Supplementary Information

Hydrogen Isotope Separation at Exceptional High Temperature Using Unsaturated Organometallic Complex

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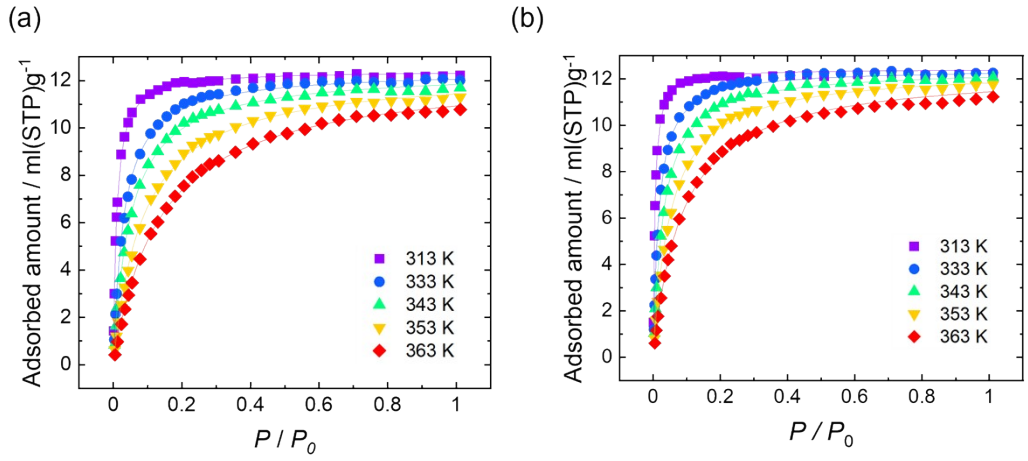
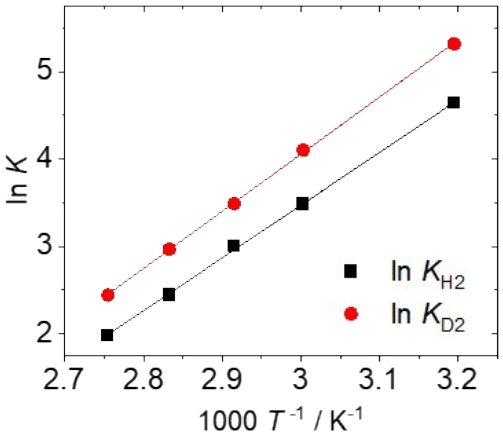


Fig S1 Adsorption isotherm of **Mn-dppe** for (a)H_2 and (b)D_2, (c) van't Hoff plot for Mn-dppe; red-point represent D_2 and black point represent H_2.



Fig, S2 van't Hoff plot for Mn-dppe; red-point represent D_2 and black point represent H_2.

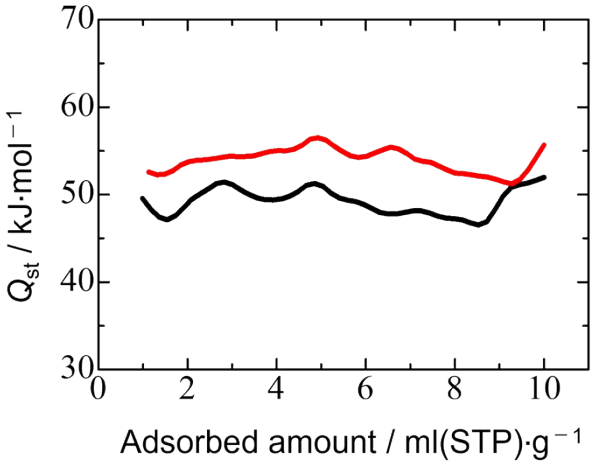


Fig S3 Equivalent differential heat of adsorption (333K, 343K, 353K), where red line represents adsorption enthalpy of D_2, black line represents adsorption enthalpy of H_2.

Table S1 Fitting parameter in Langmuir fitting of the H_2 and D_2 adsorption isotherms

Gas	T / K	V_m /ml(STP)·g^{-1}	K	R^2 value
H_2	313	12.423(16)	104.0(16)	0.9990
	333		32.7(4)	0.9986
	343		20.1(2)	0.9989
	353		11.57(12)	0.9989
	363		7.29(7)	0.9993
D_2	313	12.437(17)	204(4)	0.9968
	333		60.3(10)	0.9985
	343		32.8(5)	0.9995
	353		19.4(3)	0.9991
	363		11.52(14)	0.9978

Table S2 Equilibrium constant of H_2 and D_2 adsorption at each temperature.

T / K	K_{H2}	K_{D2}	K_{H2}/K_{D2}
313	104.02	204.17	1.96
333	32.74	60.41	1.85
343	20.12	32.84	1.63
353	11.57	19.45	1.68
363	7.29	11.54	1.58

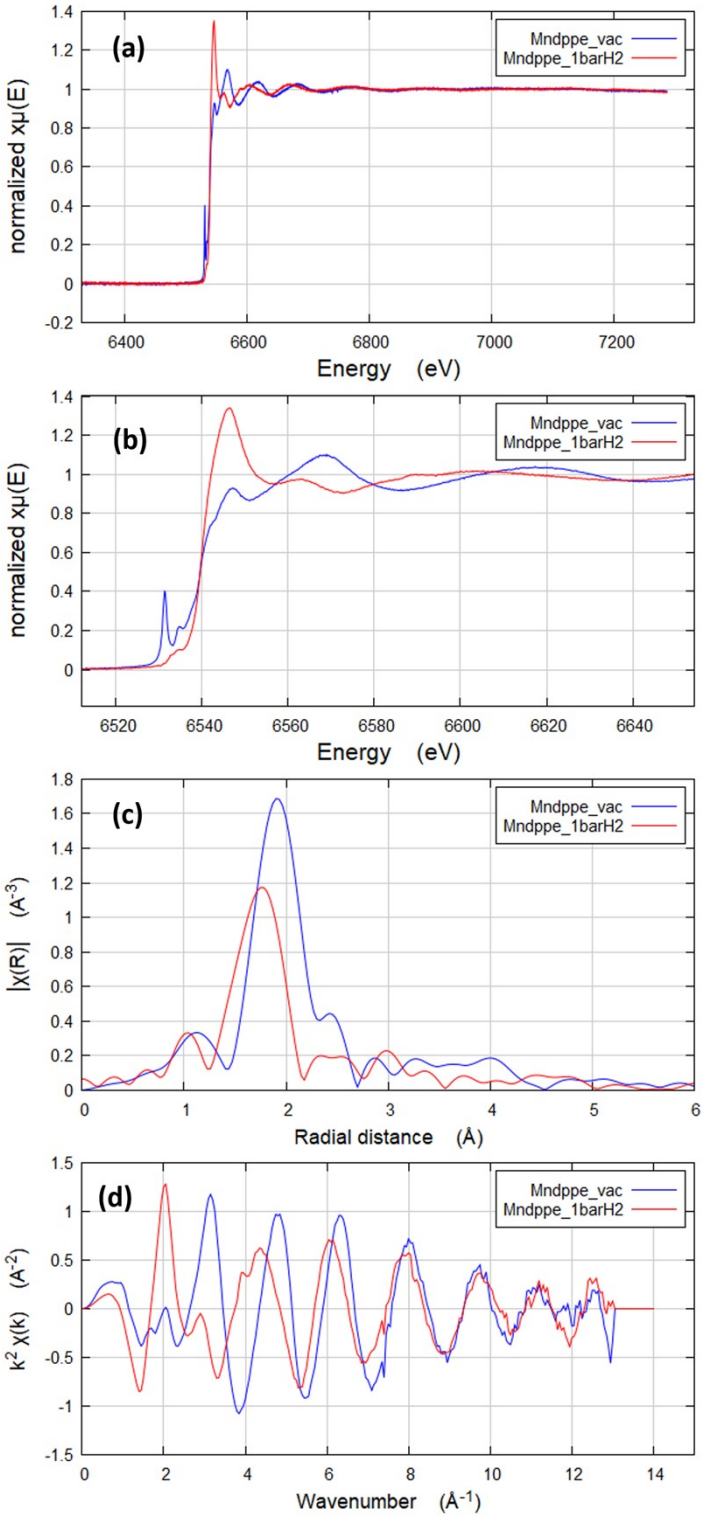


Fig S4 (a) XAFS spectra, (b) XANES region, (c) R-plots and (d) k-plots of EXAFS spectra in **Mn-dppe** before dihydrogen adsorption (red) and after dihydrogen adsorption (blue) at 313 K.

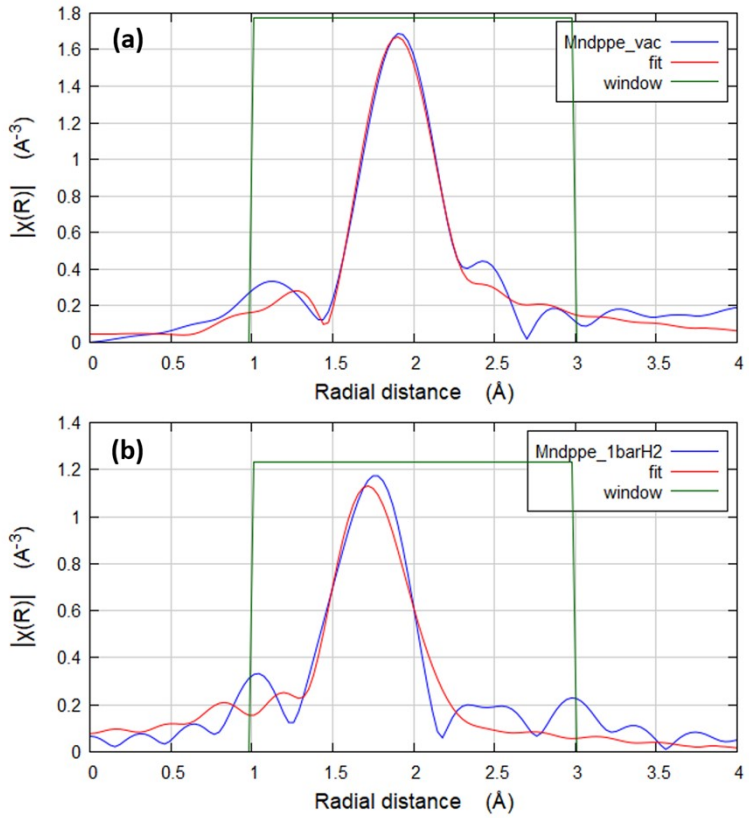


Fig S5 Measured (blue) and fitted (red) curves of the R-plots in the EXAFS spectra for **Mn-dppe** before dihydrogen adsorption (a) and after dihydrogen adsorption (b) at 313 K.

