Supporting Information

Synthesis and Comparison of Nickel, Palladium, and Platinum Bis(N-Heterocyclic Carbene) Pincer Complexes for Electrocatalytic CO_2 Reduction

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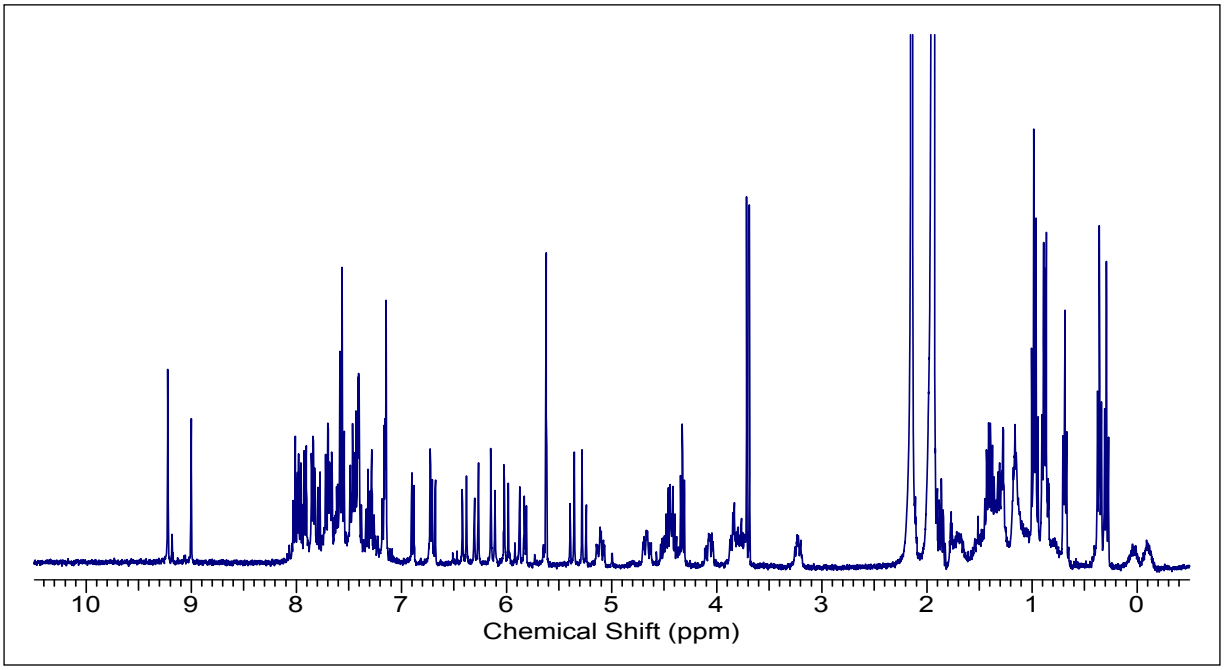

Figure S1. ^{1}H NMR spectrum of isolated impurities from column chromatography of as-synthesized [Ni(bC^N^bC)Cl]OTf wherein $NiCl_2$(DME) was slowly added to the silver carbene proligand species.

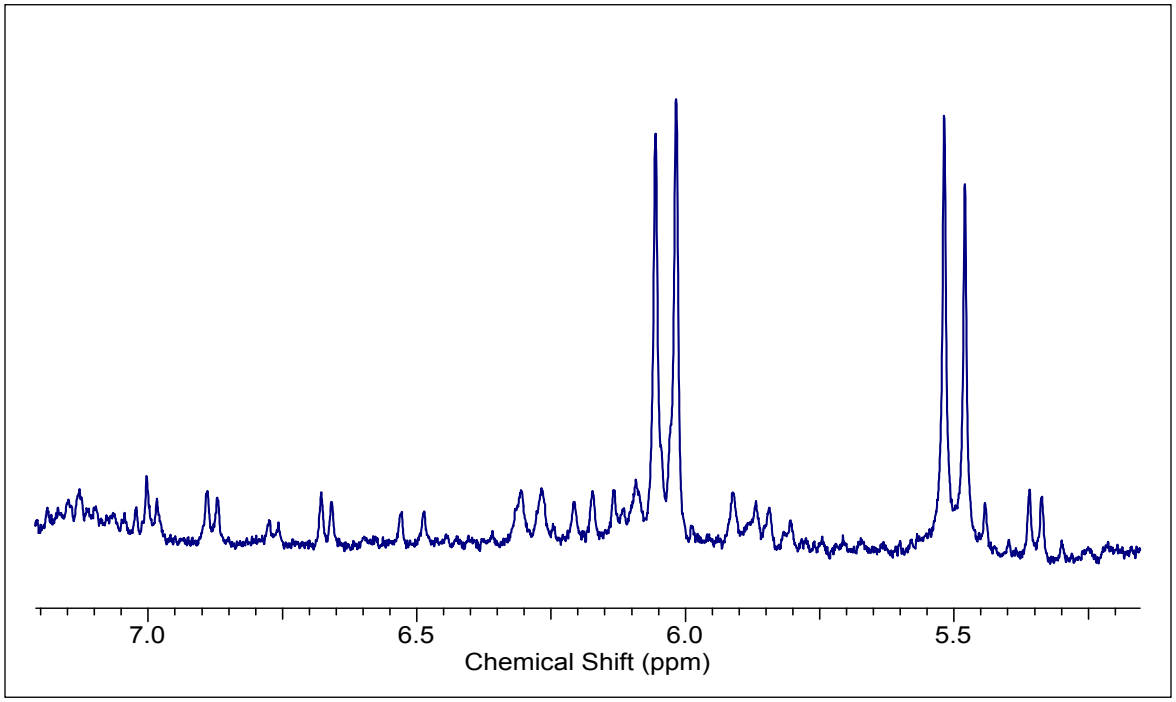

Figure S2. ^{1}H NMR spectrum from 5.0 to 7.5 ppm of as-synthesized [Pt(bC^N^bC)Br]OTf prepared from $PtBr_2$ before purification by column chromatography.

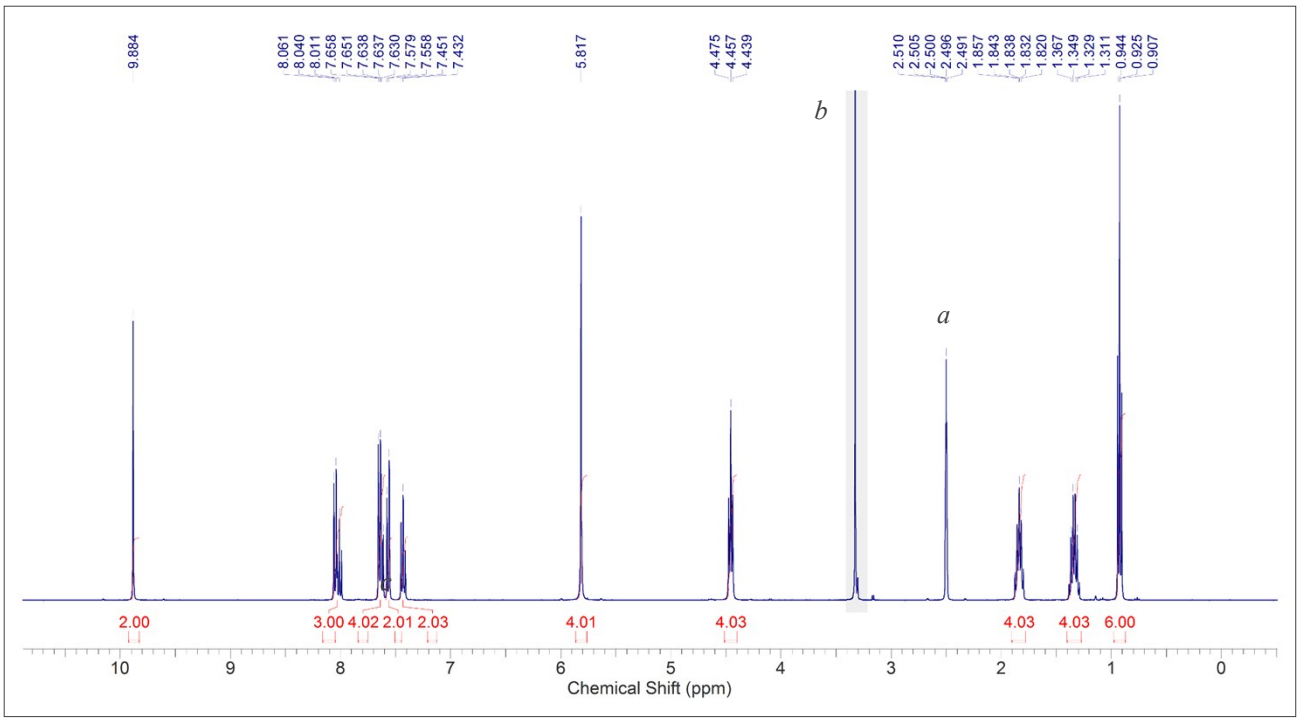

Figure S3. ^{1}H NMR spectrum of bC^N^bC · 2HBr in $(CD_3)_2SO$. Residual solvent[a] and water[b] indicated.

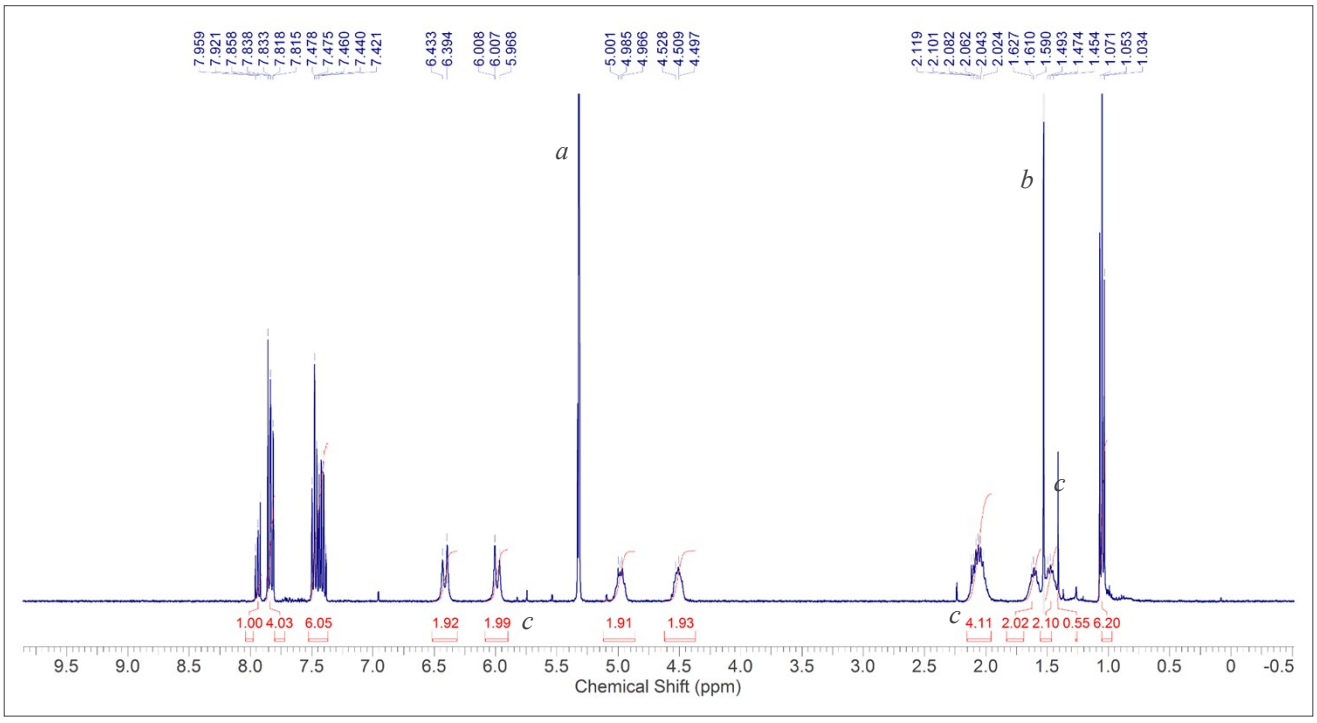

Figure S4. ^{1}H NMR spectrum of [Ni(bC^N^bC)Cl]OTf in CD_2Cl_2. Residual solvent[a], water[b], and BHT[c] indicated.

