

## Supporting Information for

### Hydrogen Evolution Reaction Mechanisms in Thiosemicarbazone Metal Complexes: A Combined Theoretical and Experimental Investigation on the Impact of Proton Source

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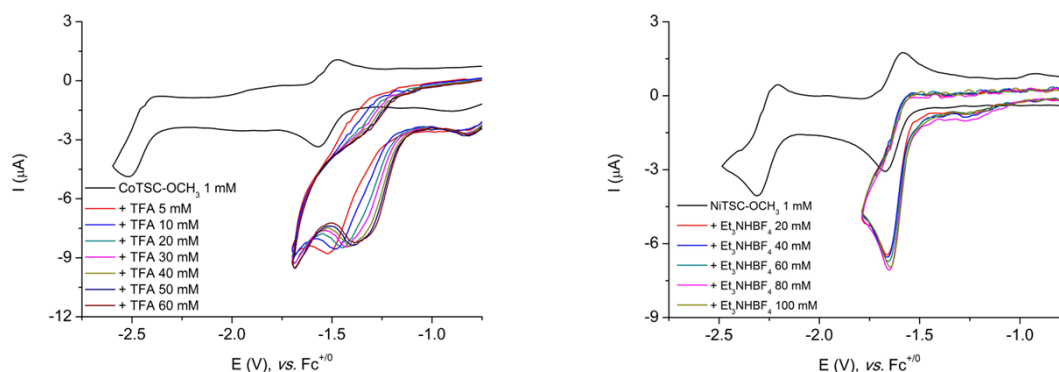
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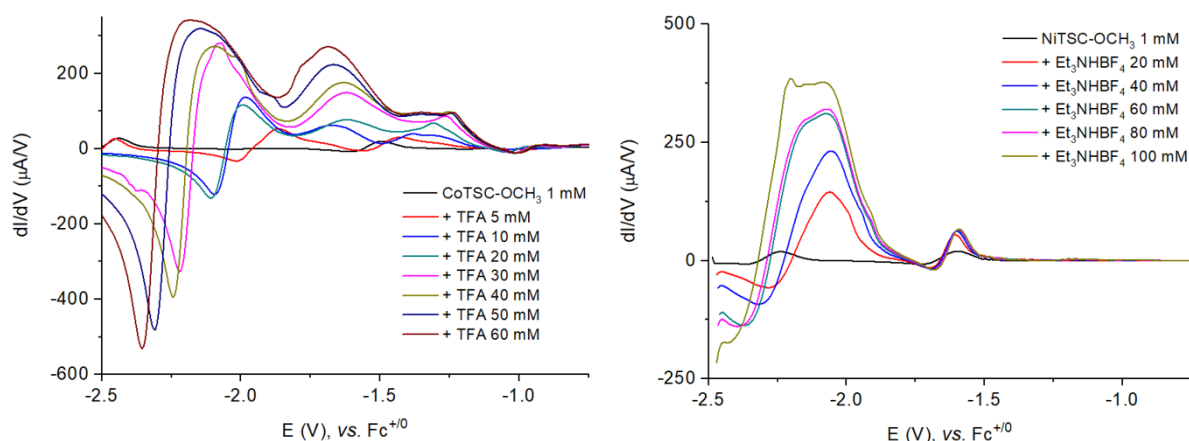
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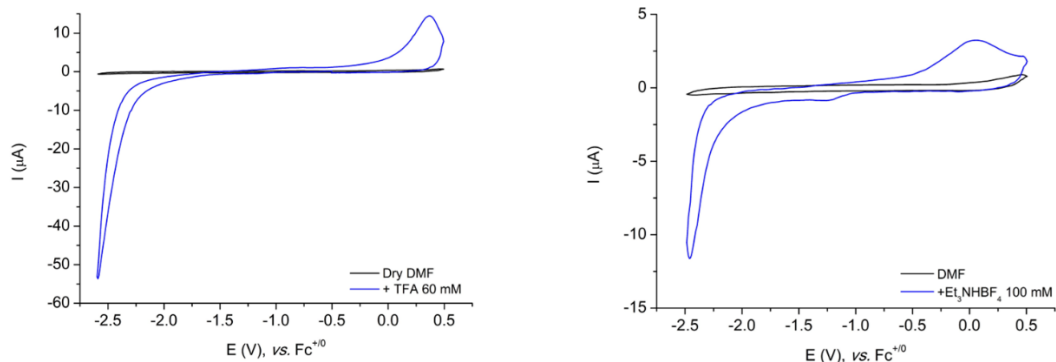
## 1. Electrocatalytic proton reduction



**Figure S1.** Successive cyclic voltammograms of a DMF solution (0.1 M NBu<sub>4</sub>PF<sub>6</sub>) with 1 mM of (left) CoTSC-OCH<sub>3</sub> in the presence of increasing amounts of TFA and (right) NiTSC-OCH<sub>3</sub> in the presence of increasing amounts of Et<sub>3</sub>NHBF<sub>4</sub>. Scan rate 500 mV.s<sup>-1</sup> at a glassy carbon working electrode.

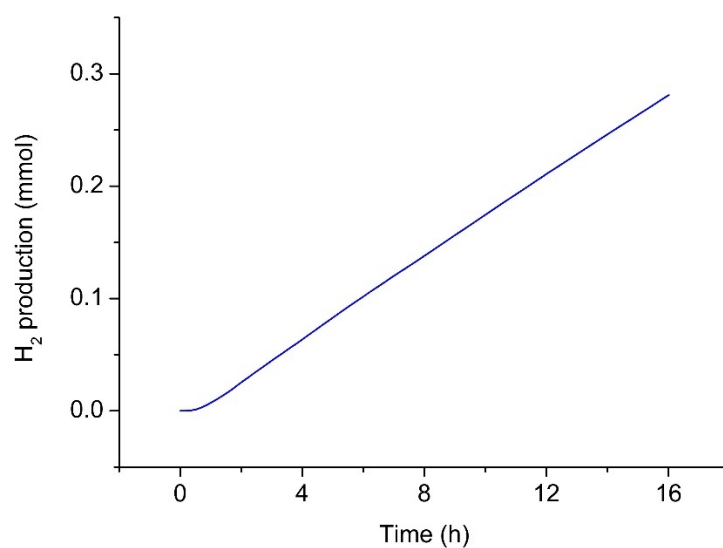


**Figure S2.** First derivative of the cyclic voltammograms of a DMF solution (0.1 M NBu<sub>4</sub>PF<sub>6</sub>) with 1 mM of (left) CoTSC-OCH<sub>3</sub> in the presence of increasing amounts of TFA and (right) NiTSC-OCH<sub>3</sub> in the presence of increasing amounts of Et<sub>3</sub>NHBF<sub>4</sub>. Scan rate 500 mV.s<sup>-1</sup> at a glassy carbon working electrode.