Table S3 Fitting parameters of EXAFS for Mn-dppe before and after H_2 adsorption.

	S^2	Mn-C distance (Å)	Mn-P distance (Å)	σ_C	σ_P	R-factor
Mn-dppe as synthesis	0.938(3)	1.80(4)	2.301(14)	0.0008(32)	0.007(3)	0.012
Mn-dppe after H_2 adsorption	0.938 (fixed)	1.84(2)	2.32(3)	-0.0004(28)	0.012(2)	0.0267

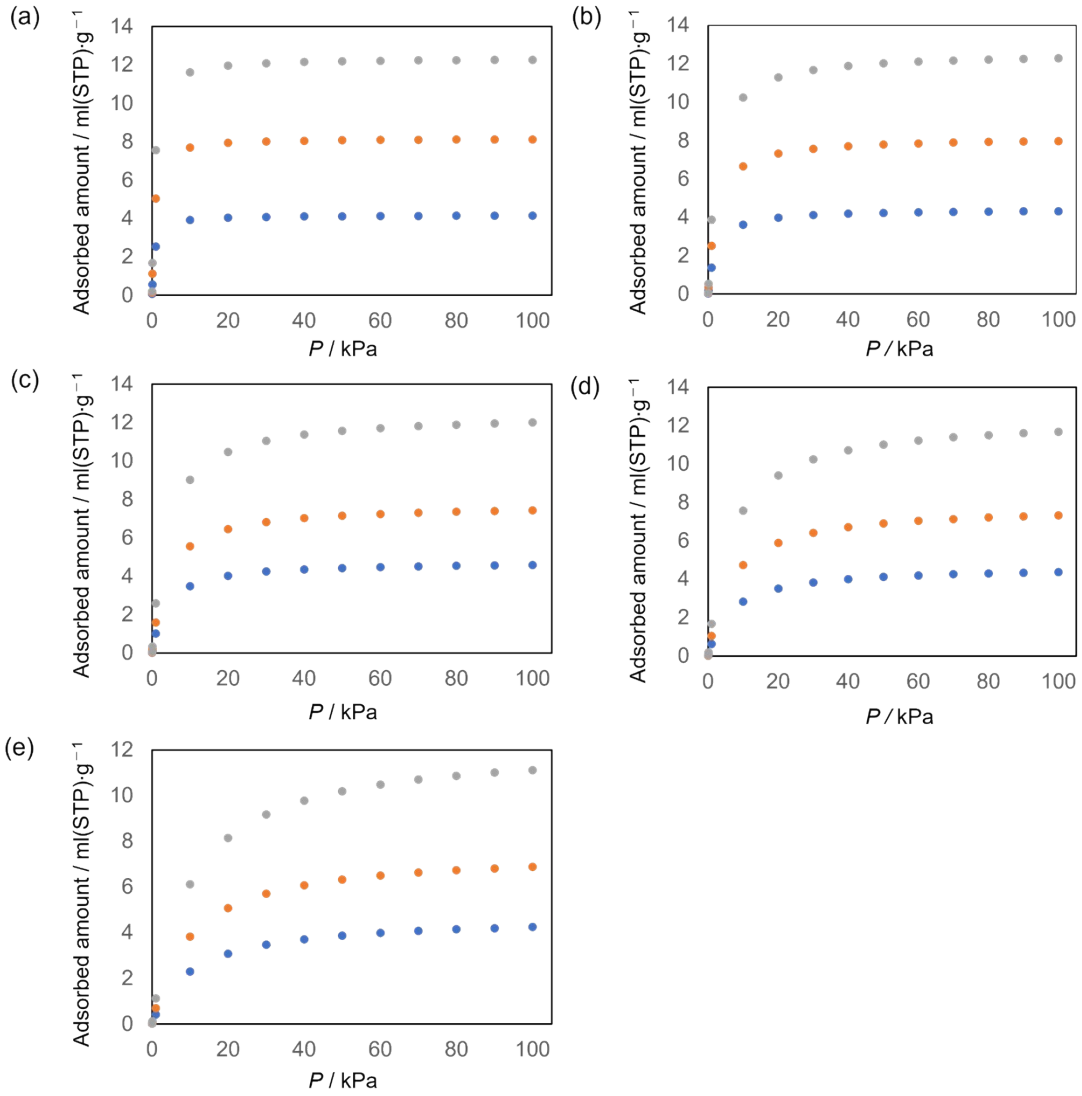


Fig S6 Mixed gas (H_2:D_2 = 1:1) adsorption isotherm calculated using pyIAST[10] at each temperature; (a) 313 K, (b) 333 K, (c) 343 K, (d) 353 K, (e) 363 K, where orange points represent D_2 uptake, blue points represent H_2 uptake, and gray points represent total uptake.

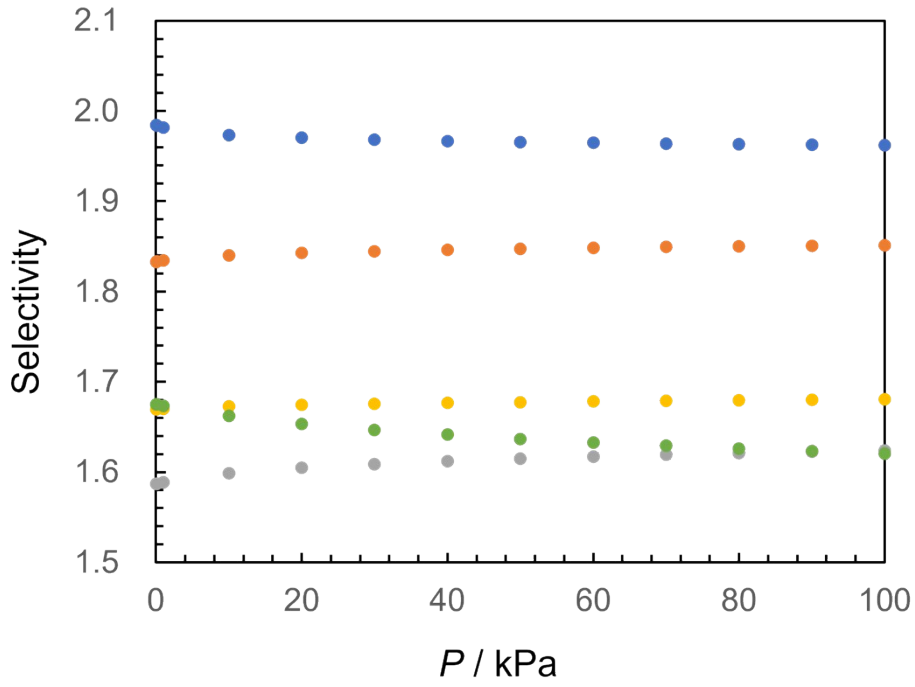


Fig S7 Calculated selectivity vs. total pressure, where blue points represent 313 K, orange points represent 333 K, gray points represent 343 K, yellow points represent 353 K, and green points represent 363 K.

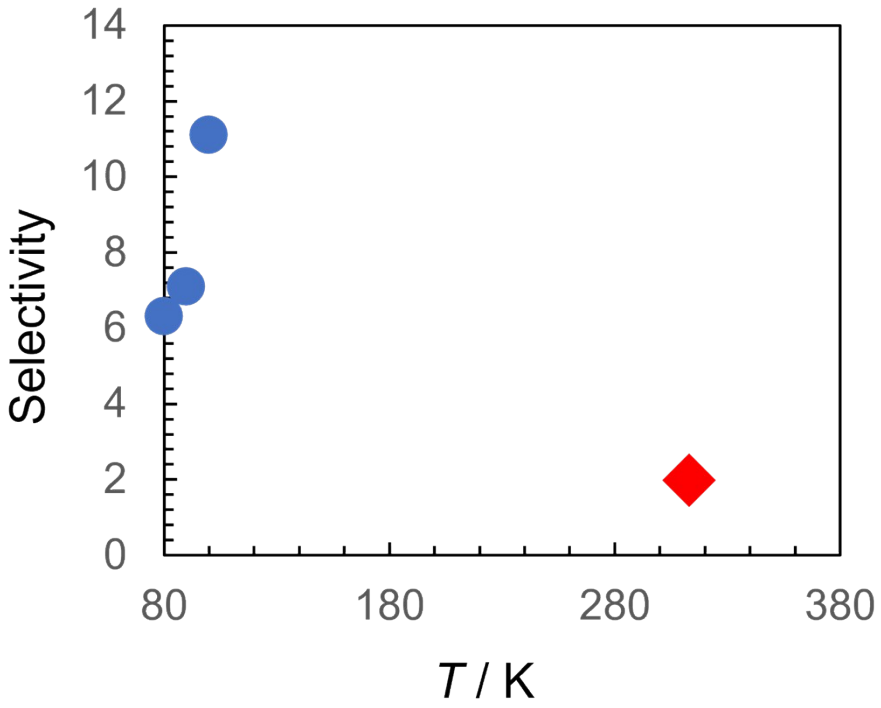


Fig S8 Plot of selectivity against temperature of the hydrogen isotope separation materials at high temperature, where blue points represent previously reported materials and red points represent the materials in this work

Table S4 Selectivity and working temperature of the hydrogen isotope separation materials (working temperature is over 80 K)