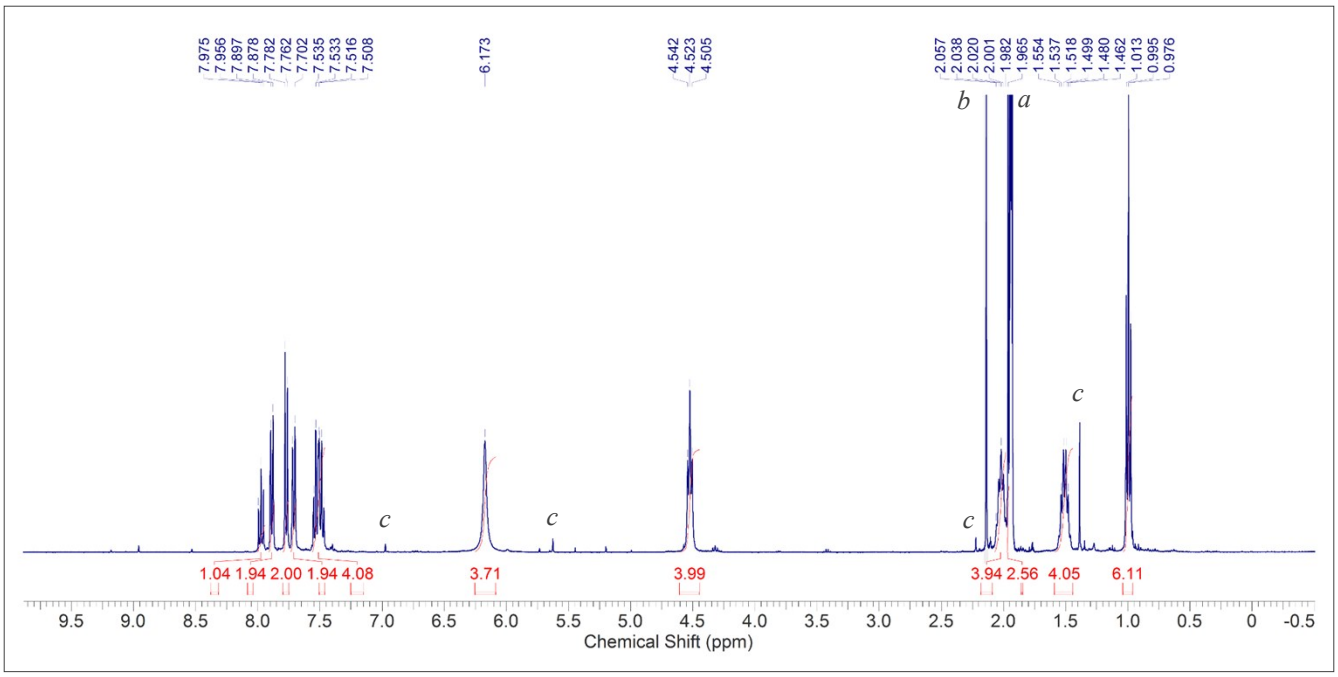

Figure S5. ^{1}H NMR spectrum of [Ni(bC^N^bC)(CH_3CN)]($OTf)_2$ in CD_3CN. Residual solvent[a], water[b], and BHT[c] indicated.

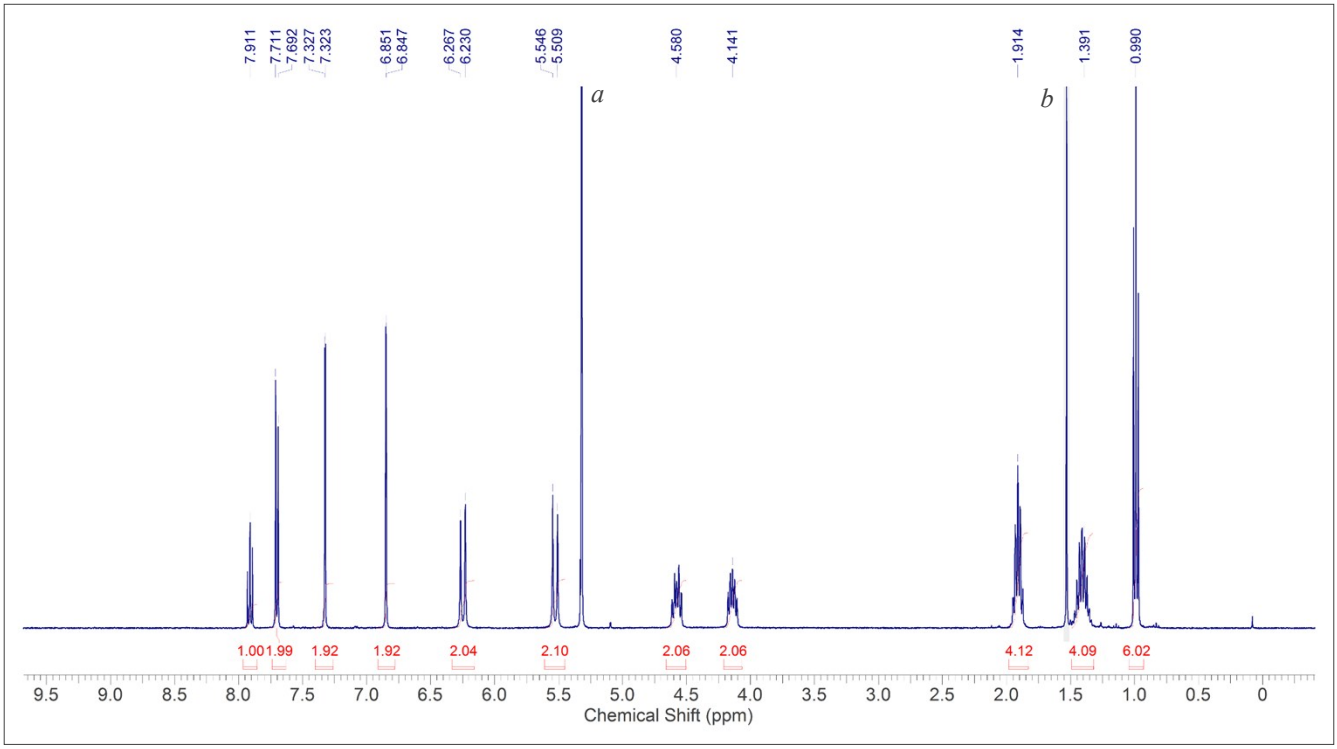

Figure S6. ^{1}H NMR spectrum of [Ni(C^N^C)Cl]OTf in CD_2Cl_2. Residual solvent[a] and water[b] indicated.

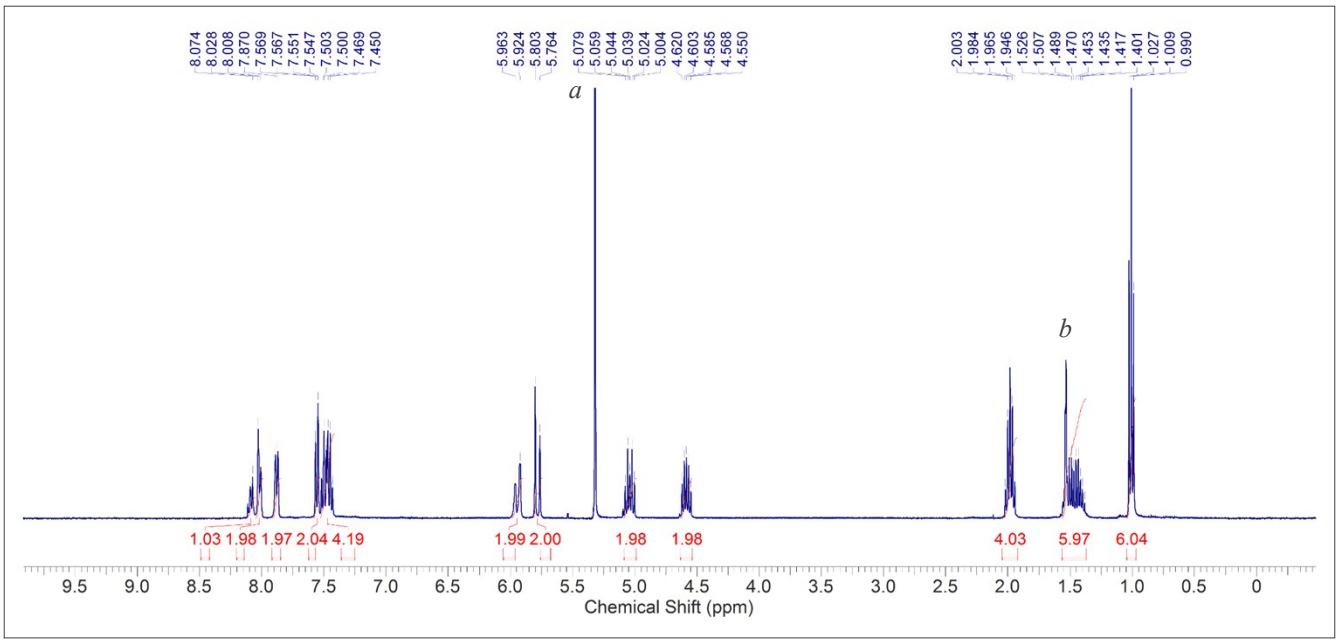

Figure S7. ^{1}H NMR spectrum of [Pd(bC^N^bC)Cl]OTf in CD_2Cl_2. Residual solvent[a] and water[b] indicated.