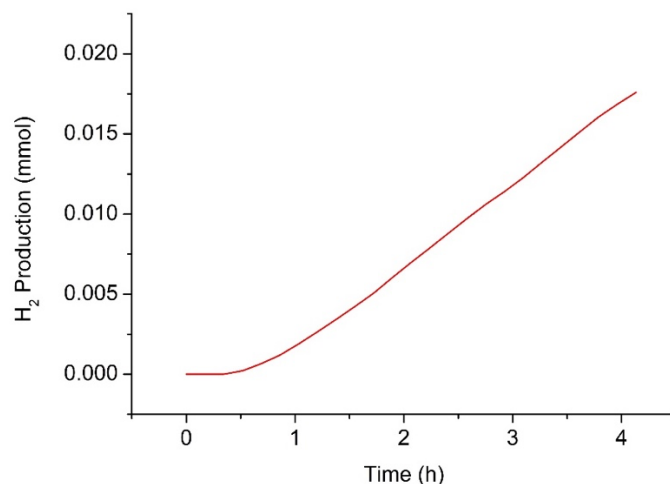


**Figure S3.** Successive cyclic voltammograms of (left) CoTSC-OCH<sub>3</sub> and (right) NiTSC-OCH<sub>3</sub> complexes recorded after electrocatalysis upon washing the glassy carbon electrode and immersion into a fresh solution of DMF (0.1 M NBu<sub>4</sub>PF<sub>6</sub>, black lines) and in the presence of (left) 60 mM of TFA and (right) 100 mM of Et<sub>3</sub>NHBF<sub>4</sub> (blue lines).

## 2. Gas Analysis

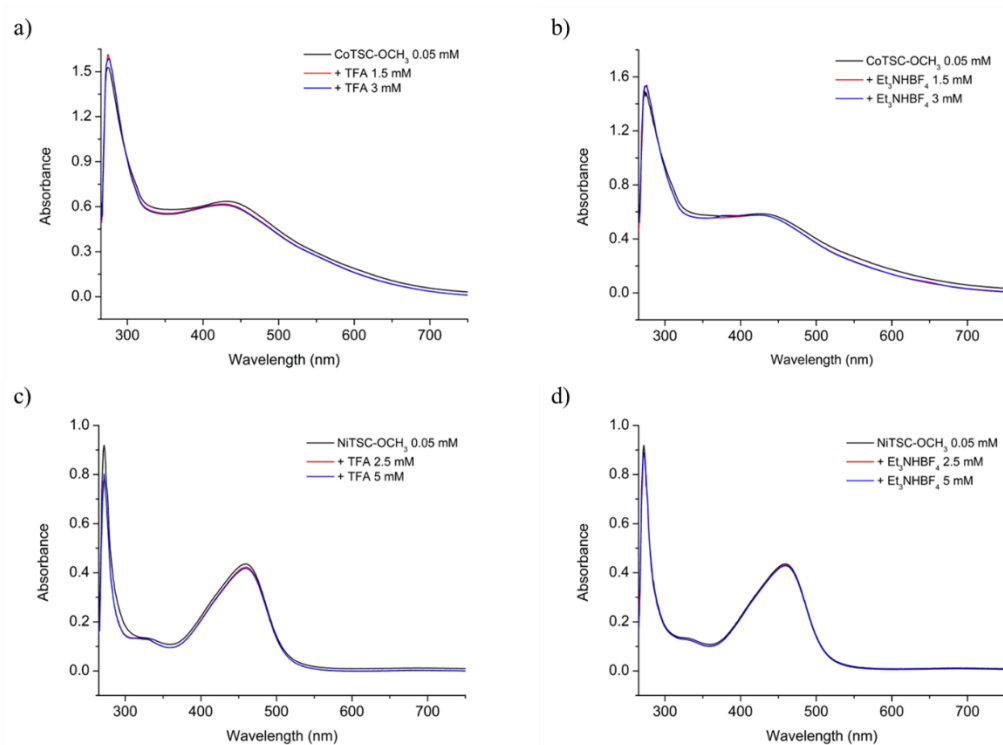


**Figure S4.** Hydrogen evolution detected by gas chromatography during bulk electrolysis experiments at -1.6 V vs. Fc<sup>+0</sup> using a pool mercury working electrode. The electrolytic solution contains 0.1 M NBu<sub>4</sub>PF<sub>6</sub> in DMF, 60 mM TFA and 1 mM of CoTSC-OCH<sub>3</sub>.



**Figure S5.** Hydrogen evolution detected by gas chromatography during bulk electrolysis experiments at  $-2.1$  V vs.  $\text{Fc}^{+/0}$  using a pool mercury working electrode. The electrolytic solution contains  $0.1$  M  $\text{NBu}_4\text{PF}_6$  in DMF,  $100$  mM  $\text{Et}_3\text{NHBF}_4$  and  $1$  mM of  $\text{NiTSC-OCH}_3$ .

### 3. UV-vis Spectroscopy



**Figure S6.** Electronic absorption spectra of  $0.05$  mM solutions of a)  $\text{CoTSC-OCH}_3$  complexes in DMF in the absence (black line) and in the presence (30 and 60 equivalents, blue and red lines, respectively) of TFA, b)  $\text{CoTSC-OCH}_3$  complexes in DMF in the absence (black line) and in the presence (30 and 60 equivalents, blue and red lines, respectively) of  $\text{Et}_3\text{NHBF}_4$ , c)  $\text{NiTSC-OCH}_3$  complexes in DMF in the absence (black line) and in the presence (50 and 100 equivalents, blue and red lines, respectively) of TFA and d)  $\text{NiTSC-OCH}_3$  complexes in DMF in the absence (black line) and in the presence (50 and 100 equivalents, blue and red lines, respectively) of  $\text{Et}_3\text{NHBF}_4$ .

## 4. Benchmarking of performances

### 4.1. TOF calculations from controlled potential electrolysis experiments (CPE)

Based on the analysis we conducted for NiTSC-OCH<sub>3</sub>,<sup>3</sup> we evaluated the TOF values of the complexes from the electrolysis data as proposed by Saveant and co-workers.<sup>4</sup> Equations 3-6 were used for the calculation under the assumption that the electron transfer to the catalyst is fast and the Nernst law is obeyed. In these equations,  $i_{el}$  is the current during electrolysis,  $F$  is Faraday's constant ( $F = 96500 \text{ C}\cdot\text{mol}^{-1}$ ),  $E_{appl}$  is the applied potential during electrolyses ( $E_{appl} = -1.70 \text{ V vs. Fc}^{+/0}$ ),  $E_{1/2}$  is the half-wave potential for the catalytic wave,  $A$  is the surface area of the mercury-pool working electrode ( $A \sim 0.47 \text{ cm}^2$ ),  $D_{cat}$  is the diffusion coefficient,  $[Cat]$  is the concentration of the catalyst ( $[Cat] = 1 \text{ mM}$ ),  $Q_{el}$  is the charge passed during the electrolysis,  $FY$  is the Faradaic yield,  $t$  is the electrolysis time and  $TOF_{max}$  is the maximum turnover frequency obtained from CVs. Electrolysis experiments were conducted at potentials close to the half-wave potentials of the catalytic processes and so TOF values determined from electrolysis were equated to  $TOF_{max}$  values.

$$TOF = \frac{i_{el}^2(1+\exp[\frac{F}{RT}(E_{appl}-E_{1/2})])}{F^2A^2D_{cat}[Cat]^2} \quad (3)$$

$$i_{el} = \frac{Q_{el}\cdot FY}{t} \quad (4)$$

$$i_p = 0.446FA[Cat]\sqrt{\frac{FvD_{cat}}{RT}} \quad (5)$$

$$TOF = \frac{TOF_{max}}{1+\exp[\frac{F}{RT}(E_{appl}-E_{1/2})]} \quad (6)$$

**Table S1.** Calculated TOF values and HER production data for CoTSC-OCH<sub>3</sub> and NiTSC-OCH<sub>3</sub> with TFA and Et<sub>3</sub>NH<sup>+</sup>.