Compound	Selectivity	Temperature / K	Reference
1	1.98	313	This work
CPO-27-Co	6.3	80	[1]
Cu-MFU-4l	7.1	90	[2]
Cu-MFU-4l	11.1	100	[2]

Table S5 Computed thermodynamic parameters for H_2 and D_2 adducts

Entry	Functional	Basis sets			ΔH° (H_2) / kJ·mol^{-1}	ΔH° (D_2) / kJ·mol^{-1}	$\Delta\Delta H^\circ$ kJ·mol^{-1}
		Mn	H_2 (D_2)	others			
1	B3LYP	def2-TZVP	cc-pVDZ	6-31G	51.16	55.53	4.37
2	B3LYP	def2-TZVP	aug-cc-pVDZ	6-31G	40.70	44.97	4.27
3	M06	def2-TZVP	cc-pVDZ	6-31G	61.71	66.73	5.03
4	M06	def2-TZVP	aug-cc-pVDZ	6-31G	50.81	55.67	4.87
5	wB97X-D	def2-TZVP	cc-pVDZ	6-31G	68.32	73.11	4.79
6	wB97X-D	def2-TZVP	aug-cc-pVDZ	6-31G	56.94	61.67	4.73

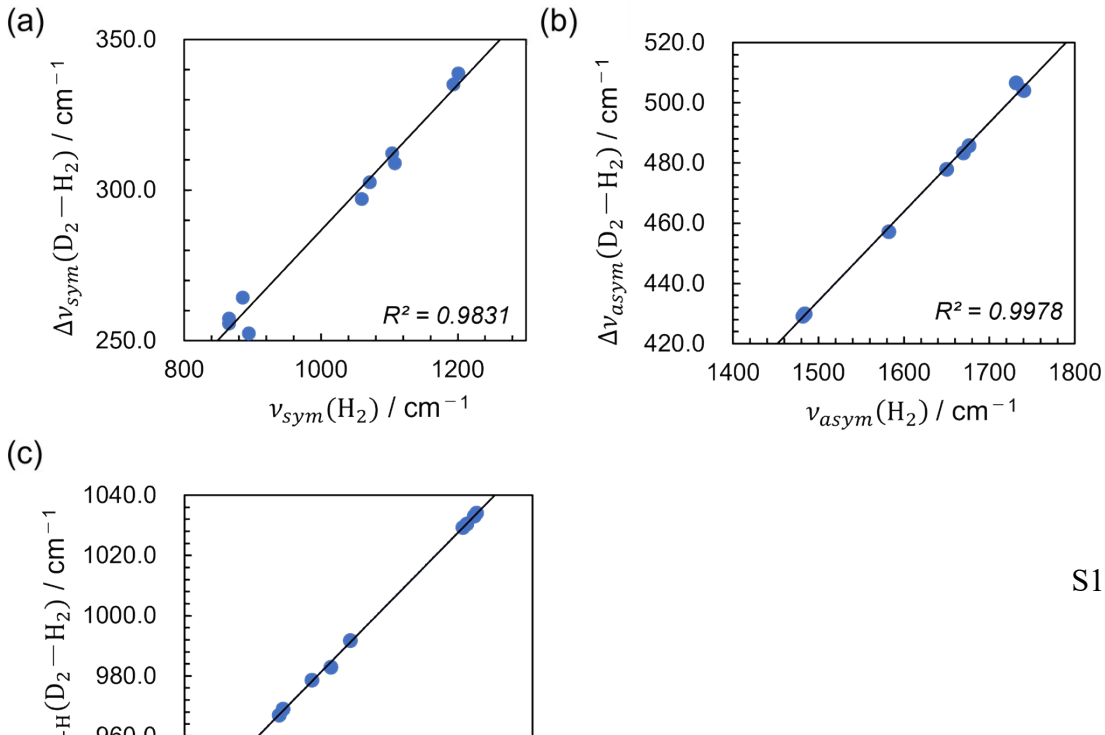
Table S6. Computed difference of vibration mode involved with dihydrogen for H_2 and D_2 adducts.

Compound	vibrational difference[a] / cm^{-1}			Total difference[b] / cm^{-1}	ΔZPE / $kJ{\cdot}mol^{-1}$	Separation factor
	$\Delta\nu_{sym}$	$\Delta\nu_{asym}$	$\Delta\nu_{H-H}$			
Mn-dppe	338.8	504.1	978.6	1821.5	10.9	2.75
$Mn(CO)_5$	297.1	457.2	967.0	1721.3	10.3	2.13
$Mn\text{-}PMe_3$	309.0	485.8	969.0	1763.8	10.5	2.31
$Mn\text{-}PH_3$	302.6	477.9	982.9	1763.5	10.5	2.35
Mn-dmpe	312.3	483.4	954.0	1749.7	10.5	2.18
Mn-bpy	255.8	429.1	1030.5	1715.4	10.3	1.89
Mn-dmbpy	264.4	429.4	1033.1	1726.9	10.3	1.93
Mn-dcbpy	257.4	429.9	1029.2	1716.5	10.3	1.88
Mn-bpyOMe	252.5	429.9	1034.0	1716.4	10.3	1.96

a, vibrational difference were calculated by following equation; $\Delta\nu_{sym} = \nu_{sym}(\text{M-H}_2) - \nu_{sym}(\text{M-D}_2)$, $\Delta\nu_{asym} = \nu_{asym}(\text{M-H}_2) - \nu_{asym}(\text{M-D}_2)$, $\Delta\nu_{H-H} = \nu_{H-H}(\text{M-H}_2) - \nu_{D-D}(\text{M-D}_2)$.

b, total difference was sum of the three vibrational differences.

Fig S9 Plot of the calculated differences in frequency in each vibration mode between H_2 adducts and D_2 adducts vs. frequency of H_2 adducts, (a) symmetric vibration between metal and dihydrogen (ν_{sym}), (b) separation factor vs. asymmetric vibration between metal and dihydrogen (ν_{asym}), (c) separation factor vs. symmetric vibration between the hydrogen (ν_{H-H})



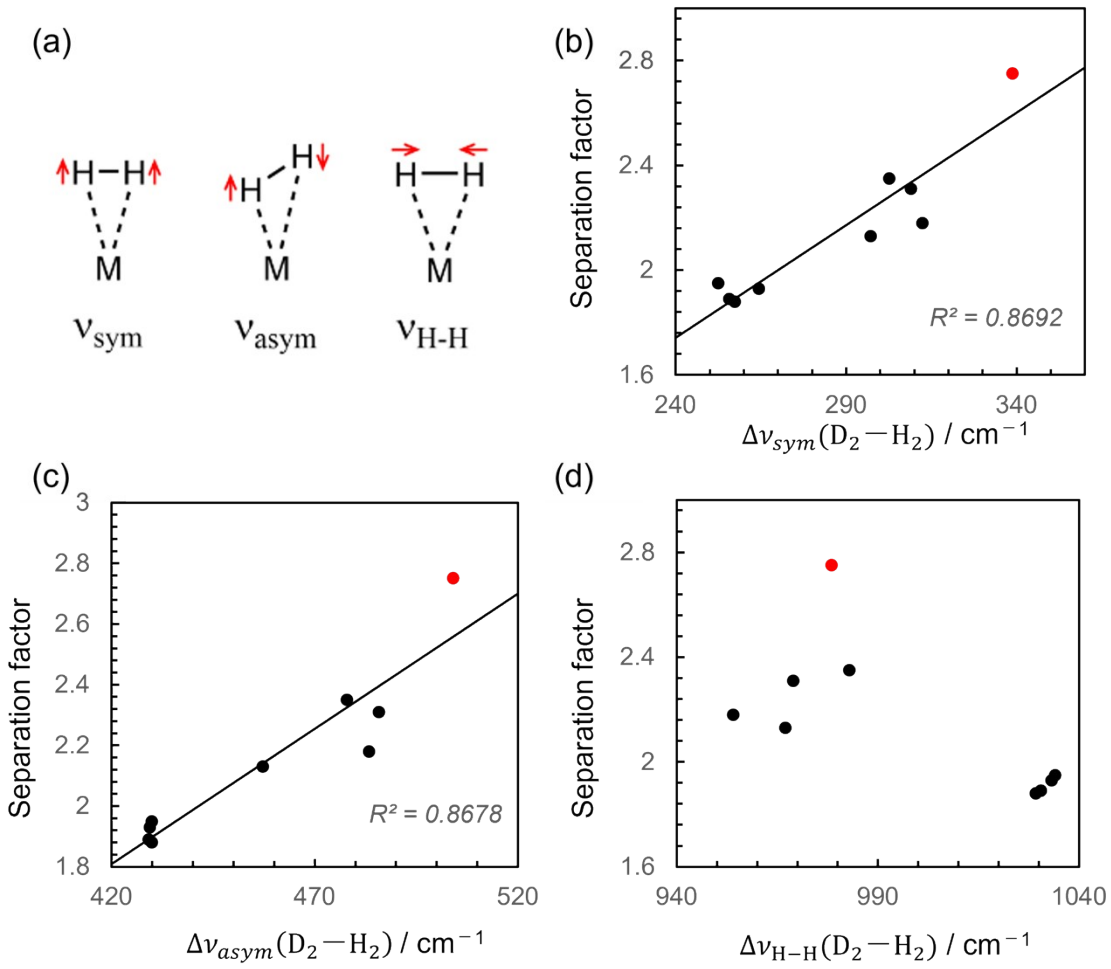


Fig S10 (a) Represented vibration mode involved with dihydrogen (b) - (d) Plot of the calculated dihydrogen isotope separation factor *vs*. the difference of represented calculated vibration energy involved with H_2 or D_2 between H_2 adducts and D_2 adducts on the corresponding unsaturated Mn complexes series, (b) separation factor vs. symmetric vibration between metal and dihydrogen ($^{\Delta\nu_{sym}}$), (c) separation factor vs. asymmetric vibration between metal and dihydrogen ($^{\Delta\nu_{asym}}$), (d) separation factor vs. symmetric vibration between the hydrogen ($^{\Delta\nu_{H-H}}$), where the red points represent Mn-dppe. Grey points represent the corresponding unsaturated Mn complexes.

