Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information

A high-spin nickel(II) borohydride complex in dehalogenation

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Table S1. Selected bond distances (Å) and angles (°) for **1**-$(BPh_4)_2$ and **2**-BPh_4.

Bond Distances (Å)			
1-$(BPh_4)_2$		**2**-BPh_4	
Ni1-N1	2.1034(10)	Ni1-N1	2.083(2)
Ni1-N2	2.1019(10)	Ni1-N2	2.1430(18)
Ni1-N3	2.0998(10)	Ni1-N3	2.0701(18)
Ni1-N4	2.1169(10)	Ni1-N4	2.0945(19)
Ni1-N5	2.0619(10)	Ni1-H1h	1.72(3)
Ni1-N6	2.0869(10)	Ni1-H2h	1.77(3)
		Ni1⋯B1	2.225(3)
Bond Angles (°)			
1-$(BPh_4)_2$		**2**-BPh_4	
N1- Ni1-N2	84.50(4)	N1-Ni1-N2	83.84(7)
N1-Ni1-N3	84.46(4)	N1-Ni1-N3	84.92(8)
N1-Ni1-N4	176.61(4)	N1-Ni1-N4	91.71(8)
N1-Ni1-N5	92.30(4)	N2-Ni1-N3	84.40(7)
N1-Ni1-N6	94.75(4)	N2-Ni1-N4	174.60(8)
N2-Ni1-N3	84.55(4)	N3-Ni1-N4	92.18(8)
N2-Ni1-N4	92.16(4)		
Ni2-Ni1-N5	176.17(4)		
Ni2-Ni1-N6	93.19(4)		

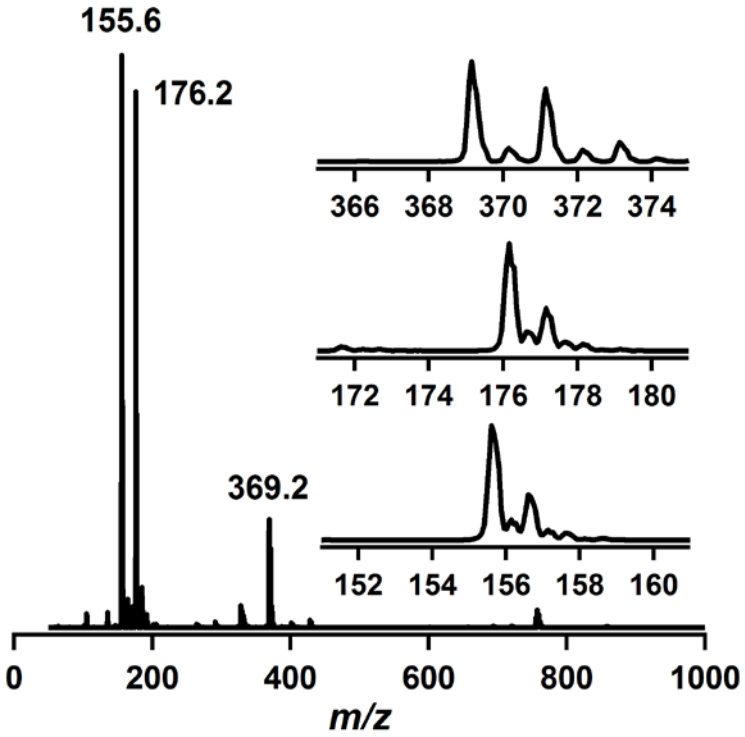

Fig. S1 ESI-MS of **1** in CH_3CN at room temperature. Mass peaks at 155.6, 176.2 and 369.2 are assigned to $[Ni(Me_3\text{-}TACN)(CH_3CN)_2]^{2+}$, $[Ni(Me_3\text{-}TACN)(CH_3CN)_3]^{2+}$ and $[Ni(Me_3\text{-}TACN)\ (CH_3CN)(ClO_4)]^{+}$, respectively. Insets show observed distribution patterns for $[Ni(Me_3\text{-}TACN)(CH_3CN)_2]^{2+}$ (bottom), $[Ni(Me_3\text{-}TACN)(CH_3CN)_3]^{2+}$ (middle) and $[Ni(Me_3\text{-}TACN)\ (CH_3CN)(ClO_4)]^{+}$ (upper).