Complex / proton source	Time (h)	Q (C)	FY (%)	Total H <sub>2</sub> (mmol)	TON	TOF (s <sup>-1</sup> )
CoTSC-OCH <sub>3</sub> / TFA	4	14.4	79	0.063	8	96
CoTSC-OCH <sub>3</sub> / TFA	16	61.9	88	0.300	35	117
NiTSC-OCH <sub>3</sub> / Et <sub>3</sub> NH <sup>+</sup>	4	5.5	58	0.017	2	24

**Table S2.** Calculated TOF values and HER production data for CoTSC-OCH<sub>3</sub> and NiTSC-OCH<sub>3</sub> with Et<sub>3</sub>NH<sup>+</sup> and TFA.<sup>6</sup>

Complex / proton source	Time (h)	Q (C)	FY (%)	Total H <sub>2</sub> (mmol)	TON	TOF (s <sup>-1</sup> )
NiTSC-OCH <sub>3</sub> / TFA	4	4.2	63	0.014	2	11
NiTSC-OCH <sub>3</sub> / TFA	16	51.2	80	0.170	21	90
CoTSC-OCH <sub>3</sub> / Et <sub>3</sub> NH <sup>+</sup>	4	19.1	65	0.072	9	130

## 4.2 Overpotential determinations

Following a previously reported protocol,<sup>1</sup> the overpotential values,  $\eta$ , of NiTSC-OCH<sub>3</sub> and CoTSC-OCH<sub>3</sub> complexes were calculated as the difference between the mid-wave catalytic potential ( $E_{1/2}^{cat}$ ) and the theoretical half-wave potential ( $E_{1/2}^T$ ) such as:

$$\eta = E_{1/2}^{cat} - E_{1/2}^T \quad (1)$$

The value of  $E_{1/2}^T$  depends on the standard potential for proton reduction in DMF ( $E_{H^+/H_2}^0$ ), the  $pK_a$  of the proton source, the total acid concentration ( $C_0$ ), the dissolved hydrogen concentration ( $C_{H_2}^0$ ), and the difference in diffusion coefficients between the acid and H<sub>2</sub> ( $\epsilon_D$ ). In the case of TFA in DMF, homoconjugation is negligible and the theoretical half-wave potential,  $E_{1/2}^T$ , is calculated as follows:

$$E_{1/2}^T = E_{H^+/H_2}^0 - (2.303 \times RT/F) \times pK_a + \epsilon_D - (RT/2F) \times \ln(C_0/C_{H_2}^0) \quad (2)$$

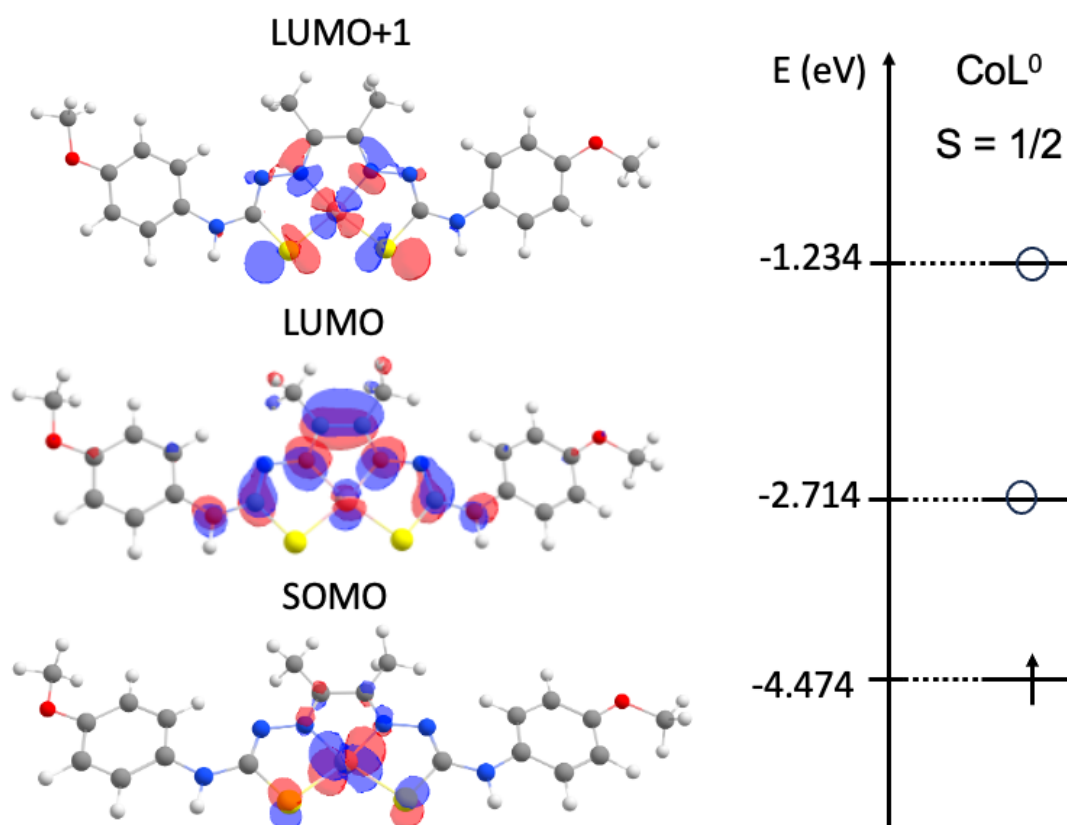
The relevant values of  $E_{H^+/H_2}^0$  (-0.62 V),  $pK_a$  (6.0 and 9.3 for TFA and Et<sub>3</sub>NHBF<sub>4</sub> in DMF, respectively),  $\epsilon_D$  (0.04 ± 0.005 V) and  $C_{H_2}^0$  (1.9.10<sup>-3</sup> M), were obtained from literature.<sup>1,2</sup> We used  $R = 8.31 \text{ J.K}^{-1}.\text{mol}^{-1}$ ,  $T = 298 \text{ K}$ ,  $F = 96500 \text{ C.mol}^{-1}$  and  $C_0 = 0.1 \text{ M}$  for Et<sub>3</sub>NHBF<sub>4</sub> and  $C_0 = 0.06 \text{ M}$  for TFA.

