Supporting Information for:

Synthesis and Characterization of Manganese Triple-Decker Complexes

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Contents

1. NMR Investigations:

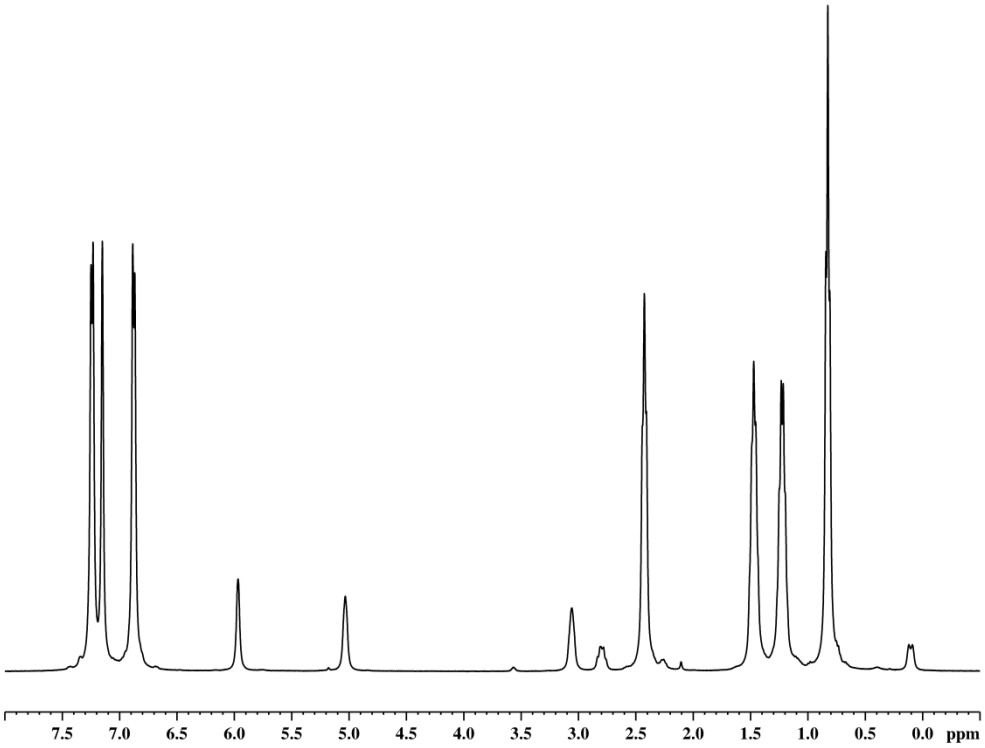

Figure S1. ^{1}H NMR spectrum of **1** in C_6D_6 at 298 K.

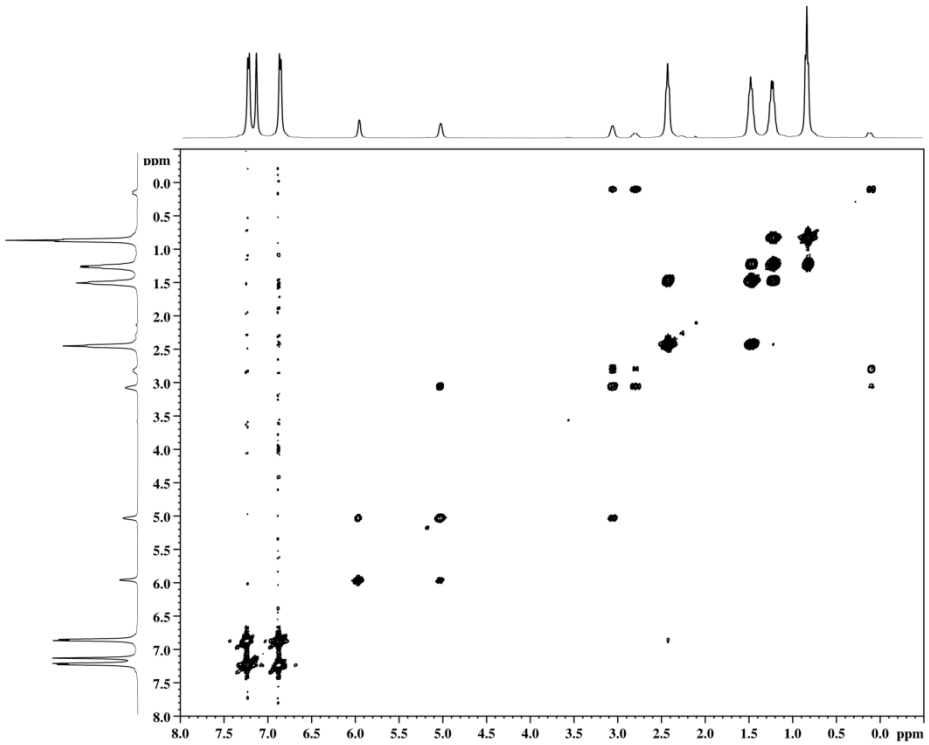

Figure S2. ^{1}H COSY NMR of **1** in C_6D_6 at 298 K.

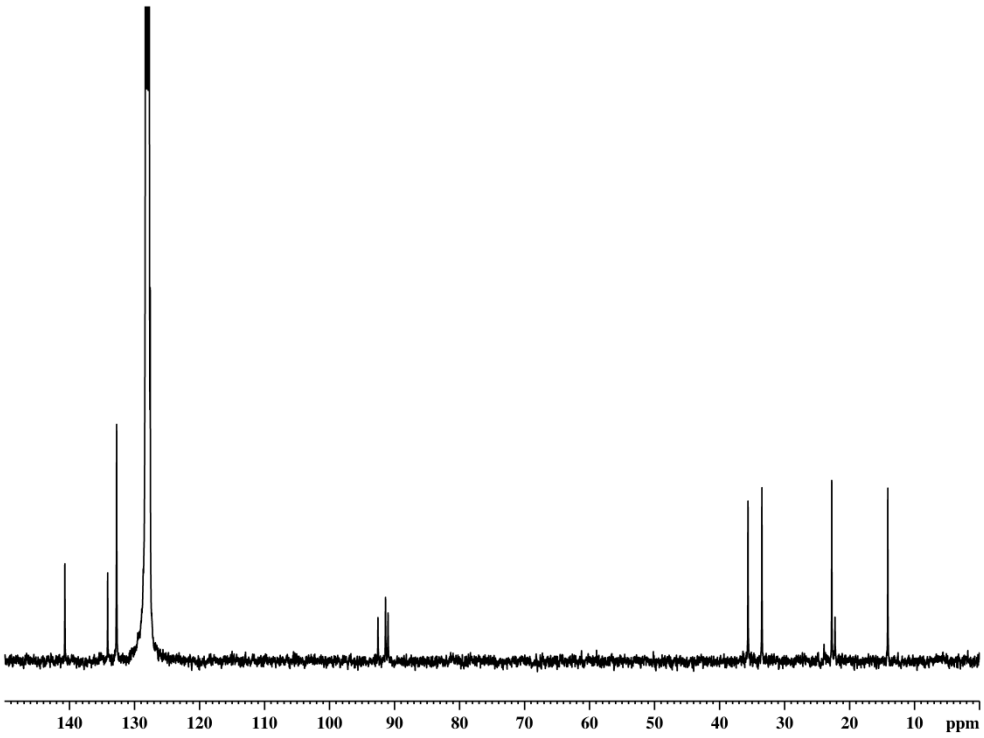

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **1** in C_6D_6 at 298 K.