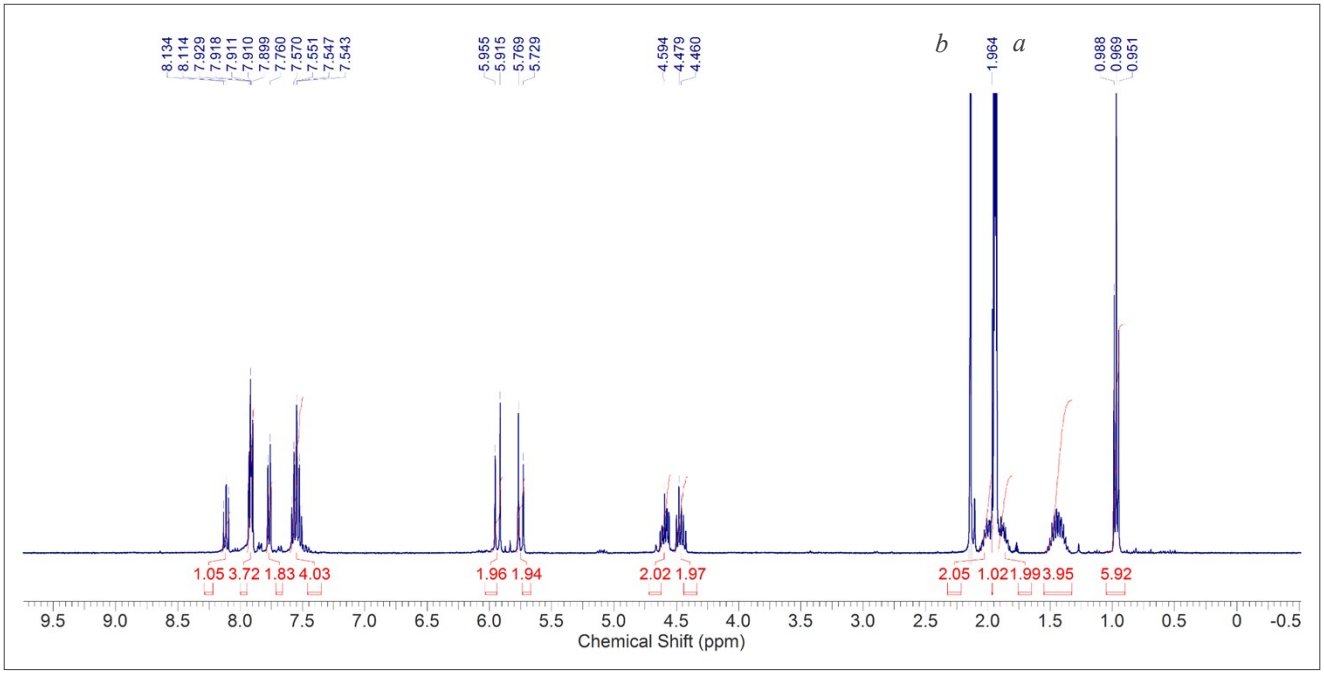

Figure S8. ^{1}H NMR spectrum of [Pd(bC^N^bC)(CH_3CN)](OTf)$_2$ in CD_3CN. Residual solvent[a] and water[b] indicated.

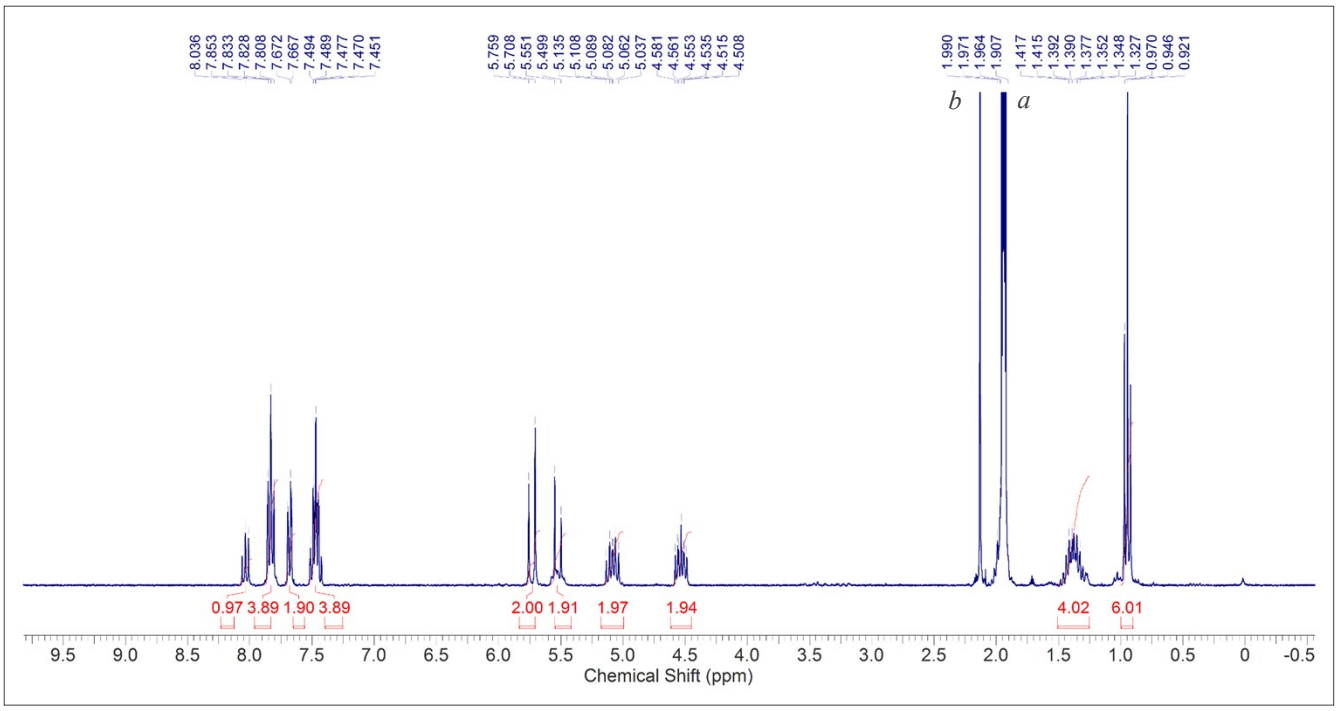

Figure S9. ^{1}H NMR spectrum of [Pt(bC^N^bC)Br]OTf in CD_3CN. Residual solvent[a] and water[b] indicated.

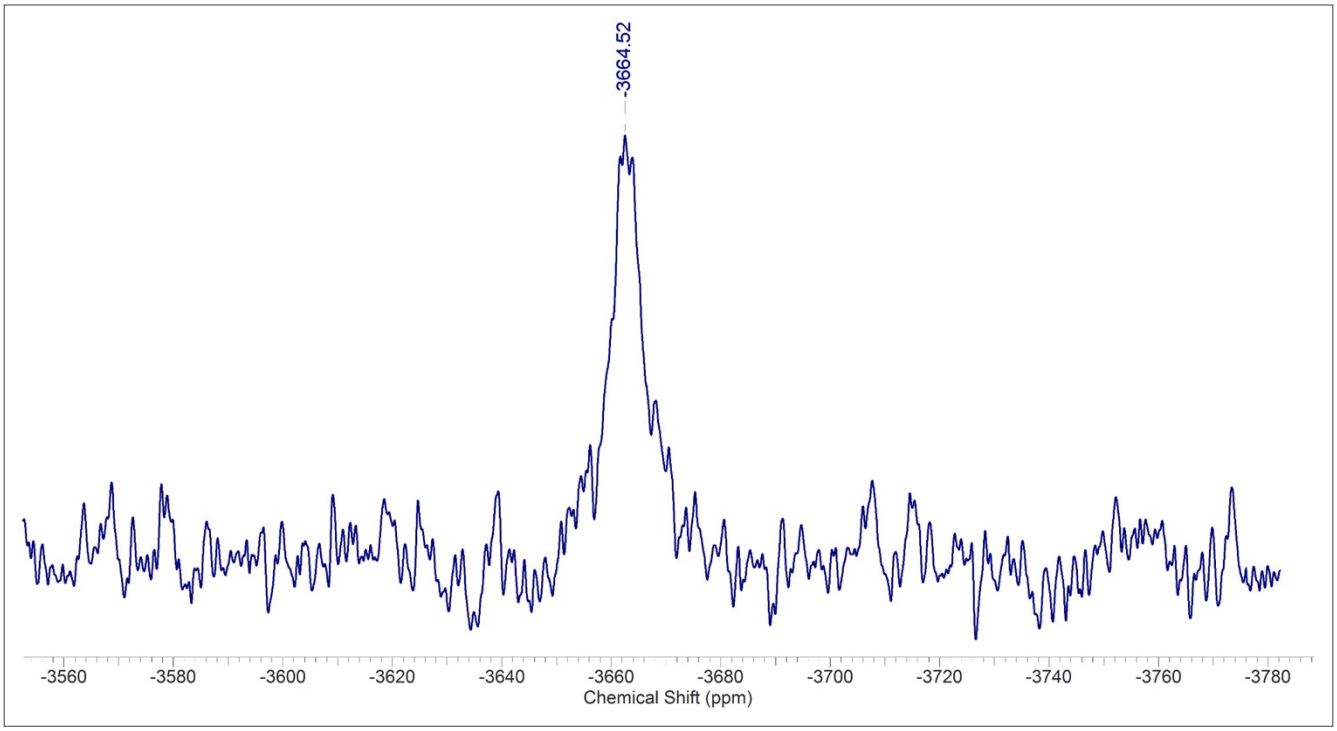

Figure S10. ^{195}Pt NMR spectrum of [Pt(bC^N^bC)Br]OTf in CD_3CN.

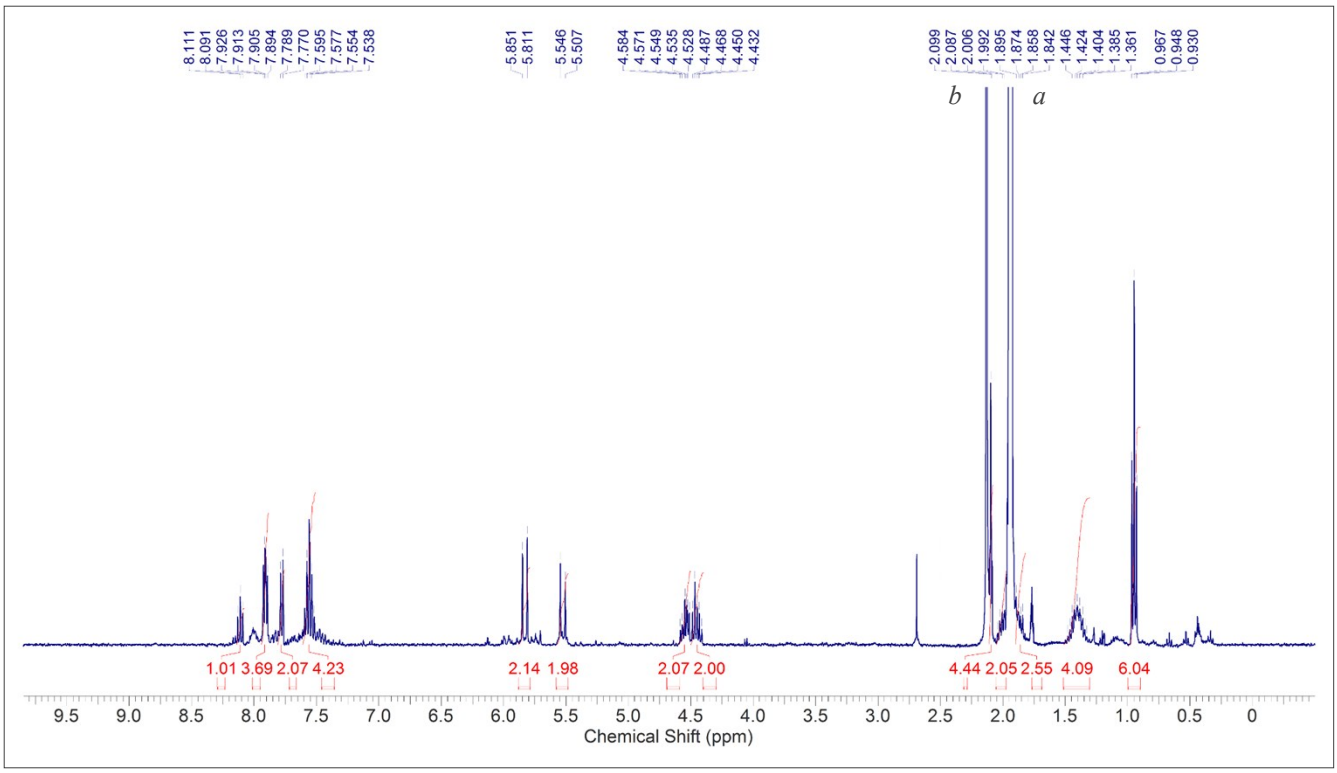

Figure S11. ^{1}H NMR spectrum of [Pt(bC^N^bC)(CH_3CN)](OTf)$_2$ in CD_3CN. Residual solvent[a] and water[b] indicated.