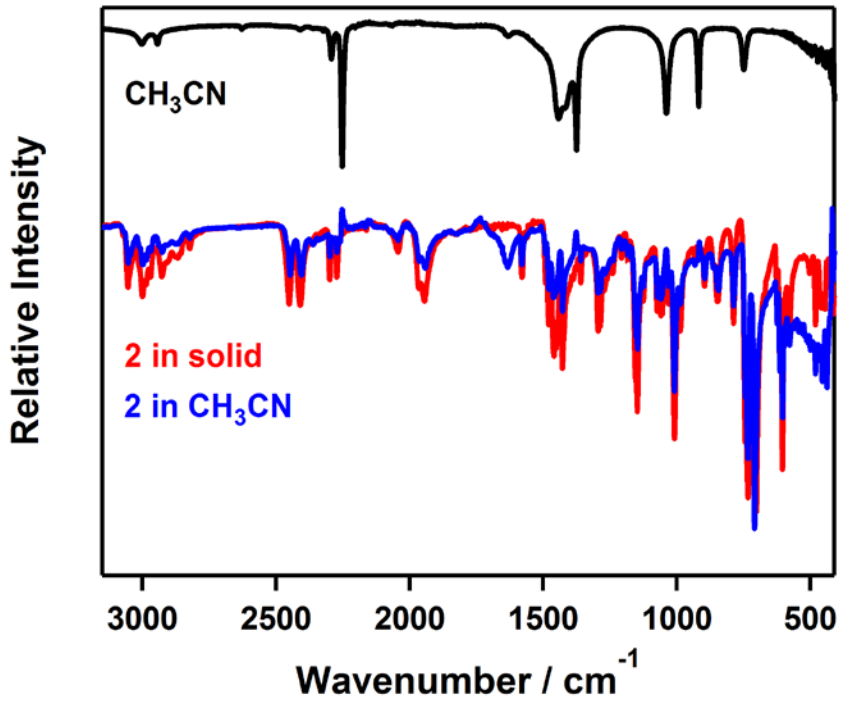

Fig. S2 (a) IR spectrum of CH_3CN (black). (b) IR spectrum of **2** in CH_3CN (blue). (c) IR spectrum of a powdered sample of **2** (red).