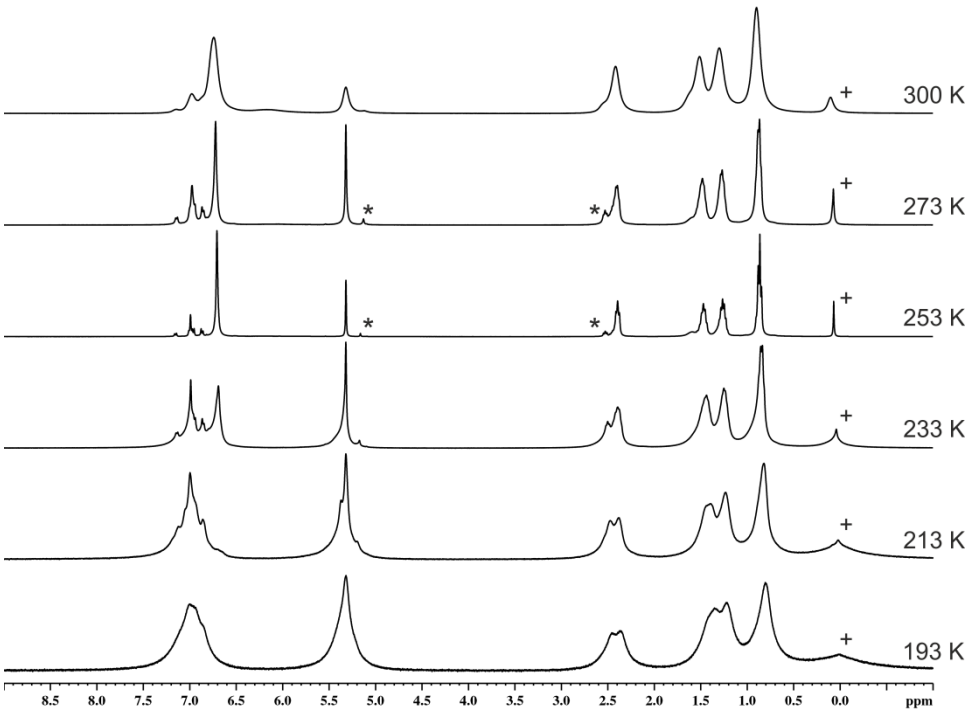

Figure S4. ^{1}H NMR spectrum of a mixture of **2** and **3** in CD_2Cl_2 at various temperatures. (* = $Cp^{BIG}H$ impurities; + = silicon grease).

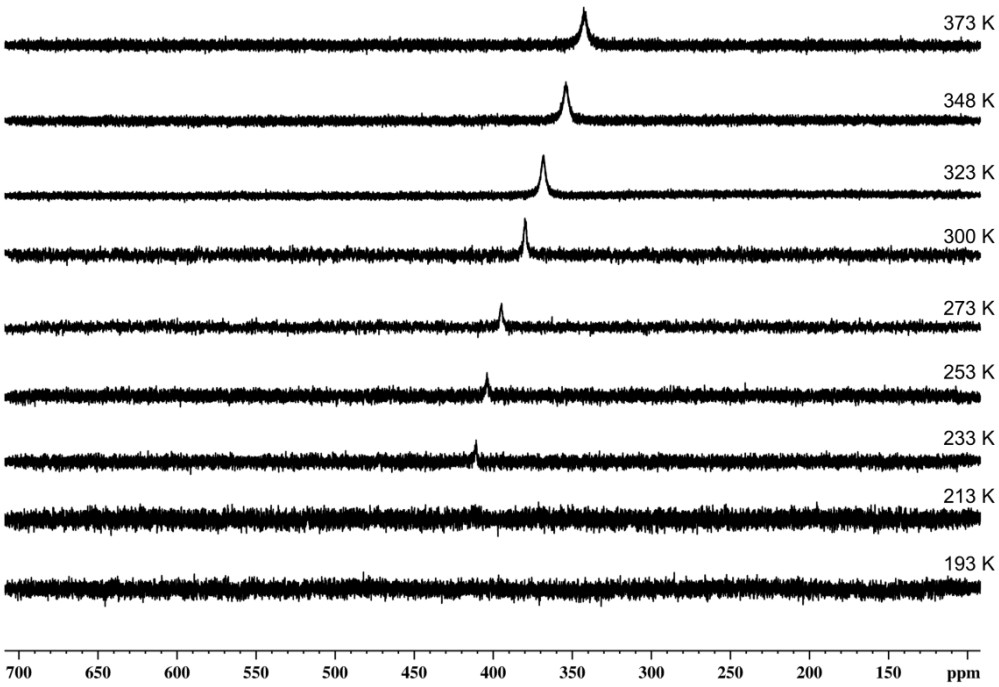

Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum of a mixture of **2** and **3** at various temperatures. Spectra from 193 K to 300 K have been collected in CD_2Cl_2 and spectra from 323 K to 373 K in d_8-toluene.

Table S1. $^{31}P\{^{1}H\}$ NMR parameters of a mixture of **2** and **3** at various temperatures. Decrease of temperature results in a signal sharpening effect.

T [K]	**Solvent**	**δ [ppm]**	**$\omega_{1/2}$ [Hz]**
373	d_8-toluene	342.9	717
348		354.1	684
323		368.2	559
300		385.2	460
300	CD_2Cl_2	380.1	379
273		394.8	329
253		404.1	375
233		410.9	293

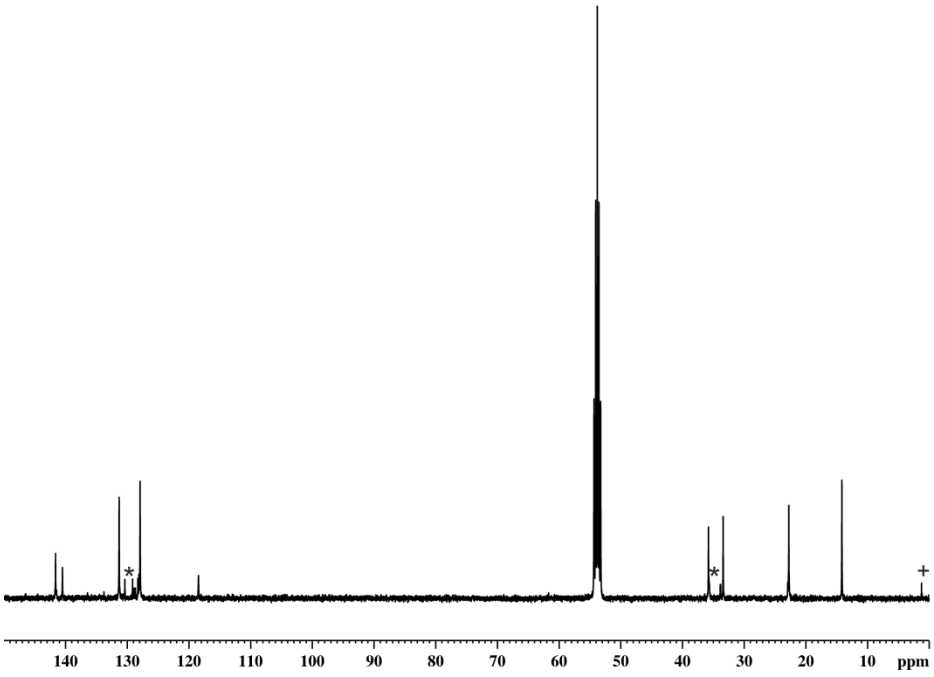

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of a mixture of **2** and **3** in CD_2Cl_2. (* = $Cp^{BIG}H$ impurities; + = silicon grease).

2. Crystallographic Details:

The crystal structure analyses were performed on an Oxford Diffraction SuperNova diffractometer. For both compounds an analytical absorption correction was carried out.[1] The structures were solved by direct methods of the program SIR-92[2] and refined with the least square method on F^2 employing SHELXL-97[3] with anisotropic displacements for non-H atoms. Hydrogen atoms were located in idealized positions and refined isotropically according to the riding model. CCDC 1048598 (**1**) and -1048599 (**2**/**3**).

