

**Using EPR to following the reversible dihydrogen addition to a paramagnetic
cluster of high hydride count: $[\text{Rh}_6(\text{PCy}_3)_6\text{H}_{12}]^+$ and $[\text{Rh}_6(\text{PCy}_3)_6\text{H}_{14}]^+$**

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Supporting Materials

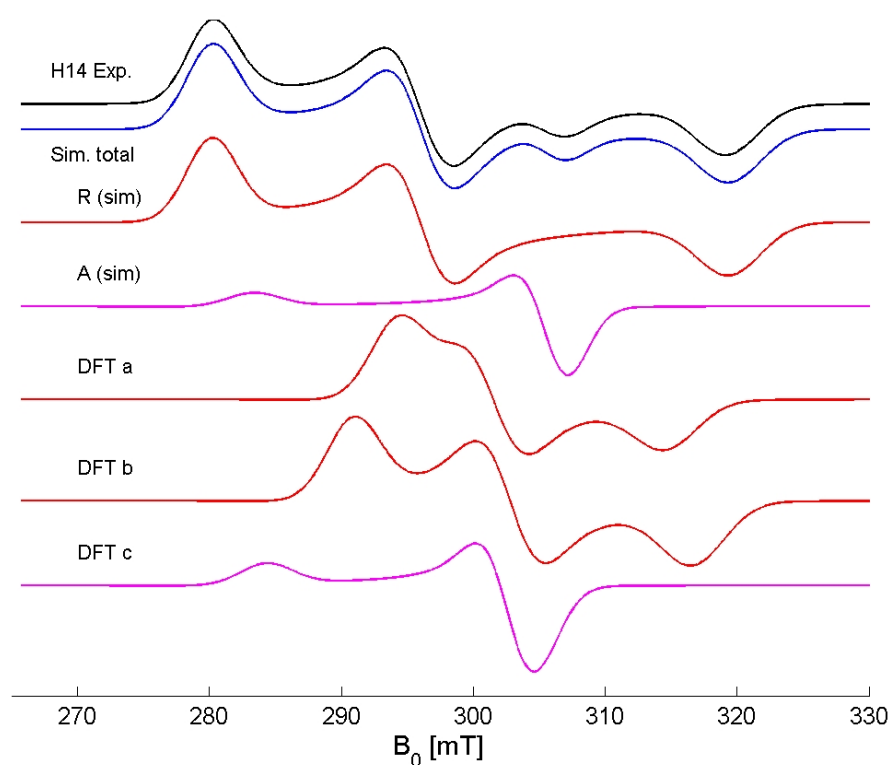


Figure S1. X-band (9.3896 GHz) CW EPR spectrum of **Cy-[H14]⁺** in **C₆H₄F₂** recorded at 20°K. Experimental trace (black), and simulation of the sum **R[•]+A[•]** (blue) and the components, isomer **R[•]** (red), isomer **A[•]** (magenta). The spectra calculated using the DFT g-values for calculated structure a, b and c, are indicated. The colour match between experimental and DFT isomers indicate our assignment. For isomer **A[•]** a good absolute match is observed, whereas for isomer **R[•]** both DFT structure a and b have the correct g-values order and rhombicity, but the DFT calculated values are all too low.