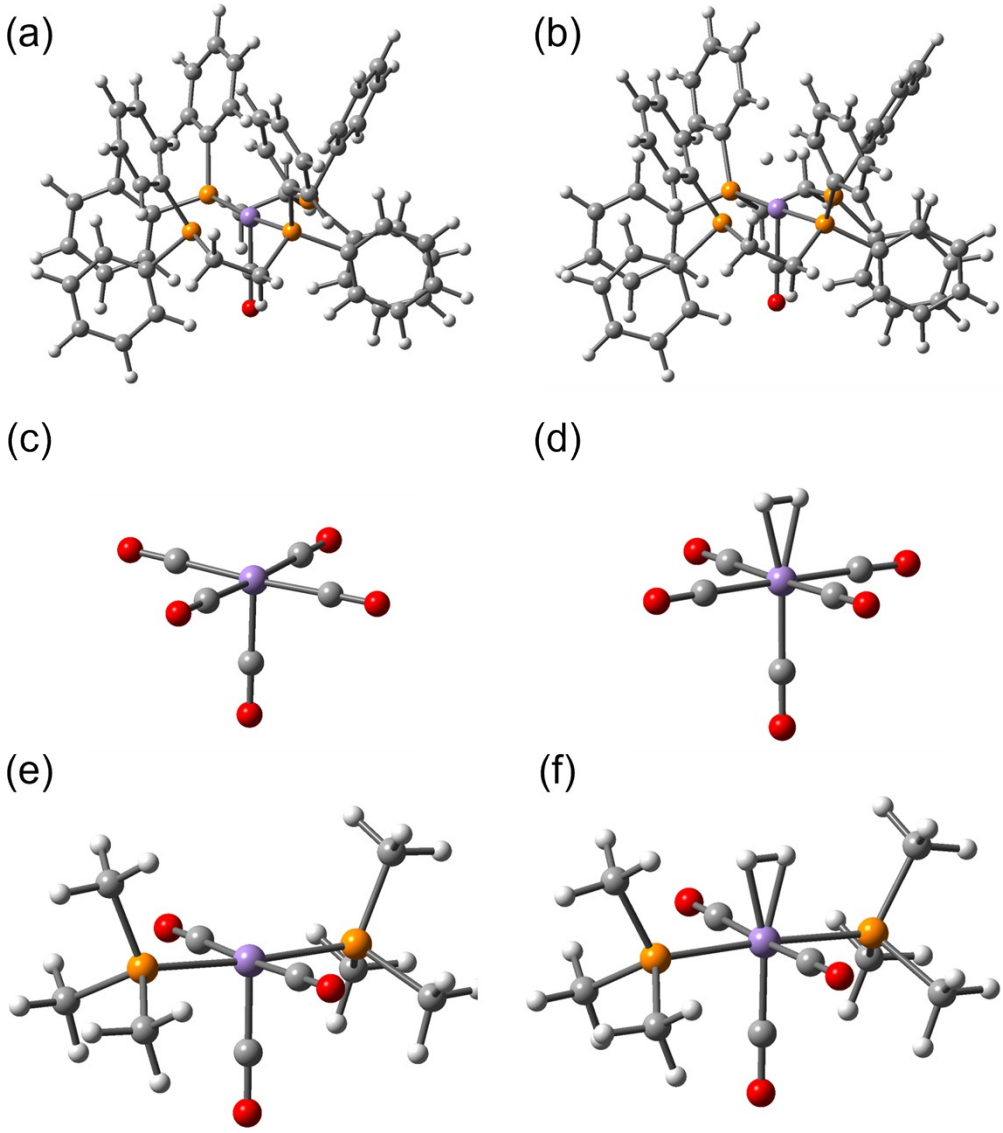


Fig S11. Optimized structures of various unsaturated Mn complexes and the H_2 adducts; 10$[Mn(dppe)_2(CO)]^+$ (a), $[Mn(dppe)_2(CO)(H_2)]^+$ (b), $[Mn(CO)_5]^+$, (c), $[Mn(CO)_5(H_2)]^+$ (d), $[Mn(PMe_3)_2(CO)_3]^+$ (e), $[Mn(PMe_3)_2(CO)_3(H_2)]^+$ (f), Mn: purple, P: orange, C: gray, O: red, H: white. The cartesian coordinate of the optimized structures were shown in Table S6-S11.

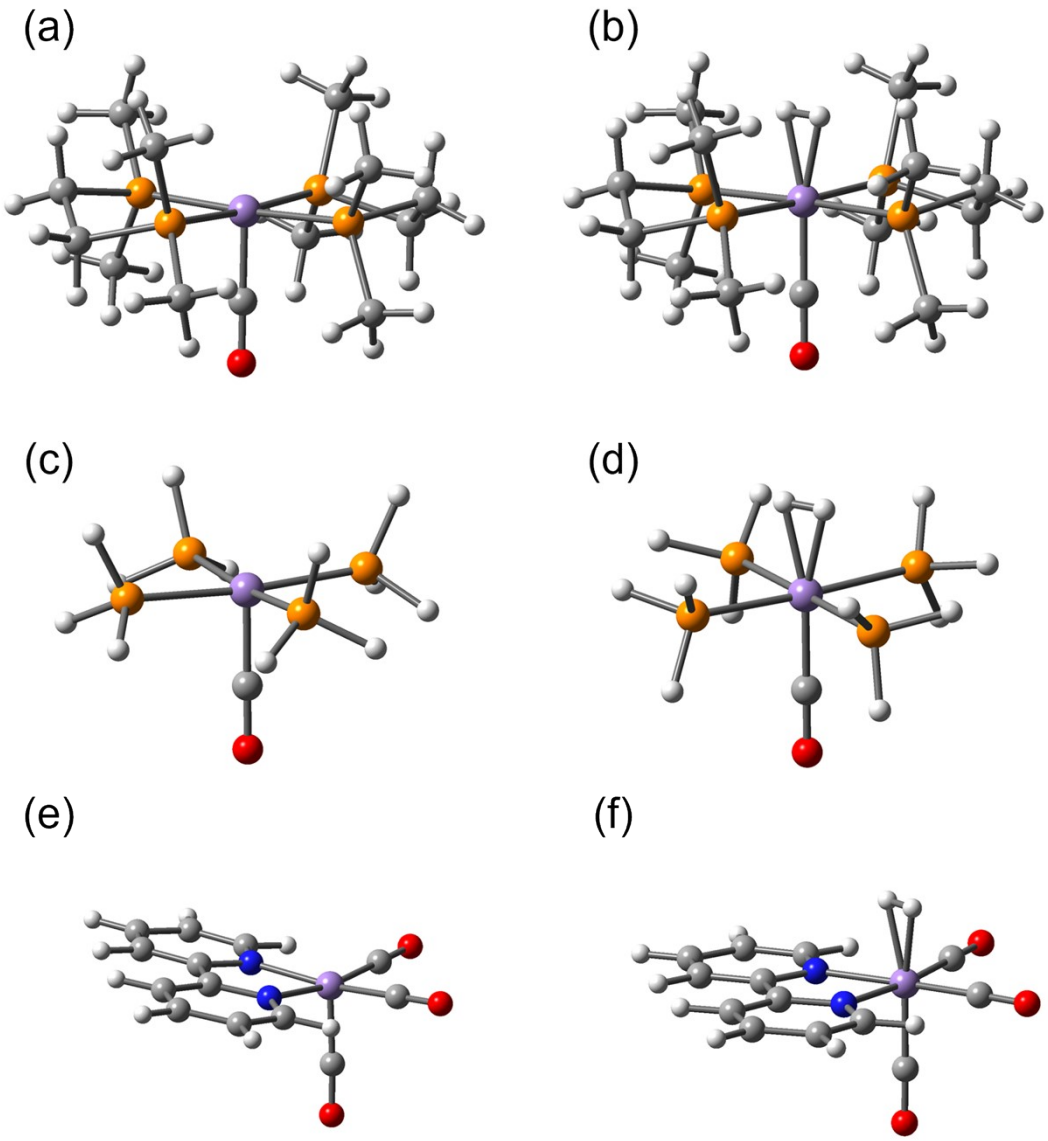


Fig S12 Optimized structures of various unsaturated Mn complexes and the H_2 adducts; $[Mn(dmpe)_2(CO)]^+$ (a), $[Mn(dmpe)_2(CO)(H_2)]^+$ (b), $[Mn(PH_3)_4(CO)]^+$, (c), $[Mn(PH_3)_4(CO)(H_2)]^+$ (d), $[Mn(bpy)(CO)_3]^+$ (e), $[Mn(bpy)(CO)_3(H_2)]^+$ (f), Mn: purple, P: orange, C: gray, O: red, N: blue, H: white. The cartesian coordinate of the optimized structures were shown in Table S12-S17.

