Electronic Supplementary Material (ESI) for Energy and Environmental Science

Proton management as a design principle for hydrogenase-inspired catalysts

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SUPPLEMENTARY INFORMATION

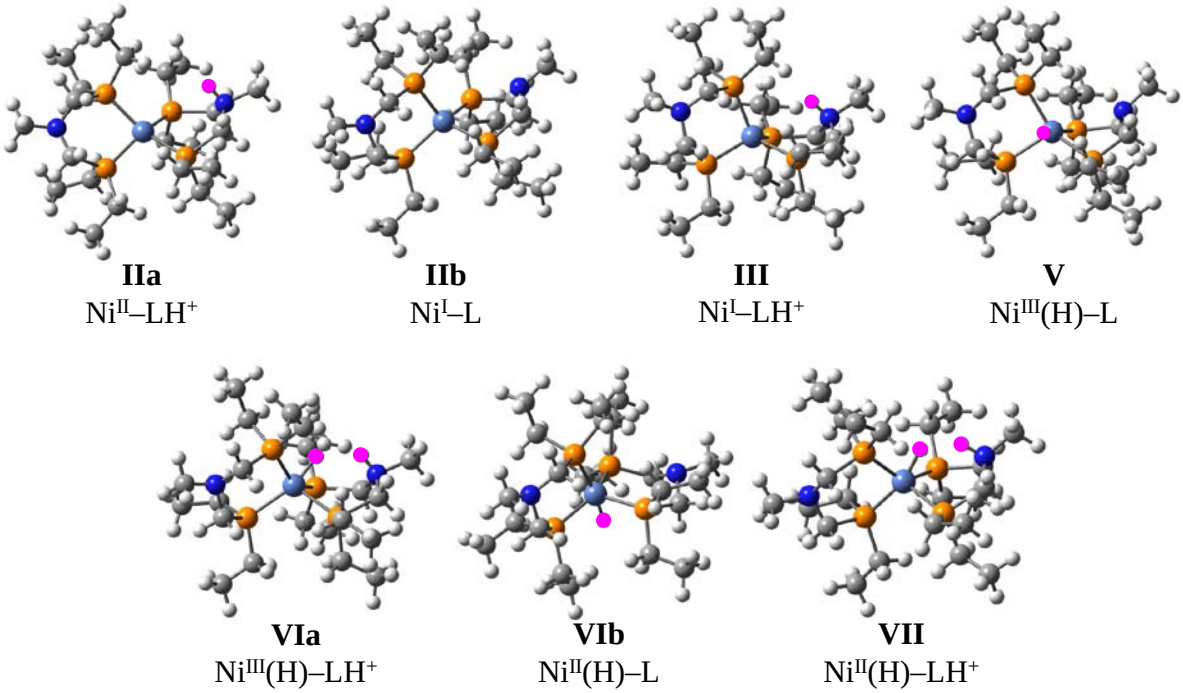
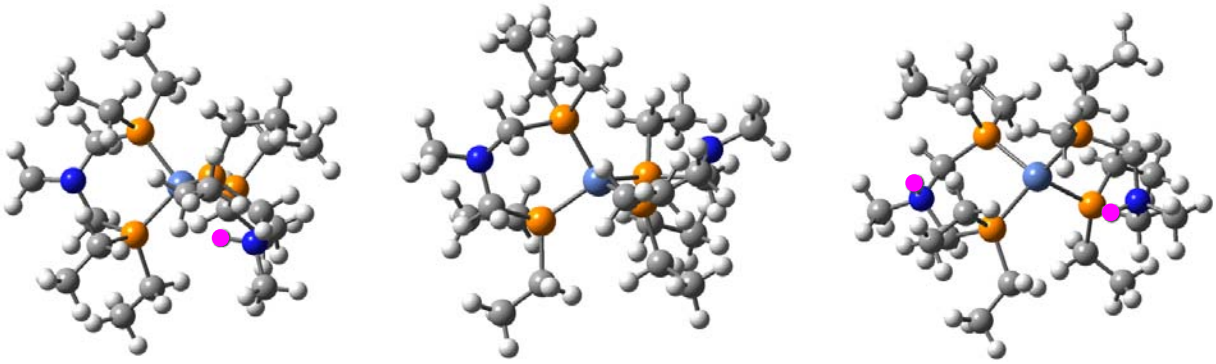


Figure S1. Calculated structures of intermediates along postulated catalytic pathway. Alternative structures for intermediates **I** and **IX** are shown in Figs. 5 and 6, respectively. Here the label "**a**" (as in **IIa**) indicates the species resulting from the protonation of the previous species in the sequence, while "**b**" indicates the reduction of that species. Hence, **IIa** is the protonated **I**, and **VIb** is the reduced **V**. The active protons are shaded in pink.