**Table S3.** Calculated overpotential values,  $\eta$ , for NiTSC-OCH<sub>3</sub> and CoTSC-OCH<sub>3</sub> complexes.

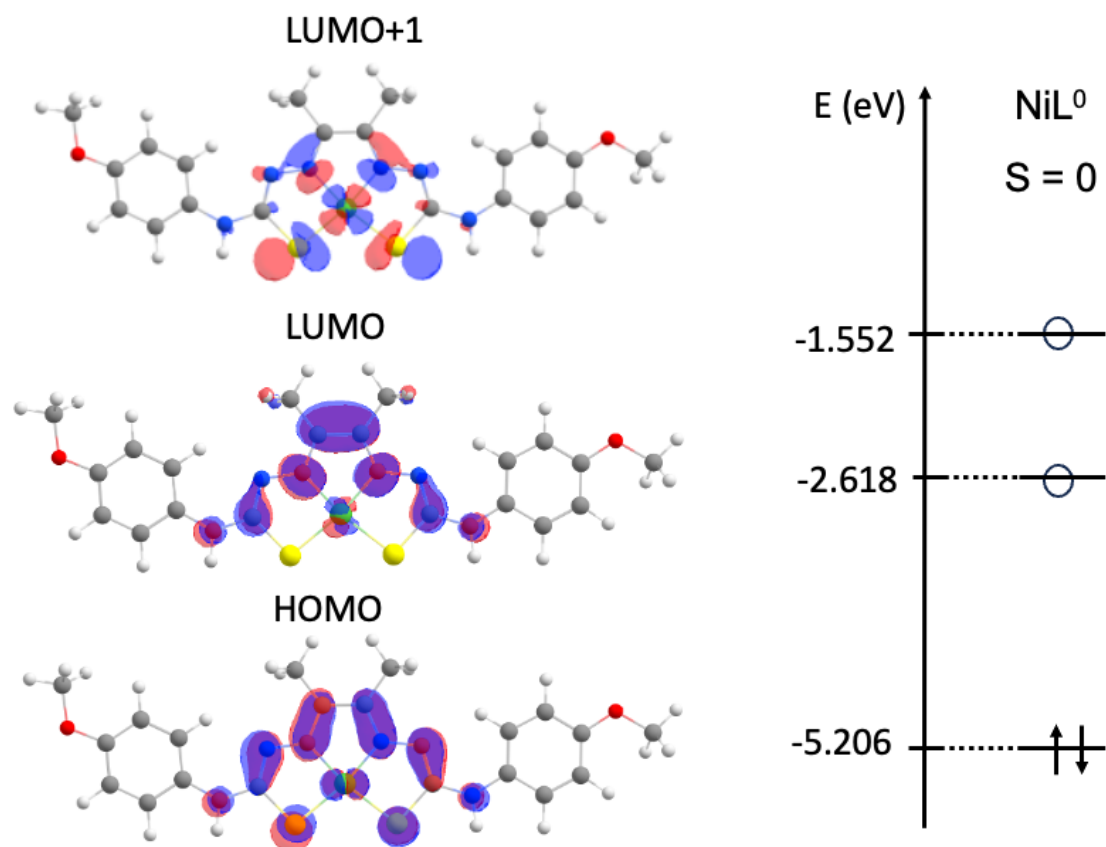
Complex / proton source	$E_{1/2}^{cat}$ (V vs. Fc <sup>+0</sup> )	$\eta$ (V vs. Fc <sup>+0</sup> )
CoTSC-OCH <sub>3</sub> / TFA	-1.28	0.294
NiTSC-OCH <sub>3</sub> / TFA <sup>6</sup>	-1.33	0.344
CoTSC-OCH <sub>3</sub> / Et <sub>3</sub> NH <sup>+</sup>	-1.48	0.311
NiTSC-OCH <sub>3</sub> / Et <sub>3</sub> NH <sup>+</sup>	-2.08	0.908

## 5. DFT calculations

We used the same methodology employed in our previous computational investigation of NiTSC-OCH<sub>3</sub> and CoTSC-OCH<sub>3</sub> catalysts. All DFT calculations were performed with ORCA program package,<sup>7,8</sup> using BP86/def2-TZVP(-f).<sup>9-12</sup> Solvation effects from DMF were included with the CPCM implicit solvation.<sup>7</sup> Oxidation states of NiTSC-OCH<sub>3</sub> and CoTSC-OCH<sub>3</sub> were determined in our previous work.<sup>13,14</sup> For the open-shell singlets, we performed Broken-Symmetry DFT calculations, using the “FlipSpin” feature of ORCA.<sup>14,15</sup> Cartesian coordinates were obtained from our previous work, where the metal center was substituted accordingly.<sup>13,14</sup> Free energy calculations were performed with the Numerical Harmonic Analysis feature of ORCA, using the “NumFreq” keyword. Finally, all potential energy surface (PES) scans were performed with a single distance constraint. The transition states were approximated as the highest point of these scans. We confirmed that those were good approximations by verifying that only one single imaginary frequency was present. All chemical structure images were generated using Chemcraft.<sup>16</sup>



**Figure S7.** Frontier orbitals of CoTSC-OCH<sub>3</sub> together with their corresponding energies.



**Figure S8.** Frontier orbitals of NiTSC-OCH<sub>3</sub> together with their corresponding energies.

**Table S4.** PES scan for the distance between the two protons forming H<sub>2</sub> for the three-proton mechanism in NiTSC-OCH<sub>3</sub> and CoTSC-OCH<sub>3</sub>, in the presence of TFA<sup>-</sup>. Energies shifted to the lowest energy point, which corresponds to the reactant state, prior to H<sub>2</sub> formation.

H-H (Å)	E <sub>Ni</sub> (kcal·mol <sup>-1</sup> )	E <sub>Co</sub> (kcal·mol <sup>-1</sup> )
0.75	4.32	3.48
0.80	5.17	4.39
0.85	6.72	6.98
0.90	10.21	8.50
0.95	41.44	40.79
1.00	55.75	54.59
1.05	49.81	48.76
1.10	44.50	43.44
1.15	39.65	38.63
1.20	35.53	34.28
1.25	31.61	30.36
1.30	28.08	26.85
1.35	24.93	23.71



1.40	23.19	21.68
1.45	20.21	18.79
1.50	17.41	16.08
1.55	14.70	13.57
1.60	12.22	11.26
1.65	9.98	9.11
1.70	8.05	7.22
1.75	6.30	5.57
1.80	4.79	4.18
1.85	3.46	2.98
1.90	2.41	1.95
1.95	1.55	1.16
2.00	0.88	0.57
2.05	0.40	0.17
2.10	0.09	-0.04
2.15	0.00	-0.08
2.20	0.05	0.00
2.25	0.25	0.30
2.30	0.57	0.73
2.35	1.00	1.35

### Cartesian coordinates from DFT calculations

- Cartesian coordinates of  $\text{CoLH}^0$  after the first PCET step (proton at  $\text{N}_d$ ), in the presence of  $\text{TFA}^-$  ( $M_s=0$ ).

C	7.30243067759414	16.04151515485567	8.22103614386849
C	7.58384486906056	17.40569794616451	8.03344380568132
C	8.79119014070075	17.92569787169609	8.51983598068377
C	9.70770296073331	17.11305223642473	9.18910947563927
C	9.41813850515335	15.75420624308887	9.38370489996213
C	8.21109981137590	15.23011974033366	8.88986071261670
N	6.74469783683684	18.29112064577918	7.31035297891280
C	5.44337227251992	18.21108667371634	6.95622524392280
S	4.83362230195408	19.28553248121777	5.73220904280824
Co	2.75357746094338	18.60803326447889	5.81461868075965
N	3.29078973196576	17.38915519621284	7.06994544032756
N	4.61356991988947	17.31838240155242	7.54255984820281
O	10.23914605468417	14.86831980473849	10.03081623380984
C	11.48017202433841	15.37847176520947	10.55212500061365
N	1.13012881722846	17.74903430123848	6.06368400096097
C	1.10815344255913	16.71444650458606	6.92540826816339
C	2.39265422311222	16.48117186408782	7.51192408309284