	Crystal Data for **1**	Crystal Data for **2**/**3** * **6C_7H_8**
Empirical Formula	$C_{62}H_{73}Mn$	$C_{152}H_{178}Mn_2P_{4.7}$
Formula Weight	873.14	2260.37
Temperature [K]	123.00(10)	123.0(2)
Crystal System	triclinic	monoclinic
Space Group	$P\bar{1}$	$P2_1/m$
a [Å]	14.1067(7)	17.11800(15)

b [Å]	14.5710(5)	23.57334(16)
c [Å]	14.6081(5)	17.22285(14)
α [°]	105.957(3)	90
β [°]	94.745(3)	110.9973(10)
γ [°]	118.726(4)	90
Volume [Å^3]	2448.1(2)	6488.41(10)
Z	2	2
ρ_{calc} [mg/mm^3]	1.184	1.157
μ [mm^{-1}]	2.469	2.503
F(000)	940	2421
Crystal Size [mm^3]	0.162 × 0.0788 × 0.0243	0.337 × 0.155 × 0.116
Radiation	Cu-K$_\alpha$ (λ = 1.54178)	Cu-K$_\alpha$ (λ = 1.54178)
2Θ Range	6.5 to 141.76°	6.65 to 147.22°
Index Ranges	-17 ≤ h ≤ 16	-20 ≤ h ≤ 21
	-17 ≤ k ≤ 12	-29 ≤ k ≤ 23
	-17 ≤ l ≤ 17	-21 ≤ l ≤ 21
Reflections Collected	20568	61294
Independent Reflections	9066	13251
	[R_{int} = 0.0244, R_{sigma} = 0.0291]	[R_{int} = 0.0378, R_{sigma} = 0.0229]
Data/Restraints/Parameters	9066/6/586	13251/162/664
Goodness-of-Fit on F^2	1.041	1.030
Final R Indexes [I > 2σ(I)]	R_1 = 0.0420, wR_2 = 0.1110	R_1 = 0.0622, wR_2 = 0.1802
Final R Indexes [All Data]	R_1 = 0.0484, wR_2 = 0.1163	R_1 = 0.0652, wR_2 = 0.1840
Largest Diff. Peak/Hole [e·Å^{-3}]	0.384/-0.356	1.238/-1.303
Flack Parameter	-	-

With the aid of PLATON,[4] two solvent accessible areas were found in the crystal structure of **2**/**3**, but it was impossible to refine any reasonable molecules from difference Fourier peaks. Therefore the midpoints, the sizes and the numbers of electrons in the voids were refined and the contribution to the calculated structure factors of the disordered solvent is taken into account by back-Fourier transformation with the program SQUEEZE[5] (Sluis and Spek, 1990). The voids are found around (-0.019 0.250 -0.014), and (0.007 0.750 0.011) and the sizes are 1056 $Å^3$ and 306 e^- and 299 e^- were detected (whole cell), respectively. The number of electrons corresponds each to six toluene molecules.

Some of the butyl groups of **2**/**3** are disordered and had to be treated with SIMU restraints to obtain reasonable displacement parameters.

In the crystal structure of **1** a disorder over two positions (78/22) of a methylene group and a neighboring methine moiety is observed (see Figure S7).

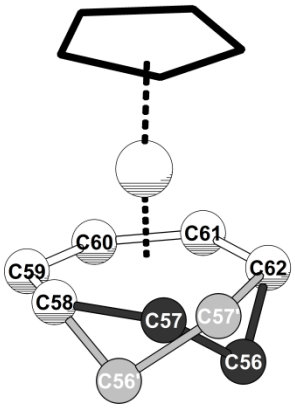

Figure S7. Schematic illustration of the disorder of the cht ligand in **1** in the crystal. Different parts are colored differently; hashed globes belong to both parts.

3. LIFDI Mass Spectrum of Compound 2/3

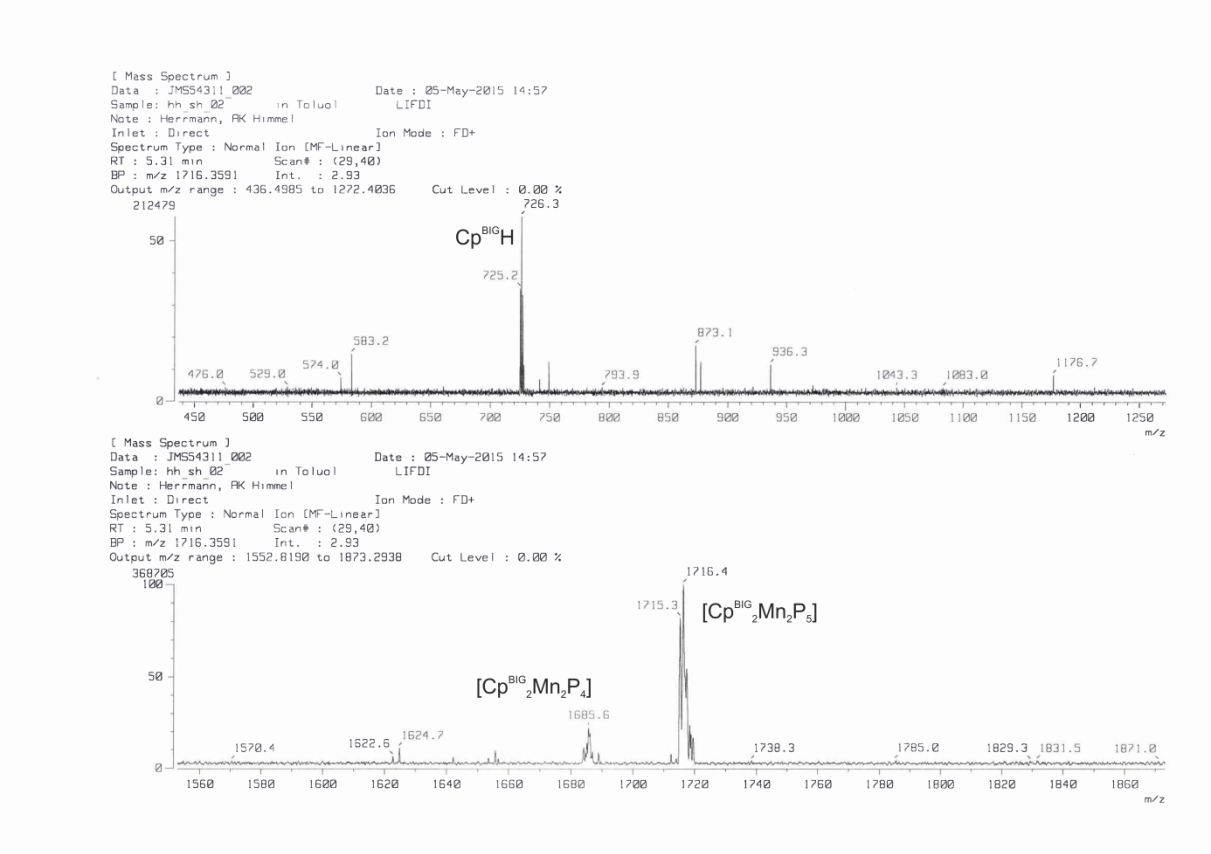

Figure S8. LIFDI mass spectrum of the compound mixture **2**/**3** in toluene.

4. DFT Calculations:

All calculations were carried out using the TURBOMOLE program.[6] The geometries were optimized using the RI-[7]BP86[8] functional together with the def2-SVP[9] basis set for all atoms. The Multipole Accelerated Resolution of Identity (MARI-J)[10] approximation was used in the geometry optimizations. The final energy of the molecules has been determined by single point calculations without using the RI formalism. The EPR g tensors for the model compound [(C_5Ph_5)Mn(μ,$\eta^{5:5}$-P_5)] (**2'**) have been computed using the Orca[11] program package. The EPR spectrum has been simulated with the EasySpin program.[12]

Table S2. Calculated g-matrix of [(C_5Ph_5)Mn(μ,$\eta^{5:5}$-P_5)] (**2'**) at the BP86/def2-SVP level of theory.

