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Unsaturation In Binuclear Heterometalic Carbonyls: The Cyclopentadienyliron Manganese Carbonyl $CpFeMn(CO)_n$ System as a Hybrid of the $Cp_2Fe_2(CO)_n$ and $Mn_2(CO)_n$ Systems

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Supporting Information

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The description of the DZP basis set

Complete Gaussian reference.

Literature References

Table S1 Theoretical Cartesian coordinates (in Å) of $CpFeMn(CO)_7$ **7CO-1S** using the M06-L and BP86 methods

Atom	M06-L			Atom	BP86		
	X	Y	Z		X	Y	Z
C	0.981176	-2.718360	1.144974	C	-3.067331	-0.718099	1.032329
C	1.802380	-1.653099	0.713390	C	-2.057573	-1.715412	0.824272
C	1.802380	-1.653099	-0.713390	C	-1.841152	-1.826987	-0.585280
C	0.981176	-2.718360	-1.144974	C	-2.688008	-0.893579	-1.242318
C	0.448973	-3.372807	0.000000	C	-3.453630	-0.201010	-0.237781
H	0.759627	-2.963427	2.173272	H	-3.456582	-0.397047	1.995401
H	2.343711	-0.974370	1.353861	H	-1.564182	-2.297723	1.596987
H	2.343711	-0.974370	-1.353861	H	-1.151757	-2.509218	-1.073341
H	0.759627	-2.963427	-2.173272	H	-2.742955	-0.729046	-2.315326
H	-0.215452	-4.222688	0.000000	H	-4.196698	0.571318	-0.417944
Fe	-0.153634	-1.395415	0.000000	Fe	-1.416201	0.177196	0.084362
Mn	0.097206	1.436474	0.000000	Mn	1.422988	-0.132435	-0.072626
C	1.917980	1.302715	0.000000	C	1.131561	-1.899944	0.285198
C	-1.753362	1.414258	0.000000	C	1.623196	1.684489	-0.309982
C	0.156891	3.228968	0.000000	C	3.124499	-0.438723	-0.536020
C	0.155277	1.105312	-1.809082	C	0.725603	-0.321520	-1.760579
C	0.155277	1.105312	1.809082	C	1.735653	0.095040	1.727070
O	3.064586	1.244867	0.000000	O	1.017174	-3.026164	0.528211
O	0.196597	4.376695	0.000000	O	4.219812	-0.645115	-0.852360
O	-2.897102	1.416522	0.000000	O	1.808830	2.814490	-0.446252
O	0.248662	0.890807	-2.932216	O	0.387534	-0.471604	-2.858981
O	0.248662	0.890807	2.932216	O	1.977753	0.209501	2.849885
O	-2.171730	-1.212055	-2.085114	O	-1.412039	2.566980	-1.579327
O	-2.171730	-1.212055	2.085114	O	-0.860523	1.715133	2.489461
C	-1.371613	-1.245211	1.259825	C	-1.004394	1.084325	1.523603
C	-1.371613	-1.245211	-1.259825	C	-1.353361	1.611376	-0.921953

Table S2 Theoretical Cartesian coordinates (in Å) of $CpFeMn(CO)_7$ **7CO-2S** using the M06-L and BP86 methods

Atom	M06-L			Atom	BP86		
	X	Y	Z		X	Y	Z
C	1.686061	-2.078161	0.709969	C	-1.720319	2.140479	0.716991
C	1.686061	-2.078161	-0.709969	C	-1.720319	2.140479	-0.716991
C	0.618423	-2.891475	-1.154079	C	-0.637215	2.945927	-1.163617
C	-0.048530	-3.382425	0.000000	C	0.046479	3.428010	0.000000
C	0.618423	-2.891475	1.154079	C	-0.637215	2.945927	1.163617
H	2.367035	-1.526943	1.341625	H	-2.422479	1.606536	1.352291
H	2.367035	-1.526943	-1.341625	H	-2.422479	1.606536	-1.352291
H	0.334305	-3.067178	-2.180077	H	-0.353046	3.127938	-2.196322
H	-0.920347	-4.020097	0.000000	H	0.922186	4.073090	0.000000
H	0.334305	-3.067178	2.180077	H	-0.353046	3.127938	2.196322
F	-0.162407	-1.315479	0.000000	Fe	0.162321	1.328670	0.000000
M	0.100784	1.309776	0.000000	Mn	-0.096518	-1.313619	0.000000
C	-0.206263	-0.113608	-1.482225	C	0.222575	0.123320	-1.470941
C	0.300920	2.488827	1.362655	C	-0.293692	-2.500876	1.355591
C	0.300920	2.488827	-1.362655	C	-0.293692	-2.500876	-1.355591
C	-1.724162	1.632691	0.000000	C	1.714498	-1.679803	0.000000
C	1.914530	1.014674	0.000000	C	-1.914965	-1.080496	0.000000
C	-0.206263	-0.113608	1.482225	C	0.222575	0.123320	1.470941
C	-1.918397	-1.418113	0.000000	C	1.909966	1.468007	0.000000
O	-0.305941	-0.161035	-2.646938	O	0.348656	0.161391	-2.643741
O	0.424479	3.225754	-2.231054	O	-0.417866	-3.260781	-2.217320
O	0.424479	3.225754	2.231054	O	-0.417866	-3.260781	2.217320
O	-2.841467	1.871932	0.000000	O	2.826781	-1.983399	0.000000
O	3.052073	0.869813	0.000000	O	-3.069603	-1.005480	0.000000
O	-3.061393	-1.531381	0.000000	O	3.059920	1.616722	0.000000
O	-0.305941	-0.161035	2.646938	O	0.348656	0.161391	2.643741

Table S3 Theoretical Cartesian coordinates (in Å) of $CpFeMn(CO)_7$ **7CO-3S** using the M06-L and BP86 methods