C	2.75237842509322	15.34941084955624	8.42062552112168
N	-0.05228823739596	18.08098556971348	5.42269411724383
C	0.12754046709626	19.08991931360552	4.60040937397483
S	1.72107514535082	19.89262935174297	4.37939608094017
N	-0.88834975556019	19.60543201693809	3.84828012175023
C	-2.24481502925454	19.24586388478090	3.74313148027684
C	-2.84508221722188	18.19408286176985	4.45192641492826
C	-4.20522975495692	17.90742792550358	4.27792033070908
C	-4.98488034373509	18.66617706336758	3.39548377506706
C	-4.38573571011323	19.72277809814075	2.68524503081692
C	-3.03867832550299	20.00634294905462	2.85730219954728
O	-6.32164047166838	18.46256282745058	3.15673932060536
C	-6.95848905109032	17.38389190501844	3.86379945867302
C	-0.13615629921508	15.92966372620912	7.19618663040786
O	4.83463258593144	17.55405668686906	10.22720619638913
C	5.04013725788137	16.74775379176170	11.18210823880584
C	5.39158550061254	17.48948085180485	12.52656465645949
F	4.33989430500581	18.25544923342401	12.95720197178972
O	4.99137089846298	15.50589259453427	11.22248222954589
F	5.69911398767436	16.64253614645527	13.54617725248743
F	6.45814384288735	18.33199920492454	12.38214940750245
H	-0.60852353597707	20.38735732846862	3.25985170989643
H	7.22083437864763	19.10225029675784	6.91780648712102
H	10.63582837161145	17.55028286853640	9.55307301178102
H	-2.58529899043523	20.82900003510048	2.29951535107137
H	-4.99208241458897	20.31490806728826	1.99811508691137
H	-4.64110745755028	17.08431097170574	4.84223002571219
H	9.02153389543002	18.98252029017679	8.37012654075711
H	-2.24383828933442	17.60246276180948	5.13842983150934
H	-0.93797931978314	16.58248775366363	7.57420604853824
H	0.04406799314787	15.14106078278805	7.93513614850930
H	-0.51731165546375	15.46159558973196	6.27521446819773
H	6.38261853937775	15.60538957969058	7.83648824352640
H	1.86553173226069	14.76263734867639	8.68307487697846
H	3.22489761063505	15.68927176259930	9.35426899937829
H	3.47146316668057	14.67186918027296	7.92943420393841
H	7.99434612248232	14.17109194627234	9.03614177660514
H	-8.00264908049472	17.39057510196156	3.53364229946771
H	-6.91282628887870	17.54175956782545	4.95237976923521
H	-6.49604619389052	16.41725993162038	3.61114506510481
H	12.11475436430801	15.77526086672380	9.74503508383131
H	11.97474245493252	14.52291350416288	11.02372466503258
H	11.30038783110047	16.16322403908670	11.30263302587558
H	4.72994449485092	17.16805247707373	8.59394563195228

- Cartesian coordinates of CoHLH<sup>+</sup> after the first PCET step (proton at N<sub>d</sub>), followed by a proton transfer (proton at Co) in the presence of TFA<sup>-</sup> (M<sub>s</sub> = 0).

C	-3.31877181021412	19.88755122628708	2.98897841268540
C	-2.50001896566073	19.09179368452383	3.81807422074525
C	-3.01443735850175	17.89257315189798	4.33280171356250
C	-4.31869926664054	17.49524598962860	4.02283380581559
C	-5.12715340334600	18.29031440369788	3.19700709270019
C	-4.61193068383492	19.49496119494026	2.68204975082995
N	-1.20123231355657	19.58013093210928	4.06838868081111
C	-0.16267424862384	19.06390468569965	4.76691001614109
S	1.33687725721028	20.03888550857879	4.75431004431566
Co	2.43333215837069	18.67955435051532	6.04933772347941
N	0.90707861846903	17.58769686741241	6.02723912086968
N	-0.26135770598612	17.90784134582895	5.40719960015513
O	-6.41182182280301	17.98714807476278	2.83986595575284
C	-6.97054713774247	16.76144924659597	3.35082105355044
S	4.41943912255349	19.57818283489404	6.12243795923354
C	5.13440326990267	18.35906199122924	7.15898969825810
N	4.41824470805826	17.29329857562944	7.57239463317868
N	3.13239414934189	17.26731716293552	7.06024154791761
C	2.34273968800088	16.21897247292034	7.23194257779020
C	2.75081281192929	14.95224082165908	7.90476067442479
N	6.41425715437371	18.52141831635287	7.53198993730492
C	7.33099589524075	17.61665767165736	8.13243301084433
C	7.25655529516645	16.22443461234658	7.95944691063600
C	8.22320913457353	15.40447326338746	8.52562922435964
C	9.28435895772409	15.95267439154538	9.26951360434478
C	9.37014761304062	17.34483476458473	9.42758783707285
C	8.39495718623741	18.16514876119940	8.85893904009150
O	10.17612456022281	15.05690485851404	9.78784461249770
C	11.27838234238398	15.58303651713950	10.55265445904831
C	1.02274381955580	16.42097388150064	6.64958157510414
C	-0.08904214347495	15.42835468062913	6.71502755291545
O	4.69323468813441	18.60076904343805	10.72400129976475
C	4.66763372677910	17.37237436592189	10.86587523608729
O	4.60679268109945	16.44450349760764	9.98817048115263
C	4.69216492750530	16.79822335214591	12.32748502492224
F	4.87584898395199	17.76222886829379	13.26479337723587
F	3.51353175411999	16.17111534373543	12.62487176026298
F	5.68639541622340	15.87993338167226	12.49875054521840
H	-0.99883026437796	20.47572398575233	3.62543207205610
H	6.79728670508920	19.44056617671478	7.31201604159412

H	10.18410269178445	17.79963066173010	9.98909845619051
H	-2.92709742733470	20.82278697893035	2.58376095902630
H	-5.24096014117823	20.11297049461840	2.04012953393123
H	-4.69196183908317	16.56020601264240	4.43724495595596
H	8.46273800105622	19.24740404432239	8.98392536277113
H	-2.39553712298786	17.27136621682508	4.97501735125364
H	-1.03029512481822	15.93259177437641	6.97396870826402
H	0.11651437149286	14.65119198966058	7.45873063631561
H	-0.24049513716039	14.94335211103153	5.73718089064926
H	6.45568718145423	15.77978092702470	7.37113756451496
H	2.26927504363987	14.09363513765188	7.42049929535861
H	2.45276436595455	14.95319677422372	8.96485793481816
H	3.83784903773142	14.81862401530339	7.86317157207157
H	8.17375117135776	14.32311472895611	8.39181150503492
H	-7.98790301522981	16.71338377258797	2.94924236417210
H	-7.00482130632802	16.77289179551840	4.45057787738796
H	-6.39255983073645	15.89123508013713	3.00523887794216
H	11.90695353098106	16.24167739930562	9.93485573452910
H	11.85735071593679	14.70995321435513	10.87041634883894
H	10.91803488743979	16.13194356005037	11.43549958096287
H	4.55530554703611	16.90570628007259	8.63946020635869
H	1.96737789849627	19.35770577479003	7.22649039892101

- Cartesian coordinates of CoHLH<sup>0</sup> after PCET and proton transfer step (protons at N<sub>d</sub> and Co), followed by a reduction in the presence of TFA (S = ½).

C	-3.21356481374867	18.62242882688124	1.39327219649187
C	-2.50956396623530	18.25643323483825	2.56249508260241
C	-3.19409057382464	17.54607093081338	3.56172452043909
C	-4.54488905539506	17.21100003272176	3.39716679622989
C	-5.23331997237292	17.57880524147588	2.23461431493688
C	-4.55073947967415	18.29055919298623	1.23096926700021
N	-1.15933962751151	18.63514293446387	2.63584810776184
C	-0.21728956700221	18.45228847271325	3.61701831906285
S	1.40757624278438	19.08478802079497	3.25485601063302
Co	2.23560471831136	18.59400360799428	5.23026827825064
N	0.59797342468780	17.77780193007630	5.57539422230828
N	-0.49960438578504	17.84790746785447	4.75333897316850
O	-6.55472576805634	17.29726125017160	1.98119518540343
C	-7.27508924981919	16.57020837376237	2.99102975345994
S	4.37641195111823	19.06815807321529	5.03079919671313
C	4.84553399276885	18.55301232948612	6.62333495800628
N	3.93556139150423	17.96680115163007	7.42830664807692
N	2.67587147869686	17.81873211675823	6.86044151167510