1.9332035	-0.0026597	0.0000001
0.0026241	1.9332197	0.0000001
0.0000002	0.0000001	2.0049926

Table S3. Calculated hyperfine coupling (all values in MHz) for [(C_5Ph_5)Mn(μ,$\eta^{5:5}$-P_5)] (**2'**) at the BP86/def2-SVP level of theory.

Mn 0			
A(FC)	88.1149	88.1149	88.1149
A(SD)	-65.9072	-65.8556	131.7628
A(tot)	22.2077	22.2593	219.8776
A(iso)	88.1149		

Mn 1			
A(FC)	88.1147	88.1147	88.1147
A(SD)	-65.9071	-65.8571	131.7642
A(tot)	22.2076	22.2575	219.8789
A(iso)	88.1147		

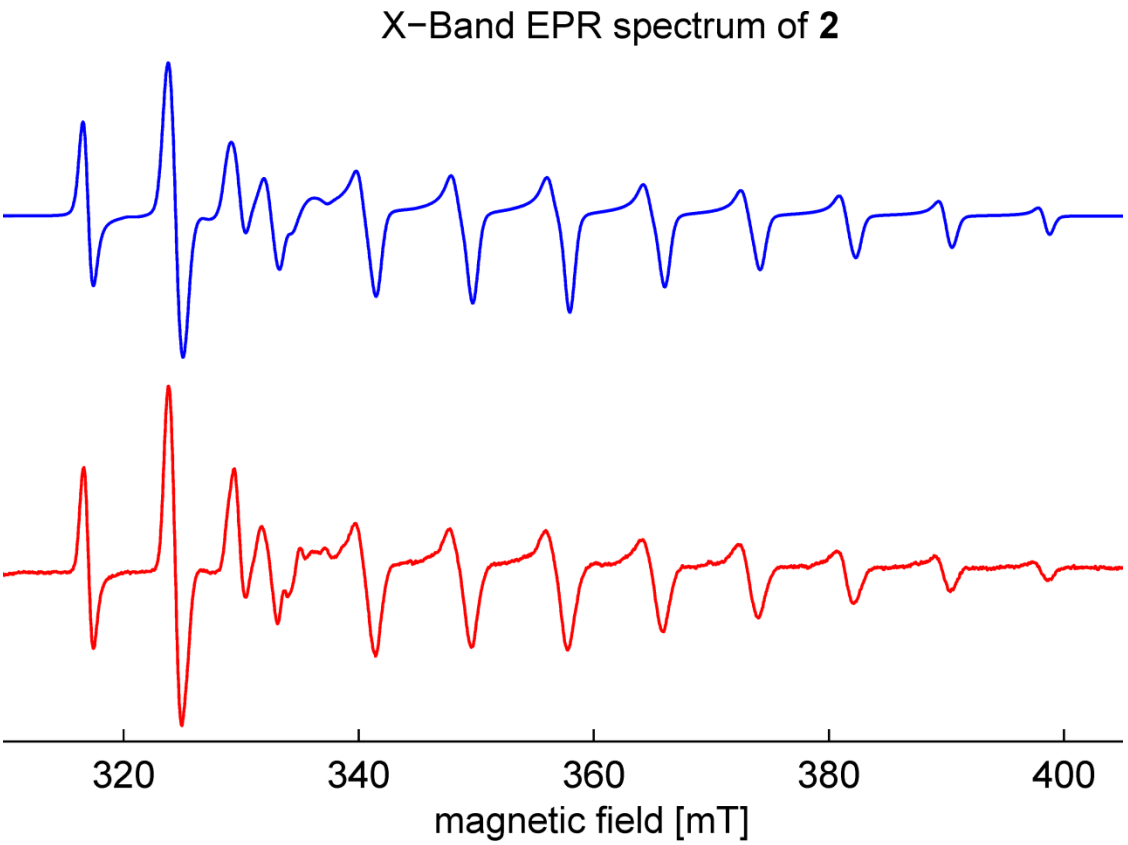

Figure S9. Experimental (red) and fitted (blue) X-Band EPR spectrum of **2** in toluene at 77 K. Parameters used for the fitting: $g_x = g_y = 1.8845$, $g_z = 1.99945$; $A_{1,1} = 215.7$, $A_{2,1} = 215.0$, $A_{1,2} = 10.5$, $A_{2,2} = 36.5$ MHz.

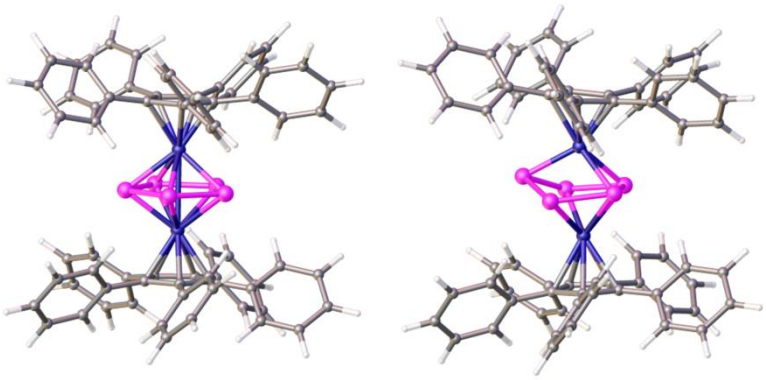

Figure S10. Calculated minimum structures of **2'** in doublet (left) and quartet (right) spin state.

Table S4. Cartesian coordinates of the optimized geometry of [(C_5Ph_5)Mn(μ,$\eta^{5:5}$-P_5)] (**2'**) in the doublet spin state at the BP86/def2-SVP level of theory.