Atom	M06-L			Atom	BP86		
	X	Y	Z		X	Y	Z
C	2.804767	0.005802	-1.771553	C	-2.840436	0.509224	1.730242
C	1.458994	-0.442488	-1.903906	C	-1.509936	0.047393	1.999417
C	1.314153	-1.598739	-1.102366	C	-1.407615	-1.286672	1.510970
C	2.545040	-1.843753	-0.455542	C	-2.662988	-1.641679	0.931712
C	3.480345	-0.854245	-0.881266	C	-3.561431	-0.534782	1.080570
H	3.226800	0.877612	-2.249641	H	-3.231003	1.493928	1.976864
H	0.687256	0.017768	-2.502599	H	-0.719632	0.617151	2.479711
H	0.398843	-2.151877	-0.954270	H	-0.517515	-1.908450	1.535364
H	2.743310	-2.643028	0.242900	H	-2.898438	-2.594320	0.462948
H	4.506248	-0.765154	-0.559597	H	-4.590388	-0.489169	0.734882
Fe	1.839830	0.060766	0.102461	Fe	-1.856964	0.043095	-0.115086
Mn	-1.895036	0.051610	0.156593	Mn	1.906052	0.038442	-0.137573
C	-2.248400	-0.752421	-1.389549	C	2.349009	-0.512661	1.496317
C	-0.000350	0.249134	0.639647	C	-0.008400	0.189611	-0.611200
C	-3.596858	0.435765	0.723056	C	3.572884	0.293165	-0.843661
C	-1.862189	-1.642824	0.876388	C	1.859401	-1.743849	-0.576097
C	-1.697616	1.582275	-0.845696	C	1.829559	1.716662	0.603160
C	1.940850	1.821591	0.172260	C	-2.123319	1.677127	-0.710419
C	2.325113	-0.127785	1.787634	C	-2.221846	-0.675490	-1.678774
O	-2.442595	-1.279269	-2.399920	O	2.634090	-0.874438	2.567170
O	-4.657878	0.680603	1.082153	O	4.619791	0.460284	-1.306563
O	-0.531654	0.759318	1.607163	O	0.524325	0.542826	-1.658255
O	-1.835239	-2.736646	1.222795	O	1.850424	-2.887151	-0.758860
O	-1.540295	2.470287	-1.555435	O	1.800219	2.732743	1.157237
O	2.651925	-0.258517	2.877336	O	-2.487057	-1.151109	-2.698605
O	2.005083	2.964307	0.209628	O	-2.324610	2.748226	-1.096078

Table S4 Theoretical Cartesian coordinates (in Å) of $CpFeMn(CO)_7$ **7CO-4S** using the M06-L and BP86 methods

Atom	M06-L			Atom	BP86		
	X	Y	Z		X	Y	Z
C	-3.520094	-0.900216	0.767563	C	-3.624524	-0.850926	0.710755
C	-2.390085	-1.772519	0.666594	C	-2.508224	-1.763591	0.698349
C	-2.003416	-1.824375	-0.690389	C	-2.044720	-1.871869	-0.643634
C	-2.847333	-0.959426	-1.428166	C	-2.834860	-1.008523	-1.461438
C	-3.801218	-0.406791	-0.519315	C	-3.823545	-0.391206	-0.616368
H	-4.047410	-0.650050	1.675506	H	-4.200212	-0.558680	1.585123
H	-1.920866	-2.306040	1.479392	H	-2.100737	-2.288877	1.558079
H	-1.168762	-2.381517	-1.088531	H	-1.210492	-2.480692	-0.981307
H	-2.788089	-0.768245	-2.488517	H	-2.721725	-0.861117	-2.531902
H	-4.580815	0.295881	-0.772563	H	-4.579292	0.321334	-0.937767
Fe	-1.847676	0.152380	0.032695	Fe	-1.856885	0.153521	0.027311
Mn	1.898710	-0.102972	-0.219221	Mn	1.910133	-0.099277	-0.201202
C	1.643988	-1.893406	0.091978	C	1.719550	-1.890205	0.127187
C	1.924398	1.740581	-0.163704	C	2.014096	1.737766	-0.188776
C	3.529391	-0.285311	-1.040896	C	3.519989	-0.299889	-1.047995
C	-1.309405	0.769698	1.607486	C	-1.391082	0.768618	1.616461
C	-1.936873	1.760133	-0.693433	C	-1.952676	1.757364	-0.695264
O	1.466811	-2.990377	0.385716	O	1.621567	-3.006564	0.424638
O	4.5399651.	-0.401708	-1.570265	O	4.524847	-0.430762	-1.606523
O	922109	2.878811	-0.026047	O	2.112218	2.885757	-0.090251
O	-2.004116	2.797619	-1.175364	O	-2.047924	2.807011	-1.171980
O	-0.963263	1.157764	2.627001	O	-1.124741	1.165147	2.668889
O	0.402170	-0.086871	-1.722874	O	0.396585	-0.101487	-1.703666
C	-0.014817	0.029467	-0.585809	C	-0.015288	0.026771	-0.554812
O	2.748124	0.023116	2.588639	O	2.803210	0.063428	2.602259
C	2.422692	-0.025240	1.483215	C	2.449960	0.002051	1.495671

Table S5 Theoretical Cartesian coordinates (in Å) of $CpFeMn(CO)_6$ **6CO-1S** using the M06-L and BP86 methods

Atom	M06-L			Atom	BP86		
	X	Y	Z		X	Y	Z
C	1.430889	-2.655147	0.705359	C	-2.602134	-0.711426	-1.565351
C	1.659694	-1.326747	1.153612	C	-1.251126	-1.163162	-1.700966
C	1.751439	-0.484610	0.000000	C	-0.395048	-0.000005	-1.717984
C	1.659694	-1.326747	-1.153612	C	-1.251130	1.163148	-1.700973
C	1.430889	-2.655147	-0.705359	C	-2.602136	0.711409	-1.565355
H	1.268414	-3.512935	1.339731	H	-3.476556	-1.349525	-1.468472
H	1.706947	-1.000005	2.180719	H	-0.923219	-2.197721	-1.737923
H	2.094320	0.585944	0.000000	H	0.704348	-0.000004	-2.027989
H	1.706947	-1.000005	-2.180719	H	-0.923227	2.197707	-1.737935
H	1.268414	-3.512935	-1.339731	H	-3.476560	1.349505	-1.468479
Fe	0.050641	-1.339417	0.000000	Fe	-1.374176	-0.000002	0.038117
Mn	0.281644	1.251102	0.000000	Mn	1.269528	0.000001	-0.231874
C	1.478705	1.523010	0.000000	C	1.578009	0.000008	1.523529
C	0.802461	2.968851	0.000000	C	2.984163	0.000002	-0.762385
C	0.172271	1.154559	-1.836834	C	1.231659	1.833058	-0.120827
C	0.172271	1.154559	1.836834	C	1.231663	-1.833054	-0.120816
O	1.113558	4.076065	0.000000	O	4.095780	0.000001	-1.094851
O	2.619940	1.655952	0.000000	O	1.770856	0.000012	2.665744
O	0.035375	1.125470	-2.973985	O	1.278424	2.980506	0.011381
O	0.035375	1.125470	2.973985	O	1.278457	-2.980502	0.011396
O	2.044037	-1.532052	-2.112354	O	-1.832021	2.104591	2.005583
O	2.044037	-1.532052	2.112354	O	-1.832023	-2.104585	2.005595
C	1.265435	-1.456592	1.267936	C	-1.627809	-1.261527	1.232888
C	1.265435	-1.456592	-1.267936	C	-1.627812	1.261528	1.232881

