587464	-0.025414
N	2.773470	3.588700	-0.000660	-1.318697	-1.304364	-0.161615
Ni	0.000030	-0.000010	-0.000350	-0.000002	0.000002	-0.160355

Table S4: Optimized geometry of **Ni(TAPPy)$_2^{2-}$** in the gas phase and with DMF solvent continuum.

	Gas Phase			DMF		
Atom	X	Y	Z	X	Y	Z
C	-5.642040	-3.537912	0.003444	-2.637589	1.174376	0.289455
C	-4.942756	-4.779759	0.004090	-3.401205	2.405720	-0.022030
C	-3.537751	-4.727698	0.003301	-4.783443	2.380101	-0.359790

C	-3.485248	-2.399405	0.001392	-5.447948	3.576951	-0.634150
C	-4.907183	-2.352566	0.002106	-4.727441	4.795427	-0.570120
C	-2.668941	-1.167013	-0.000005	-3.366991	4.730219	-0.223820
C	-2.668939	1.167008	-0.000832	-2.638091	-1.173832	0.289425
C	2.668924	1.167011	0.000244	-3.402432	-2.404907	-0.021430
C	2.668905	-1.167010	-0.000982	-4.784794	-2.378712	-0.358590
C	5.642053	3.537883	0.003141	-5.450008	-3.575332	-0.632250
C	4.942788	4.779737	0.003757	-4.730076	-4.794138	-0.568090
C	3.537781	4.727693	0.003166	-3.369442	-4.729485	-0.222410
C	3.485244	2.399407	0.001483	2.644528	-1.174542	0.311927
C	4.907178	2.352544	0.002003	3.402220	-2.404875	-0.011640
C	5.642051	-3.537873	-0.001654	4.780666	-2.380356	-0.367620
C	4.907177	-2.352535	-0.001178	5.440034	-3.576640	-0.654710
C	3.485247	-2.399404	-0.001471	4.719200	-4.795238	-0.585140
C	3.537784	-4.727698	-0.002697	3.363719	-4.729433	-0.220160
C	4.942783	-4.779730	-0.002446	2.644771	1.173738	0.312807
C	-5.642043	3.537910	-0.002278	3.402505	2.404105	-0.010500
C	-4.907182	2.352564	-0.001708	4.780759	2.379530	-0.367270
C	-3.485246	2.399417	-0.001389	5.440134	3.575826	-0.654250
C	-3.537759	4.727705	-0.002187	4.719513	4.794510	-0.583810
C	-4.942762	4.779758	-0.002536	3.364224	4.728755	-0.218090
H	-6.745311	-3.511965	0.004014	-2.769182	5.657945	-0.159700
H	-5.471285	-5.746900	0.005168	-5.207635	5.763313	-0.777470
H	-2.955847	-5.671337	0.003779	-6.517180	3.570884	-0.899660
H	-5.381638	-1.361194	0.001602	-5.302983	1.412884	-0.400270
H	-1.081343	-2.308468	0.000182	-2.772066	-5.657481	-0.158190
H	-1.081341	2.308471	-0.000914	-5.210854	-5.761864	-0.774820
H	1.081328	2.308489	0.000392	-6.519353	-3.568840	-0.897290
H	1.081384	-2.308537	-0.001843	-5.303874	-1.411252	-0.399150
H	6.745324	3.511915	0.003570	-1.096774	-2.320149	0.605260
H	5.471321	5.746876	0.004644	-1.095969	2.320079	0.605849
H	2.955892	5.671342	0.003618	2.765920	-5.656926	-0.150980
H	5.381635	1.361174	0.001497	5.195640	-5.762845	-0.802290
H	6.745322	-3.511922	-0.001417	6.505621	-3.570750	-0.934760
H	5.381620	-1.361159	-0.000567	5.300642	-1.413517	-0.412030
H	2.955882	-5.671335	-0.003317	2.766600	5.656308	-0.148210
H	5.471336	-5.746859	-0.002846	5.195972	5.762127	-0.800880
H	-6.745314	3.511960	-0.002519	6.505565	3.569905	-0.934900
H	-5.381634	1.361191	-0.001498	5.300551	1.412625	-0.412420
H	-2.955854	5.671343	-0.002374	1.105634	2.318012	0.645638
H	-5.471297	5.746897	-0.003005	1.105048	-2.318754	0.643511
N	-2.803325	-3.601805	0.001980	-1.347388	1.317779	0.691240
N	-3.358546	0.000004	-0.000398	-2.704257	3.589498	0.051561