Atom	x	y	z	Atom	x	y	z
Mn	0.001052	-0.0008043	1.438787	C	5.310225	-1.43749	3.944381
Mn	0.0010462	-0.0008075	-1.4387371	H	5.804816	-0.08309	2.313421
P	-1.8824285	-0.1772805	0.0000291	C	0.965445	-3.54151	-2.65858
P	-0.4134781	-1.8469821	0.0000282	C	-0.65845	-3.30378	-4.44699
P	1.6286256	-0.9659119	0.0000229	C	-3.06926	-2.01278	-2.65655
P	1.4219527	1.2486721	0.0000212	C	-3.34617	-0.39465	-4.44452
P	-0.7480431	1.7362972	0.0000249	C	-2.8618	2.298489	-2.6556
C	0.0454834	-1.2351883	3.2128637	C	-1.40909	3.060238	-4.44485
C	-1.160607	-0.424958	3.2119433	C	1.301008	3.431885	-2.65549
C	1.1887648	-0.3385772	3.2130098	C	2.474369	2.286809	-4.44549
C	0.1058738	-2.709742	3.413599	C	2.936989	-1.64438	-4.45176
C	-0.7626528	0.9725086	3.211654	C	3.666855	-0.18005	-2.65862
C	-2.544442	-0.9379756	3.4116304	H	-4.64924	3.474777	2.308724
C	0.6893918	1.0258883	3.2120231	C	-3.45176	4.285365	3.936044
C	2.6095139	-0.7371777	3.4150733	H	-2.05515	4.83353	5.513972
C	0.9654743	-3.5414995	2.6586674	H	1.866291	5.495744	2.308534
C	-0.6584083	-3.3037539	4.4470806	C	3.006982	4.60832	3.936493
C	-1.6779281	2.1304483	3.411376	H	3.959646	3.450542	5.515355
C	-3.0692723	-2.0127205	2.6565411	H	1.581363	-3.10221	-1.86134
C	-3.3461974	-0.3945948	4.4445184	C	1.046734	-4.91789	-2.91747
C	1.5073283	2.2545014	3.4117376	H	-1.31746	-2.67534	-5.06282
C	2.937019	-1.6444451	4.4517102	C	-0.57433	-4.68066	-4.70611
C	3.6668521	-0.1801128	2.6585636	H	-2.46078	-2.46272	-1.85956
H	1.5813209	-3.102226	1.8613621	C	-4.35305	-2.5158	-2.91516
C	1.0468584	-4.9178632	2.9176511	H	-2.95269	0.426755	-5.06014
H	-1.3174921	-2.6753184	5.0628524	C	-4.6295	-0.90066	-4.70345
C	-0.5741985	-4.6806066	4.7063058	H	-3.10173	1.581227	-1.85818
C	0.0454727	-1.2351952	-3.2128125	C	-3.73642	3.364481	-2.91401
C	-1.1606183	-0.4249663	-3.2118902	H	-0.50679	2.938892	-5.06097
C	-0.762667	0.9725011	-3.2116053	C	-2.28629	4.124992	-4.70354
C	0.6893773	1.0258826	-3.2119793	H	0.544887	3.437461	-1.858
C	1.1887519	-0.338582	-3.2129666	C	2.043895	4.59355	-2.91381
C	-2.8617778	2.2985091	2.6556365	H	2.637955	1.391454	-5.06197
C	-1.4090588	3.0602636	4.4448759	C	3.21516	3.450594	-4.70419
H	-2.4607215	-2.4627776	1.8596759	H	2.134879	-2.07409	-5.06859
C	-4.3531715	-2.5155748	2.9149788	C	4.272106	-1.9898	-4.71287
H	-2.9526482	0.4266905	5.0602511	H	3.440042	0.538428	-1.85848
C	-4.6296296	-0.900434	4.7032674	C	5.000659	-0.52792	-2.91955
C	1.3009978	3.4319027	2.6555624	H	1.721057	-5.54368	-2.31283
C	2.4743602	2.2868215	4.4455559	C	0.274887	-5.49547	-3.9393
H	2.1349396	-2.0739847	5.0686999	H	-1.1778	-5.11782	-5.51662
C	4.2721178	-1.9901103	4.7125921	H	-4.73936	-3.35075	-2.31053
H	3.4400418	0.538532	1.8585675	C	-5.14133	-1.96049	-3.93675
C	5.0006382	-0.5282237	2.9192593	H	-5.23211	-0.46199	-5.51379
H	1.7212326	-5.5436413	2.3130694	H	-4.64933	3.474693	-2.30877
C	0.2750584	-5.4954155	3.9395309	C	-3.45184	4.285281	-3.93609
H	-1.1776008	-5.1177529	5.5168691	H	-2.05524	4.833435	-5.51402
C	0.1058611	-2.709751	-3.413533	H	1.866456	5.495659	-2.30831
C	-2.5444477	-0.9379925	-3.4115932	C	3.00713	4.608246	-3.93629
C	-1.677946	2.1304368	-3.4113338	H	3.959809	3.450467	-5.51514

C	1.5073161	2.254495	-3.4116883	H	4.500564	-2.69616	-5.52593
C	2.6094992	-0.7371703	-3.4150663	C	5.310238	-1.43708	-3.94477
H	-3.1017312	1.5812167	1.8582506	H	5.80486	-0.08265	-2.31384
C	-3.7363529	3.3645439	2.913995	H	0.338207	-6.57606	4.140297
H	-0.5067875	2.9388926	5.0610236	H	-6.14965	-2.35459	4.136944
C	-2.2862281	4.1250606	4.7035159	H	-4.13793	5.122717	4.136316
H	-4.7395321	-3.3504262	2.3102488	H	3.590562	5.520123	4.13688
C	-5.1414941	-1.9601952	3.9364967	H	6.3572104	-1.711444	4.1465517
H	-5.232297	-0.4616639	5.513506	H	0.3379799	-6.576126	-4.140007
H	0.5449438	3.4374513	1.8580119	H	6.3572332	-1.71089	-4.14708
C	2.0437875	4.5936094	2.9139737	H	-6.149424	-2.354984	-4.137303
H	2.6380155	1.3914319	5.0619742	H	-4.138034	5.1226063	-4.136389
C	3.2150535	3.4506475	4.7043511	H	3.5907646	5.520026	-4.136622
H	4.5005798	-2.6966028	5.5255272				

Table S5. Cartesian coordinates of the optimized geometry of [(C_5Ph_5)Mn(μ,$\eta^{4:3}$-P_5)] (**2'**) in the quartet spin state at the BP86/def2-SVP level of theory.

Atom	x	y	z	Atom	x	y	z
Mn	-0.0624735	-0.1911833	1.6008121	C	5.2539884	-1.621206	4.1176793
Mn	-0.0257799	-0.0714212	-1.5606218	H	5.7487031	-0.566309	2.2789972
P	-1.9085371	-0.4435226	-0.1426019	C	1.0522828	-3.508108	-3.032862
P	-0.6372244	-2.1223567	0.5123983	C	-0.528837	-3.223461	-4.853048
P	1.3483396	-1.4168045	-0.1385719	C	-2.963619	-2.112009	-2.933343
P	1.430057	0.8257953	0.1013866	C	-3.342833	-0.426089	-4.640114
P	-0.7378658	1.4757771	0.096471	C	-2.898113	2.1972079	-2.700549
C	-0.0004119	-1.2717109	3.4737666	C	-1.517123	3.118368	-4.472762
C	-1.1877332	-0.434881	3.4225062	C	1.2014715	3.423014	-2.610034
C	1.1663902	-0.416371	3.3708429	C	2.4616186	2.49463	-4.468726
C	0.0374511	-2.7296277	3.7739988	C	3.0437191	-1.440561	-4.68631
C	-0.7541651	0.9437676	3.2949111	C	3.6379006	-0.095824	-2.75185
C	-2.5847755	-0.8801762	3.6880728	H	-4.592207	3.4413054	2.2157008
C	0.7007725	0.9537359	3.2703191	C	-3.369361	4.3557212	3.7672858
C	2.5760014	-0.8514958	3.5791614	H	-1.952119	5.00502	5.2873301
C	0.8838331	-3.6164714	3.0672101	H	1.9421025	5.3038769	1.9587145
C	-0.7336431	-3.2478924	4.8408711	C	3.1473016	4.5101777	3.5887914
C	-1.6419921	2.1332061	3.4114919	H	4.1552677	3.4481055	5.1999582
C	-3.1844826	-1.9610357	3.0026157	H	1.6314191	-3.09297	-2.19479
C	-3.3259117	-0.2498269	4.7172013	C	1.1649421	-4.871	-3.346503
C	1.5591297	2.169398	3.3308897	H	-1.184708	-2.580045	-5.45715
C	2.8973514	-1.6118412	4.7298206	C	-0.413511	-4.586198	-5.166395
C	3.6254535	-0.4809904	2.7084078	H	-2.319287	-2.566582	-2.16698
H	1.5049793	-3.2326579	2.2446259	C	-4.233082	-2.652206	-3.185859
C	0.9474916	-4.9753444	3.4084645	H	-2.995206	0.4381035	-5.224126
H	-1.3845654	-2.5745059	5.4166392	C	-4.612651	-0.969163	-4.892187
C	-0.6676278	-4.6084997	5.1816453	H	-3.091589	1.4253844	-1.941448
C	0.0945302	-1.1986888	-3.5136846	C	-3.809945	3.2501083	-2.86646
C	-1.1294579	-0.4366745	-3.4483193	H	-0.626851	3.0645117	-5.115969
C	-0.7732273	0.9835636	-3.3823202	C	-2.431487	4.1699023	-4.638393
C	0.6659171	1.083259	-3.4245666	H	0.4268735	3.3200349	-1.836186
C	1.2032512	-0.2595214	-3.4571923	C	1.9298902	4.6168708	-2.715503
C	-2.8254013	2.2615001	2.6476864	H	2.6654124	1.6707277	-5.167936
C	-1.3466489	3.1373691	4.3639468	C	3.1881532	3.6907388	-4.57279
H	-2.6238274	-2.4781566	2.2095426	H	2.2854144	-1.841091	-5.37449
C	-4.4812622	-2.38895	3.3240917	C	4.3986301	-1.743398	-4.891322
H	-2.8740884	0.581502	5.2772614	H	3.3455238	0.5511856	-1.911626
C	-4.6222386	-0.6798981	5.0399475	C	4.991219	-0.403894	-2.956092
C	1.3431573	3.2913556	2.4966084	H	1.8319361	-5.510665	-2.748197
C	2.5826121	2.2519192	4.3056686	C	0.4315302	-5.41786	-4.412497
H	2.0979041	-1.8995387	5.4281366	H	-0.988591	-4.999572	-6.009401
C	4.2219688	-1.991513	4.9959039	H	-4.574847	-3.525839	-2.609745
H	3.3983191	0.1110899	1.810272	C	-5.064899	-2.082201	-4.164499
C	4.9489062	-0.8633403	2.9747592	H	-5.252033	-0.517116	-5.666177
H	1.6111381	-5.6461195	2.841454	H	-4.708129	3.29371	-2.23144
C	0.1696611	-5.4788665	4.4649564	C	-3.580635	4.2430459	-3.833645
H	-1.2766829	-4.9886965	6.0163255	H	-2.243421	4.9366684	-5.405813
C	0.1997158	-2.659868	-3.776593	H	1.716958	5.4450133	-2.022088
C	-2.497803	-0.9865603	-3.6527642	C	2.9272438	4.7567055	-3.695626
C	-1.7316599	2.1158862	-3.4961122	H	3.963104	3.7895582	-5.348597
C	1.4560856	2.3397726	-3.4839782	H	4.6893401	-2.386959	-5.735953
C	2.6410582	-0.6117216	-3.6116251	C	5.3780307	-1.229164	-4.025321