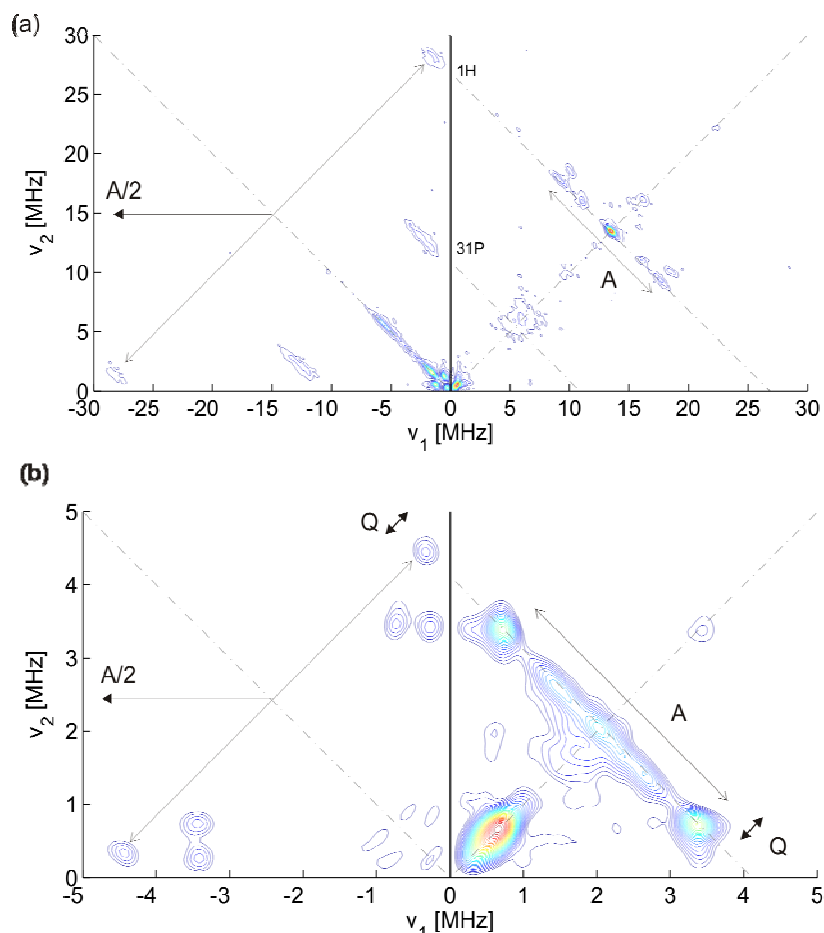


Figure S2. X-band hyperfine sublevel correlated (HYSCORE) spectra of (a) **Cy-[H14]⁺** and (b) **Cy-[D14]⁺**. Spectrum (a) shows ¹H signals with hyperfine couplings *A* from *A*~0MHz (peaks at +15,+15) to *A*~30MHz (cross-peaks in the (-,+) quadrant at (-26,3)MHz and (-3,26)MHz). Indicated are ³¹P signals observed in the (-,+) quadrant with hyperfine couplings *A*~6-18MHz. According to DFT both the interstitial proton (*A*_{DFT}=[-15,-2,1]MHz) and hydride proton hyperfine couplings (*A*_{DFT}=0-20MHz) have a similar range making assignment base on this spectrum impossible. (b) Deuterium signals are observed with hyperfine couplings corresponding to those observed in the ¹H sample (*A*(²H)=*A*(¹H)/6.5144). The nuclear quadrupole interaction would split the ²H signals in each quadrant in the directions indicated by the arrows (labeled with *Q*). A lack of resolved splittings shows that all the ²H quadrupole couplings are small (<0.5 MHz). According to DFT the interstitial proton has a smaller quadrupole coupling (*Q*=[-7,-1,8] kHz) than the hydride protons (*Q*~[-25,5,20]kHz) but all are too small to be resolved by the HYSCORE data.

Experimental (Fig S2): The HYSCORE experiments at 7.5K (²H) and 15K (¹H) at 9.716GHz and 312mT employed the pulse sequence $\pi/2-\tau-\pi/2-t_1-\pi-t_2-\pi/2-\tau$ -echo with mw pulses of lengths $t_{\pi/2} = t_{\pi} = 16$ ns, $\tau = 116$ ns, and starting times $t_{1,0} = t_{2,0} = 64$ ns with increments $\Delta t = 16$ ns (data matrix 256×256). An eight-step phase cycle was used to remove unwanted echoes. The HYSCORE data were processed with MATLAB 7.0 (The MathWorks, Inc.). The time traces were baseline corrected with an exponential, apodized with a Gaussian window and zero filled. After a two-dimensional Fourier transformation absolute-value spectra were calculated.