C	1.70467972490353	17.12446512690179	7.49712832821461
C	1.94391834625599	16.42946162397220	8.79942219519009
N	6.12015600280455	18.77350490885822	7.03820918332099
C	6.90012520599853	18.14611500410229	8.03966525977856
C	6.56190508060920	16.92298992957308	8.64423197898487
C	7.41760505072704	16.34626496014704	9.57590255426940
C	8.62669611975742	16.96918712384902	9.92780791411591
C	8.97194323271999	18.18691015102700	9.32303677024928
C	8.10889121168738	18.76495558643910	8.39035775609041
O	9.39339299451715	16.31613149441328	10.85941369947653
C	10.63593987854451	16.93422077313761	11.23919165770977
C	0.49220562309719	17.11718450542788	6.75400974883765
C	-0.78904582110116	16.46304085528063	7.16624905922768
O	4.01493994576626	19.01649281052995	9.89320239714452
C	4.17007271555868	18.53401325660107	11.05561544825507
O	4.14464704014145	17.35974544754067	11.45934054015043
C	4.41626356196425	19.65404459195317	12.13531088059495
F	5.49736780848482	20.43155038103095	11.82484595952531
F	3.33997956864326	20.49624479656424	12.23160122102980
F	4.63699679690671	19.16048369098467	13.38387165621200
H	-0.81380048374912	19.13952928168443	1.82283862011540
H	6.63524097898807	19.41454707546487	6.43738539070608
H	9.90284484693822	18.69537712084444	9.56840038606224
H	-2.69650905330612	19.17507206242202	0.60533905575483
H	-5.08519459453867	18.57876031355710	0.32432290054184
H	-5.04512083301108	16.65954072029053	4.19211068565160
H	8.38375020397529	19.71220569006603	7.92179664308001
H	-2.66662444762978	17.25775653584699	4.46799396406358
H	-1.59829165512870	17.20440465971158	7.26031770780508
H	-0.68209486707123	15.94908325556213	8.12807377970428
H	-1.11840275460790	15.72927050033363	6.41431305204870
H	5.63787055596952	16.40987405675552	8.38497829375468
H	1.08199384321984	15.81516821312006	9.08083059061916
H	2.14513969943402	17.13580266921523	9.61854421344947
H	2.82476345444443	15.77100373466701	8.72929145822049
H	7.15517319886986	15.39661705533320	10.04425362126798
H	-8.29151235974923	16.45099379602823	2.60090578980298
H	-7.30548926429743	17.13098474785892	3.93813758604475
H	-6.82603084541523	15.57974218702545	3.16330985986834
H	11.30942651507889	17.03318437407826	10.37398636536014
H	11.08401685689531	16.26424427832029	11.98049163916927
H	10.46420221680407	17.92376691643729	11.68973519616504
H	3.98675619543764	18.16526519465375	8.48219506961228
H	1.84893376401658	19.88738235375203	5.81452758053397

- Cartesian coordinates of CoH-LH<sub>2</sub><sup>+</sup> after third proton transfer step (protons at both N<sub>d</sub> and Co) in presence of TFA<sup>-</sup> (S = ½)

C	7.96845201720491	18.72542697783052	8.37977954034094
C	6.82985657108870	18.10531686061826	7.84927479853697
C	6.57212868179495	16.76026873625231	8.16510411889652
C	7.43319058791939	16.06600214798089	9.00567331146719
C	8.57108018948186	16.69160243480873	9.54534011265920
C	8.83935660960099	18.02983569332345	9.22075323478991
N	6.03150812380545	18.85764944808241	6.95052269080929
C	4.74325350659328	18.69739610044653	6.57003640729412
N	3.88012459094668	17.97120585114049	7.30622340921952
N	2.60566564557525	17.89039337175355	6.76984925486209
C	1.67351724724679	17.07475528801118	7.31278974000897
C	0.42681655910496	17.16641343489729	6.62887198031308
C	-0.83203568035426	16.43586129850570	6.96778243600939
O	9.35021139253605	15.91841946192531	10.36436093447032
C	10.52212613948887	16.53165622325216	10.93333766762393
S	4.19952020938823	19.47099151111987	5.10614615258781
Co	2.09172118600367	18.91842925260705	5.30897352849424
N	0.49743871727034	18.02478597107297	5.58920630257166
N	-0.59532634058306	18.27376679197722	4.79218585603245
C	-0.41226478657237	19.10138619991037	3.74494679130891
S	1.17373016744588	19.75220687096169	3.48309500172361
N	-1.43995763430944	19.41878984449841	2.92778840198313
C	-2.75949075631896	18.88714526958093	2.93371484338670
C	-3.83688587817772	19.76755435651955	2.73234625308906
C	-5.13812780817491	19.28494105323610	2.69441765464374
C	-5.39329765158392	17.91188102169504	2.87085402872095
C	-4.31963062660475	17.02900773498486	3.06208742415769
C	-3.00949555618638	17.51706094132705	3.08038061617235
O	-6.70682450415439	17.53811627068554	2.83334590340395
C	-7.00363687725350	16.13769206213736	3.00009248382076
C	1.95903528623761	16.16470651145704	8.46349633264253
O	4.20630752998280	20.35789731353725	9.81654891757921
C	4.13822156777329	19.26518538006452	10.39985877186516
C	4.18181701891070	19.27810223506163	11.97179782948262
F	3.04464224789114	18.73744737177902	12.50711384990927
O	4.02980387296802	18.08671830503888	9.93212741826381
F	5.23178795136526	18.54732343346336	12.45241442705859
F	4.30303657874603	20.52863663592525	12.48972653231785
H	-1.25800081431725	20.19219718836990	2.29055752179328
H	6.52103374341856	19.59963073391826	6.45282241419184

H	9.71555136113142	18.54123708329081	9.61539207465303
H	-3.64673955188929	20.83463538597491	2.60736807279421
H	-5.97657794343867	19.96475783182995	2.53751743362368
H	-4.48483411643288	15.95936132616038	3.17687970639719
H	8.17974473722615	19.76728722380897	8.13147031836782
H	-2.18428962399034	16.80999970969026	3.17258556078968
H	-1.64229971067905	17.13328017451582	7.23934345160784
H	-0.68165999016039	15.76533889283245	7.81983918151897
H	-1.18247019856994	15.82484823154162	6.11976360164055
H	5.70780440433558	16.24845195418930	7.74520530723803
H	1.18308081735562	15.39673675835755	8.55337106820729
H	2.01853044407315	16.71178957514872	9.41638319823596
H	2.92583350430112	15.65885059328070	8.32113858264236
H	7.23748181557457	15.02091099408051	9.25000991861867
H	-8.09436337807894	16.06130228320319	2.94632023074425
H	-6.65281381955371	15.77489675832452	3.97785846188554
H	-6.54873182864680	15.54084179042195	2.19549992962573
H	11.22003293509193	16.85538162788517	10.14625406297644
H	10.99144011746758	15.75550080545975	11.54669139096180
H	10.25047773263836	17.39075597501098	11.56517580106522
H	3.97717020399060	17.98285200531008	8.40538812615134
H	-1.52773881156282	17.99316929420192	5.10366686222688
H	1.74443987461800	20.08369413572264	6.12228976352482

- Cartesian coordinates of **Co-LH<sub>3</sub><sup>+</sup>** after third proton transfer step (protons at both N<sub>d</sub> and N<sub>Co</sub>) in presence of TFA<sup>-</sup>, used for the H<sub>2</sub> potential energy surface scan to study tunnelling (S = ½)