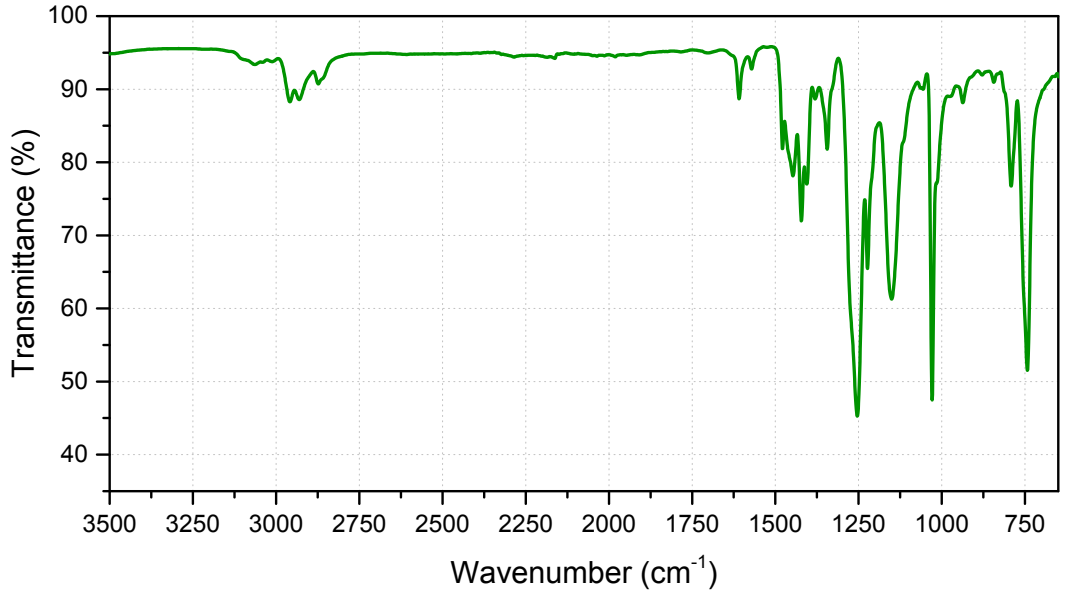

Figure S12. ATR-FTIR spectrum of [Ni(bC^N^bC)Cl]OTf.

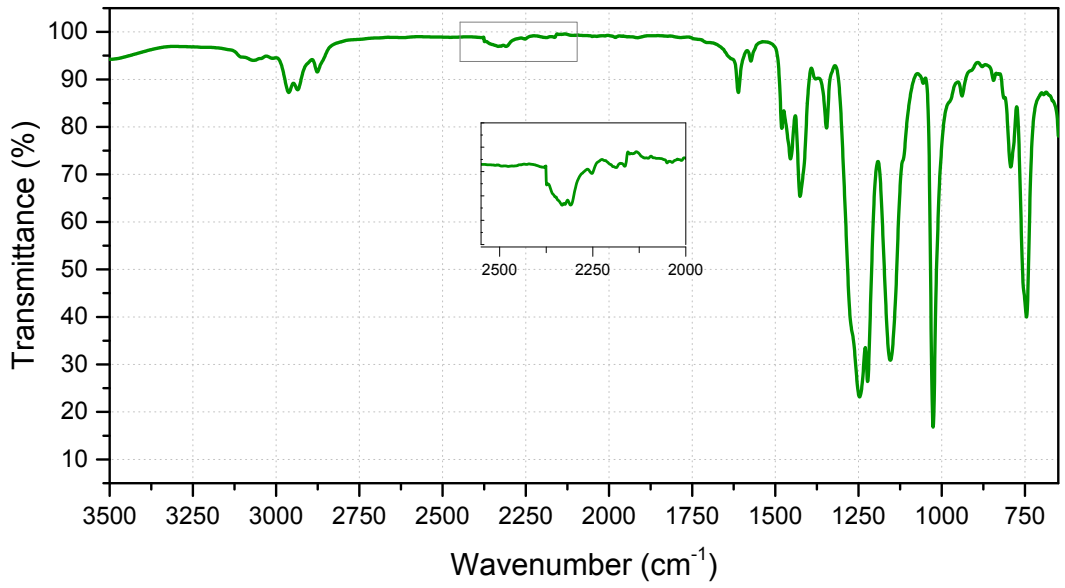

Figure S13. ATR-FTIR spectrum of [Ni(bC^N^bC)(CH_3CN)]($OTf)_2$.

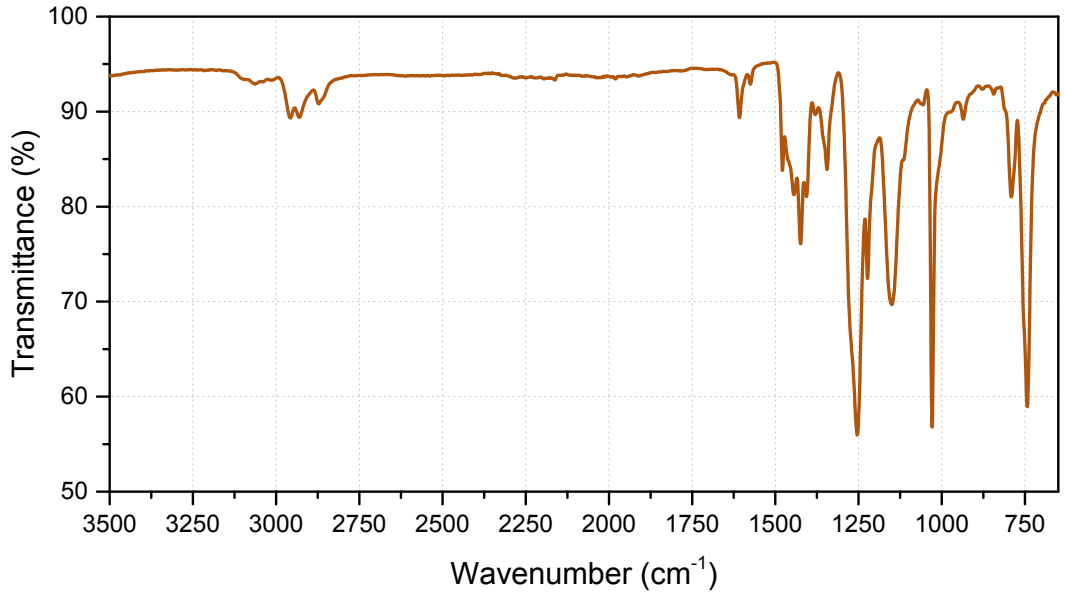

Figure S14. ATR-FTIR spectrum of [Pd(bC^N^bC)Cl]OTf.

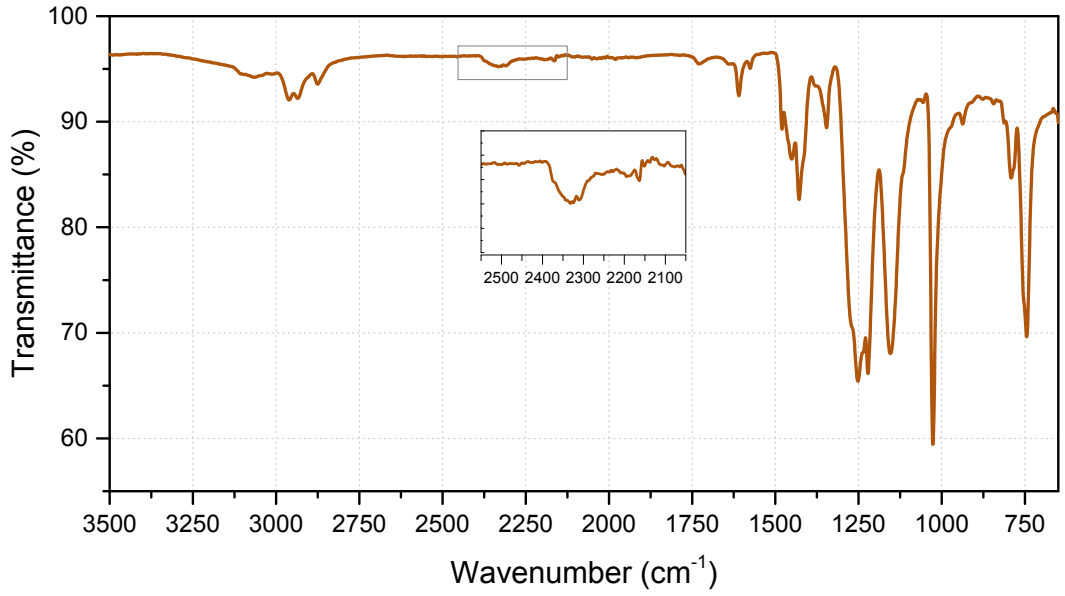

Figure S15. ATR-FTIR spectrum of [Pd(bC^N^bC)(CH_3CN)]($OTf)_2$.

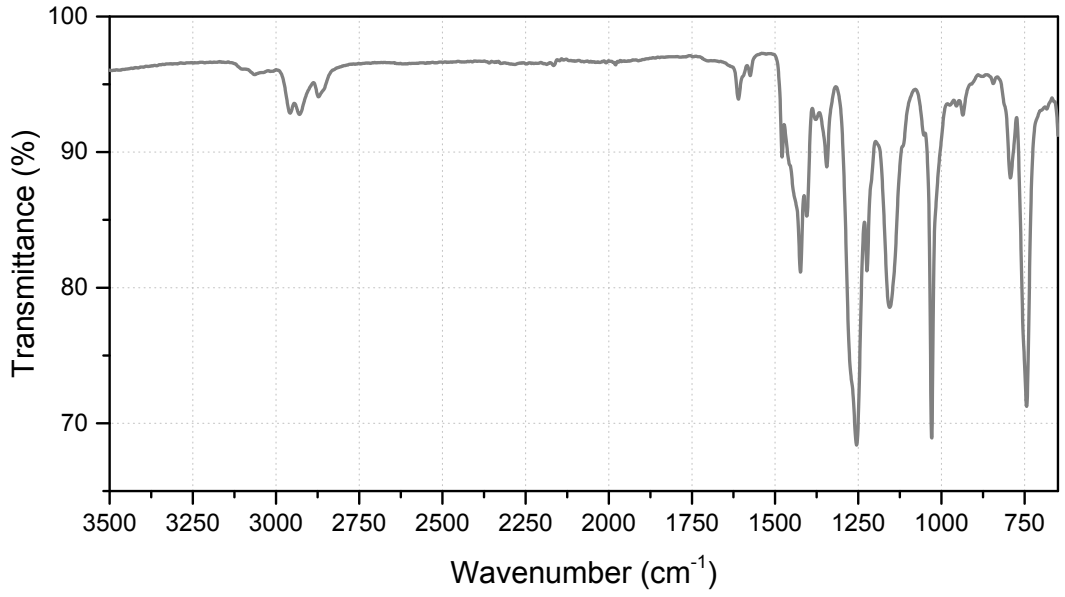

Figure S16. ATR-FTIR spectrum of [Pt(bC^N^bC)Br]OTf.