N	-1.325204	-1.303777	-0.000967	-3.299801	0.000411	0.134573
N	-1.325205	1.303781	-0.000618	-2.706027	-3.588984	0.052284
N	1.325190	1.303799	-0.000465	-1.347787	-1.317749	0.690610
N	1.325176	-1.303823	-0.001315	1.357900	-1.316953	0.732200
N	3.358502	-0.000001	-0.000181	2.705367	-3.589258	0.067792
N	2.803343	3.601810	0.002062	3.303950	-0.000417	0.147352
N	2.803344	-3.601802	-0.002253	2.705871	3.588566	0.069813
N	-2.803332	3.601807	-0.001638	1.358324	1.316109	0.733724
Ni	-0.000006	-0.000005	-0.000792	0.003170	-0.000190	0.694962

Table S5: Optimized geometry of **Ni(TAPPh)$_2$** in the gas phase.

Atom	X	Y	Z
C	5.638761	-3.510264	-0.224920
C	5.135428	-4.703029	0.325932
C	3.819451	-4.739488	0.819329
C	3.500991	-2.396673	0.182279
C	4.832910	-2.364180	-0.287717
C	2.649886	-1.166094	0.083441
C	2.651617	1.169712	-0.050045
C	-2.645004	1.169870	-0.014416
C	-2.644756	-1.170785	-0.052976
C	-5.637193	3.495085	-0.394164
C	-5.152977	4.691374	0.166518
C	-3.848003	4.737284	0.687865
C	-3.502421	2.396449	0.061583
C	-4.823087	2.353883	-0.439300
C	-5.638050	-3.493256	0.335205
C	-4.825262	-2.350784	0.371083
C	-3.500660	-2.398966	-0.118805
C	-3.838976	-4.748725	-0.714798
C	-5.148189	-4.696789	-0.204713
C	5.650800	3.451115	-0.619637
C	4.841092	2.308293	-0.547961
C	3.505814	2.401504	-0.095840
C	3.828540	4.804015	0.251809

C	5.148017	4.703797	-0.223040
C	3.009450	-3.595179	0.749028
C	-3.029265	3.598087	0.636688
C	-3.021736	-3.608052	-0.673296
C	3.015077	3.661913	0.316000
H	6.670768	-3.472502	-0.606266
H	3.424739	-5.660545	1.274703
H	5.214206	-1.421768	-0.703669
H	1.038373	-2.292223	-0.040063
H	1.040753	2.276817	-0.295971
H	-1.032349	2.295406	-0.131761
H	-1.032331	-2.292214	0.105945
H	-6.660007	3.451350	-0.798988
H	-3.469277	5.661877	1.149657
H	-5.185145	1.407484	-0.864605
H	-6.664158	-3.444898	0.731084
H	-5.191317	-1.398961	0.780589
H	-3.455628	-5.679275	-1.160527
H	6.685432	3.363893	-0.985433
H	5.221853	1.320858	-0.841963
H	3.433672	5.775200	0.587043
H	5.770921	-5.600144	0.380088
H	-5.794853	5.584759	0.205514
H	-5.788953	-5.591273	-0.236403
H	5.786267	5.599097	-0.274496
H	1.994522	-3.627637	1.176731
H	-2.023465	3.635828	1.085120
H	-2.012275	-3.651110	-1.112818
H	1.996870	3.750086	0.727701
N	3.324531	0.004090	0.066961
N	1.322286	-1.303577	0.019334
N	1.323998	1.300881	-0.126095
N	-1.316989	1.307004	-0.069955
N	-1.316753	-1.306381	0.010601
N	-3.317964	-0.000512	-0.040953
Ni	0.002288	-0.000048	-0.040045

Table S6: Optimized geometry of **Ni(TAPPh)$_2$**$^-$ in the gas phase.

Atom	X	Y	Z
C	-5.627000	-3.566852	-0.336757
C	-5.012488	-4.778835	-0.716808
C	-3.610547	-4.821342	-0.842688