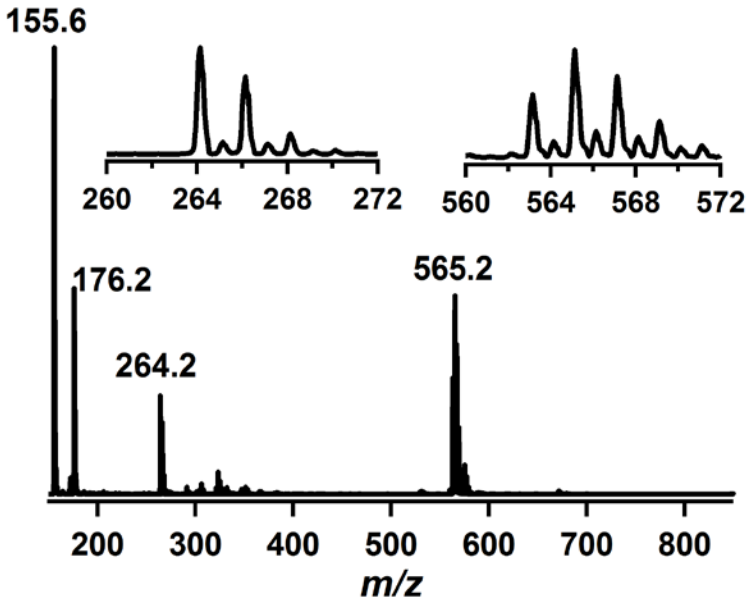

Fig. S3 ESI-MS spectrum showing the formation of $[Ni(Me_3\text{-}TACN)(Cl)]^+$ after the reaction of **2** and $CHCl_3$. Mass peaks at 155.6, 176.2, 264.2 and 565.2 are assigned to $[Ni(Me_3\text{-}TACN)(CH_3CN)_2]^{2+}$, $[Ni(Me_3\text{-}TACN)(CH_3CN)_3]^{2+}$, $[Ni(Me_3\text{-}TACN)(Cl)]^+$ and $[Ni_2(Me_3\text{-}TACN)_2(Cl)_3]^+$, respectively. Insets show observed distribution patterns for $[Ni(Me_3\text{-}TACN)(Cl)]^+$ (left) and $[Ni_2(Me_3\text{-}TACN)_2(Cl)_3]^+$ (right).

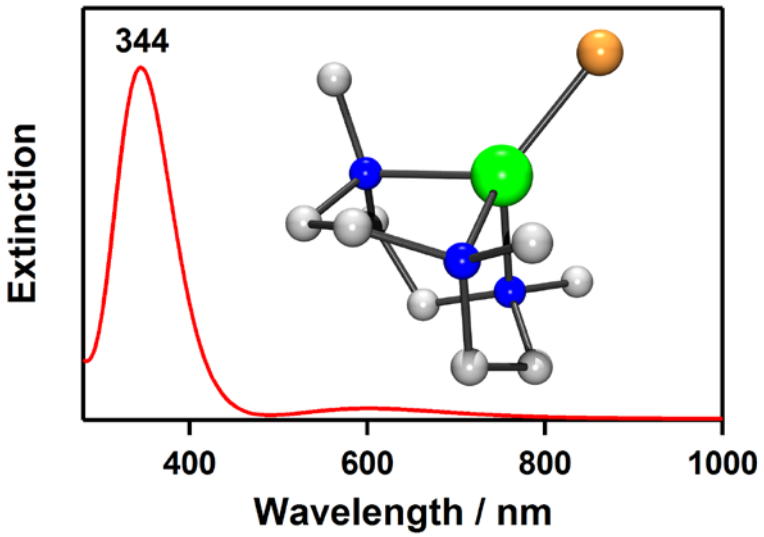

Fig. S4 TD-DFT predicted absorption spectrum of $[Ni(Me_3\text{-}TACN)(Cl)]^+$. Inset shows DFT structure of $[Ni(Me_3\text{-}TACN)(Cl)]^+$ (gray, C; blue, N; green, Ni; gold, Cl).

Coordinates in xyz-format

$[Ni(Me_3\text{-}TACN)(BH_4)(CH_3CN)]^+$

C	0.540141990789	-1.910107262329	-3.339115379300
C	2.598635500717	-1.215857630127	-2.271431301980
C	-0.870075162044	-1.520954368623	-3.760113434469
C	1.578786011763	0.259925035689	-3.920281918564
C	-2.527329408721	-1.523360240791	-1.973383907107
C	1.253121585663	1.672907839219	-3.455214746106
C	-2.214208355842	0.501162661760	-3.301166064797
C	-1.193714309899	1.511244250221	-3.825170941530
C	-0.258417909946	3.092451665042	-2.205437313636
C	-2.206842997904	1.423529222414	0.727943471123
C	-2.913588099744	1.851000180526	1.917392105009
H	3.205635267900	-1.720377687148	-3.031228884446
H	1.044823080704	-2.406418889837	-4.177430103760
H	0.497944410581	-2.625787231692	-2.517302832770
H	2.400709199324	-1.898484473105	-1.450321143179
H	-1.444436307466	-2.428235500753	-3.957311708826
H	3.151988217855	-0.368913125300	-1.873592313032
H	2.626528588432	0.225446774025	-4.224825824757
H	-0.851517162677	-0.969572122090	-4.698264562861
H	1.002282534207	0.006556027999	-4.808307383334
H	1.997943109191	-0.858443523761	0.561596704916
H	-2.008872972450	-2.363996245178	-1.515837782629
H	-3.312594114889	-1.905281182294	-2.633694479479
H	0.139792599204	-1.063318462701	-0.178218127886
H	1.124493428981	0.733668878815	-0.289208769952
H	-2.903415297491	0.224744977343	-4.107470094000
H	-2.981649184290	-0.931043413969	-1.183522061972
H	-0.760414289878	1.162661006421	-4.760527468198
H	1.966917946085	1.980303870221	-2.690148159647
H	0.429277482494	0.054995946950	1.475545880128
H	1.352315278251	2.370728515664	-4.295383797790
H	-2.806361259142	0.952768267464	-2.507240646068
H	-1.709259406785	2.443495053188	-4.062837932938
H	0.484893951837	3.211803891073	-1.419079223959
H	-0.138778513489	3.897715747444	-2.937557429219
H	-1.246740424017	3.164827505470	-1.759802533736
H	-2.663500650948	1.184386065824	2.743559915322
H	-2.619115467966	2.867740603075	2.178380272448
H	-3.989566741025	1.822893122252	1.743221165290