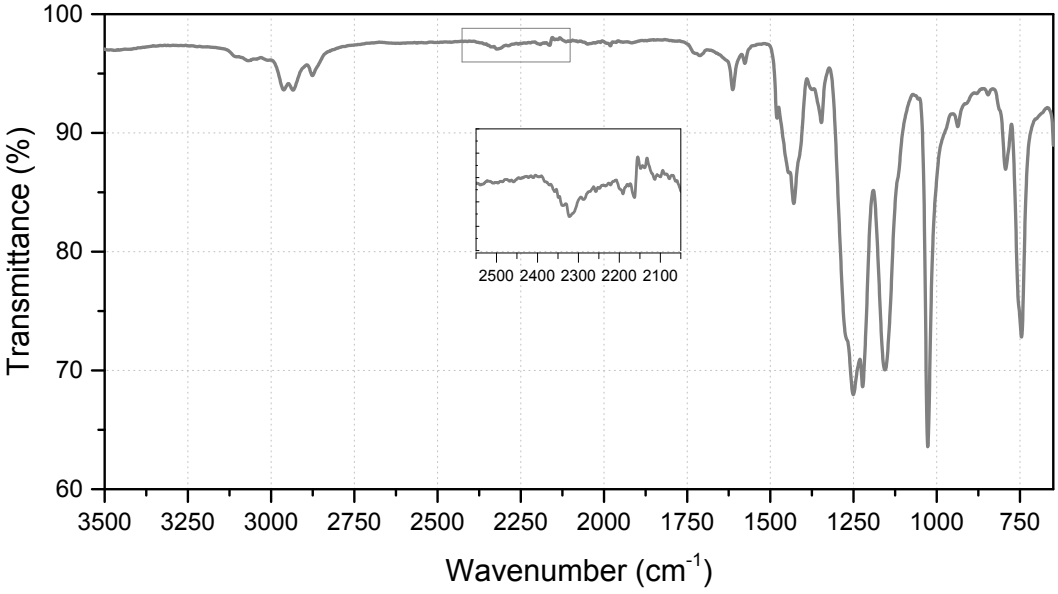

Figure S17. ATR-FTIR spectrum of [Pt(bC^N^bC)(CH_3CN)]($OTf)_2$.

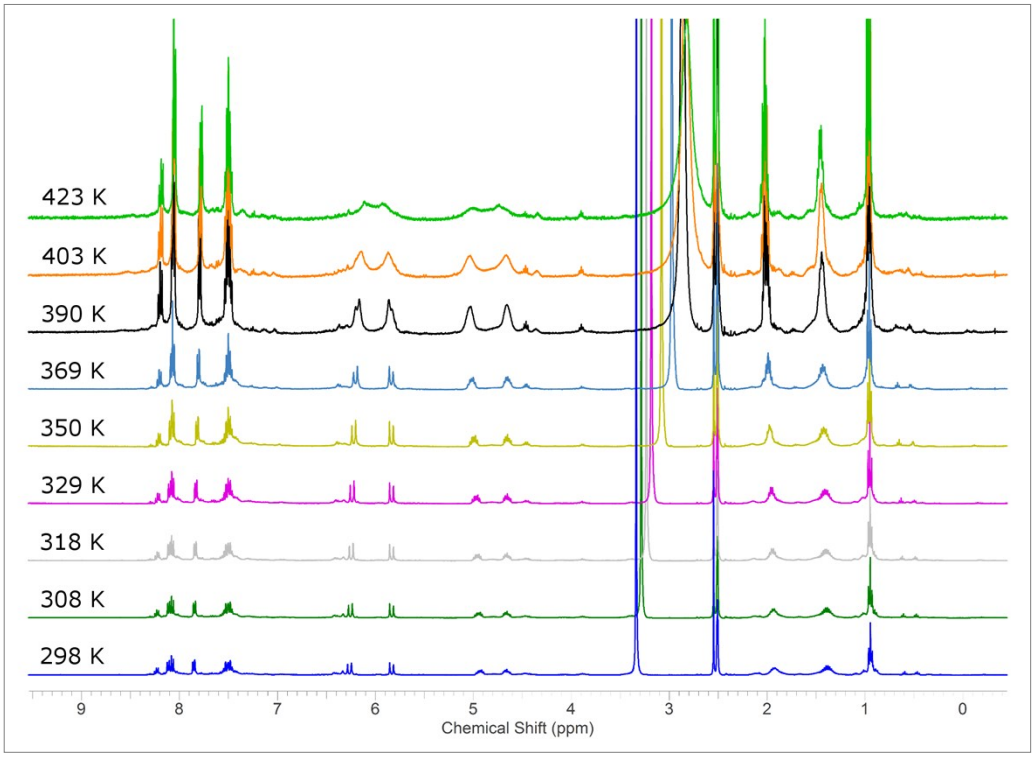

Figure S18. Variable temperature ^{1}H NMR spectra of [Pd(bC^N^bC)Cl]BF_4 in $(CD_3)_2SO$.

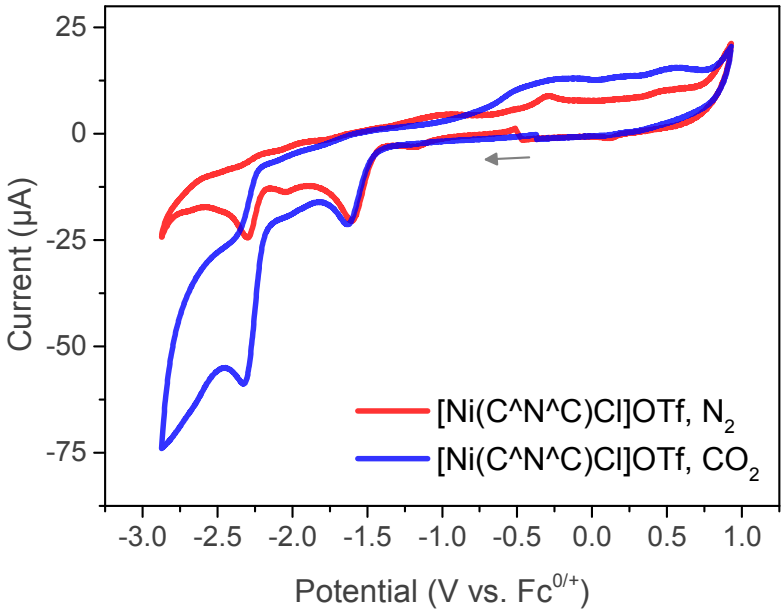

Figure S19. Overlaid cyclic voltammograms of [Ni(C^N^C)Cl]OTf taken at a scan rate of 100 mV/s under N_2 and CO_2.

DFT Sample Input Code

A typical example of the input used for geometry optimization of reduced species in Gaussian is given below for input files used in sequence:

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%chk=Ni2-bC^N^bC-Cl-cpcm.chk
# opt freq=noraman wb97xd/genecp scrf=(cpcm,solvent=acetonitrile) nosymm
pop=npa

Ni(bC^N^bC)Cl Geometry Optimization

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 N                  0.44807000    2.69941600   -0.36773900
 N                  1.03464400   -2.91625900    1.19969900
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 C                  0.82651300   -4.19008800    0.66992000
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H	1.65440800	-3.12302500	3.18985500
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Cl	0.00000000	0.00000000	2.95654800
C	-0.12565200	-4.05485000	-0.34590100
C	-0.56267900	-5.15137100	-1.09124600
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H	1.30869900	5.06426000	-1.87664900

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 H                  1.37311700   -7.50465600    0.45616500
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H C N Cl 0
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geom=check guess=read

Ni(bC^N^bC)Cl, 1e reduced

0 2

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D95(d)
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@./basis/sdd-ni.gbs


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A typical example of the input used for modelling the approach of CO_2 to a reduced complex is given below:

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CO_2 Scan from 3.25A to 1.75A - 0.25A/6steps

0 2

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N	1.08874500	-2.79501100	1.11373100
N	-0.58155800	-2.62139300	-0.26013100
N	0.00000000	0.00000000	-1.24639500
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C	0.84565400	-4.07556000	0.62634100
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C	-0.19915124	1.91398907	0.56672417
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C	0.74251200	0.95259400	-3.35427000
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H	2.21512600	-1.40371100	2.16875000
H	-3.13063700	2.81229700	1.55883000
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H	2.26437200	1.42858600	-0.54165800
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C	1.46584900	-5.29939500	0.88198000

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 H                  2.29476200   -5.38538700    1.57868800
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 O                  3.32990022   -0.35204785   -0.28762613

B 51 52 S 6 -0.250000

H C N O Cl 0
D95(d)
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DFT Optimized Geometries

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C	-1.463248639	-1.948882257	-1.198929540
C	0.000000010	0.000000008	-4.117756668
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C	0.227153261	3.964446341	-0.270290272
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C	-0.000000001	0.000000000	-4.103510137
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H	3.130636968	-2.812297631	1.558829771
H	2.215126534	-1.403710991	2.168749763
H	-3.130636974	2.812297636	1.558829771
H	-2.215126540	1.403710991	2.168749758
H	2.002243628	2.654703174	-1.798074515
H	2.264371923	1.428585936	-0.541657783
H	-2.002243628	-2.654703174	-1.798074515
H	-2.264371923	-1.428585936	-0.541657783
H	-0.000000002	0.000000000	-5.188473524
H	-1.332992918	-1.715019172	-3.857843637
H	1.332992918	1.715019177	-3.857843642
H	-2.050213668	2.982813389	2.970131614
H	2.050213668	-2.982813389	2.970131614
Ni	0.000000002	0.000000000	0.659575524
Cl	0.000000010	0.000000001	2.893983553
C	-0.227153261	-3.964446341	-0.270290272
C	-0.726286715	-5.075518317	-0.952357268
C	-0.107039687	-6.300723265	-0.701262997
C	1.465849270	-5.299395817	0.881979753
C	0.969611405	-6.411837945	0.201528822
C	-0.845654079	4.075560688	0.626341071
C	-1.465849270	5.299395817	0.881979753
C	-0.969611405	6.411837945	0.201528824
C	0.726286715	5.075518317	-0.952357268
C	0.107039687	6.300723318	-0.701262992
H	-2.294761699	5.385387173	1.578687766
H	-1.423357580	7.384418897	0.369988344
H	0.464725900	7.189731835	-1.213033870
H	1.554959300	4.999671951	-1.650258243
H	2.294761699	-5.385387173	1.578687766
H	1.423357580	-7.384418897	0.369988342
H	-0.464725900	-7.189731835	-1.213033876
H	-1.554959300	-4.999671951	-1.650258243