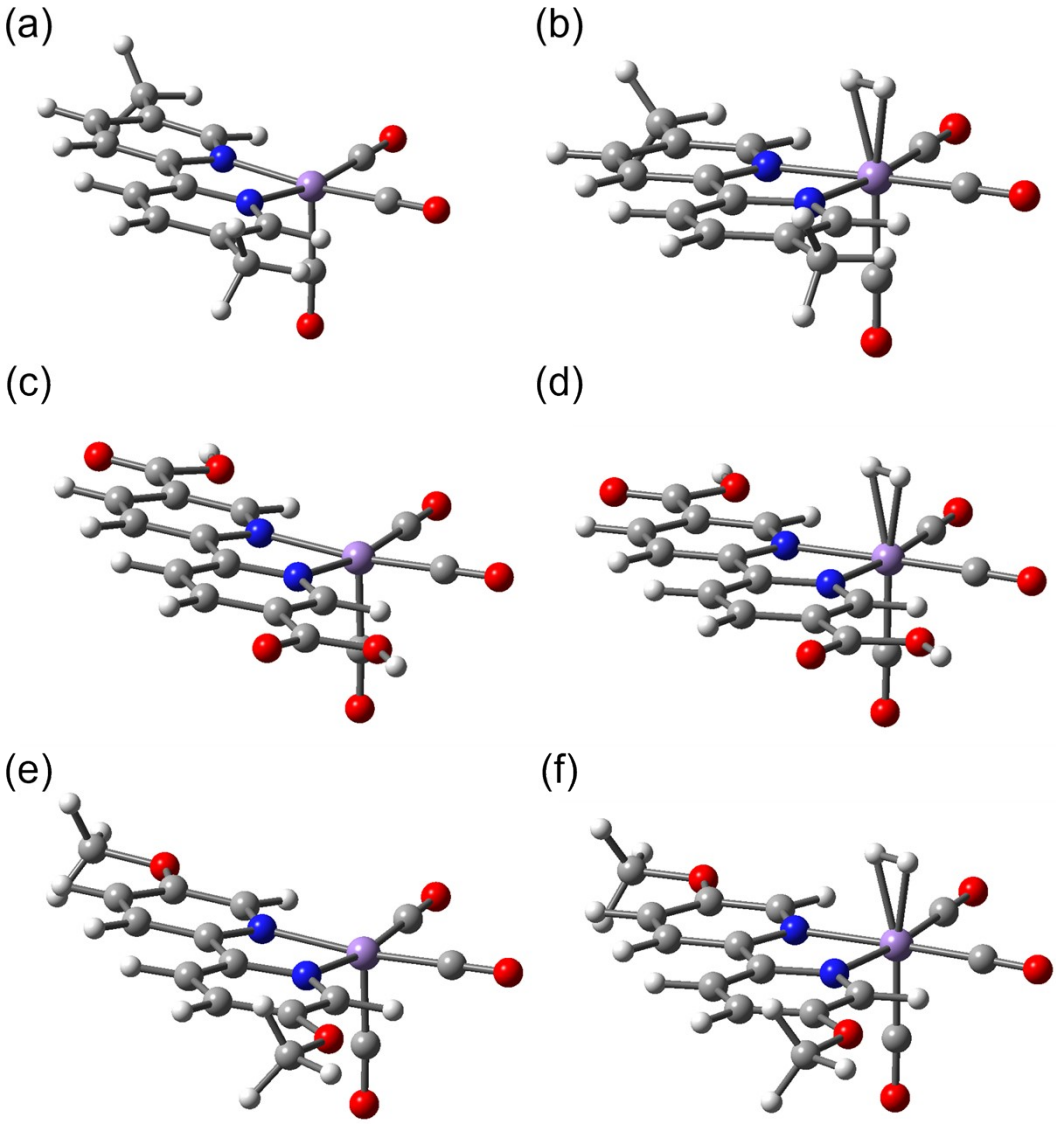


Fig S13 Optimized structures of various unsaturated Mn complexes and the H_2 adducts; $[Mn(dmbpy)(CO)_3]^+$ (a), $[Mn(dmbpy)(CO)_3(H_2)]^+$ (b), $[Mn(dcbpy)(CO)_3]^+$, (c), $[Mn(dcbpy)(CO)_3(H_2)]^+$ (d), $[Mn(dOMebpy)(CO)_3]^+$ (e), $[Mn(dOMebpy)(CO)_3(H_2)]^+$ (f), Mn: purple, P: orange, C: gray, O: red, N: blue, H: white. The cartesian coordinate of the optimized structures were shown in Table S18-S23.

Table S7. The cartesian coordinates of the optimized structure for $[Mn(dppe)_2(CO)]^+$

Symbol	X	Y	Z
P	1.385604	-1.86006	-0.27875
P	-1.70841	-1.62093	-0.35041
P	1.707804	1.621582	-0.34628
P	-1.38546	1.863988	-0.25424
C	0.926797	3.346813	-0.68076
C	-0.47851	3.208666	-1.24751
H	1.591076	3.896182	-1.35772
H	0.896142	3.87301	0.281842
H	-0.47031	2.886758	-2.29657
H	-1.04009	4.148398	-1.17806
C	0.475609	-3.1967	-1.27944
C	-0.92579	-3.34181	-0.70407
H	1.038524	-4.13652	-1.22269
H	0.45895	-2.86479	-2.32538
H	-0.88719	-3.87586	0.253902
H	-1.59355	-3.88724	-1.38077
C	-0.01848	0.019399	-2.14143
O	-0.04039	0.040125	-3.3356
C	3.104891	1.59428	-1.59213
C	4.430495	1.407202	-1.19146
C	2.805579	1.779818	-2.94864
C	5.452544	1.419909	-2.14175
H	4.670551	1.255767	-0.14171
C	3.831079	1.790902	-3.89321
H	1.776462	1.908756	-3.2771
C	5.156091	1.616039	-3.49002
H	6.48143	1.276365	-1.8239
H	3.594235	1.941551	-4.94232
H	5.954575	1.633093	-4.22605
C	2.602061	1.87877	1.277062

C	3.149788	3.118663	1.626546
C	2.720467	0.801351	2.160736
C	3.783191	3.280834	2.858565
H	3.097223	3.957811	0.93614
C	3.353126	0.963334	3.394196
H	2.318946	-0.17235	1.886453
C	3.879478	2.206503	3.745838
H	4.205986	4.245103	3.124466
H	3.43424	0.119166	4.073495
H	4.371633	2.337926	4.704847
C	1.419915	-2.70158	1.394333
C	2.068974	-3.92803	1.589006
C	0.66579	-2.15281	2.437866
C	1.967787	-4.58606	2.814518
H	2.657635	-4.36855	0.786475
C	0.554427	-2.81565	3.660511
H	0.133578	-1.21175	2.294767
C	1.209697	-4.03223	3.849
H	2.475682	-5.53468	2.960729
H	-0.04813	-2.38616	4.455613
H	1.126857	-4.55277	4.798292
C	3.133074	-1.95055	-0.91221
C	3.342482	-1.85732	-2.29427
C	4.228156	-2.05937	-0.04816
C	4.637326	-1.90521	-2.80709
H	2.501067	-1.73166	-2.97373
C	5.5229	-2.1079	-0.56753
H	4.076133	-2.1185	1.027372
C	5.727366	-2.03912	-1.94525
H	4.794489	-1.8303	-3.87906
H	6.369681	-2.20424	0.105802
H	6.735091	-2.08244	-2.34807

C	-3.11369	-1.58896	-1.58709
C	-4.43613	-1.40004	-1.1767
C	-2.82442	-1.7735	-2.94583
C	-5.46492	-1.41002	-2.11964
H	-4.66819	-1.24825	-0.12521
C	-3.85657	-1.78175	-3.88313
H	-1.79785	-1.90356	-3.28172
C	-5.17838	-1.60535	-3.47021
H	-6.49127	-1.26504	-1.79437
H	-3.62751	-1.93144	-4.9341
H	-5.98215	-1.62036	-4.20052
C	-2.59444	-1.89175	1.275277
C	-3.13358	-3.13628	1.621378
C	-2.71744	-0.81827	2.163131
C	-3.76251	-3.30705	2.854581
H	-3.07786	-3.97244	0.927638
C	-3.34581	-0.98885	3.397619
H	-2.32261	0.158895	1.891567
C	-3.8632	-2.23668	3.746105
H	-4.17851	-4.27495	3.117983
H	-3.43058	-0.1477	4.080184
H	-4.35195	-2.37478	4.705913
C	-3.12938	1.956251	-0.89687
C	-4.23095	2.094646	-0.04576
C	-3.3262	1.838407	-2.27921
C	-5.52002	2.149364	-0.57913
H	-4.08878	2.171538	1.029964
C	-4.61513	1.893906	-2.80559
H	-2.47987	1.684643	-2.94708
C	-5.71171	2.058313	-1.95732
H	-6.37213	2.268136	0.083824
H	-4.76275	1.800523	-3.87747

H	-6.71481	2.107256	-2.37091
C	-1.41853	2.694253	1.423967
C	-2.06221	3.922188	1.626942
C	-0.66507	2.136204	2.463138
C	-1.9571	4.572113	2.8565
H	-2.64895	4.370942	0.827584
C	-0.54928	2.791226	3.689543
H	-0.13702	1.193887	2.313322
C	-1.19981	4.009024	3.88652
H	-2.46099	5.521851	3.009179
H	0.052829	2.354561	4.481037
H	-1.11363	4.523403	4.838866
Mn	-0.00141	0.002305	-0.40207

Table S8 The cartesian coordinates of the optimized structure for $[Mn(dppe)_2(CO)(H_2)]^+$

Symbol	X	Y	Z
P	1.46927	-1.81717	-0.15443
P	-1.66088	-1.67303	-0.2214
P	1.661144	1.672678	-0.22162
P	-1.46917	1.817151	-0.15432
C	0.799289	3.36825	-0.47473
C	-0.56356	3.180932	-1.1214
H	1.45989	4.000896	-1.07866
H	0.690523	3.821066	0.519764
H	-0.4843	2.853839	-2.16562
H	-1.1581	4.101766	-1.09178
C	0.563802	-3.18122	-1.12129
C	-0.79898	-3.36855	-0.47447
H	1.158435	-4.102	-1.09148
H	0.484413	-2.85437	-2.16559

H	-0.69001	-3.82128	0.520046
H	-1.45965	-4.00127	-1.07823
C	-0.00126	0.001347	-1.97043
O	-0.00316	0.003727	-3.15994
C	2.980526	1.757404	-1.55326
C	4.33712	1.626376	-1.24347
C	2.592179	1.997403	-2.87852
C	5.296834	1.743176	-2.25021
H	4.651062	1.437842	-0.21956
C	3.55478	2.112802	-3.88021
H	1.541252	2.090924	-3.141
C	4.909203	1.989667	-3.56646
H	6.349328	1.641879	-2.00057
H	3.245723	2.304844	-4.90344
H	5.659034	2.087415	-4.34603
C	2.658315	1.945812	1.337264
C	3.192639	3.202992	1.645842
C	2.900259	0.868194	2.195108
C	3.936596	3.379889	2.812293
H	3.042651	4.044079	0.972409
C	3.648592	1.04403	3.360562
H	2.514254	-0.11984	1.951165
C	4.161525	2.302762	3.672361
H	4.344772	4.358175	3.048066
H	3.829298	0.198111	4.017989
H	4.74176	2.445037	4.579057
C	1.782088	-2.78272	1.433229
C	2.5701	-3.94305	1.38635
C	1.166637	-2.43069	2.639725
C	2.749155	-4.72342	2.527035
H	3.058103	-4.23486	0.458642
C	1.345642	-3.21432	3.782973