Table S6 Theoretical Cartesian coordinates (in Å) of $CpFeMn(CO)_6$ **6CO-2T** using the M06-L and BP86 methods

Atom	M06-L			Atom	BP86		
	X	Y	Z		X	Y	Z
C	0.982155	2.885639	0.710344	C	-2.917407	1.010164	0.685491
C	-0.362816	2.903078	1.146267	C	-2.926618	-0.331570	1.166891
C	-1.198543	2.903629	0.000000	C	-2.931684	-1.210509	0.039260
C	-0.362816	2.903078	1.146267	C	-2.929245	-0.404414	-1.141525
C	0.982155	2.885639	0.710344	C	-2.919064	0.965087	-0.745726
H	1.857366	2.850371	1.341895	H	-2.890941	1.909784	1.295194
H	-0.698236	2.878125	2.172255	H	-2.903779	-0.635891	2.210223
H	-2.278287	2.898711	0.000000	H	-2.925933	-2.297043	0.073595
H	-0.698236	2.878125	2.172255	H	-2.908917	-0.773583	-2.163770
H	1.857366	2.850371	1.341895	H	-2.894363	1.824446	-1.411044
Fe	-0.010440	1.137582	0.000000	Fe	-1.141280	-0.007066	-0.001113
Mn	0.009746	1.170759	0.000000	Mn	1.178344	0.006150	0.000863
C	-0.818964	0.056096	1.382119	C	-0.063166	-0.776103	1.401427
C	0.778194	2.159045	1.331665	C	2.176045	0.733094	-1.341467
C	-1.516787	2.177654	0.000000	C	2.190085	-1.510909	0.040712
C	-0.818964	0.056096	1.382119	C	-0.067720	-0.847960	-1.359718
C	0.778194	2.159045	1.331665	C	2.175105	0.806027	1.301123
O	-1.420932	0.117324	2.376319	O	-0.123245	-1.351286	2.423411
O	-2.475932	2.802483	0.000000	O	2.832800	-2.470656	0.066119
O	1.260892	2.770976	2.170319	O	2.808991	1.192789	-2.191861
O	-1.420932	0.117324	2.376319	O	-0.121741	-1.475312	-2.350894
O	1.260892	2.770976	2.170319	O	2.806766	1.312722	2.125429
O	2.761545	0.159950	0.000000	O	-0.150410	2.768869	-0.074432
C	1.602119	0.058297	0.000000	C	-0.067443	1.597969	-0.042971

Table S7 Theoretical Cartesian coordinates (in Å) of $CpFeMn(CO)_6$ **6CO-3S** using the M06-L and BP86 methods

Atom	M06-L			Atom	BP86		
	X	Y	Z		X	Y	Z
C	3.085339	-0.723022	-0.872305	C	3.091930	-0.745304	-0.934925
C	2.163267	-1.707035	-0.405783	C	2.200126	-1.742650	-0.410931
C	1.859303	-1.418904	0.948249	C	1.976539	-1.458754	0.972407
C	2.570761	-0.257181	1.323521	C	2.714027	-0.289718	1.310985
C	3.343207	0.163663	0.195098	C	3.413387	0.147445	0.126845
H	3.502611	-0.660420	-1.865319	H	3.454208	-0.680733	-1.957155
H	1.758875	-2.523104	-0.985044	H	1.769679	-2.569595	-0.969323
H	1.179028	-1.971558	1.578986	H	1.341694	-2.026580	1.647472
H	2.532712	0.226132	2.287808	H	2.745340	0.187913	2.286400
H	3.985805	1.030457	0.158044	H	4.062773	1.016388	0.055778
Fe	1.335695	0.190894	-0.284263	Fe	1.354183	0.185977	-0.241874
Mn	1.361342	-0.115929	-0.138145	Mn	-1.379634	-0.103645	-0.140351
C	1.030394	-1.924100	-0.118025	C	-1.115980	-1.916354	-0.111466
C	1.711725	1.705779	-0.054684	C	-1.740380	1.707470	-0.035448
C	3.134661	-0.437019	-0.101002	C	-3.158252	-0.399245	-0.171707
C	0.982010	-0.079984	1.596942	C	-1.069086	-0.087277	1.605574
O	0.857603	-3.054553	-0.035854	O	-1.009903	-3.065163	-0.023701
O	4.261199	-0.652116	-0.040337	O	-4.299324	-0.599241	-0.157446
O	1.988377	2.807873	0.064775	O	-2.048771	2.810374	0.099569
O	0.739361	-0.064101	2.724190	O	-0.904733	-0.084248	2.756739
O	1.221656	3.067710	0.137816	O	1.342806	3.076801	0.139436
O	0.758691	0.069208	-2.308990	O	-0.695343	0.107589	-2.331155
C	0.181609	0.155184	-1.591504	C	0.196066	0.169427	-1.537344
C	1.224481	1.929500	-0.030973	C	1.296715	1.924864	-0.002860

Table S8 Theoretical Cartesian coordinates (in Å) of $CpFeMn(CO)_6$ **6CO-4S** using the M06-L and BP86 methods