[Pd(bC^N^bC)Cl]$^+$

N	3.007707347	-1.171964144	0.772147051
N	2.626548918	0.328401067	-0.748592382
N	-3.008050614	-1.171982030	-0.771767928
N	-2.626363838	0.328620951	0.748592340
N	0.000082598	1.364571565	-0.000337259
C	-2.835020851	-2.168310070	-1.818680508
C	2.834327353	-2.168063235	1.819219157
C	-4.244491629	-0.622161195	-0.438886185
C	-2.031554037	-0.589523771	-0.049867775
C	2.031464166	-0.589606349	0.049820914
C	4.001683771	0.352571334	-0.536155695
C	1.852467454	1.226960752	-1.594246340
C	-1.852021881	1.227224378	1.593945031
C	0.000278905	4.139271782	-0.000321671
C	-0.908009130	3.431251356	0.783744918
C	0.908513044	3.431136101	-0.784343682
C	-0.882837612	2.040311460	0.762049471
C	0.883159040	2.040200782	-0.762641451
H	-3.250108792	-1.783655885	-2.754438126
H	-1.771882352	-2.370238435	-1.939106660
H	3.249216499	-1.783253345	2.755001451
H	1.771143425	-2.369876917	1.939426632
H	2.535602235	1.890384168	-2.123369501
H	1.305247552	0.643048774	-2.340629010
H	-2.534987977	1.890750067	2.123156529
H	-1.304677273	0.643352252	2.340268408
H	0.000360069	5.224828869	-0.000307318
H	-1.632626020	3.947016311	1.404810965
H	1.633264764	3.946805233	-1.405331824
H	3.348970321	-3.092202333	1.542896985
H	-3.349670136	-3.092351095	-1.542041739
Pd	-0.000033466	-0.710278606	-0.000413138
Cl	-0.000102863	-3.040201788	-0.000410807
C	-4.001556022	0.352849722	0.536536850
C	-5.035724326	1.110827000	1.088911404
C	-6.322399741	0.851100800	0.618775376
C	-5.531455281	-0.886060556	-0.911060852
C	-6.567086432	-0.130435640	-0.363712274
C	4.244276328	-0.622280869	0.439514204
C	5.531087556	-0.886168513	0.912113868
C	6.566921117	-0.130698300	0.364939241
C	5.036057745	1.110396186	-1.088355975
C	6.322578338	0.850680384	-0.617792377
H	5.719007975	-1.642377847	1.668483325
H	7.584826523	-0.300444645	0.703643353
H	7.156980949	1.418594572	-1.019021526
H	4.859749406	1.868204984	-1.845782865
H	-5.719642036	-1.642397315	-1.667236546
H	-7.585102595	-0.300191290	-0.702079613
H	-7.156652542	1.419125713	1.020158066
H	-4.859150001	1.868751301	1.846160386

[Pd(bC^N^bC)Cl] (1e$^-$ reduced)

N	-1.064783531	2.918097578	1.177700748
N	0.505668656	2.697560583	-0.305848723
N	1.078849946	-2.918305089	1.176041269
N	-0.496917344	-2.698232379	-0.301916546
N	0.002285424	-0.000613922	-1.364905328
C	2.123963688	-2.629613537	2.144939343
C	-2.105735707	2.629536081	2.151097262
C	0.845466766	-4.188365884	0.656871937
C	0.261527990	-2.018866520	0.584620583
C	-0.249052871	2.018649351	0.584196326
C	0.176535812	4.046299583	-0.305548978
C	1.422543309	1.987694831	-1.211750965
C	-1.417355604	-1.988812438	-1.204625974
C	-0.003284583	-0.001663276	-4.153792019
C	-0.666239448	-1.019335264	-3.468580635
C	0.662464261	1.016476056	-3.472010471
C	-0.692901340	-0.951248340	-2.015014115
C	0.694916982	0.949468156	-2.018501954
H	3.089783654	-2.953084745	1.745761708
H	2.140112363	-1.556912784	2.332500265
H	-3.073617220	2.950870361	1.755176036
H	-2.119543804	1.557100367	2.340420530
H	1.875393370	2.721414962	-1.880532755
H	2.225477898	1.562485666	-0.597594692
H	-1.872948545	-2.722940141	-1.871095387
H	-2.217798837	-1.563221021	-0.587480337
H	-0.005583472	-0.002066951	-5.243699467
H	-1.183798373	-1.822572389	-3.983220221
H	1.177822697	1.819455493	-3.989257546
H	-1.901280187	3.157584611	3.086742192
H	1.922443980	-3.155815455	3.082263601
Pd	0.006641937	0.000037118	0.698671510
Cl	0.013232093	0.001211041	3.052890358
C	-0.168703876	-4.047191019	-0.301457893
C	-0.643934722	-5.141863248	-1.027448314
C	-0.060071182	-6.378956088	-0.755858171
C	1.432117908	-5.425223055	0.931813073
C	0.960337039	-6.519464343	0.207462338
C	-0.834159296	4.187833404	0.656408039
C	-1.420661919	5.424556556	0.932165066
C	-0.952214787	6.518399321	0.204994206
C	0.648448372	5.140556530	-1.034307266
C	0.064852417	6.377571231	-0.761783443
H	-2.203582014	5.532791242	1.677194503
H	-1.380821821	7.500075136	0.385670253
H	0.402430583	7.253996126	-1.307710443
H	1.430297041	5.042419879	-1.781571223
H	2.217531439	-5.533250780	1.674231460
H	1.388895684	-7.501276315	0.387578484
H	-0.400225965	-7.255705051	-1.299613211
H	-1.428366809	-5.043953889	-1.772030390

[Pt(bC^N^bC)Cl]$^+$

N	-1.042175454	2.921074750	1.195701336
N	0.503506998	2.695358820	-0.312757672
N	1.042162510	-2.921062431	1.195694447
N	-0.503525210	-2.695371001	-0.312763473
N	-0.000017485	-0.000006193	-1.338482016
C	2.070934746	-2.647506469	2.188402242
C	-2.070946330	2.647535849	2.188415053
C	0.828523690	-4.186199951	0.652709466
C	0.231308860	-2.019517360	0.604690424
C	-0.231341515	2.019515328	0.604692446
C	0.161536464	4.043297577	-0.327395960
C	1.412579737	2.004999689	-1.216256576
C	-1.412601417	-2.005021708	-1.216266826
C	-0.000004229	-0.000007764	-4.117472965
C	-0.688645649	-0.980618355	-3.408083208
C	0.688632732	0.980601993	-3.408077604
C	-0.673447059	-0.955265441	-2.018075151
C	0.673421632	0.955250344	-2.018069547
H	3.034050653	-3.006432453	1.814956957
H	2.120263559	-1.573633415	2.360965985
H	-3.034059379	3.006474311	1.814974272
H	-2.120286303	1.573663615	2.360981855
H	1.862296148	2.733478796	-1.889715436
H	2.215283203	1.536350157	-0.638369439
H	-1.862306499	-2.733505260	-1.889728401
H	-2.215312646	-1.536380310	-0.638383822
H	0.000000697	-0.000008194	-5.202902325
H	-1.234584963	-1.763688958	-3.923192936
H	1.234579089	1.763670448	-3.923183136
H	-1.829537325	3.154959325	3.126109000
H	1.829538267	-3.154931247	3.126098697
Pt	-0.000038994	-0.000004287	0.719374940
Cl	-0.000038310	-0.000004327	3.067057428
C	-0.161534028	-4.043304424	-0.327401634
C	-0.610582908	-5.129604328	-1.080012262
C	-0.022043447	-6.364679309	-0.810031734
C	1.418584634	-5.420959738	0.927014075
C	0.974922455	-6.508898948	0.176367420
C	-0.828517832	4.186208841	0.652716101
C	-1.418557090	5.420978365	0.927023458
C	-0.974877512	6.508910961	0.176377457
C	0.610603181	5.129590892	-1.080005558
C	0.022084640	6.364675499	-0.810023204
H	-2.185640492	5.532140513	1.687573240
H	-1.407427630	7.489152282	0.354366486
H	0.340622057	7.236754261	-1.373711176
H	1.378143988	5.029932719	-1.841551913
H	2.185671830	-5.532109556	1.687561837
H	1.407490020	-7.489133020	0.354354155
H	-0.340566435	-7.236762728	-1.373720659
H	-1.378125647	-5.029958088	-1.841558232

[Pt(bC^N^bC)Cl] (1e$^-$ reduced)

N	-1.023231623	2.922749803	1.200642201
N	0.527764896	2.702242765	-0.305534040
N	1.023332902	-2.922797667	1.200618155
N	-0.527640079	-2.702204690	-0.305557599
N	0.000127121	-0.000010419	-1.296717278
C	2.053581886	-2.643961738	2.188204737
C	-2.053505050	2.643808341	2.188171706
C	0.820441900	-4.185873464	0.653770122
C	0.202770996	-2.020413570	0.609871250
C	-0.202669089	2.020404007	0.609837869
C	0.173437475	4.044209222	-0.324484620
C	1.429003700	2.002776113	-1.225741485
C	-1.428846577	-2.002719068	-1.225770781
C	-0.000049070	0.000143747	-4.149439595
C	-0.679068335	-0.997774509	-3.400763195
C	0.679052819	0.997987630	-3.400744663
C	-0.680151338	-0.976859805	-2.027178296
C	0.680303911	0.976931545	-2.027160161
H	3.023277515	-2.973298861	1.803086771
H	2.076565472	-1.572264565	2.380050456
H	-3.023295464	2.972583922	1.802807667
H	-2.076047413	1.572162767	2.380365173
H	1.892151678	2.736775163	-1.885914657
H	2.218422906	1.532803590	-0.624772415
H	-1.891998296	-2.736707333	-1.885953853
H	-2.218269477	-1.532744016	-0.624807055
H	-0.000118766	0.000201980	-5.234184220
H	-1.221837745	-1.793529358	-3.906116402
H	1.221758744	1.793796365	-3.906081239
H	-1.833765758	3.172417793	3.120069140
H	1.833482288	-3.172166619	3.120248309
Pt	0.000112198	0.000013820	0.735160562
Cl	0.000166063	0.000068771	3.117493274
C	-0.173425396	-4.044201295	-0.324474526
C	-0.613302414	-5.131981239	-1.081168435
C	-0.015600946	-6.365090903	-0.818961823
C	1.419861983	-5.417922631	0.920263488
C	0.983742136	-6.506831030	0.165091826
C	-0.820453737	4.185824944	0.653747833
C	-1.419997088	5.417825686	0.920182482
C	-0.983963829	6.506749272	0.164981483
C	0.613233811	5.132006142	-1.081199921
C	0.015415376	6.365070266	-0.819043766
H	-2.190048041	5.526726765	1.678382183
H	-1.424898417	7.484420750	0.337598267
H	0.327986639	7.236621755	-1.387276053
H	1.381931336	5.032765505	-1.841841310
H	2.189881388	-5.526872554	1.678488034
H	1.424582837	-7.484537327	0.337750942
H	-0.328234026	-7.236630328	-1.387178546
H	-1.381971987	-5.032695464	-1.841832113

Crystallography Details for [Ni(bC^N^bC)]OTf

Data Collection

A yellow irregular crystal of $C_{30}H_{33}N_5O_3F_3SClNi$ having approximate dimensions of 0.02 × 0.17 × 0.21 mm was mounted on a glass fiber. All measurements were made on a Bruker APEX DUO diffractometer with a TRIUMPH curved-crystal monochromator with Mo-Kα radiation.

The data were collected at a temperature of -183.0 ± 0.1°C to a maximum 2θ value of 60.4°. Data were collected in a series of ϕ and ω scans in 0.5° oscillations using 10.0-second exposures. The crystal-to-detector distance was 40.13 mm.