H	-3.077799	1.4867717	1.9097398	H	5.7495675	0.0053978	-2.271065
C	-3.6780833	3.3614223	2.823887	H	0.2183371	-6.546231	4.7303436
H	-0.4414446	3.0483171	4.9819499	H	-6.226571	-2.083896	4.5917356
C	-2.2016428	4.2368575	4.5390606	H	-4.038355	5.2196094	3.9025453
H	-4.9265635	-3.2305837	2.7716103	H	3.7650386	5.4163179	3.6854423
C	-5.208033	-1.748889	4.3418419	H	6.2928999	-1.92165	4.3238543
H	-5.1771765	-0.1739446	5.8450477	H	0.5192853	-6.487908	-4.656145
H	0.54373	3.2617441	1.7418921	H	6.4404407	-1.470508	-4.183892
C	2.1289008	4.4462689	2.6230298	H	-6.06225	-2.50533	-4.360279
H	2.7566372	1.4026638	4.9812944	H	-4.29682	5.0692855	-3.962029
C	3.3668938	3.4091148	4.4324653	H	3.4989178	5.6941387	-3.776016
H	4.4472083	-2.5813435	5.8978903				

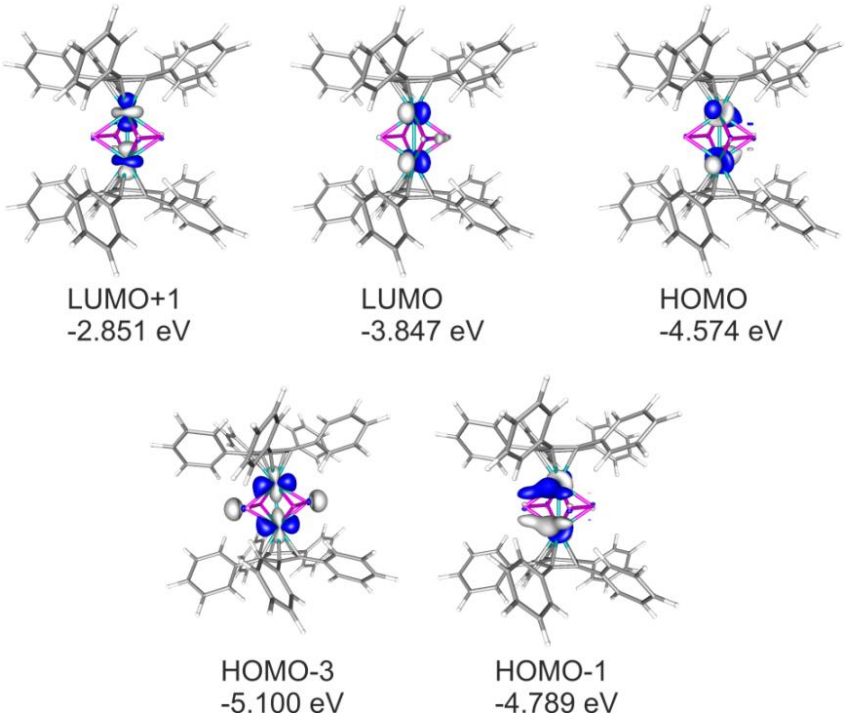

Figure S11. Selected molecular orbitals in $[(C_5Ph_5)Mn(\mu,\eta^{2:2}\text{-}P_2)_2]$ (**3'**). Calculated at the BP86/def2-SVP level of theory.

Table S6. Cartesian coordinates of the optimized geometry of $[(C_5Ph_5)Mn(\mu,\eta^{4:3}\text{-}P_5)]$ (**3'**) in the singlet spin state at the BP86/def2-SVP level of theory.

Atom	x	y	z	Atom	x	y	z
Mn	-0.1195806	0.0991271	0.0835406	C	3.749817	6.127878	2.6798709
Mn	-0.1195849	2.6959809	0.0835199	C	3.4836867	6.3724826	-2.6965108
P	-0.5156862	1.3975386	-1.7461554	C	4.5881455	4.4336897	-1.7465684
P	-1.9719006	1.3975484	-0.1397941	C	-0.9833635	-2.6853589	-5.3150265
P	0.1636388	1.3975689	1.9232613	C	-5.5862202	-2.3787811	-0.7285272
P	1.716637	1.397558	0.4154819	C	-2.5918863	-2.2360847	5.0220311
C	-0.3532298	-1.7448837	-1.1384484	C	3.8015714	-2.6165852	3.8866637
C	-1.3579812	-1.7152952	-0.0856847	C	4.6371798	-2.7888649	-2.5511169
C	-0.6624749	-1.7035135	1.1890557	C	-0.9831866	5.4804695	-5.3150965
C	0.7647095	-1.7589714	0.9230306	C	-5.5862838	5.1737018	-0.7284805
C	0.9536436	-1.764825	-0.5158657	C	-2.591824	5.0311435	5.0220346
C	-0.3532358	4.5399688	-1.1384985	C	3.8017637	5.4113868	3.8865107
C	-1.3579929	4.5103965	-0.0857389	C	4.6371791	5.5841579	-2.5510509
C	-0.6624929	4.498638	1.1890059	H	0.7811527	-0.5084434	-3.3383807
C	0.7646937	4.5540951	0.9229875	H	-1.9983119	-3.6305904	-2.1804242
C	0.9536347	4.5599314	-0.5159083	H	-2.9929843	-0.4998946	-1.9514015
C	-0.5999992	-2.0087433	-2.5846524	H	-3.0060353	-3.3945328	1.285119
C	-2.8214632	-1.8985348	-0.2892797	H	-2.5702492	-0.0894684	2.3407912
C	-1.307794	-1.8444305	2.5253956	H	-0.208423	-3.6610605	3.008723
C	1.8288414	-1.9979961	1.9373541	H	1.1588319	-0.4961137	3.364664
C	2.2292033	-2.0548895	-1.2368702	H	2.7420811	-3.6076172	0.7834851
C	-0.599998	4.803792	-2.5847117	H	1.3993341	-3.8448813	-2.1627033