Atom	M06-L			Atom	BP86		
	X	Y	Z		X	Y	Z
C	1.370480	2.446873	0.705415	C	1.381934	2.527248	0.709492
C	0.112186	2.946892	1.139618	C	0.092869	2.980982	1.148532
C	-0.666316	3.273577	0.000000	C	-0.700191	3.287095	0.000000
C	0.112186	2.946892	-1.139618	C	0.092869	2.980982	-1.148532
C	1.370480	2.446873	-0.705415	C	1.381934	2.527248	-0.709492
H	2.174935	2.110928	1.341274	H	2.204261	2.222930	1.350711
H	-0.204333	3.046101	2.167470	H	-0.225139	3.079970	2.183762
H	-1.666911	3.676382	0.000000	H	-1.721357	3.657491	0.000000
H	-0.204333	3.046101	-2.167470	H	-0.225139	3.079970	-2.183762
H	2.174935	2.110928	-1.341274	H	2.204261	2.222930	-1.350711
Fe	-0.229577	1.243348	0.000000	Fe	-0.203466	1.230282	0.000000
Mn	0.189537	-1.192386	0.000000	Mn	0.169990	-1.215901	0.000000
C	-1.202576	0.498635	1.264214	C	-1.194616	0.505274	1.263062
C	0.703552	-2.329345	-1.274094	C	0.712390	-2.345083	-1.263442
C	-1.513878	-1.936278	0.000000	C	-1.513279	-1.989915	0.000000
C	-1.202576	0.498635	-1.264214	C	-1.194616	0.505274	-1.263062
C	0.703552	-2.329345	1.274094	C	0.712390	-2.345083	1.263442
O	-1.908594	0.212532	2.135712	O	-1.928815	0.258757	2.135893
O	-2.504916	-2.508761	0.000000	O	-2.492312	-2.604025	0.000000
O	1.038566	-3.028352	-2.122363	O	1.074600	-3.046438	-2.113619
O	-1.908594	0.212532	-2.135712	O	-1.928815	0.258757	-2.135893
O	1.038566	-3.028352	2.122363	O	1.074600	-3.046438	2.113619
O	2.916452	-0.014262	0.000000	O	2.895475	-0.029427	0.000000
C	1.810319	-0.341832	0.000000	C	1.769255	-0.331124	0.000000

Table S9 Theoretical Cartesian coordinates (in Å) of $CpFeMn(CO)_6$ **6CO-5S** using the M06-L and BP86 methods

Atom	M06-L			Atom	BP86		
	X	Y	Z		X	Y	Z
C	1.625800	-1.694514	1.157324	C	1.489598	-2.122960	1.164134
C	1.972936	-0.927454	0.000000	C	2.042909	-1.487866	0.000000
C	1.625800	-1.694514	-1.157324	C	1.489598	-2.122960	-1.164134
C	0.985544	-2.864896	-0.719569	C	0.554006	-3.090823	-0.726029
C	0.985544	-2.864896	0.719569	C	0.554006	-3.090823	0.726029
H	1.767124	-1.389305	2.183242	H	1.711911	-1.870057	2.197159
H	2.523976	0.006297	0.000000	H	2.811906	-0.718158	0.000000
H	1.767124	-1.389305	-2.183242	H	1.711911	-1.870057	-2.197159
H	0.574444	-3.638029	-1.350316	H	-0.047869	-3.734016	-1.362737
H	0.574444	-3.638029	1.350316	H	-0.047869	-3.734016	1.362737
Fe	-0.078452	-1.223911	0.000000	Fe	-0.081376	-1.205934	0.000000
Mn	0.123362	1.188989	0.000000	Mn	0.177281	1.253606	0.000000
C	0.795501	2.184254	-1.362410	C	0.822366	2.304674	-1.327786
C	-1.364416	2.141081	0.000000	C	-1.336193	2.146784	0.000000
C	-0.521766	-0.045734	-1.452153	C	-0.318908	-0.008197	-1.476075
C	0.795501	2.184254	1.362410	C	0.822366	2.304674	1.327786
O	1.186349	2.825954	-2.230562	O	1.222487	2.989713	-2.171303
O	-2.351605	2.729609	0.000000	O	-2.355435	2.703145	0.000000
O	-0.935398	-0.091494	-2.544735	O	-0.622809	-0.065920	-2.616560
O	1.186349	2.825954	2.230562	O	1.222487	2.989713	2.171303
O	-2.707301	-2.479185	0.000000	O	-2.906884	-1.948938	0.000000
O	-0.935398	-0.091494	2.544735	O	-0.622809	-0.065920	2.616560
C	-0.521766	-0.045734	1.452153	C	-0.318908	-0.008197	1.476075
C	-1.677906	-1.973416	0.000000	C	-1.792929	-1.636626	0.000000

Table S10 Theoretical Cartesian coordinates (in Å) of $CpFeMn(CO)_5$ **5CO-1S** using the M06-L and BP86 methods

Atom	M06-L			Atom	BP86		
	X	Y	Z		X	Y	Z
C	0.648243	-2.600290	1.139238	C	-2.633692	1.163335	0.634021
C	1.464922	-2.373931	0.000000	C	-2.382426	0.050906	1.499622
C	0.648243	-2.600290	-1.139238	C	-2.608806	-1.132130	0.729832
C	-0.654664	-2.983341	-0.702344	C	-3.026113	-0.747787	-0.593767
C	-0.654664	-2.983341	0.702344	C	-3.042907	0.664247	-0.652665
H	0.946671	-2.465532	2.168575	H	-2.519197	2.212552	0.896037
H	2.502128	-2.076284	0.000000	H	-2.070991	0.096452	2.539164
H	0.946671	-2.465532	-2.168575	H	-2.468326	-2.153765	1.074936
H	-1.499149	-3.185912	-1.343454	H	-3.244210	-1.428470	-1.412567
H	-1.499149	-3.185912	1.343454	H	-3.279139	1.269879	-1.523567
Fe	-0.120773	-1.079250	0.000000	Fe	-1.071130	0.002221	-0.118871
Mn	0.033346	1.119218	0.000000	Mn	1.121911	-0.000204	0.037833
C	-0.326872	2.398769	1.212005	C	2.407682	-1.201656	-0.317169
C	-0.326872	2.398769	-1.212005	C	1.321960	-0.007044	1.807833
C	-0.782371	-0.194432	-1.454925	C	-0.201088	-1.437520	-0.829847
C	1.807970	1.309249	0.000000	C	2.408539	1.203251	-0.307004
O	-0.554186	3.198850	-2.004911	O	1.429416	-0.012024	2.964553
O	-0.554186	3.198850	2.004911	O	3.223004	-1.996418	-0.538845
O	-1.257467	-0.120840	-2.512653	O	-0.119471	-2.485398	-1.347918
O	2.955794	1.393834	0.000000	O	3.224432	1.999348	-0.521751
O	-1.257467	-0.120840	2.512653	O	-0.115856	2.490184	-1.343067
C	-0.782371	-0.194432	1.454925	C	-0.201272	1.441924	-0.826352