XI $Ni^0–LH^+$ **XII** $Ni^0–L$ **XIII** $Ni^I–LH^+–LH^+$

Figure S2. Calculated structures of additional intermediates along the catalytic pathway involving Ni(0) species. The active protons are shaded in pink.

Details of adjustments in calculated free energies.

Table S1. Calculated and adjusted (where appropriate) absolute free energies (in Hartree) of possible intermediate species of the $Ni(PNP)_2^{2+}$ catalyst complex.

Label	Species	$G^o_{species}$	Adj. $G^o_{species}$
I	Ni^{II}–L	-3853.025619	
IIa	Ni^{II}–LH^+	-3853.459210	
IIb	Ni^{I}–L	-3853.171810	
III	Ni^{I}–LH^+	-3853.615948	
V	Ni^{III}(H)–L	-3853.594856	
VIa	Ni^{III}(H)–LH^+	-3854.025917	
VIb	Ni^{II}(H)–L	-3853.754855	-3853.756327
VII	Ni^{II}(H)–LH^+	-3854.198985	-3854.205507
IXb	Ni^{0}–$(LH^+)_2$	-3854.182174	-3854.201740
IXc	$Ni^{IV}(H)_2$–L	-3854.177866	
XI	Ni^{0}–LH^+	-3853.729874	-3853.749440
XII	Ni^{0}–L	-3853.262130	-3853.281696
XIII	Ni^{I}–$(LH^+)_2$	-3854.054329	

Table S2. Cartesian coordinates (xyz format) of calculated structure of square-planar $Ni(PNP)_2^{2+}$ at the B3LYP/6-31G(d,p) level of theory in the gas phase.

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   83
scf done: -3853.557491
 C    -3.248909    -1.143590    -0.958712
 P    -1.611485    -1.573572    -0.190216
Ni     0.000248     0.060148     0.000076
 P     1.650179     1.659282     0.050488
 C     3.286955     1.235148     0.827405
 N     3.885529     0.006186     0.348042
 P    -1.650106     1.659154    -0.050577
 C    -3.286574     1.235090    -0.828168
 N    -3.885467     0.006229    -0.348983
 P     1.611570    -1.573690     0.190272
 C     3.249222    -1.143555     0.958199
 H     3.949078     2.069961     0.586217
 H     3.144813     1.246739     1.923935
 H     3.116333    -1.042705     2.051033
 H     3.881290    -2.020315     0.793630
 H    -3.948707     2.069994    -0.587312
 H    -3.143956     1.246609    -1.924638
 H    -3.880996    -2.020345    -0.794197
 H    -3.115665    -1.042929    -2.051521
 C     5.347302    -0.007454     0.545947
 H     5.792645     0.841843     0.022341
 H     5.634267     0.044599     1.607508
 H     5.762592    -0.921851     0.115868
 C    -5.347142    -0.007356    -0.547656
 H    -5.792706     0.842015    -0.024359
 H    -5.633537     0.044612    -1.609374
 H    -5.762695    -0.921695    -0.117708
 C    -2.048116     2.068278     1.730498
 H    -1.320089     2.816975     2.056236
 H    -1.817762     1.162516     2.302425
 C     1.353590     3.214762     1.044184
 H     0.308862     3.506694     0.965407
 H     1.498402     2.898689     2.084533
 C    -1.353582     3.215164    -1.043512
 H    -1.498466     2.899718    -2.084040
 H    -0.308846     3.507056    -0.964652
 C     2.047663     2.068799    -1.730606
 H     1.319301     2.817245    -2.056157
 H     1.817535     1.162974    -2.302526
 C     1.153763    -2.973457     1.341640
 H     0.898631    -2.448935     2.271682
 H     0.231169    -3.440890     0.997556
 C     2.156411    -2.074280    -1.519406
 H     1.311992    -1.950037    -2.201371
 H     2.872241    -1.278454    -1.761763
 C    -2.156716    -2.073527     1.519538
 H    -2.872387    -1.277455     1.761547
 H    -1.312352    -1.949324     2.201581
 C    -1.153649    -2.973819    -1.341019
 H    -0.898282    -2.449646    -2.271189
 H    -0.231173    -3.441227    -0.996593
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C	2.194288	-4.064211	1.649776
H	3.103471	-3.664036	2.102846
H	1.759776	-4.760546	2.372954
H	2.471692	-4.640393	0.766443
C	2.805350	-3.450385	-1.724004
H	2.103286	-4.269600	-1.546779
H	3.146858	-3.531317	-2.759861
H	3.677259	-3.601100	-1.082743
C	-2.239042	4.431655	-0.727416
H	-1.980539	5.246797	-1.409307
H	-3.303895	4.227932	-0.861145
H	-2.084571	4.796764	0.291620
C	3.475388	2.530477	-2.058431
H	3.752986	3.445993	-1.532187
H	4.207399	1.753809	-1.827638
H	3.541277	2.737251	-3.130462
C	2.238998	4.431483	0.728839
H	2.084286	4.797342	-0.289888
H	1.980627	5.246104	1.411397
H	3.303884	4.227672	0.862169
C	-3.476078	2.529405	2.058027
H	-3.542328	2.736002	3.130069
H	-3.753890	3.444886	1.531838
H	-4.207732	1.752493	1.826904
C	-2.194208	-4.064577	-1.648999
H	-3.103236	-3.664485	-2.102453
H	-1.759584	-4.761223	-2.371809
H	-2.471898	-4.640401	-0.765529
C	-2.806028	-3.449408	1.724452
H	-3.147760	-3.529930	2.760266
H	-3.677847	-3.600126	1.083072
H	-2.104111	-4.268835	1.547632