C	-2.8214768	4.6936281	-0.2893457	H	3.3679981	-0.3721382	-0.4702731
C	-1.3078045	4.6395487	2.5253514	H	0.7810194	3.3033475	-3.3383996
C	1.8288318	4.7930829	1.9373143	H	-1.9982688	6.4256885	-2.1805338
C	2.2291914	4.8500391	-1.2369022	H	-2.9929602	3.2950419	-1.9515177
C	0.0882389	-1.317604	-3.6079378	H	-3.0060568	6.1896864	1.2849954
C	-1.4721659	-3.0594927	-2.9586053	H	-2.5702448	2.8845737	2.3407563
C	-3.5248021	-1.2196945	-1.313722	H	-0.2084175	6.4561668	3.0086914
C	-3.5323903	-2.8345258	0.4997858	H	1.1587823	3.2911949	3.3645993
C	-2.3014247	-0.9469886	2.9758665	H	2.7420942	6.4027247	0.7834895
C	-0.9714492	-2.9449914	3.3478698	H	1.3992685	6.6400103	-2.1627281
C	1.8853675	-1.2970289	3.1642123	H	3.3680482	3.1673394	-0.470281
C	2.7765493	-3.0276513	1.7160067	H	0.4401277	-1.0927264	-5.7352673
C	2.2933165	-3.2148898	-2.0477639	H	-2.3459809	-4.2135516	-4.5739004
C	3.3986692	-1.2768855	-1.0955676	H	-5.4151313	-0.9104827	-2.3270554
C	0.0882629	4.1126377	-3.6079727	H	-5.4283254	-3.8046395	0.9092225
C	-1.4721522	5.8545401	-2.9586983	H	-3.7097383	-0.4305432	4.5419357
C	-3.5248085	4.014771	-1.3137832	H	-1.3275491	-3.9981493	5.2119255
C	-3.5324198	5.6296126	0.4997149	H	2.8885126	-1.0306417	5.0661491
C	-2.301401	3.7420791	2.9758443	H	4.4721039	-4.1400781	2.4829795
C	-0.9714509	5.7401022	3.3478326	H	3.5072221	-4.4838838	-3.3207261
C	1.885375	4.0920562	3.1641379	H	5.484662	-1.0115378	-1.6228877
C	2.7765954	5.8226875	1.7159659	H	0.440505	3.8879977	-5.7352687
C	2.2932744	6.0100531	-2.0477796	H	-2.3461401	7.0083984	-4.5740444
C	3.3986914	4.0720899	-1.0955726	H	-5.4151637	3.7054298	-2.3270295
C	-0.1037669	-1.6500278	-4.9571965	H	-5.428388	6.5996451	0.9091952
C	-1.6621643	-3.3924196	-4.308921	H	-3.7095799	3.225526	4.5419992
C	-4.8906946	-1.455642	-1.5273366	H	-1.327556	6.793263	5.2118859
C	-4.8990418	-3.0705346	0.2822605	H	2.8886137	3.825499	5.0660017
C	-2.9384355	-1.1422472	4.2098505	H	4.4723104	6.9349165	2.4828726
C	-1.6065922	-3.1367229	4.5856805	H	3.5071493	7.2791043	-3.3207147
C	2.8625642	-1.5990566	4.1237263	H	5.4847095	3.8068417	-1.6228442
C	3.7496638	-3.3329907	2.6799719	H	-6.6589966	5.3562885	-0.8961242
C	3.4837274	-3.5772563	-2.6965322	H	5.5705697	5.8656533	-3.0626033
C	4.5881201	-1.6384185	-1.7466054	H	5.5705609	-3.0702942	-3.0627227
C	-0.103566	4.4451713	-4.9572295	H	-1.1362354	-2.9430266	-6.374441
C	-1.6621529	6.187421	-4.3090256	H	-6.658894	-2.5615014	-0.8962739
C	-4.8907285	4.2506209	-1.5273313	H	-1.1359348	5.7382089	-6.3745116
C	-4.8990949	5.8655379	0.2822436	H	-3.0882056	-2.3847907	5.9934161
C	-2.9383514	3.9372888	4.2098673	H	4.5684116	-2.8523347	4.6407182
C	-1.606575	5.9318179	4.5856559	H	-3.0881563	5.179859	5.9934118
C	2.8626654	4.3939478	4.1235993	H	4.5687036	5.6470019	4.6405061

5. $[(CO)_3Mn(\eta^5\text{-}P_5)]$: Calculations and Considerations

The compound $[(CO)_3Mn(\eta^5\text{-}P_5)]$ was only characterized by ^{31}P NMR, a mass spectrum and an IR spectrum.[13] However, the IR spectrum show one CO band in the region of bridging CO ligands (1778 cm^{-1}), which is inconsistent with the proposed molecule. We therefore optimized the geometry of $[(CO)_3Mn(\eta^5\text{-}P_5)]$ (Figure S12) and calculated the CO-stretching frequencies using the BP86 and the B3LYP functionals together with the def2-TZVP basis set. In both cases we obtain stretching frequencies for the CO groups around 2000 cm^{-1}. The BP86 gives 1984 and 2032 cm^{-1} and B3LYP gives 2069 and 2114 cm^{-1}. After correction (f = 1.028 and f = 0.999 for BP86 and B3LYP respectively)[14] we obtain 2039 and 2089 cm^{-1} with BP86 as well as 2067 and 2112 cm^{-1} with B3LYP. This results clearly show that the CO absorption band observed by Baudler et al. do not originate from $[(CO)_3Mn(\eta^5\text{-}P_5)]$.

Table S7. Cartesian coordinates of the optimized geometry of $[(CO)_3Mn(\eta^5\text{-}P_5)]$ (B3LYP/def2-TZVP level of theory)

Atom	x	y	z	Atom	x	y	z
Mn	-0.0933961	0.9846118	1.0403097	C	-1.62144	0.2728989	1.7358938
P	-1.4622769	0.9375486	-1.0956563	C	0.8580236	-0.4972944	1.5118109
P	0.6219415	3.2768558	0.2662724	C	0.2853036	1.7518013	2.6528269
P	1.8407213	1.7114059	-0.4819839	O	-2.5669626	-0.1718192	2.1940903
P	-1.4190772	2.8473216	-0.133404	O	1.448938	-1.420525	1.8284692
P	0.520512	0.2449487	-1.3138373	O	0.5125685	2.2025295	3.6758177

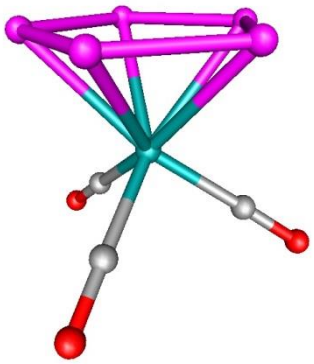

Figure S12. Optimized geometry of $[(CO)_3Mn(\eta^5\text{-}P_5)]$ (B3LYP/def2-TZVP level of theory).