Table S11 Theoretical Cartesian coordinates (in Å) of $CpFeMn(CO)_5$ **5CO-2T** using the M06-L and BP86 methods

Atom	M06-L			Atom	BP86		
	X	Y	Z		X	Y	Z
C	0.861012	2.981467	0.711775	C	0.904069	2.896710	0.715720
C	-0.481452	2.862846	1.149118	C	-0.455807	2.866093	1.159747
C	-1.305606	2.786766	0.000000	C	-1.289947	2.834912	0.000000
C	-0.481452	2.862846	-1.149118	C	-0.455807	2.866093	-1.159747
C	0.861012	2.981467	-0.711775	C	0.904069	2.896710	-0.715720
H	1.727756	3.042985	1.353037	H	1.781319	2.896809	1.357398
H	-0.809680	2.807561	2.176038	H	-0.790153	2.836274	2.193365
H	-2.377346	2.648091	0.000000	H	-2.375861	2.763125	0.000000
H	-0.809680	2.807561	-2.176038	H	-0.790153	2.836274	-2.193365
H	1.727756	3.042985	-1.353037	H	1.781319	2.896809	-1.357398
Fe	0.082471	1.131259	0.000000	Fe	-0.021538	1.113257	0.000000
Mn	0.027995	-1.183503	0.000000	Mn	0.068017	-1.200938	0.000000
C	0.439774	-2.437430	-1.237355	C	0.398187	-2.455982	-1.265400
C	0.439774	-2.437430	1.237355	C	0.398187	-2.455982	1.265400
C	0.449802	0.035834	-1.522760	C	0.501723	0.079534	-1.485082
C	-1.725532	-1.514613	0.000000	C	-1.693573	-1.447269	0.000000
O	0.715459	-3.228034	-2.021241	O	0.616953	-3.257442	-2.070504
O	0.715459	-3.228034	2.021241	O	0.616953	-3.257442	2.070504
O	0.756945	0.127646	-2.645949	O	0.868191	0.165227	-2.604101
O	-2.863026	-1.689204	0.000000	O	-2.848271	-1.579650	0.000000
O	0.756945	0.127646	2.645949	O	0.868191	0.165227	2.604101
C	0.449802	0.035834	1.522760	C	0.501723	0.079534	1.485082

Table S12 Theoretical Cartesian coordinates (in Å) of $CpFeMn(CO)_5$ **5CO-3S** using the M06-L and BP86 methods

Atom	M06-L			Atom	BP86		
	X	Y	Z		X	Y	Z
C	2.879924	-0.863045	-0.885908	C	3.106535	-0.542945	-0.831278
C	1.850300	-1.753395	-0.457649	C	2.222913	-1.645267	-0.565443
C	1.539181	-1.453932	0.894973	C	1.793494	-1.563687	0.799584
C	2.354783	-0.374366	1.300310	C	2.388951	-0.406186	1.374534
C	3.194269	-0.017464	0.197565	C	3.207575	0.217963	0.364953
H	3.323871	-0.828991	-1.868743	H	3.600299	-0.328366	-1.774768
H	1.374250	-2.512055	-1.060385	H	1.925894	-2.408090	-1.280557
H	0.795008	-1.948725	1.500554	H	1.127599	-2.257740	1.304019
H	2.335827	0.103662	2.267983	H	2.248427	-0.054498	2.392862
H	3.918900	0.782558	0.188886	H	3.786812	1.129006	0.493423
Fe	1.200552	0.203806	-0.326343	Fe	1.199922	0.164764	-0.290288
Mn	-1.376240	0.146890	-0.171483	Mn	-1.303552	-0.024097	-0.161456
C	-1.578375	-1.578538	-0.030527	C	-2.264337	-1.496217	-0.211966
C	-3.155159	0.438465	-0.087536	C	-2.800345	0.914417	0.069845
C	-1.016883	0.245858	1.556055	C	-0.927698	-0.189764	1.544378
O	-1.654486	-2.727656	0.062288	O	-2.841130	-2.507868	-0.232024
O	-4.288196	0.613435	-0.009025	O	-3.742157	1.573224	0.241108
O	-0.790935	0.290490	2.687748	O	-0.757950	-0.316060	2.691672
O	1.174271	3.049623	0.285988	O	0.892670	3.017599	0.273459
O	-0.963361	0.505728	-2.241702	O	-0.821370	0.245794	-2.384895
C	0.047432	0.361029	-1.613889	C	0.116488	0.188587	-1.643721
C	1.155439	1.925287	0.036827	C	0.966639	1.879224	0.054839

Table S13 Theoretical Cartesian coordinates (in Å) of $CpFeMn(CO)_5$ **5CO-4S** using the M06-L and BP86 methods

Atom	M06-L			Atom	BP86		
	X	Y	Z		X	Y	Z
C	-3.041422	0.377771	0.578901	C	-3.131039	0.205534	0.558937
C	-2.043705	-0.129771	1.472112	C	-2.100357	-0.212226	1.483187
C	-1.593803	-1.381296	0.971786	C	-1.528728	-1.432107	0.993613
C	-2.263172	-1.611454	-0.256610	C	-2.157937	-1.726989	-0.254504
C	-3.159181	-0.522498	-0.490696	C	-3.148964	-0.714386	-0.513753
H	-3.564640	1.315717	0.685833	H	-3.749664	1.093853	0.655687
H	-1.708124	0.345722	2.381511	H	-1.835700	0.288924	2.410499
H	-0.880223	-2.037574	1.445436	H	-0.782338	-2.040131	1.495387
H	-2.105188	-2.448842	-0.919957	H	-1.920687	-2.562544	-0.908610
H	-3.785635	-0.399496	-1.361466	H	-3.775133	-0.652441	-1.400542
Fe	-1.193980	0.149179	-0.365667	Fe	-1.217517	0.156603	-0.350618
Mn	1.217831	-0.098278	-0.100869	Mn	1.239508	-0.074111	-0.065220
C	2.220680	-1.560564	-0.162657	C	2.248468	-1.518075	-0.212389
C	0.247817	-0.171160	-1.662501	C	0.258505	-0.086084	-1.607763
C	2.665443	0.910484	-0.376287	C	2.669586	0.919440	-0.417618
C	1.166255	-0.015019	1.708475	C	1.313431	0.023290	1.746786
C	-0.654784	1.807663	-0.042342	C	-0.880706	1.862057	-0.023188
O	2.824362	-2.541442	-0.192034	O	2.862595	-2.501875	-0.308083
O	-0.639273	-0.010793	-2.437677	O	-0.588172	0.060160	-2.444562
O	3.564564	1.602105	-0.570638	O	3.571006	1.608930	-0.668120
O	1.098679	0.000432	2.857174	O	1.362272	0.064966	2.905620
O	-0.426241	2.896927	0.262752	O	-0.772987	2.984157	0.261934