H	0.531299	-1.55123	2.703553
C	2.13841	-4.3588	3.728549
H	3.364598	-5.61673	2.477247
H	0.859668	-2.92948	4.711422
H	2.277646	-4.96811	4.616349
C	3.148544	-1.76296	-0.96716
C	3.214684	-1.63972	-2.36113
C	4.33082	-1.80199	-0.21882
C	4.452849	-1.59443	-2.99992
H	2.305523	-1.56356	-2.95483
C	5.567806	-1.75621	-0.86319
H	4.292599	-1.88399	0.86514
C	5.629837	-1.66216	-2.25312
H	4.496682	-1.49915	-4.08082
H	6.481506	-1.79958	-0.27738
H	6.593025	-1.63294	-2.75427
C	-2.98034	-1.75799	-1.55292
C	-4.33695	-1.62712	-1.24313
C	-2.59198	-1.99845	-2.87808
C	-5.29665	-1.74441	-2.24983
H	-4.65094	-1.43861	-0.21923
C	-3.55455	-2.1144	-3.87972
H	-1.54103	-2.09206	-3.14047
C	-4.90898	-1.9913	-3.566
H	-6.34916	-1.64322	-2.00024
H	-3.24548	-2.30683	-4.90288
H	-5.65881	-2.08941	-4.34553
C	-2.65795	-1.94576	1.337611
C	-3.19107	-3.20307	1.647643
C	-2.90114	-0.86728	2.194042
C	-3.93504	-3.37922	2.81421
H	-3.04014	-4.04485	0.975295

C	-3.64947	-1.04238	3.3596
H	-2.51607	0.120783	1.948843
C	-4.16117	-2.30125	3.672896
H	-4.3423	-4.35761	3.051152
H	-3.83113	-0.19581	4.015928
H	-4.74141	-2.44297	4.579678
C	-3.14815	1.76245	-0.96765
C	-4.33071	1.803539	-0.21985
C	-3.21379	1.637226	-2.36149
C	-5.56747	1.757818	-0.86464
H	-4.29287	1.887022	0.864003
C	-4.45177	1.592308	-3.00068
H	-2.30448	1.559094	-2.95474
C	-5.62901	1.662068	-2.25449
H	-6.48137	1.802745	-0.27927
H	-4.49522	1.495823	-4.08149
H	-6.59201	1.633096	-2.756
C	-1.78233	2.782852	1.433116
C	-2.5698	3.943546	1.385906
C	-1.1678	2.430359	2.639941
C	-2.74917	4.723845	2.526586
H	-3.05713	4.235681	0.457947
C	-1.34716	3.213889	3.783196
H	-0.53287	1.550617	2.704008
C	-2.13936	4.358754	3.728431
H	-3.36415	5.617463	2.476535
H	-0.86193	2.928683	4.71192
H	-2.27888	4.968015	4.616224
Mn	0.000011	-3.2E-05	-0.19935
H(Iso=1)	0.362423	0.203397	1.438627
H(Iso=1)	-0.36227	-0.2031	1.438624

Table S9 The cartesian coordinates of the optimized structure for $[Mn(CO)_5]^+$

Symbol	X	Y	Z
Mn	0.00004	-3.9E-05	-0.32984
C	1.381611	-1.3087	-0.38294
O	2.217112	-2.1002	-0.40127
C	-1.38154	1.308623	-0.38281
O	-2.21701	2.100153	-0.40106
C	0.000091	-9.8E-05	1.503441
O	0.000139	-0.00015	2.658852
C	-1.30876	-1.38147	-0.38313
C	1.30862	1.381593	-0.38312
O	-2.10045	-2.2168	-0.40218
O	2.100067	2.217165	-0.40216

Table S10 The cartesian coordinates of the optimized structure for $[Mn(CO)_5(H_2)]^+$

Symbol	X	Y	Z
Mn	-4E-06	0.000079	-0.32325
H(Iso=1)	-0.4051	-0.10762	-1.98685
H(Iso=1)	0.405537	0.105902	-1.98687
C	0.424217	-1.84696	-0.35992
O	0.681885	-2.96927	-0.37576
C	-0.42444	1.846981	-0.36301
O	-0.68193	2.969298	-0.38055
C	-0.00063	0.002895	1.547039
O	-0.00103	0.004728	2.69987
C	-1.84427	-0.4247	-0.31368
C	1.844856	0.422308	-0.31372
O	-2.9665	-0.68382	-0.29208
O	2.967724	0.678637	-0.29214

Table S11 The cartesian coordinates of the optimized structure for $[Mn(PMe_3)_2(CO)_3]^+$

Symbol	X	Y	Z
Mn	-8E-06	0.000006	-0.1624
P	-2.35073	-7.8E-05	-0.25267
P	2.350723	0.000069	-0.25268
C	-0.00019	1.847524	-0.20883
O	-0.00036	3.013733	-0.21382
C	0.000174	-1.84751	-0.20878
O	0.000404	-3.01372	-0.21375
C	0.000006	0.000029	1.615359
O	0.000033	0.000063	2.787844
C	-3.10405	-1E-06	-1.96584
C	-3.16731	-1.45819	0.581953
C	-3.16722	1.457908	0.582242
C	3.104056	-0.00023	-1.96584
C	3.16718	-1.45784	0.582409
C	3.167321	1.45826	0.581779
H	-4.1961	-4.8E-05	-1.87589
H	-2.8931	-2.3873	0.072726
H	-2.8929	2.387108	0.07324
H	4.1961	-0.0002	-1.87588
H	2.892833	-2.38709	0.073524
H	2.893144	2.387318	0.072437
H	2.789319	0.892402	-2.51457
H	2.789364	-0.89306	-2.51427
H	4.255414	1.336834	0.550973
H	2.84016	1.511453	1.625629
H	2.839994	-1.51045	1.626288
H	4.255293	-1.33663	0.551577
H	-2.78929	-0.8927	-2.51445
H	-2.78937	0.89277	-2.51438

H	-4.25533	1.336675	0.551433
H	-2.84003	1.510664	1.626111
H	-2.84016	-1.51125	1.625814
H	-4.2554	-1.33679	0.551117

Table S12 The cartesian coordinates of the optimized structure for $[Mn(PMe_3)_2(CO)_3(H_2)]^+$

Symbol	X	Y	Z
Mn	-9E-06	0.000005	-0.26544
H(Iso=1)	0.416345	0.000311	-1.91308
H(Iso=1)	-0.41637	-0.00019	-1.91309
P	-2.35107	0.000079	-0.18351
P	2.351067	-5.3E-05	-0.18353
C	0.000083	1.843798	-0.30881
O	0.000232	3.010118	-0.31515
C	-0.00015	-1.84379	-0.30894
O	-0.00022	-3.01011	-0.31532
C	-7E-06	-4.9E-05	1.542028
O	0.000066	-0.00019	2.711859
C	-3.26817	-9.9E-05	-1.81098
C	-3.08509	-1.45699	0.725298
C	-3.08506	1.457327	0.725043
C	3.268176	0.000364	-1.81099
C	3.085091	-1.4574	0.72484
C	3.085058	1.456916	0.725473
H	-4.34753	-0.00028	-1.62232
H	-2.84802	-2.38722	0.19968
H	-2.84787	2.387499	0.19939
H	4.34753	0.00056	-1.62233
H	2.84792	-2.38751	0.199062
H	2.847964	2.387205	0.199973
H	3.00335	0.894059	-2.38523

H	3.003698	-0.89329	-2.38545
H	4.172731	1.341634	0.783097
H	2.672684	1.502212	1.739173
H	2.67277	-1.50301	1.738553
H	4.172768	-1.34217	0.782441
H	-3.00337	-0.89373	-2.38533
H	-3.00366	0.893625	-2.38532
H	-4.17274	1.342107	0.782625
H	-2.67274	1.502785	1.738763
H	-2.67271	-1.50242	1.73899
H	-4.17276	-1.34169	0.782942

Table S13 The cartesian coordinates of the optimized structure for $[Mn(dmpe)_2(CO)]^+$

Symbol	X	Y	Z
P	1.630623	-1.64391	-0.19199
P	1.793478	1.489468	-0.18058
P	-1.79351	-1.4895	-0.18048
P	-1.63064	1.643885	-0.19206
C	-3.40788	-0.50584	-0.41973
C	-3.28288	0.835551	0.287173
H	-4.24754	-1.10131	-0.03868
H	-3.55335	-0.37549	-1.50159
H	-3.2621	0.710981	1.379853
H	-4.10683	1.517035	0.038779
C	3.282862	-0.83556	0.28718
C	3.407854	0.505805	-0.41978
H	4.106812	-1.51705	0.038799
H	3.262104	-0.71094	1.379855
H	3.553325	0.375405	-1.50164
H	4.247512	1.101295	-0.03875
C	-1.8E-05	0.000047	1.629468
O	0.000348	0.000254	2.821084