Data Reduction

Of the 39661 reflections that were collected, 9056 were unique (R_{int} = 0.043); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT[1] software package. The linear absorption coefficient, μ, for Mo-Kα radiation is 8.43 cm^{-1}. Data were corrected for absorption effects using the multi-scan technique (SADABS[2]), with minimum and maximum transmission coefficients of 0.902 and 0.983, respectively. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods.[3] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. The final cycle of full-matrix least-squares refinement[4] on F^2 was based on 9056 reflections and 399 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1\ (I>2.00\sigma(I)) = \Sigma\ ||Fo| - |Fc|| / \Sigma\ |Fo| = 0.034$$

$$wR2\ (all\ data) = [\ \Sigma\ (\ w\ (Fo^2 - Fc^2)^2\ )/\ \Sigma\ w(Fo^2)^2]^{1/2} = 0.080$$

The standard deviation of an observation of unit weight[5] was 1.02. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.51 and –0.45 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[6] Anomalous dispersion effects were included in Fcalc[7]; the values for Δf' and Δf'' were those of Creagh and McAuley.[8] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[9] All refinements were performed using the XL[10] via the OLEX2[11] interface.

References

(1) SAINT. Version 8.34A Bruker AXS Inc., Madison, Wisconsin, USA. (1997-2013).

(2) SADABS 2014/5 - Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Crystallogr.* **48**.

(3) SHELXT: Sheldrick, G. M.; Acta Cryst., A71, 3-8 (2015).

(4) Least Squares function minimized:

$$\Sigma w(F_o^2-F_c^2)^2$$

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

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

where: N_o = number of observations

N_v = number of variables

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

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

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

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

(10) XL Sheldrick, G. M.; Acta Cryst., A64, 112-122 (2008).

(11) OLEX2 – V1.2.6 Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H., OLEX2: A complete structure solution, refinement and analysis program (2009). J. Appl. Cryst., 42, 339-341

Experimental Details:

A. Crystal Data

Empirical Formula	$C_{30}H_{33}N_5O_3F_3SClNi$
Formula Weight	694.83
Crystal Colour, Habit	yellow, irregular
Crystal Dimensions	0.02 x 0.17 x 0.21 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 10.561(3) Å b = 10.647(3) Å c = 14.867(4) Å α = 89.824(4)^o β = 89.273(8)^o γ = 67.244(8)^o V = 1541.4(8) Å^3
Space Group	*P -1* (#2)
Z value	2
D_{calc}	1.497 g/cm^3
F_{000}	720.00
μ(Mo-Kα)	8.43 cm^{-1}

B. Intensity Measurements

Diffractometer	Bruker APEX DUO
Radiation	Mo-Kα (λ = 0.71073 Å)
Data Images	2288 exposures @ 10.0 seconds
Detector Position	40.13 mm
$2\theta_{max}$	60.4^o
No. of Reflections Measured	Total: 39661
Corrections	Unique: 9056 (R_{int} = 0.043) Absorption (T_{min} = 0.902, T_{max}= 0.983) Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (XT)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w (Fo^2 - Fc^2)^2
Least Squares Weights	$w=1/(\sigma^2(Fo^2)+(0.0325P)^2 + 0.8300P)$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>0.00σ(I))	9056
No. Variables	399
Reflection/Parameter Ratio	22.70
Residuals (refined on F^2, all data): R1; wR2	0.051; 0.080
Goodness of Fit Indicator	1.02
No. Observations (I>2.00σ(I))	7233
Residuals (refined on F^2): R1; wR2	0.034; 0.074
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.51 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.45 $e^-/Å^3$

Table S1. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for [Ni(bC^N^bC)Cl]OTf. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Ni1	2684.0(2)	7141.6(2)	7302.3(2)	9.03(5)
Cl1	1681.0(4)	8906.3(4)	8154.4(2)	12.93(8)
N1	2545.9(13)	9393.0(13)	6003.9(9)	10.8(2)
N2	1862.4(13)	7841.8(13)	5516.3(8)	9.9(2)
N3	3579.6(13)	5577.5(13)	6548.6(8)	9.6(2)
N4	4341.9(13)	5002.4(13)	8392.9(8)	10.1(2)
N5	2327.7(13)	5761.0(13)	9030.1(8)	9.9(2)
C1	2384.9(16)	8232.2(15)	6244.6(10)	10.6(3)
C2	1655.8(15)	8757.6(15)	4809.6(10)	10.3(3)
C3	1134.4(16)	8796.9(16)	3945.9(10)	12.5(3)
C4	1088.9(17)	9878.9(17)	3402.0(11)	15.3(3)
C5	1524.9(17)	10886.2(17)	3715.9(11)	16.0(3)
C6	2028.6(17)	10855.5(16)	4579.8(11)	14.5(3)
C7	2093.7(16)	9757.0(15)	5122(1)	10.9(3)
C8	3138.1(17)	10148.6(16)	6576.4(11)	13.3(3)
C9	4564.7(17)	9268.2(17)	6909.8(12)	17.5(3)
C10	5192(2)	10094(2)	7461.4(13)	23.2(4)
C11	4335(2)	10795(2)	8284.9(13)	28.5(4)
C12	1674.2(16)	6548.6(15)	5498.3(10)	11.0(3)
C13	2992.2(16)	5410.0(15)	5777.3(10)	10.7(3)
C14	3574.9(17)	4243.5(16)	5254.3(10)	13.1(3)
C15	4808.9(17)	3240.4(17)	5518.8(11)	15.8(3)
C16	5426.2(17)	3428.4(16)	6298.2(11)	13.7(3)
C17	4789.4(16)	4596.8(16)	6802.7(10)	10.7(3)
C18	5371.3(16)	4822.6(16)	7685(1)	11.9(3)
C19	3046.8(16)	5943.5(15)	8315.3(10)	10.1(3)
C20	4473.2(16)	4202.0(15)	9156.8(10)	10.5(3)
C21	5587.2(17)	3142.3(16)	9522.1(10)	12.8(3)
C22	5341.1(18)	2569.7(16)	10313.2(11)	15.7(3)
C23	4031.8(19)	3045.1(17)	10719.1(11)	16.7(3)
C24	2927.7(17)	4114.0(16)	10360.2(10)	13.9(3)
C25	3176.1(16)	4689.9(16)	9566(1)	11.2(3)
C26	849.2(16)	6494.3(16)	9191.3(10)	12.4(3)
C27	524.3(17)	7472.6(17)	9994.0(11)	15.1(3)
C28	-1020.2(18)	8183.3(18)	10169.9(12)	19.7(3)
C29	-1803(2)	9077(2)	9392.3(14)	29.1(4)
S1	8728.5(4)	5281.7(4)	6898.1(3)	12.89(8)
F1	10952.0(12)	3226.2(12)	6398.6(9)	36.3(3)
F2	10473.8(14)	3247.5(15)	7812(1)	48.8(4)

F3	11334.3(11)	4636.5(13)	7284.4(8)	29.8(3)
O1	7966.5(13)	4426.5(13)	6759.3(8)	19.6(3)
O2	8912.7(13)	5960.2(13)	6095.7(8)	19.9(3)
O3	8380.5(15)	6103.3(15)	7701.6(9)	31.2(3)
C30	10455.5(19)	4038.5(19)	7114.5(12)	21.2(4)

Table S2. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for [Ni(bC^N^bC)Cl]OTf. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Ni1	9.83(10)	8.55(10)	7.25(9)	-0.18(7)	0.02(7)	-1.94(8)
Cl1	14.47(18)	11.49(17)	10.07(16)	-1.70(13)	-0.27(13)	-1.96(14)
N1	10.8(6)	9.6(6)	11.0(6)	-0.2(5)	-0.5(5)	-2.8(5)
N2	11.3(6)	9.5(6)	8.6(6)	0.6(5)	-0.4(5)	-3.6(5)
N3	8.9(6)	10.3(6)	9.6(6)	0.4(5)	1.5(5)	-3.9(5)
N4	8.5(6)	11.4(6)	9.2(6)	0.4(5)	0.4(5)	-2.6(5)
N5	8.1(6)	12.4(6)	8.1(6)	-1.0(5)	0.2(5)	-2.8(5)
C1	9.1(7)	9.8(7)	11.4(7)	-1.3(5)	0.6(5)	-1.9(6)
C2	8.4(7)	8.6(7)	11.3(7)	1.0(5)	1.2(5)	-0.4(6)
C3	9.0(7)	13.8(7)	11.6(7)	-1.4(6)	-0.2(6)	-1.2(6)
C4	13.8(8)	15.8(8)	10.9(7)	1.9(6)	-0.2(6)	0.0(6)
C5	15.1(8)	13.5(7)	15.2(8)	4.6(6)	1.3(6)	-1.0(6)
C6	13.3(8)	10.6(7)	17.2(8)	1.0(6)	1.6(6)	-1.9(6)
C7	8.5(7)	11.0(7)	10.8(7)	1.2(5)	0.7(5)	-1.3(6)
C8	15.2(8)	10.8(7)	14.7(7)	-1.9(6)	-2.3(6)	-5.7(6)
C9	14.4(8)	18.1(8)	19.5(8)	-1.5(6)	-2.2(6)	-5.6(7)
C10	22.4(9)	27.6(10)	25.4(9)	2.8(7)	-7.2(7)	-16.0(8)
C11	35.3(11)	26.7(10)	26.9(10)	-5.8(8)	-8.9(8)	-15.4(9)
C12	11.5(7)	10.1(7)	11.5(7)	0.8(5)	-1.7(6)	-4.2(6)
C13	11.8(7)	12.1(7)	9.8(7)	1.5(5)	0.3(5)	-6.5(6)
C14	13.3(7)	14.9(8)	10.9(7)	-1.9(6)	0.0(6)	-5.3(6)
C15	17.2(8)	11.9(7)	16.1(8)	-4.7(6)	3.2(6)	-3.3(7)
C16	10.7(7)	13.2(7)	14.1(7)	-0.2(6)	1.9(6)	-1.2(6)
C17	9.8(7)	12.6(7)	9.6(7)	0.8(5)	2.0(5)	-4.4(6)
C18	9.0(7)	14.2(7)	11.3(7)	0.2(6)	1.3(5)	-3.3(6)
C19	9.9(7)	11.1(7)	9.2(7)	-2.5(5)	-0.3(5)	-4.0(6)
C20	11.9(7)	10.7(7)	9.4(7)	0.2(5)	-2.1(5)	-4.7(6)
C21	12.3(7)	13.3(7)	12.8(7)	-1.2(6)	-3.2(6)	-4.7(6)
C22	19.8(8)	12.8(7)	14.0(7)	2.5(6)	-6.6(6)	-5.7(7)
C23	25.4(9)	16.8(8)	11.1(7)	3.2(6)	-4.5(6)	-11.6(7)
C24	18.3(8)	15.8(8)	10.5(7)	-1.2(6)	0.4(6)	-9.9(7)
C25	13.0(7)	12.5(7)	9.4(7)	-0.6(5)	-2.9(5)	-6.2(6)

C26	9.0(7)	16.2(8)	11.2(7)	-2.0(6)	1.2(5)	-3.9(6)
C27	13.2(8)	20.2(8)	11.6(7)	-3.3(6)	-0.1(6)	-6.2(7)
C28	15.2(8)	21.9(9)	19.6(8)	-7.8(7)	5.0(7)	-4.4(7)
C29	17.6(9)	27.4(10)	31.7(11)	-5.5(8)	-1.8(8)	3.0(8)
S1	13.71(19)	14.70(19)	11.09(17)	-2.32(14)	2.38(14)	-6.46(16)
F1	21.1(6)	25.7(6)	53.6(8)	-14.1(6)	2.9(6)	0.1(5)
F2	35.0(7)	58.6(9)	54.6(9)	43.9(7)	-15.5(6)	-19.7(7)
F3	21.5(6)	43.6(7)	31.8(6)	3.8(5)	-8.0(5)	-20.5(6)
O1	17.0(6)	23.1(6)	22.9(6)	-0.1(5)	2.3(5)	-12.5(5)
O2	21.6(6)	21.2(6)	18.7(6)	6.4(5)	-2.2(5)	-10.2(5)
O3	35.4(8)	35.6(8)	23.0(7)	-17.3(6)	10.1(6)	-14.3(7)
C30	19.5(9)	24.8(9)	21.8(9)	6.9(7)	-2.5(7)	-11.4(8)