Table S14 Theoretical harmonic vibrational frequencies (cm^{-1}) and IR intensities (km/mol) of $CpFeMn(CO)_n$ (n = 7, 6, 5) by M06-L and BP86 methods

	M06-L	BP86
$CpFeMn(CO)_7$ **7CO-1S**	12.1 (A", 0.1)	9.8 (A, 0.2)
	54.5 (A', 0.2)	39.1 (A, 0.3)
	69.2 (A", 0.1)	50.2 (A, 0.0)
	70.4 (A', 0.1)	54.1 (A, 0.2)
	71.5 (A", 0.1)	63.7 (A, 0.1)
	80.2 (A", 0.2)	71.9 (A, 0.0)
	85.5 (A', 0.2)	78.2 (A, 0.1)
	93.6 (A", 0.0)	89.3 (A, 0.1)
	97.1 (A', 0.9)	97.2 (A, 0.3)
	100.1 (A", 0.4)	100.8 (A, 0.6)
	106.5 (A', 0.0)	102.2 (A, 0.5)
	111.2 (A', 0.1)	102.8 (A, 0.1)
	112.0 (A", 0.0)	108.4 (A, 0.4)
	114.0 (A', 0.9)	115.2 (A, 0.5)
	128.5 (A", 0.1)	125.9 (A, 0.2)
	140.1 (A', 3.0)	132.2 (A, 3.2)
	166.8 (A', 0.7)	162.9 (A, 0.7)
	360.5 (A', 1.8)	333.0 (A, 3.2)
	376.5 (A", 3.7)	357.4 (A, 3.3)
	392.6 (A", 0.1)	385.3 (A, 0.5)
	413.6 (A', 0.4)	388.5 (A, 0.1)
	414.0 (A", 0.0)	397.6 (A, 6.9)
	427.4 (A', 7.8)	420.7 (A, 0.3)
	433.0 (A', 0.7)	439.6 (A, 5.3)
	438.4 (A', 1.2)	442.8 (A, 2.9)
	457.6 (A", 0.1)	447.6 (A, 0.7)
	472.7 (A', 19.9)	466.4 (A, 5.5)
	473.4 (A", 8.0)	493.9 (A, 5.8)
	484.0 (A', 13.3)	496.5 (A, 8.3)
	506.6 (A', 0.1)	507.9 (A, 2.1)
	514.4 (A", 0.1)	509.1 (A, 8.4)
	515.9 (A', 13.2)	523.3 (A, 16.5)
	559.6 (A", 3.8)	552.0 (A, 6.8)
	573.4 (A", 35.0)	563.3 (A, 4.1)
	580.5 (A", 0.9)	571.1 (A, 24.4)
	584.3 (A', 63.8)	578.5 (A, 35.5)
	597.4 (A', 62.2)	581.5 (A, 34.4)
	616.3 (A", 2.8)	586.9 (A, 9.8)
	618.1 (A', 54.5)	592.6 (A, 48.9)
	648.6 (A', 33.8)	640.0 (A, 30.6)
	673.0 (A', 111.7)	673.5 (A, 110.5)

	689.3 (A", 98.8) 693.0 (A', 242.1) 833.7 (A", 0.0) 833.8 (A', 1.0) 848.4 (A', 14.7) 855.2 (A', 27.5) 873.9 (A", 5.8) 934.3 (A", 0.3) 934.5 (A', 3.3) 1027.0 (A', 3.2) 1040.5 (A", 3.9) 1083.8 (A", 0.0) 1086.6 (A', 2.7) 1148.7 (A', 4.8) 1277.8 (A", 0.0) 1406.3 (A', 3.4) 1408.7 (A", 0.8) 1462.7 (A', 4.2) 1464.5 (A", 2.2) 2022.7 (A", 32.6) 2035.1 (A', 178.9) 2043.0 (A', 762.0) 2055.4 (A", 1767.2) 2064.2 (A', 279.4) 2069.2 (A', 1431.6) 2142.1 (A', 437.0) 3226.9 (A', 0.3) 3229.8 (A", 0.2) 3245.8 (A", 0.3) 3249.5 (A', 0.9) 3257.9 (A', 0.0)	680.8 (A, 94.1) 684.8 (A, 247.8) 818.5 (A, 12.7) 822.8 (A, 2.8) 826.0 (A, 26.5) 835.1 (A, 11.8) 844.3 (A, 7.2) 903.1 (A, 0.6) 911.3 (A, 1.0) 991.0 (A, 5.0) 1004.3 (A, 4.2) 1050.8 (A, 0.2) 1052.4 (A, 2.5) 1111.7 (A, 1.6) 1244.6 (A, 0.0) 1350.5 (A, 2.0) 1355.5 (A, 0.6) 1407.8 (A, 3.1) 1419.0 (A, 6.7) 1948.4 (A, 13.3) 1968.2 (A, 367.6) 1972.6 (A, 793.4) 1979.8 (A, 929.8) 1992.7 (A, 1428.8) 2005.4 (A, 487.2) 2072.5 (A, 477.7) 3153.4 (A, 0.2) 3159.7 (A, 0.0) 3170.8 (A, 0.9) 3172.4 (A, 0.2) 3184.1 (A, 0.1)
$CpFeMn(CO)_7$ **7CO-2S**	16.6 (A", 0.6) 45.0 (A", 0.1) 56.3 (A", 0.0) 62.6 (A', 0.4) 73.4 (A', 0.0) 79.2 (A", 0.0) 85.3 (A", 0.2) 89.4 (A', 0.2) 90.5 (A", 0.1) 97.5 (A", 0.3) 99.3 (A', 0.6) 102.4 (A', 0.8) 111.9 (A', 0.0)	26.9 (A", 0.4) 39.1 (A", 0.2) 49.4 (A", 0.0) 56.8 (A', 0.4) 74.7 (A', 0.0) 86.7 (A", 0.2) 92.1 (A', 0.2) 92.7 (A", 0.0) 96.1 (A", 0.0) 97.1 (A', 0.3) 102.3 (A", 0.2) 104.4 (A', 0.7) 107.3 (A', 0.3)