B	0.950388772884	-0.296294272819	0.458608608331
N	1.321223203556	-0.749233046637	-2.853549794293
N	-1.556711336720	-0.696485346854	-2.722572670573
N	-0.096068481454	1.767518513081	-2.843073972243
N	-1.636268123659	1.073758752954	-0.206755145065
Ni	-0.082138453419	0.163115139869	-1.420693796011

$[Ni(Me_3\text{-}TACN)(BH_4)]^+$

C	0.614133357328	-1.906288728906	-3.551474049915
C	2.780351495561	-1.324878900944	-2.584407875827
C	-0.833578038916	-1.453367118763	-3.726327989218
C	1.650279535469	0.300570836305	-4.030908830348
C	-2.199273737041	-1.591572068709	-1.692221778771
C	1.423704434195	1.667569758124	-3.387573570649
C	-2.024673474164	0.544852841382	-2.860633883962
C	-1.055959564112	1.576094509827	-3.432021298395
C	0.114378036743	2.899492187053	-1.732495290403
C	-5.408794077906	2.407040344746	5.945918748203
C	-6.290065261234	2.540016475912	7.095236272421
H	3.325402128075	-1.795674010349	-3.407728774767
H	0.997948331399	-2.304533050589	-4.497559583741
H	0.665646702389	-2.710210804104	-2.816653616008
H	2.626472212284	-2.053024964331	-1.791106165299
H	-1.460668537664	-2.324519259840	-3.924637733116
H	3.375406523246	-0.506694806361	-2.183358123596
H	2.654512714420	0.263724562933	-4.458076086592
H	-0.929307970532	-0.808589105752	-4.597558601977
H	0.965208990342	0.150613545066	-4.862975206222
H	0.952197789162	-0.336487804856	1.633052482890
H	-1.660610691554	-2.499384940818	-1.428206984749
H	-3.111577007644	-1.861066373800	-2.232396556933
H	0.599655012244	-1.335481922387	-0.124266331184
H	1.612759576097	0.388773394329	-0.168366766815
H	-2.844164451349	0.371070709752	-3.567025908772
H	-2.464802664753	-1.072453474895	-0.773504154389
H	-0.768584306652	1.311026449810	-4.447448301706
H	2.239659003034	1.895127946586	-2.700940793217
H	-0.347332603075	0.390520810319	0.221572945042
H	1.419012483993	2.445703546535	-4.159408723608
H	-2.466579634544	0.922245943550	-1.937749403735
H	-1.557038982054	2.543505553570	-3.502699824526
H	0.962130472939	2.905817452960	-1.051041727147

H	0.126739135802	3.810452498433	-2.338193919451
H	-0.798951438884	2.880329417921	-1.140479108472
H	-7.106787365241	3.224646449295	6.863131140973
H	-6.704850262789	1.566419355500	7.359761864000
H	-5.739032191482	2.928642215962	7.951873929135
B	0.720909055161	-0.230823952062	0.480637409174
N	1.472588467813	-0.805387120559	-3.043151242266
N	-1.330182468640	-0.724187177282	-2.520445430696
N	0.172858847304	1.692961438592	-2.589358992767
N	-4.713307297959	2.300920557031	5.033179421853
Ni	0.342357618856	-0.059403461935	-1.441497975135