C	-2.06781	2.461649	-1.82876
H	-2.93617	3.116868	-1.69617
H	-1.22063	3.055991	-2.1858
H	-2.3019	1.699578	-2.57896
C	1.988162	2.852759	-1.45772
H	1.248126	3.639041	-1.27437
H	2.991168	3.288708	-1.38576
H	1.840195	2.450668	-2.46478
C	-1.98819	-2.85285	-1.45754
H	-1.24816	-3.63912	-1.27415
H	-2.9912	-3.28879	-1.38556
H	-1.84023	-2.45081	-2.46463
C	-2.1616	-2.41972	1.407124
H	-3.07147	-3.01762	1.285744
H	-1.32266	-3.07706	1.6564
H	-2.29349	-1.70599	2.22649
C	-1.57634	3.111686	0.968485
H	-1.36114	2.75774	1.982658
H	-0.79126	3.80872	0.656142
H	-2.53901	3.635145	0.960085
C	1.576325	-3.11165	0.968629
H	2.539	-3.63509	0.960272
H	1.361107	-2.75766	1.98278
H	0.79126	-3.80871	0.656311
C	2.06777	-2.46175	-1.82866
H	1.220579	-3.05612	-2.18565
H	2.30183	-1.69972	-2.5789
H	2.93614	-3.11696	-1.69606
C	2.161548	2.419762	1.406976
H	3.07148	3.017579	1.285624
H	1.32264	3.077183	1.656161
H	2.293316	1.706058	2.226388

Mn	-9E-06	-8E-06	-0.11081

Table S14 The cartesian coordinates of the optimized structure for $[Mn(dmpe)_2(CO)(H_2)]^+$

Symbol	X	Y	Z
P	1.656215	-1.61072	-0.20188
P	1.745691	1.524865	-0.11387
P	-1.74563	-1.52485	-0.11423
P	-1.65622	1.610734	-0.20208
C	-3.36981	-0.58802	-0.435
C	-3.30019	0.769916	0.247258
H	-4.21055	-1.19521	-0.07525
H	-3.46945	-0.48367	-1.52529
H	-3.30883	0.667134	1.342446
H	-4.13374	1.424582	-0.03818
C	3.300139	-0.76995	0.247763
C	3.369905	0.588016	-0.43442
H	4.133712	-1.42462	-0.03758
H	3.308603	-0.66722	1.342957
H	3.469712	0.483711	-1.5247
H	4.210601	1.195172	-0.07451
C	-0.00015	-3.5E-05	1.617744
O	-0.00023	-0.0001	2.803802
Mn	0.000012	0.000016	-0.15424
C	-2.08143	2.443125	-1.8306
H	-2.9488	3.101137	-1.70702
H	-1.22745	3.034481	-2.17797
H	-2.30728	1.68099	-2.58426
C	-1.64488	3.06111	0.980544
H	-0.86267	3.772773	0.694472
H	-2.61315	3.573879	0.960416
H	-1.44605	2.696756	1.9945

C	2.128855	2.395553	1.502186
H	2.321613	1.653734	2.283747
H	3.007919	3.037436	1.379163
H	1.273315	3.004429	1.811628
C	1.871805	2.942872	-1.33404
H	2.851961	3.426025	-1.25011
H	1.738223	2.564516	-2.35344
H	1.092959	3.684158	-1.124
C	1.644624	-3.06113	0.980697
H	2.612883	-3.57392	0.960737
H	1.445602	-2.6968	1.994626
H	0.862453	-3.77277	0.694449
C	-2.12902	-2.39561	1.501734
H	-2.32186	-1.65382	2.283304
H	-3.00809	-3.03747	1.378563
H	-1.27354	-3.00453	1.811257
C	-1.87151	-2.94281	-1.33447
H	-1.09267	-3.68408	-1.12433
H	-2.85166	-3.426	-1.25072
H	-1.73777	-2.56441	-2.35384
C	2.081666	-2.44306	-1.83036
H	2.948985	-3.10112	-1.70666
H	1.227709	-3.03436	-2.1779
H	2.307673	-1.6809	-2.58395
H(Iso=1)	-0.28773	-0.30349	-1.81519
H(Iso=1)	0.288022	0.303584	-1.81512

Table S15 The cartesian coordinates of the optimized structure for $[Mn(PH_3)_2(CO)_3]^+$

Symbol	X	Y	Z
Mn	0.000026	0.000038	-0.23082
P	1.628125	1.716297	-0.34692
H	1.323228	2.973565	0.263668

H	2.899722	1.476337	0.263211
H	2.081467	2.193749	-1.61895
P	1.716279	-1.62806	-0.34703
H	2.97353	-1.32322	0.263618
H	1.476281	-2.8997	0.262994
H	2.193773	-2.08131	-1.61908
P	-1.62808	-1.7162	-0.34716
H	-1.32315	-2.97361	0.263127
H	-2.8996	-1.47634	0.263164
H	-2.08158	-2.19338	-1.61924
P	-1.71624	1.628131	-0.34703
H	-2.19376	2.081336	-1.61908
H	-2.97347	1.323287	0.263655
H	-1.47626	2.899796	0.262955
C	-1.3E-05	0.000003	1.536932
O	-0.00026	-0.0005	2.717626

Table S16 The cartesian coordinates of the optimized structure for $[Mn(PH_3)_2(CO)_3(H_2)]^+$

Symbol	X	Y	Z
Mn	0.000002	-9.8E-05	-0.2617
P	-1.70569	1.628834	-0.24874
H	-2.35277	1.876212	1.001281
H	-1.39187	2.979448	-0.61031
H	-2.86568	1.449605	-1.07012
P	1.660849	1.673528	-0.32192
H	1.291304	3.031642	-0.59208
H	2.433531	1.887611	0.860929
H	2.730982	1.552616	-1.26722
P	1.705803	-1.62883	-0.2484
H	1.391323	-2.98021	-0.60656
H	2.864177	-1.45124	-1.07241

H	2.355387	-1.87366	1.000831
P	-1.66085	-1.67368	-0.32177
H	-2.72871	-1.5553	-1.26994
H	-1.29038	-3.0324	-0.58758
H	-2.43634	-1.88496	0.859744
C	-0.00011	0.000145	1.532426
O	-0.00023	0.000566	2.70868
H(Iso=1)	0.131371	-0.3919	-1.92779
H(Iso=1)	-0.13153	0.391748	-1.92774

Table S17 The cartesian coordinates of the optimized structure for $[Mn(bpy)(CO)_3]^+$

Symbol	X	Y	Z
C	1.67178	-0.73217	-0.09954
C	0.326164	-2.65215	-0.11535
C	1.441472	-3.48016	-0.0722
C	2.708284	-2.90253	-0.04691
C	2.822	-1.51356	-0.05992
C	1.671716	0.732307	-0.09955
C	0.325931	2.652171	-0.11535
C	1.441166	3.480275	-0.07224
C	2.708031	2.902757	-0.04699
C	2.821869	1.5138	-0.05998
H	-0.67306	-3.07039	-0.13335
H	1.310903	-4.55559	-0.05867
H	3.597549	-3.52242	-0.01459
H	3.801944	-1.05104	-0.03654
H	-0.67333	3.070323	-0.13331
H	1.310503	4.555696	-0.05873
H	3.597243	3.522728	-0.01471
H	3.801854	1.051368	-0.03664
N	0.429055	1.30274	-0.13354
N	0.429171	-1.30271	-0.13356

Mn	-1.12198	-5.3E-05	-0.21656
C	-2.37453	1.291159	-0.53466
C	-2.37442	-1.29136	-0.53474
C	-1.49791	-0.00014	1.534227
O	-3.16529	2.124191	-0.73496
O	-1.69223	-4E-06	2.683741
O	-3.16511	-2.12443	-0.73509

Table S18 The cartesian coordinates of the optimized structure for $[Mn(bpy)(CO)_3(H_2)]^+$

Symbol	X	Y	Z
C	1.676559	-0.70688	-0.10625
C	0.375546	-2.65507	-0.14958
C	1.507259	-3.45923	-0.09095
C	2.76146	-2.8552	-0.04228
C	2.844063	-1.4656	-0.04879
C	1.650708	0.756636	-0.10299
C	0.279902	2.658037	-0.16315
C	1.380693	3.5021	-0.08242
C	2.654826	2.943104	-0.01217
C	2.788106	1.557443	-0.0215
H	-0.61418	-3.09467	-0.18614
H	1.39937	-4.53732	-0.08331
H	3.66308	-3.45602	0.002838
H	3.813063	-0.98166	-0.00843
H	-0.72481	3.060222	-0.21753
H	1.233755	4.575556	-0.07358
H	3.532993	3.576028	0.052393
H	3.77293	1.108893	0.038536
N	0.404371	1.311532	-0.17747
N	0.449763	-1.30504	-0.16164
Mn	-1.14461	-0.02759	-0.26779

C	-2.43981	1.245303	-0.45657
C	-2.39934	-1.34902	-0.36506
C	-1.28539	0.021122	1.557753
O	-3.25498	2.072209	-0.5639
O	-1.3503	0.056849	2.717323
O	-3.19058	-2.20492	-0.40744
H(Iso=1)	-1.09273	-0.44189	-1.972
H(Iso=1)	-0.74777	0.285597	-1.9485

Table S19 The cartesian coordinates of the optimized structure for $[Mn(dmbpy)(CO)_3]^+$

Symbol	X	Y	Z
O	-2.12606	3.277467	-0.73744
N	1.30425	-0.31039	-0.12801
C	0.730726	-1.54927	-0.09257
C	-1.29166	2.488051	-0.53467
C	2.653055	-0.20703	-0.11003
H	3.070406	0.794276	-0.12973
C	3.503461	-1.31259	-0.0647
C	2.903745	-2.57777	-0.03865
H	3.52613	-3.46768	-0.0052
C	1.518873	-2.69618	-0.05151
H	1.059975	-3.67813	-0.02713
N	-1.30426	-0.31039	-0.12801
C	-0.73074	-1.54927	-0.09257
C	-2.65306	-0.20702	-0.11004
H	-3.07041	0.794286	-0.12974
C	-3.50347	-1.31257	-0.0647
C	-2.90376	-2.57776	-0.03865
H	-3.52615	-3.46767	-0.00519
C	-1.51889	-2.69617	-0.05151
H	-1.05999	-3.67813	-0.02712
O	2.126115	3.277416	-0.73744