	148.5 (A', 0.3)	145.8 (A', 0.3)
	199.8 (A", 1.3)	201.1 (A", 1.4)
	215.4 (A', 0.8)	215.5 (A', 1.0)
	238.5 (A', 1.1)	238.9 (A', 1.4)
	318.4 (A", 0.8)	305.9 (A", 0.1)
	344.9 (A', 4.6)	311.5 (A', 6.0)
	373.4 (A", 8.4)	353.0 (A", 10.5)
	393.1 (A', 8.3)	379.9 (A', 0.5)
	399.9 (A", 0.3)	398.3 (A", 0.2)
	405.3 (A', 8.5)	404.6 (A', 17.4)
	423.7 (A', 0.8)	423.2 (A', 0.3)
	425.1 (A', 2.7)	432.7 (A", 0.4)
	437.1 (A", 1.0)	439.5 (A', 1.3)
	468.2 (A', 20.0)	477.7 (A", 0.0)
	479.8 (A", 2.7)	484.2 (A', 5.5)
	480.2 (A', 28.8)	491.3 (A', 22.1)
	497.3 (A", 10.3)	494.9 (A", 6.9)
	518.7 (A', 1.4)	509.4 (A", 10.3)
	522.8 (A", 11.1)	523.8 (A', 10.3)
	552.5 (A', 17.9)	537.2 (A', 17.6)
	555.4 (A', 43.9)	553.7 (A', 26.4)
	581.8 (A", 3.0)	564.7 (A", 3.1)
	589.8 (A', 5.2)	575.6 (A", 0.1)
	590.6 (A", 6.8)	578.1 (A', 5.9)
	614.9 (A', 37.3)	595.0 (A', 10.4)
	619.7 (A", 11.2)	596.9 (A", 13.6)
	638.9 (A', 419.6)	634.5 (A', 421.5)
	651.7 (A', 178.1)	648.2 (A', 162.5)
	680.9 (A', 242.0)	677.6 (A', 268.7)
	683.3 (A", 86.3)	682.4 (A", 86.0)
	835.4 (A", 1.9)	814.0 (A", 3.4)
	837.6 (A', 5.1)	816.3 (A', 67.3)
	838.1 (A", 3.5)	823.0 (A", 1.7)
	846.6 (A', 44.9)	823.8 (A', 0.3)
	880.5 (A', 5.4)	861.1 (A', 4.9)
	929.3 (A", 0.2)	905.3 (A", 0.2)
	942.7 (A', 2.9)	917.7 (A', 3.1)
	1031.3 (A', 2.6)	995.5 (A', 3.4)
	1038.5 (A", 5.9)	1006.8 (A", 7.7)
	1082.1 (A', 2.0)	1052.0 (A', 1.9)
	1084.9 (A", 0.5)	1053.5 (A", 0.5)
	1152.6 (A', 1.8)	1115.7 (A', 0.5)
	1278.2 (A", 0.0)	1246.1 (A", 0.0)
	1407.7 (A', 0.7)	1353.4 (A', 0.8)

	1409.1 (A", 0.0) 1459.7 (A', 3.7) 1472.3 (A", 1.1) 1892.5 (A", 860.3) 1916.7 (A', 20.4) 2041.8 (A', 650.4) 2060.9 (A', 516.0) 2063.1 (A", 950.6) 2075.0 (A', 1203.7) 2141.9 (A', 649.3) 3226.8 (A', 0.5) 3227.7 (A", 0.0) 3240.7 (A', 0.6) 3249.5 (A", 0.1) 3256.0 (A', 0.1)	1354.0 (A", 0.1) 1408.0 (A', 5.9) 1425.7 (A", 2.3) 1821.8 (A", 779.7) 1844.0 (A', 12.4) 1970.5 (A', 631.1) 1988.4 (A', 625.6) 1992.4 (A", 851.4) 2001.8 (A', 933.8) 2067.7 (A', 622.8) 3152.3 (A', 0.4) 3155.7 (A", 0.0) 3166.5 (A', 0.4) 3172.8 (A", 0.5) 3180.1 (A', 0.1)
$CpFeMn(CO)_7$ **7CO-3S**	21.3 (A, 0.2) 35.8 (A, 0.0) 39.4 (A, 0.1) 42.4 (A, 0.1) 59.4 (A, 0.2) 70.6 (A, 0.4) 73.1 (A, 0.1) 75.0 (A, 0.1) 83.5 (A, 0.0) 92.3 (A, 0.5) 94.9 (A, 0.6) 100.8 (A, 0.1) 122.9 (A, 0.1) 130.0 (A, 0.1) 170.6 (A, 0.0) 192.3 (A, 1.1) 304.9 (A, 0.6) 353.3 (A, 0.9) 367.9 (A, 3.4) 376.7 (A, 0.7) 389.4 (A, 8.0) 401.1 (A, 15.8) 428.4 (A, 4.7) 439.2 (A, 6.6) 449.8 (A, 4.5) 456.8 (A, 5.9) 465.2 (A, 16.0) 471.9 (A, 1.3) 502.3 (A, 3.8)	15.2 (A, 0.2) 27.9 (A, 0.1) 35.2 (A, 0.0) 38.8 (A, 0.3) 56.2 (A, 0.4) 71.5 (A, 0.4) 74.4 (A, 0.1) 78.1 (A, 0.1) 86.2 (A, 0.0) 95.4 (A, 0.4) 98.3 (A, 0.4) 106.4 (A, 0.1) 120.4 (A, 0.2) 130.6 (A, 0.1) 171.1 (A, 0.0) 188.7 (A, 0.3) 295.6 (A, 2.1) 336.1 (A, 4.4) 349.9 (A, 0.4) 362.0 (A, 2.7) 374.1 (A, 0.4) 395.5 (A, 26.0) 434.3 (A, 2.2) 444.3 (A, 2.2) 445.7 (A, 0.2) 451.5 (A, 3.1) 475.9 (A, 4.1) 476.5 (A, 5.4) 501.7 (A, 1.9)