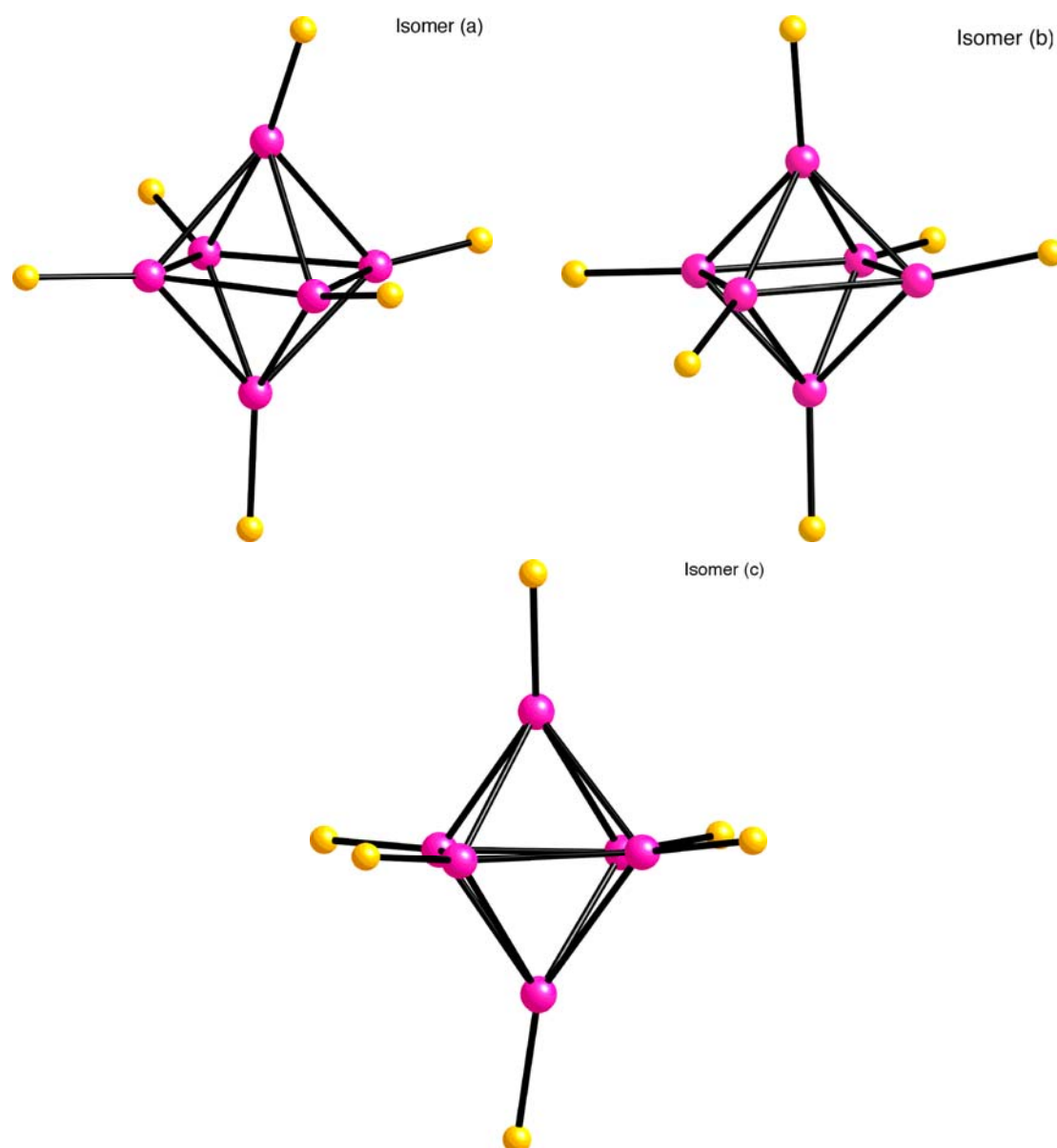


Figure S3. {RhP}₆ cluster cores for the calculated isomers (a) – (c) highlighting the pseudo symmetry associated with each: (a) C_s; (b) C₁; (c) C_{2h}.