Table S3. Bond Lengths for [Ni(bC^N^bC)Cl]OTf.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ni1	Cl1	2.1675(6)	C9	C10	1.534(2)
Ni1	N3	1.9207(14)	C10	C11	1.526(3)
Ni1	C1	1.9075(16)	C12	C13	1.512(2)
Ni1	C19	1.9150(15)	C13	C14	1.389(2)
N1	C1	1.3574(19)	C14	C15	1.388(2)
N1	C7	1.4023(19)	C15	C16	1.389(2)
N1	C8	1.4730(19)	C16	C17	1.381(2)
N2	C1	1.3583(19)	C17	C18	1.514(2)
N2	C2	1.3918(19)	C20	C21	1.392(2)
N2	C12	1.4655(19)	C20	C25	1.395(2)
N3	C13	1.3552(19)	C21	C22	1.390(2)
N3	C17	1.358(2)	C22	C23	1.404(3)
N4	C18	1.462(2)	C23	C24	1.387(2)
N4	C19	1.353(2)	C24	C25	1.397(2)
N4	C20	1.3935(19)	C26	C27	1.532(2)
N5	C19	1.3550(19)	C27	C28	1.529(2)
N5	C25	1.400(2)	C28	C29	1.528(3)
N5	C26	1.468(2)	S1	O1	1.4462(12)
C2	C3	1.398(2)	S1	O2	1.4423(12)
C2	C7	1.397(2)	S1	O3	1.4400(14)
C3	C4	1.391(2)	S1	C30	1.824(2)
C4	C5	1.404(2)	F1	C30	1.340(2)
C5	C6	1.392(2)	F2	C30	1.329(2)
C6	C7	1.398(2)	F3	C30	1.340(2)
C8	C9	1.522(2)			

Table S4. Bond angles for [Ni(bC^N^bC)Cl]OTf.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N3	Ni1	Cl1	179.78(4)	N3	C13	C12	117.55(13)
C1	Ni1	Cl1	92.35(5)	N3	C13	C14	121.70(14)
C1	Ni1	N3	87.69(6)	C14	C13	C12	120.75(14)
C1	Ni1	C19	176.21(6)	C15	C14	C13	118.97(14)
C19	Ni1	Cl1	91.43(5)	C14	C15	C16	119.24(15)
C19	Ni1	N3	88.52(6)	C17	C16	C15	119.42(15)
C1	N1	C7	110.22(12)	N3	C17	C16	121.53(14)
C1	N1	C8	125.08(13)	N3	C17	C18	116.60(13)
C7	N1	C8	124.68(13)	C16	C17	C18	121.83(14)
C1	N2	C2	111.34(12)	N4	C18	C17	108.28(12)
C1	N2	C12	121.64(12)	N4	C19	Ni1	116.94(11)
C2	N2	C12	126.83(12)	N4	C19	N5	106.34(13)
C13	N3	Ni1	120.75(11)	N5	C19	Ni1	136.72(12)
C13	N3	C17	119.11(13)	N4	C20	C25	105.49(13)
C17	N3	Ni1	120.08(10)	C21	C20	N4	132.31(15)
C19	N4	C18	121.08(13)	C21	C20	C25	122.19(14)
C19	N4	C20	111.33(13)	C22	C21	C20	116.64(15)
C20	N4	C18	127.28(13)	C21	C22	C23	121.29(15)
C19	N5	C25	110.22(13)	C24	C23	C22	121.95(15)
C19	N5	C26	125.54(13)	C23	C24	C25	116.72(15)
C25	N5	C26	124.07(13)	C20	C25	N5	106.61(13)
N1	C1	Ni1	135.92(11)	C20	C25	C24	121.20(15)
N1	C1	N2	106.21(13)	C24	C25	N5	132.19(15)
N2	C1	Ni1	117.86(11)	N5	C26	C27	113.07(13)
N2	C2	C3	132.16(14)	C28	C27	C26	112.07(13)
N2	C2	C7	105.63(13)	C29	C28	C27	113.81(15)
C7	C2	C3	122.21(14)	O1	S1	C30	102.42(8)
C4	C3	C2	116.53(15)	O2	S1	O1	113.96(7)
C3	C4	C5	121.33(15)	O2	S1	C30	103.10(8)
C6	C5	C4	122.12(15)	O3	S1	O1	115.77(8)
C5	C6	C7	116.57(15)	O3	S1	O2	115.48(9)
C2	C7	N1	106.58(13)	O3	S1	C30	103.57(9)
C2	C7	C6	121.24(14)	F1	C30	S1	110.62(12)
C6	C7	N1	132.19(14)	F2	C30	S1	111.75(13)
N1	C8	C9	112.86(13)	F2	C30	F1	107.50(16)
C8	C9	C10	111.91(14)	F2	C30	F3	107.66(15)
C11	C10	C9	113.95(15)	F3	C30	S1	111.98(13)
N2	C12	C13	109.24(12)	F3	C30	F1	107.10(15)

Table S5. Torsion Angles for [Ni(bC^N^bC)Cl]OTf.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Ni1	N3	C13	C12	4.87(18)	C13	N3	C17	C18	-178.17(13)
Ni1	N3	C13	C14	-175.52(11)	C13	C14	C15	C16	0.1(2)
Ni1	N3	C17	C16	176.81(11)	C14	C15	C16	C17	1.1(2)
Ni1	N3	C17	C18	-0.69(17)	C15	C16	C17	N3	-0.9(2)
N1	C8	C9	C10	176.90(14)	C15	C16	C17	C18	176.51(14)
N2	C2	C3	C4	-179.27(16)	C16	C17	C18	N4	-120.90(15)
N2	C2	C7	N1	0.08(16)	C17	N3	C13	C12	-177.67(13)
N2	C2	C7	C6	-179.83(14)	C17	N3	C13	C14	1.9(2)
N2	C12	C13	N3	50.64(17)	C18	N4	C19	Ni1	-6.18(18)
N2	C12	C13	C14	-128.97(14)	C18	N4	C19	N5	174.18(12)
N3	C13	C14	C15	-1.6(2)	C18	N4	C20	C21	7.7(3)
N3	C17	C18	N4	56.59(17)	C18	N4	C20	C25	-173.64(14)
N4	C20	C21	C22	179.59(15)	C19	N4	C18	C17	-53.48(18)
N4	C20	C25	N5	-0.09(16)	C19	N4	C20	C21	-178.65(16)
N4	C20	C25	C24	179.92(13)	C19	N4	C20	C25	0.02(17)
N5	C26	C27	C28	-177.84(13)	C19	N5	C25	C20	0.14(17)
C1	N1	C7	C2	-0.86(17)	C19	N5	C25	C24	-179.88(16)
C1	N1	C7	C6	179.04(17)	C19	N5	C26	C27	-111.11(16)
C1	N1	C8	C9	55.4(2)	C20	N4	C18	C17	119.62(15)
C1	N2	C2	C3	-179.16(16)	C20	N4	C19	Ni1	179.71(10)
C1	N2	C2	C7	0.72(17)	C20	N4	C19	N5	0.06(17)
C1	N2	C12	C13	-50.41(18)	C20	C21	C22	C23	-0.1(2)
C2	N2	C1	Ni1	177.90(10)	C21	C20	C25	N5	178.74(13)
C2	N2	C1	N1	-1.25(17)	C21	C20	C25	C24	-1.2(2)
C2	N2	C12	C13	124.17(15)	C21	C22	C23	C24	-0.8(2)
C2	C3	C4	C5	-1.0(2)	C22	C23	C24	C25	0.7(2)
C3	C2	C7	N1	179.98(14)	C23	C24	C25	N5	-179.66(15)
C3	C2	C7	C6	0.1(2)	C23	C24	C25	C20	0.3(2)
C3	C4	C5	C6	0.3(3)	C25	N5	C19	Ni1	-179.66(12)
C4	C5	C6	C7	0.6(2)	C25	N5	C19	N4	-0.13(16)
C5	C6	C7	N1	179.30(16)	C25	N5	C26	C27	74.12(18)
C5	C6	C7	C2	-0.8(2)	C25	C20	C21	C22	1.1(2)
C7	N1	C1	Ni1	-177.63(13)	C26	N5	C19	Ni1	5.0(2)
C7	N1	C1	N2	1.28(17)	C26	N5	C19	N4	-175.51(13)
C7	N1	C8	C9	-123.18(16)	C26	N5	C25	C20	175.61(13)
C7	C2	C3	C4	0.9(2)	C26	N5	C25	C24	-4.4(3)
C8	N1	C1	Ni1	3.6(3)	C26	C27	C28	C29	-62.2(2)
C8	N1	C1	N2	-177.46(13)	O1	S1	C30	F1	62.07(13)
C8	N1	C7	C2	177.89(14)	O1	S1	C30	F2	-57.66(15)
C8	N1	C7	C6	-2.2(3)	O1	S1	C30	F3	-178.54(12)
C8	C9	C10	C11	58.5(2)	O2	S1	C30	F1	-56.49(13)

C12	N2	C1	Ni1	-6.75(19)	O2	S1	C30	F2	-176.23(13)
C12	N2	C1	N1	174.10(13)	O2	S1	C30	F3	62.89(14)
C12	N2	C2	C3	5.8(3)	O3	S1	C30	F1	-177.19(12)
C12	N2	C2	C7	-174.33(14)	O3	S1	C30	F2	63.08(16)
C12	C13	C14	C15	177.95(14)	O3	S1	C30	F3	-57.81(14)
C13	N3	C17	C16	-0.7(2)					

Table S6. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for [Ni(bC^N^bC)Cl]OTf.

Atom	***x***	***y***	***z***	**U(eq)**
H3	827	8120	3741	15
H4	756	9937	2806	18
H5	1474	11612	3326	19
H6	2313	11545	4790	17
H8A	2522	10525	7101	16
H8B	3190	10924	6231	16
H9A	5172	8852	6387	21
H9B	4507	8522	7286	21
H10A	6115	9478	7662	28
H10B	5309	10794	7068	28
H11A	3474	11510	8090	43
H11B	4850	11200	8646	43
H11C	4131	10124	8647	43
H12A	1427	6374	4884	13
H12B	919	6594	5915	13
H14	3136	4134	4724	16
H15	5226	2435	5171	19
H16	6279	2759	6483	16
H18A	6223	4029	7822	14
H18B	5596	5642	7645	14
H21	6471	2826	9245	15
H22	6073	1843	10584	19
H23	3898	2622	11256	20
H24	2046	4438	10641	17
H26A	425	5824	9299	15
H26B	432	7017	8645	15
H27A	967	6958	10537	18
H27B	914	8168	9877	18
H28A	-1402	7483	10291	24
H28B	-1171	8755	10716	24
H29A	-1739	8506	8864	44

H29B	-1403	9745	9247	44
H29C	-2769	9554	9567	44