Table S8. Calculated characteristics of the vibrational frequencies of $[(CO)_3Mn(\eta^5\text{-}P_5)]$ (BP86/def2-TZVP level of theory)

# mode	symmetry	wave number cm^{-1}	IR intensity km/mol	IR	RAMAN
1		0	0	-	-
2		0	0	-	-
3		0	0	-	-
4		0	0	-	-
5		0	0	-	-
6		0	0	-	-
7	a	3.45	0.00145	YES	YES
8	a	92.16	0.22243	YES	YES
9	a	93.84	0.12317	YES	YES
10	a	107.77	0.03533	YES	YES
11	a	114.07	0.03667	YES	YES
12	a	115.93	0.0052	YES	YES
13	a	191.26	0.03183	YES	YES
14	a	191.8	0.28234	YES	YES
15	a	225.81	1.95886	YES	YES
16	a	234.15	1.14323	YES	YES
17	a	236.65	0.9585	YES	YES
18	a	299.41	0.00062	YES	YES
19	a	301.18	0.60539	YES	YES
20	a	411.5	0.00057	YES	YES
21	a	443.75	0.01499	YES	YES
22	a	457.91	0.86272	YES	YES
23	a	459.26	0.9278	YES	YES
24	a	471.23	0.03512	YES	YES
25	a	471.92	0.11741	YES	YES
26	a	484.04	0.17231	YES	YES
27	a	484.71	0.00804	YES	YES
28	a	509.78	4.60349	YES	YES
29	a	523.92	13.53345	YES	YES
30	a	529.03	8.37407	YES	YES
31	a	611.07	34.84748	YES	YES
32	a	616.5	38.08434	YES	YES
33	a	651.19	104.64508	YES	YES
34	a	1984.01	533.9885	YES	YES
35	a	1984.11	537.0265	YES	YES
36	a	2032.29	1016.17487	YES	YES

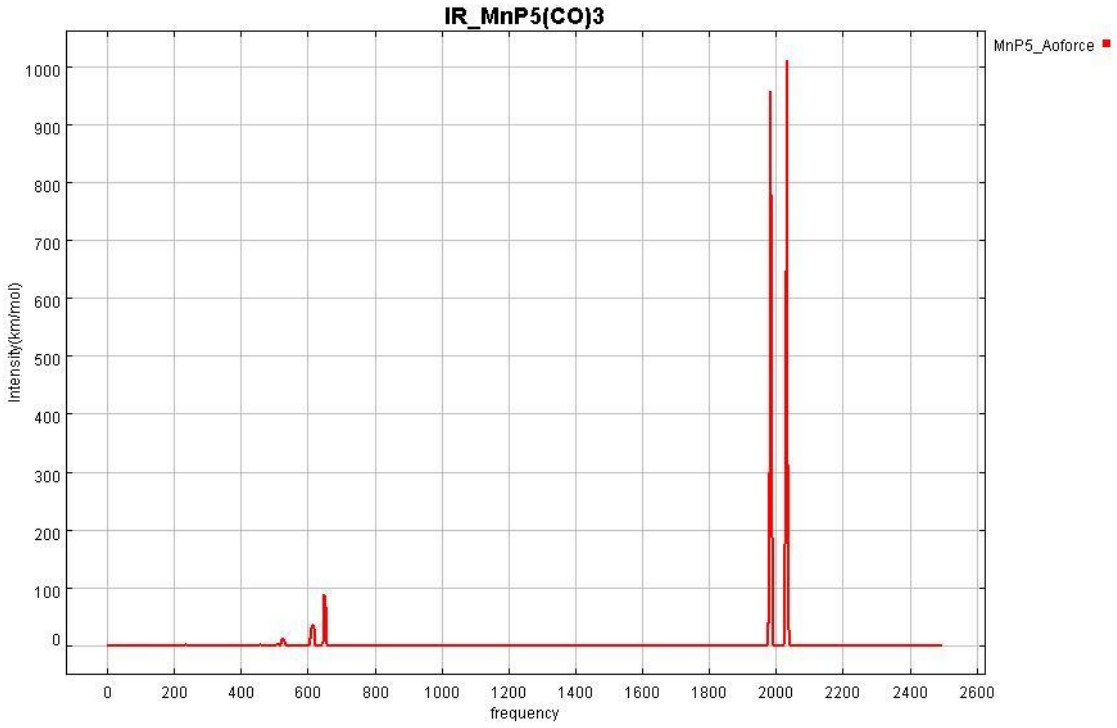

Figure S13. Calculated IR spectrum of $[(CO)_3Mn(\eta^5\text{-}P_5)]$ (BP86/def2-TZVP level of theory; without correction).

Table S9. Calculated characteristics of the vibrational frequencies of [$(CO)_3Mn(\eta^5\text{-}P_5)$] (B3LYP/def2-TZVP level of theory)

# mode	symmetry	wave number cm-1	IR intensity km/mol	IR	RAMAN
1		0	0	-	-
2		0	0	-	-
3		0	0	-	-
4		0	0	-	-
5		0	0	-	-
6		0	0	-	-
7	a	7.47	0.00055	YES	YES
8	a	95.57	0.18037	YES	YES
9	a	97.35	0.10957	YES	YES
10	a	110.55	0.12203	YES	YES
11	a	116.08	0.07613	YES	YES
12	a	119.54	0.03159	YES	YES
13	a	199.88	0.70223	YES	YES
14	a	201.98	0.0397	YES	YES
15	a	207.23	0.90845	YES	YES
16	a	217.47	0.03272	YES	YES
17	a	224.07	0.70754	YES	YES
18	a	307.29	0.00548	YES	YES
19	a	309.12	0.76651	YES	YES
20	a	409.66	0.00151	YES	YES
21	a	450.23	0.74908	YES	YES
22	a	453.06	0.82796	YES	YES
23	a	454.43	0.19371	YES	YES
24	a	478.64	0.98961	YES	YES
25	a	480.38	12.44824	YES	YES
26	a	482.81	3.96582	YES	YES
27	a	500.99	0.42453	YES	YES
28	a	501.38	1.87867	YES	YES
29	a	520.34	23.78628	YES	YES
30	a	525.84	19.09098	YES	YES
31	a	614.41	35.19604	YES	YES
32	a	618.89	39.21034	YES	YES
33	a	654.18	113.47399	YES	YES
34	a	2068.99	619.29384	YES	YES
35	a	2069.16	613.32325	YES	YES
36	a	2113.61	1203.65191	YES	YES

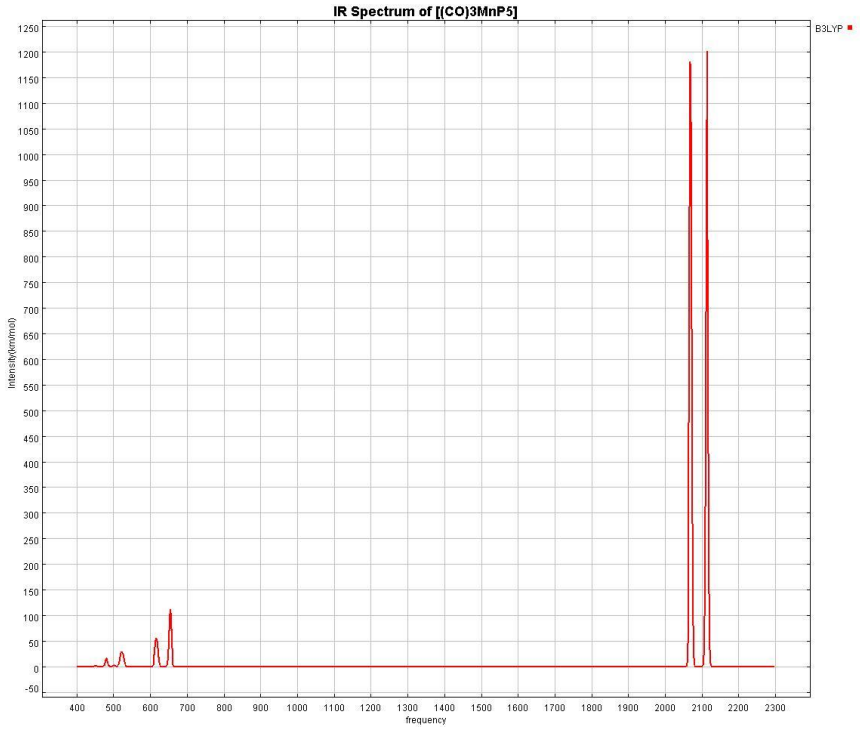

Figure S14. Calculated IR spectrum of [$(CO)_3Mn(\eta^5\text{-}P_5)$] (B3LYP/def2-TZVP level of theory; without correction).

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