Table S3. Cartesian coordinates of calculated structure of "tetrahedral" $Ni^{II}(PNP)_2^{2+}$ at the B3LYP/6-31G(d,p) level of theory in the gas phase.

83
scf done: -3853.562844

C	3.296693	-1.104996	0.269141
P	1.546300	-1.347384	0.863241
Ni	0.031400	0.085788	-0.048623
P	-1.590892	1.578728	0.436616
C	-3.177860	1.520391	-0.527030
N	-3.746205	0.187176	-0.637935
P	1.712401	1.473334	-0.592092
C	3.060523	0.541891	-1.501325
N	3.202994	-0.869983	-1.169259
P	-1.514941	-1.440218	-0.638430
C	-2.970884	-0.677215	-1.515240
H	-3.891481	2.163045	-0.004798
H	-2.976299	1.991668	-1.508308
H	-2.616714	-0.170932	-2.431033
H	-3.604279	-1.506984	-1.839176
H	2.825650	0.617700	-2.565961
H	3.998804	1.104232	-1.340188

H	3.837492	-2.036298	0.452120
H	3.833847	-0.321002	0.823210
C	-5.168116	0.240646	-1.026775
H	-5.721211	0.834509	-0.294975
H	-5.322035	0.680790	-2.024064
H	-5.584382	-0.769346	-1.021992
C	4.307870	-1.470896	-1.934636
H	4.121472	-1.336056	-3.003172
H	5.286489	-1.026736	-1.693923
H	4.350772	-2.543746	-1.732841
C	1.241512	2.792673	-1.826754
H	0.886539	3.639574	-1.234345
H	0.372834	2.411829	-2.375854
C	-1.247620	3.406520	0.448356
H	-0.235309	3.539989	0.840373
H	-1.219197	3.710456	-0.603143
C	2.536785	2.342480	0.830335
H	2.945809	1.558777	1.476627
H	1.728719	2.802578	1.410417
C	-1.993733	1.121826	2.205005
H	-1.302168	1.710507	2.820215
H	-1.709871	0.074463	2.351853
C	-0.771656	-2.544878	-1.947886
H	0.044642	-1.974623	-2.406225
H	-0.297801	-3.377645	-1.423458
C	-2.332357	-2.440387	0.691571
H	-1.594937	-2.618094	1.480708
H	-3.071635	-1.746975	1.109198
C	1.372017	-3.188602	0.689640
H	1.661066	-3.390601	-0.347738
H	0.310919	-3.433825	0.774429
C	1.453295	-0.952764	2.686698
H	1.122909	0.088690	2.777951
H	0.629168	-1.560833	3.079309
C	-1.709808	-3.083919	-3.041174
H	-2.131701	-2.287142	-3.657959
H	-1.134787	-3.735194	-3.705644
H	-2.529778	-3.678699	-2.632737
C	-3.004283	-3.756617	0.275881
H	-2.289098	-4.475377	-0.133685
H	-3.469279	-4.218887	1.151069
H	-3.793489	-3.600304	-0.464353
C	3.614121	3.389876	0.514972
H	4.024048	3.778779	1.451330
H	4.448238	2.972595	-0.055570
H	3.208175	4.238804	-0.040113
C	-3.446851	1.319833	2.666310
H	-3.774678	2.357722	2.586420
H	-4.131010	0.692778	2.090199
H	-3.530192	1.029552	3.717549
C	-2.219585	4.307902	1.226274
H	-2.218351	4.088349	2.296329
H	-1.908265	5.349755	1.108068
H	-3.245894	4.236395	0.857633
C	2.308188	3.275085	-2.825493
H	1.896777	4.113461	-3.394939
H	3.218072	3.626989	-2.335743

H	2.582242	2.504203	-3.548898
C	2.729467	-1.155180	3.523171
H	3.537554	-0.493450	3.199681
H	2.514396	-0.917232	4.568795
H	3.096703	-2.181588	3.487328
C	2.176198	-4.074301	1.653001
H	2.041249	-5.122154	1.369901
H	3.250028	-3.870023	1.621705
H	1.835988	-3.969953	2.685919