C	8.32365589592105	17.95861337334109	8.27863836634352
C	7.12141754456418	17.43769486581538	7.78679190056211
C	6.77295913491386	16.10917910278378	8.08153244591083
C	7.60865033502483	15.33202175074604	8.87460273466925
C	8.81271748723110	15.85732499874548	9.37713674484769
C	9.17161752266480	17.17838105416006	9.06738144916938
N	6.33522273609770	18.26885090555353	6.93819422358537
C	5.00014469502412	18.33334295907358	6.78438266864033
N	4.18406780278262	17.60035955763163	7.57484213764445
N	2.77069145312736	17.94703055899150	7.46752470276050
C	1.86446309859737	16.78981685839988	7.60426134993751
C	0.71059106674661	16.95033466603997	6.88834483169935
C	-0.49204635750567	16.05832293690385	6.94245918555199
O	9.56185902413301	15.00943347262525	10.14477943543614
C	10.80503426560252	15.51389564853537	10.66965411217677
S	4.35831333144480	19.36175713009423	5.53099238806198

Co	2.25967540720051	19.00078377878953	5.92227258628224
N	0.72012929941946	18.06130602363438	6.05087628357554
N	-0.38527432884794	18.35080833577229	5.27707517673783
C	-0.27152093479261	19.38870758171403	4.43337264014045
S	1.25131432529107	20.21528828056077	4.40213290684848
N	-1.31108754504001	19.78436722468299	3.65097463797212
C	-2.56369179770238	19.14835509790351	3.46049298098449
C	-3.70355499936230	19.95669183114457	3.29295495980396
C	-4.94723619272398	19.38353811673162	3.06292569562812
C	-5.08809820252283	17.98454685166083	3.01067444877999
C	-3.95533292139212	17.17364998561004	3.16972830305237
C	-2.70074641585699	17.75600858421733	3.38130320132478
O	-6.35681046925015	17.51656174247718	2.79716819433485
C	-6.53077322721360	16.08909586909813	2.72642983800556
C	2.22765105587788	15.69476175465331	8.54880500944533
O	2.77290111775377	19.32521968150344	9.89809735878726
C	3.63829102352037	18.74537793108232	10.60531501662928
C	3.68842795841369	19.25268626743111	12.08894451872299
F	4.62375573640500	18.62333995390502	12.84461722702096
O	4.45055296809097	17.83428360081898	10.29995024606206
F	3.96582832537943	20.58881409147747	12.14019963822759
F	2.48498242519656	19.07017550329666	12.70825361278217
H	-1.20425807095971	20.70834652962008	3.23893178760832
H	6.85395327393100	18.93698164979338	6.36962148828590
H	10.10041996098577	17.61113254698353	9.43458691299768
H	-3.60690263259254	21.04259652645490	3.34485285019655
H	-5.82956469740391	20.01136843188939	2.93112585780667
H	-4.02782257154025	16.08893813378618	3.11318424962759
H	8.60399476186119	18.98675601674216	8.04274355420158
H	-1.82587731656131	17.10811064912744	3.44245807950513
H	-1.38037476404274	16.60591412105806	7.29744927233341
H	-0.33121116639011	15.21911151246520	7.62649357549045
H	-0.72204043295150	15.64304706576199	5.94877910697840
H	5.86013661982227	15.67262761700455	7.67866758458099
H	1.42919796457349	14.94572297193414	8.60007977490115
H	2.40753674672527	16.07196468275488	9.56873495166964
H	3.14645057023500	15.17592140825711	8.22981469353482
H	7.34400364445836	14.29917991541213	9.10476800334887
H	-7.60057737751269	15.93159466491561	2.55487396952487
H	-6.23093983243897	15.60804666743987	3.66983214761887
H	-5.95398912112573	15.66232004311810	1.89195801014685
H	11.48902518473893	15.79958490283607	9.85635526394389
H	11.23740598815743	14.68768469774205	11.24326208884469
H	10.63259657127967	16.37571658856323	11.33165718384442



H	2.62107490400571	18.58041242257491	8.31086714720219
H	4.45361631636036	17.51958378872563	8.59893085379418
H	-1.29229716782904	17.94230451743331	5.51095843386731

- Cartesian coordinates of  $\text{NiLH}^0$  after successive reduction and proton transfer steps (proton at  $\text{N}_d$ ,  $S=\frac{1}{2}$ ).

C	-2.79710519914366	18.16151836387775	4.58108724007778
C	-2.21019245144145	19.13894088186046	3.76151101814720
C	-3.04004599558704	19.86816568479837	2.88067427326652
C	-4.40540739875369	19.62860793705286	2.82316414016108
C	-4.99028180403173	18.64855553679179	3.64642059221972
C	-4.17625767493111	17.91990492901882	4.52280648965326
N	-0.84093711043408	19.45061295464436	3.74833805368446
C	0.21142529567540	18.94970587524001	4.47009741477806
N	0.05998423130340	17.97322823755692	5.34246033298196
N	1.22234199062466	17.69539369498749	6.00059347175299
C	1.27773094028572	16.63331281980619	6.84090760084232
C	0.07332758871461	15.78632166251600	7.10319466671893
O	-6.34662638263605	18.48380529107095	3.51759393164818
C	-6.97230971829224	17.48804974428189	4.34084012849341
Ni	2.85380591263469	18.53451730194399	5.64447376268338
S	1.79233373865647	19.69912313212715	4.13970224084720
N	3.49578144872308	17.23050715912500	6.80092200353419
C	2.57193746807164	16.43561401621374	7.39514490123570
C	2.93744852505048	15.49800020801463	8.50034519057566
N	4.77056784695880	17.34457691217995	7.30376747051739
C	5.55669692895385	18.30603859048452	6.79453752373224
S	4.85306907322923	19.44766650157863	5.69520451207964
N	6.86921577008667	18.38398569277378	7.13293911302297
C	7.63844383509134	17.45624631807916	7.88282925740995
C	8.57508887784279	17.94553610217793	8.80228561786432
C	9.38828246619012	17.07324410869592	9.52942639608249
C	9.25711987314140	15.68644723785865	9.35334211528973
C	8.32323675390396	15.19351830633445	8.42457382062694
C	7.53041726283437	16.06683341907239	7.68757413777053
O	9.98980725705202	14.74796295368570	10.02345260207704
C	10.96392825535608	15.21430764953655	10.97281601729209
H	-0.57770003669340	20.17846537965712	3.08786818520505
H	7.31309553133282	19.27335561491674	6.91385473589202
H	10.10923169625923	17.48484026674603	10.23365414521121
H	-2.59943894388634	20.63183477661629	2.23543511909498
H	-5.03791255157909	20.19698120214918	2.13940168031227
H	-4.59918862137558	17.15445480563429	5.17204117755608
H	8.67090609674053	19.02237571529174	8.95143413760994
H	-2.17132619095049	17.59052049065864	5.26293537395325
H	-0.75818017177992	16.38992228862499	7.49874746552169
H	0.29652413143252	14.98871213823864	7.82081810131330
H	-0.28807651467876	15.32148281752374	6.17231529864984
H	6.85391667413146	15.66348418142445	6.93328446262019

H	3.70985110652020	14.77572268222447	8.18626761153073
H	2.06692149925964	14.92465673764706	8.83555326387751
H	3.32919117644743	16.04362464937425	9.37593039799333
H	8.24282085541378	14.11640276531628	8.27229253201478
H	-8.03689934736113	17.51751199236162	4.08523955402302
H	-6.84194779305619	17.71707617241928	5.41016507515869
H	-6.56831790735862	16.48581695313653	4.12810794997888
H	11.73038358239940	15.83222162295694	10.48054094747369
H	11.42656883666117	14.31257614841841	11.38709466323054
H	10.48544378293499	15.79009240827105	11.77968161565220
H	5.09504750405662	16.70022796700614	8.02728246905943

- Cartesian coordinates of  $\text{NiLH}_2^+$  after reduction and two successive proton transfer steps (both protons at  $N_d$ ,  $S=1/2$ ).