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[H14]⁺ Isomer A

Rh 0.094893 0.068823 -0.033270
Rh 2.857114 -0.026348 -0.000996
Rh 1.586574 2.336647 0.017168
P 1.526272 4.346700 0.900185
H 1.621264 5.483603 0.045090
H 2.538572 4.705464 1.840980
H 0.378079 4.742528 1.652767
H 0.132080 1.427355 0.928148
H 2.811251 1.457314 0.969950
H 0.424583 2.989747 -1.061003
Rh 1.498405 -0.760130 -2.202856
P 1.109895 -2.186486 -3.829953
H 1.842627 -3.414487 -3.841122
H -0.201928 -2.725277 -3.989462
H 1.331428 -1.801786 -5.188225
H 0.291525 0.111567 -3.127052
Rh 0.101576 1.719367 -2.348849
P -1.192371 3.400647 -2.923240
H -2.220974 3.814418 -2.023170
H -0.597905 4.679932 -3.144380
H -1.976563 3.339017 -4.111475
H 1.614538 2.250126 -3.168265
Rh 2.975006 1.596899 -2.269918
P 4.328923 2.035067 -3.922643
H 3.864798 1.887595 -5.263872
H 5.534155 1.277063 -4.040992
H 4.890306 3.346389 -4.043368
H 2.863339 0.181727 -3.116706
H 2.851378 2.936973 -0.831494
H -0.488434 1.092640 -3.677003
H 0.288686 -1.397739 -1.225740
P 4.408920 -1.045018 1.169019
H 4.035031 -2.150246 1.989972
H 5.139415 -0.291189 2.135092
H 5.507753 -1.644893 0.486287
H 2.743671 -1.403140 -1.014471
H 4.015711 0.687110 -1.106789
P -1.547618 -0.695064 1.198038
H -1.337099 -0.782638 2.607157
H -2.814213 -0.037395 1.217940
H -2.008892 -2.027818 0.968088
H -0.973772 0.893085 -1.152649
H 1.447628 -0.616342 0.897448
H 1.491629 0.853472 -1.166425

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[H14]⁺ Isomer B

Rh 1.204879 1.395027 -1.930992

Rh	-0.011087	0.077952	0.025743
Rh	2.771423	-0.05367	-0.173439
Rh	2.573861	2.693508	-0.046727
Rh	-0.046495	2.699422	0.048814
P	-1.631048	4.221099	0.271485
H	-2.682852	4.263732	-0.691874
H	-2.441375	4.254726	1.446584
H	-1.273459	5.602884	0.242551
H	1.264153	3.871348	0.024314
H	-0.055589	2.642086	-1.68037
H	0.1837	2.56196	1.780309
H	-1.196059	1.437425	0.107161
P	4.303276	4.06174	0.011854
H	5.055422	4.280947	-1.183186
H	4.089117	5.428344	0.363693
H	5.400189	3.809271	0.888937
H	2.358685	2.578369	-1.952824
H	3.734677	1.436348	-0.1947
H	2.672028	2.689789	1.599218
P	4.813866	-0.889067	-0.168622
H	5.8448	-0.240417	0.575139
H	5.508131	-0.99768	-1.411564
H	5.046124	-2.21516	0.29885
H	1.281388	-1.084742	-0.105821
H	2.393499	-1.60768	-0.248461
H	2.719813	0.051112	1.611371
Rh	1.390912	1.324561	2.003251
P	0.6827	1.488183	4.085084
H	-0.710358	1.730272	4.265532
H	0.817564	0.37827	4.968057
H	1.186679	2.505032	4.954203
H	0.292642	0.062524	1.860947
H	2.507394	0.291293	2.622207
P	-1.298936	-1.714489	0.139581
H	-1.060196	-2.730072	1.116444
H	-1.433542	-2.571387	-0.993053
H	-2.689879	-1.524227	0.403647
H	-0.111676	0.071814	-1.646474
P	1.219363	1.482497	-4.127628
H	0.599339	2.604067	-4.756063
H	0.580245	0.444097	-4.87178
H	2.458307	1.50705	-4.832927
H	2.443049	0.202723	-1.90994344

[H14]⁺ Isomer C

Rh	1.15898447	1.42736343	-2.07328389
Rh	0.03741770	-0.03464904	0.12596343
Rh	2.72666007	0.03471229	-0.14049560
Rh	2.60293863	2.72790885	0.01125459
Rh	-0.08170079	2.65871585	0.10820845