O	0.000022	1.815822	2.685041
C	-1.3E-05	1.619321	1.535457
C	1.291655	2.488061	-0.53465
Mn	0	1.23874	-0.21291
C	4.989681	-1.14297	-0.04378
H	5.421367	-1.57208	0.868306
H	5.456531	-1.6536	-0.89429
H	5.278267	-0.08882	-0.08622
C	-4.98969	-1.14296	-0.04378
H	-5.45654	-1.65359	-0.89428
H	-5.42138	-1.57205	0.868312
H	-5.27827	-0.0888	-0.08623

Table S20 The cartesian coordinates of the optimized structure for $[Mn(dmbpy)(CO)_3(H_2)]^+$

Symbol	X	Y	Z
O	-2.14099	3.349856	-0.40187
N	1.304971	-0.31213	-0.1717
C	0.722032	-1.54295	-0.09444
C	-1.30045	2.54154	-0.36011
C	2.653175	-0.21431	-0.158
H	3.074794	0.783951	-0.21516
C	3.497002	-1.3223	-0.07442
C	2.890396	-2.58319	-0.00266
H	3.508021	-3.47453	0.063452
C	1.506431	-2.69317	-0.01136
H	1.04169	-3.67071	0.050297
N	-1.31565	-0.30468	-0.15423
C	-0.73871	-1.53927	-0.09648
C	-2.66322	-0.20345	-0.14211
H	-3.08241	0.79676	-0.18139
C	-3.51175	-1.30946	-0.07953

C	-2.91053	-2.5737	-0.0283
H	-3.53159	-3.46377	0.019956
C	-1.52694	-2.68826	-0.03541
H	-1.06575	-3.66851	0.007349
O	2.139898	3.325221	-0.56693
O	0.090569	1.461396	2.720295
C	0.050655	1.400562	1.560288
C	1.295023	2.52831	-0.45693
Mn	-0.00451	1.262401	-0.26375
C	4.984191	-1.16058	-0.05908
H	5.412981	-1.55883	0.868279
H	5.448253	-1.7051	-0.88987
H	5.279187	-0.1104	-0.13983
C	-4.99827	-1.14194	-0.06586
H	-5.4616	-1.66608	-0.91011
H	-5.43215	-1.55871	0.850919
H	-5.28866	-0.08899	-0.12448
H(Iso=1)	0.289078	0.836121	-1.9403
H(Iso=1)	-0.41429	1.227576	-1.96943

Table S21 The cartesian coordinates of the optimized structure for $[Mn(dcbpy)(CO)_3]^+$

Symbol	X	Y	Z
O	-2.11799	3.438541	-0.71928
N	1.302176	-0.16909	-0.12508
O	5.707495	-2.0312	-0.00477
C	0.731734	-1.41406	-0.08414
C	-1.29091	2.642096	-0.52155
C	2.648001	-0.06353	-0.10959
H	3.085207	0.927993	-0.13361
C	3.473209	-1.18478	-0.06115
C	2.897161	-2.45355	-0.02807
H	3.543473	-3.32582	0.008232

C	1.510609	-2.56635	-0.03914
H	1.048755	-3.54611	-0.01015
C	4.949132	-1.06811	-0.04406
N	-1.30217	-0.1691	-0.12512
O	-5.70749	-2.03121	-0.00475
C	-0.73173	-1.41406	-0.08417
C	-2.648	-0.06354	-0.10969
H	-3.0852	0.927985	-0.13373
C	-3.4732	-1.18479	-0.06129
C	-2.89715	-2.45356	-0.02818
H	-3.54347	-3.32583	0.008091
C	-1.5106	-2.56636	-0.0392
H	-1.04875	-3.54612	-0.0102
C	-4.94913	-1.06812	-0.04428
O	2.118015	3.438529	-0.71927
O	-8.4E-05	1.953578	2.694173
C	-2.2E-05	1.758398	1.545115
C	1.290928	2.642102	-0.52148
Mn	0.000003	1.384795	-0.20747
O	5.354133	0.225767	-0.07779
H	6.329763	0.313183	-0.06582
O	-5.35413	0.225766	-0.07758
H	-6.32975	0.313188	-0.06535

Table S22 The cartesian coordinates of the optimized structure for $[Mn(dcbpy)(CO)_3(H_2)]^+$

Symbol	X	Y	Z
O	-2.13547	3.501829	-0.39339
N	1.303985	-0.17035	-0.15818
O	5.701865	-2.04255	0.014527
C	0.726418	-1.40852	-0.07746
C	-1.30149	2.688858	-0.34918

C	2.649039	-0.06911	-0.14956
H	3.088719	0.919935	-0.20877
C	3.469835	-1.19134	-0.06765
C	2.888868	-2.45647	0.010539
H	3.531428	-3.32966	0.075461
C	1.503285	-2.56268	0.00618
H	1.037282	-3.53871	0.071036
C	4.945928	-1.07959	-0.06054
N	-1.31121	-0.16684	-0.14215
O	-5.71201	-2.03657	-0.00577
C	-0.73619	-1.40696	-0.07878
C	-2.656	-0.06521	-0.13424
H	-3.09551	0.924731	-0.17783
C	-3.47852	-1.18749	-0.07077
C	-2.89947	-2.45437	-0.01078
H	-3.54309	-3.32776	0.038997
C	-1.51401	-2.56177	-0.01399
H	-1.04906	-3.53928	0.034166
C	-4.95436	-1.07382	-0.06516
O	2.128017	3.484643	-0.54477
O	0.079649	1.628785	2.735858
C	0.044533	1.55374	1.577139
C	1.291978	2.680065	-0.43735
Mn	-0.00475	1.405216	-0.24927
O	5.356407	0.210608	-0.14785
H	6.332474	0.293218	-0.14181
O	-5.36312	0.218105	-0.13538
H	-6.33911	0.301616	-0.12991
H(Iso=1)	0.312513	1.029174	-1.93352
H(Iso=1)	-0.42816	1.345753	-1.94987

Table S23 The cartesian coordinates of the optimized structure for $[Mn(dOMebpy)(CO)_3]^+$

Symbol	X	Y	Z
O	-2.1232	3.48649	-0.72111
N	1.305358	-0.10942	-0.13289
C	0.728492	-1.35237	-0.08431
C	-1.29198	2.692711	-0.52486
C	2.64357	0.002739	-0.12431
H	3.094432	0.987739	-0.15449
C	3.486068	-1.11589	-0.07277
C	2.910763	-2.38822	-0.02893
H	3.521927	-3.28312	0.011331
C	1.523761	-2.49347	-0.03478
H	1.067175	-3.47637	0.001584
N	-1.30533	-0.10943	-0.13292
C	-0.72846	-1.35238	-0.08431
C	-2.64355	0.002716	-0.12435
H	-3.09442	0.987711	-0.15456
C	-3.48604	-1.11592	-0.07279
C	-2.91072	-2.38824	-0.02891
H	-3.52188	-3.28315	0.011371
C	-1.52372	-2.49349	-0.03475
H	-1.06712	-3.47638	0.001639
O	2.123227	3.486523	-0.72095
O	-0.00025	1.990472	2.689815
C	-8.1E-05	1.804642	1.538523
C	1.292005	2.692745	-0.52469
Mn	0.000008	1.439648	-0.21344
O	-4.80968	-0.84017	-0.07098
O	4.809706	-0.84013	-0.07094
C	5.770891	-1.92631	-0.01335
H	6.745061	-1.44221	-0.02106

H	5.647038	-2.50093	0.911086
H	5.6702	-2.5761	-0.88955
C	-5.77085	-1.92636	-0.01337
H	-5.647	-2.50095	0.911086
H	-6.74503	-1.44227	-0.0211
H	-5.67015	-2.57617	-0.88955

Table S24 The cartesian coordinates of the optimized structure for $[Mn(dOMebpy)(CO)_3(H_2)]^+$

Symbol	X	Y	Z
O	-2.13986	3.551922	-0.38557
N	1.306968	-0.11115	-0.17627
C	0.721435	-1.34651	-0.09074
C	-1.3025	2.740628	-0.34957
C	2.644417	-0.00394	-0.17003
H	3.098219	0.978323	-0.23243
C	3.481113	-1.12433	-0.08402
C	2.899629	-2.39247	0.000133
H	3.506405	-3.28847	0.070042
C	1.513382	-2.4902	-0.00355
H	1.051695	-3.4689	0.066123
N	-1.31665	-0.10542	-0.15464
C	-0.73523	-1.34395	-0.09154
C	-2.65349	0.003289	-0.14777
H	-3.10648	0.987046	-0.19041
C	-3.4932	-1.11647	-0.08296
C	-2.91527	-2.38731	-0.02226
H	-3.52412	-3.28314	0.029168
C	-1.52918	-2.4877	-0.02657
H	-1.06958	-3.4687	0.021464
O	2.133693	3.529715	-0.56687
O	0.098174	1.647569	2.722311

C	0.054897	1.592334	1.562124
C	1.292983	2.729179	-0.45575
Mn	-0.00542	1.460717	-0.26233
O	4.806579	-0.85623	-0.09042
O	-4.81802	-0.84466	-0.0863
C	-5.77526	-1.93289	-0.01212
H	-5.64922	-2.49341	0.920644
H	-6.75122	-1.45246	-0.02667
H	-5.67277	-2.59567	-0.87834
C	5.76093	-1.94553	0.004257
H	6.738118	-1.46798	-0.01891
H	5.633141	-2.48822	0.947259
H	5.656908	-2.62394	-0.84959
H(Iso=1)	-0.41313	1.446838	-1.96828
H(Iso=1)	0.272987	1.025539	-1.93867

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2 Weinrauch, I.; Savchenko, I.; Denysenko, D.; Souliou, S. M.; Kim, H.-H.; Le Tacon, M.; Daemen, L. L.; Cheng, Y.; Mavrandonakis, A.; Ramirez-Cuesta, A. J.; Volkmer, D.; Schütz, G.; Hirscher, M.; Heine, T. *Nat. Commun.* **2017**, *8* (1), 14496.