C	-3.440993	-2.458142	-0.180782
C	-4.857038	-2.425658	-0.080949
C	-2.640590	-1.237590	0.128930
C	-2.694740	1.110004	0.268914
C	2.615796	1.226373	0.175706
C	2.690909	-1.125671	0.240242
C	5.585496	3.593667	-0.163881
C	4.972821	4.790277	-0.593437
C	3.578379	4.810225	-0.790400
C	3.411341	2.454794	-0.104999
C	4.820751	2.444170	0.069651
C	5.735390	-3.278750	-0.564467
C	4.882479	-2.175546	-0.433611
C	3.585212	-2.315390	0.123086
C	4.048562	-4.709310	0.439233
C	5.324826	-4.558383	-0.133107
C	-5.799285	3.321616	0.090489
C	-4.969565	2.198715	0.196212
C	-3.556726	2.319671	0.122160
C	-3.851605	4.740025	-0.207198
C	-5.249794	4.605925	-0.108193
C	-2.837711	-3.680712	-0.579823
C	2.809435	3.662011	-0.550086
C	3.192458	-3.604571	0.571242
C	-3.019393	3.616564	-0.094821
H	-6.724110	-3.513729	-0.242242
H	-3.113093	-5.751708	-1.161625
H	-5.323667	-1.473174	0.205999
H	-1.038065	-2.344380	0.474829
H	-1.135880	2.242123	0.721171
H	0.997986	2.313708	0.500470
H	1.102102	-2.293181	0.306112
H	6.676721	3.560195	-0.010544
H	3.084806	5.728801	-1.147279
H	5.283242	1.503074	0.399769
H	6.733349	-3.144188	-1.012870
H	5.182588	-1.171592	-0.765771
H	3.719300	-5.697183	0.800381
H	-6.892408	3.197084	0.160810
H	-5.384685	1.191713	0.340326
H	-3.403486	5.731080	-0.385404
H	-5.619024	-5.675536	-0.919487
H	5.575637	5.693308	-0.778291

H	5.996008	-5.425704	-0.235789
H	-5.903052	5.488665	-0.192097
H	-1.745763	-3.730644	-0.720377
H	1.725239	3.690340	-0.746170
H	2.216004	-3.739536	1.063140
H	-1.931028	3.746032	-0.210521
N	-3.324027	-0.070827	0.064569
N	-1.335354	-1.358758	0.440907
N	-1.390656	1.254565	0.577234
N	1.305413	1.330950	0.467541
N	1.368095	-1.305183	0.435213
N	3.314468	0.068130	0.123269
Ni	-0.005807	-0.017908	0.468971

Table S7**:** Optimized geometry of **Ni(TAPPh)$_2^{2-}$** in the gas phase.

Atom	X	Y	Z
C	5.550147	3.597915	-0.579757
C	4.908023	4.830472	-0.861145
C	3.497259	4.871904	-0.814746
C	3.383155	2.484200	-0.182973
C	4.809853	2.457418	-0.257268
C	2.624919	1.271654	0.203719
C	2.711648	-1.081856	0.352505
C	-2.598347	-1.259425	0.210214
C	-2.710060	1.096531	0.296649
C	-5.516457	-3.635754	-0.421929
C	-4.866706	-4.847168	-0.771680
C	-3.455273	-4.857795	-0.816721
C	-3.353029	-2.481629	-0.144602
C	-4.781875	-2.485101	-0.123576
C	-5.788921	3.194553	-0.534733
C	-4.929554	2.104829	-0.368045
C	-3.603921	2.266316	0.134017
C	-4.071595	4.686299	0.316074
C	-5.371933	4.509002	-0.199527
C	5.823906	-3.237541	-0.145678
C	4.984839	-2.130911	0.008902
C	3.570210	-2.273005	0.149819
C	3.899932	-4.714503	-0.067709
C	5.297736	-4.554028	-0.180958

C	2.752348	3.732298	-0.483754
C	-2.714499	-3.708755	-0.509793
C	-3.207124	3.595157	0.487976
C	3.056494	-3.607103	0.093839
H	6.652091	3.533112	-0.619323
H	2.966699	5.810641	-1.052339
H	5.301111	1.497048	-0.045195
H	1.005933	2.352534	0.594894
H	1.155241	-2.222222	0.828810
H	-0.954961	-2.317147	0.544485
H	-1.119589	2.266739	0.370135
H	-6.619704	-3.596863	-0.385768
H	-2.921681	-5.779655	-1.107579
H	-5.277325	-1.541242	0.147253
H	-6.802479	3.027692	-0.940137
H	-5.236639	1.082583	-0.633048
H	-3.727751	5.695576	0.603363
H	6.912482	-3.079833	-0.246098
H	5.383960	-1.106861	0.027841
H	3.456876	-5.724808	-0.114976
H	5.492378	5.730230	-1.114413
H	-5.446632	-5.754778	-1.006339
H	-6.048676	5.369164	-0.332310
H	5.959752	-5.427492	-0.299304
H	1.651752	3.796070	-0.490242
H	-1.615546	-3.744541	-0.590512
H	-2.216975	3.764358	0.940291
H	1.968468	-3.776501	0.148682
N	3.318923	0.109386	0.127075
N	1.330161	1.374813	0.607296
N	1.414393	-1.229786	0.734974
N	-1.291564	-1.344069	0.571851
N	-1.387840	1.290364	0.569738
N	-3.312373	-0.108124	0.158587
Ni	0.006152	0.019796	0.594659

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