P	-1.77213000	4.14413615	0.12425346
H	-2.84308259	3.97253093	-0.79587317
H	-2.55035962	4.31329787	1.30372494
H	-1.50349407	5.51669544	-0.13827341
H	1.26845293	3.85014884	0.06359288
H	-0.12733858	2.65921410	-1.59841434
H	0.17118158	2.49459223	1.91131661
H	-1.17898254	1.30599103	0.17057694
P	4.16831438	4.32997896	-0.19892662
H	4.80014773	4.56485667	-1.45258710
H	3.84115611	5.67714740	0.11438328
H	5.34547543	4.22164296	0.59535963
H	2.36901356	2.70838844	-1.70854894
H	3.81260015	1.40127737	-0.15933496
H	2.58940440	2.66549732	1.79389331
P	4.44338598	-1.36857574	-0.48773228
H	5.52166468	-1.43424903	0.44043858
H	5.23049105	-1.18438236	-1.65952422
H	4.23105707	-2.76952441	-0.62728841
H	1.37153477	-1.15085758	0.00833492
H	2.71960609	0.09955977	1.75705149
Rh	1.41161793	1.35716815	2.10489913
P	0.94549633	1.57835233	4.29717143
H	-0.42177706	1.65538103	4.66759488
H	1.34632581	0.55630493	5.19894701
H	1.42869410	2.70070627	5.02402160
H	0.26478141	0.10915383	1.96163558
H	2.64217300	0.34350250	2.66725658
P	-1.48359448	-1.68643262	0.00698588
H	-1.44396897	-2.68432635	1.02047917
H	-1.53811995	-2.55626041	-1.11632232
H	-2.87274606	-1.38185790	0.08718082
H	0.04939064	0.09161903	-1.61632650
P	1.86400786	1.60312745	-4.18751405
H	1.43716812	2.68544027	-5.00519237
H	1.57797821	0.54217628	-5.08659164
H	3.26140072	1.69722377	-4.41998708
H	2.34996139	0.20042039	-1.83807364
H	-0.03369440	0.71558642	-2.83994990

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H-[H12]+

Rh	-0.0338	0.0194	-1.9401
P	0.0316	-0.0941	-4.1249
H	0.2683	1.1338	-4.8185
H	1.0193	-0.8933	-4.7745
H	-1.1040	-0.5400	-4.8642
H	0.0094	-1.5430	-2.1300
H	-1.7880	0.0210	-1.7410
Rh	0.0273	0.0013	1.9508

P	-0.0225	0.1046	4.1431
H	-0.3802	1.3153	4.8072
H	-0.9268	-0.7690	4.8241
H	1.1565	-0.1907	4.8944
H	0.0432	1.5614	2.1263
H	-1.7106	0.0477	1.7768
Rh	0.0472	-1.9065	-0.0163
P	-0.0597	-4.0991	0.0320
H	-0.5287	-4.7655	1.2019
H	-0.9140	-4.7380	-0.9198
H	1.1164	-4.8833	-0.1835
H	0.0646	-2.1188	1.5353
Rh	-0.0373	1.9277	0.0235
P	0.0242	4.1173	-0.0758
H	-0.0109	2.1568	-1.5310
H	0.1404	4.8335	1.1553
H	1.0794	4.7573	-0.7904
H	-1.0669	4.8450	-0.6392
Rh	1.8856	0.0427	-0.0080
P	4.0762	-0.0720	-0.0019
H	4.8529	1.1148	0.1500
H	4.7254	-0.8628	0.9922
H	4.7493	-0.6042	-1.1450
Rh	-1.8740	-0.0108	0.0146
P	-4.0739	-0.0402	0.0372
H	-1.8051	1.7307	0.0117
H	-4.7976	1.1886	0.0748
H	-4.7773	-0.6508	-1.0472
H	-4.7494	-0.7018	1.1075
H	-1.6730	-1.7863	0.0586
H	1.6806	1.8348	0.0049
H	1.8148	-1.6909	0.0389
H	1.7740	0.0490	1.7463
H	1.6925	0.0277	-1.7802