C	-2.79429351320412	18.91568380020055	4.95206171061773
C	-2.16480851753084	19.17399614936522	3.72793354152906
C	-2.89217400969443	19.03543200206526	2.53308855544331
C	-4.21911909743383	18.62838858965822	2.56528522308667
C	-4.84480083521311	18.33810491669285	3.79261385324009
C	-4.12461715660855	18.48731515545810	4.98813245948454
N	-0.81819776785932	19.62702779217472	3.65132062129271
C	0.25023818607434	19.18479376306848	4.34649129336522
N	0.14603243460626	18.10278249017168	5.14201279767279
N	1.23442193643796	17.77597567784653	5.90805954335589
C	1.29755766755833	16.60337820989033	6.56919186480774
C	0.14463044673178	15.65577067411621	6.62584685283509
O	-6.14380428590971	17.92971695075576	3.71927750854822
C	-6.82043100317572	17.62226397632674	4.95141353001728
Ni	2.83149672915632	18.71620808126975	5.67960122103715
S	1.78207694451339	19.98335447777430	4.22224838906637
N	3.47965844108124	17.30417828412224	6.71709094794359
C	2.58142748818060	16.40622398382122	7.16689016052944
C	2.93172267615245	15.36372301962142	8.17710920264158
N	4.73400410569062	17.39120448953391	7.26229130674275
C	5.49352761479187	18.44432056989726	6.90412418088011
S	4.78620105996415	19.69007612681643	5.92989901494671
N	6.77719130465173	18.52969230080933	7.30956179266902
C	7.54838914456443	17.55009905863067	7.99535862189875
C	8.39339900443519	17.96779762343003	9.03046246291172
C	9.19823519201183	17.04934616357616	9.70717264427429
C	9.15139573744314	15.68974480369213	9.35733753413443
C	8.31059826283447	15.27261423924708	8.30932624666619
C	7.52447136848333	16.19344467962300	7.62596870942633
O	9.88359699060840	14.71121896674538	9.96230241382283

C	10.76457868409925	15.09785581163214	11.03246600342829
H	-0.60400466910104	20.30561289102770	2.92232081258151
H	7.20912554753835	19.44252339465942	7.17674354039340
H	9.84691248381894	17.40191511456169	10.50704447030987
H	-2.40874253053941	19.24705836837296	1.57803501753754
H	-4.78799614584252	18.51888211814846	1.64111708584294
H	-4.59043110479976	18.29514863848808	5.95288759195519
H	8.42186789056660	19.02165110177573	9.31250703766341
H	-2.26661295893188	19.08024035275283	5.89225709068306
H	-0.73827594053745	16.11896872103446	7.09594056479771
H	0.39779183908075	14.76015484576078	7.20207104188764
H	-0.14640220443197	15.32637400201598	5.61438214663150
H	6.92162054613316	15.85801548250395	6.78132386060370
H	3.75234877670273	14.71766450862051	7.82494204764647
H	2.07265378091621	14.72150447864662	8.39575987142923
H	3.25028678859426	15.82460541752819	9.12727270276221
H	8.29930122310729	14.21984927900590	8.02449694526230
H	-7.83045100162028	17.31391901526816	4.66290854478341
H	-6.87408116761259	18.50719249550633	5.60337127932377
H	-6.31747290429753	16.79939213424015	5.48170456578460
H	11.53075662014193	15.80305599840824	10.67632326886402
H	11.24178959328043	14.17181147199822	11.36889771536772
H	10.20105015544895	15.54878005512029	11.86321259369395
H	5.04773192720825	16.70107355305968	7.94786838689913
H	-0.68408977826482	17.50612973346250	5.14329160897983

- Cartesian coordinates of  $\text{NiLH}_2^0$  after successive reduction and proton transfer steps (both protons at  $N_d$ ,  $M_s=0$ ).

C	-2.75960723832609	18.85282388948297	4.83668475586606
C	-2.14458569416957	19.03808939100504	3.58910012587431
C	-2.92926274724936	18.92458893124195	2.42474429207819
C	-4.28407071667078	18.62822514513648	2.50812898662774
C	-4.89159238272137	18.41735834856691	3.75911496490526
C	-4.11954101684782	18.53296901839639	4.92372608819579
N	-0.78199334866812	19.38712822372680	3.45201335282880
C	0.28594168870104	18.98619894011207	4.21306432099655
N	0.17719804290345	17.96270612645466	5.06768948473302
N	1.17931993199079	17.78615578607587	6.01585309983113
C	1.29089160460544	16.53980375643756	6.62220180503664
C	0.14818237872587	15.57126684335856	6.61330174167166
O	-6.22678999938669	18.11182507635245	3.73737671725173
C	-6.87826511725404	17.89579818839302	4.99936545985324
Ni	2.80152354759308	18.68390938505699	5.72552795789977
S	1.81030440018705	19.79289942047516	4.10869828053108
N	3.49397748897244	17.22153452228014	6.67621644989221

C	2.54527274956875	16.34335592215759	7.18827960678538
C	2.91121904821621	15.33476142683109	8.23368039351370
N	4.65193372036266	17.43585211235224	7.41623081640698
C	5.38000489832544	18.52706193753555	7.15222253514681
S	4.65865353873495	19.76505218600241	6.18685564966509
N	6.66248556830099	18.64882762033953	7.62220305346157
C	7.49201200720372	17.64720722578193	8.17705292455526
C	8.36930568171249	17.99219453461818	9.21536921581332
C	9.24631473266809	17.05117806717720	9.76184247247802
C	9.24114496863762	15.73159477953167	9.28470620590748
C	8.36727560045848	15.38172895636101	8.24085562184712
C	7.51145549975048	16.32715157787380	7.68429740759794
O	10.04465022707648	14.72931789919355	9.76025932974286
C	10.95482302700154	15.05629415993825	10.82261310186228
H	-0.53057663304520	19.89729138251071	2.60913333843086
H	6.99502326158194	19.60650345370875	7.70137272285241
H	9.91697377633355	17.35647322758143	10.56349420037024
H	-2.46560271136659	19.07189290400495	1.44738722800708
H	-4.88795540012741	18.54396361569013	1.60331124594410
H	-4.56424264279579	18.39635198111296	5.90811224904761
H	8.36914545769982	19.01333119502982	9.60182675003483
H	-2.19461242580765	18.99101829756059	5.75898075032247
H	-0.78487726544918	16.02140232608657	6.99412422719340
H	0.37082218304311	14.69958190321505	7.23974166016095
H	-0.05960142336151	15.19351859891135	5.59630688144539
H	6.88202196392387	16.04130354576746	6.84101388048769
H	3.77340894348837	14.71491523377669	7.93249354121794
H	2.07326257370862	14.65628109970840	8.43185567631249
H	3.17082265729109	15.81642145330414	9.19326010381594
H	8.38226374826487	14.36081324822571	7.85623153074864
H	-7.92110557402414	17.66432634268572	4.75836335500619
H	-6.83506647840157	18.79899631950723	5.62759758768473
H	-6.42578478535421	17.04912529632062	5.53872437021753
H	11.67021532516087	15.83155194679167	10.50698812317536
H	11.49202612591643	14.12902617155070	11.04791825883685
H	10.41255037593072	15.39710396392994	11.71821522479823
H	4.99114111481069	16.70035518479413	8.03843013474152
H	-0.67115725782393	17.39684490997820	5.12446074029047

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