	506.1 (A, 2.4)	504.2 (A, 12.5)
	514.1 (A, 19.3)	523.9 (A, 11.3)
	543.5 (A, 4.4)	534.0 (A, 2.4)
	553.6 (A, 9.7)	545.0 (A, 3.3)
	578.8 (A, 19.0)	571.2 (A, 13.1)
	591.4 (A, 60.9)	580.0 (A, 5.4)
	601.6 (A, 85.3)	580.7 (A, 50.7)
	612.1 (A, 7.9)	589.8 (A, 62.4)
	616.4 (A, 7.1)	602.0 (A, 27.0)
	642.4 (A, 38.5)	635.5 (A, 23.8)
	655.3 (A, 73.5)	647.9 (A, 87.1)
	674.0 (A, 73.3)	668.5 (A, 63.0)
	692.2 (A, 78.3)	686.0 (A, 66.0)
	742.2 (A, 398.6)	723.1 (A, 411.9)
	834.1 (A, 7.3)	813.6 (A, 43.9)
	840.3 (A, 1.7)	820.8 (A, 4.3)
	843.2 (A, 17.1)	825.1 (A, 0.9)
	853.6 (A, 43.3)	828.3 (A, 41.9)
	880.9 (A, 7.7)	859.6 (A, 7.0)
	940.6 (A, 1.1)	913.5 (A, 0.3)
	941.0 (A, 1.2)	917.2 (A, 1.5)
	1028.5 (A, 4.0)	999.0 (A, 4.6)
	1040.7 (A, 4.2)	1003.9 (A, 6.3)
	1083.2 (A, 1.0)	1051.9 (A, 0.2)
	1083.6 (A, 0.4)	1053.6 (A, 1.4)
	1152.4 (A, 1.1)	1114.9 (A, 0.2)
	1278.5 (A, 0.0)	1246.5 (A, 0.0)
	1406.0 (A, 4.5)	1351.1 (A, 1.6)
	1408.2 (A, 1.4)	1353.4 (A, 6.4)
	1461.9 (A, 2.2)	1411.6 (A, 5.1)
	1474.8 (A, 2.2)	1421.9 (A, 2.5)
	1642.9 (A, 140.1)	1571.1 (A, 138.1)
	2004.9 (A, 714.3)	1938.2 (A, 657.2)
	2027.4 (A, 1110.2)	1958.3 (A, 1064.4)
	2050.4 (A, 587.0)	1981.1 (A, 515.0)
	2072.4 (A, 954.1)	1995.5 (A, 907.2)
	2099.5 (A, 1239.9)	2027.3 (A, 1092.3)
	2126.2 (A, 307.4)	2052.1 (A, 291.6)
	3227.2 (A, 0.3)	3153.5 (A, 0.3)
	3229.3 (A, 0.1)	3156.9 (A, 0.0)
	3242.4 (A, 0.2)	3171.4 (A, 0.0)
	3246.8 (A, 0.1)	3173.9 (A, 0.2)
	3255.6 (A, 0.3)	3183.0 (A, 0.2)
$CpFeMn(CO)_7$	8.9 (A, 0.2)	12.7 (A, 0.3)

7CO-4S	31.7 (A, 0.1)	30.6 (A, 0.2)
	39.8 (A, 0.1)	36.4 (A, 0.1)
	54.6 (A, 0.1)	40.7 (A, 0.2)
	57.2 (A, 0.0)	55.0 (A, 0.0)
	69.9 (A, 0.0)	69.3 (A, 0.0)
	73.7 (A, 0.3)	75.6 (A, 0.3)
	76.0 (A, 0.5)	80.0 (A, 0.6)
	85.8 (A, 0.3)	86.6 (A, 0.1)
	91.8 (A, 0.4)	92.7 (A, 0.2)
	93.3 (A, 0.4)	97.5 (A, 0.5)
	97.9 (A, 0.2)	102.4 (A, 0.0)
	120.2 (A, 0.1)	120.5 (A, 0.5)
	124.3 (A, 0.7)	124.1 (A, 0.3)
	173.2 (A, 0.2)	170.8 (A, 0.0)
	183.3 (A, 1.2)	180.8 (A, 0.7)
	296.7 (A, 0.6)	289.2 (A, 0.5)
	351.8 (A, 0.5)	335.5 (A, 9.1)
	366.5 (A, 11.0)	344.6 (A, 1.7)
	382.6 (A, 10.8)	364.3 (A, 17.6)
	387.9 (A, 12.5)	378.0 (A, 15.0)
	402.0 (A, 4.1)	383.7 (A, 3.6)
	427.9 (A, 5.6)	439.0 (A, 0.3)
	444.4 (A, 1.3)	443.9 (A, 2.9)
	451.8 (A, 4.8)	447.0 (A, 1.3)
	457.2 (A, 15.2)	458.5 (A, 2.7)
	464.7 (A, 4.3)	472.0 (A, 4.5)
	469.8 (A, 1.7)	475.6 (A, 5.1)
	498.5 (A, 13.1)	500.1 (A, 2.1)
	503.9 (A, 1.7)	508.5 (A, 15.7)
	514.8 (A, 7.4)	510.2 (A, 7.4)
	541.5 (A, 6.9)	530.9 (A, 3.6)
	545.8 (A, 8.8)	538.1 (A, 8.9)
	572.3 (A, 44.3)	570.3 (A, 15.0)
	577.3 (A, 35.0)	574.8 (A, 34.2)
	609.1 (A, 0.8)	582.1 (A, 5.9)
	615.8 (A, 45.0)	586.6 (A, 3.4)
	619.7 (A, 29.1)	605.1 (A, 56.3)
	640.5 (A, 10.7)	635.3 (A, 3.9)
	656.0 (A, 103.7)	650.8 (A, 122.0)
	671.6 (A, 53.6)	664.9 (A, 36.4)
	691.1 (A, 71.8)	685.2 (A, 57.7)
	749.7 (A, 493.0)	731.1 (A, 537.6)
	835.6 (A, 9.7)	816.9 (A, 40.2)
	838.0 (A, 6.2)	822.2 (A, 3.0)

	851.7 (A, 25.2) 855.8 (A, 3.1) 867.9 (A, 13.2) 928.7 (A, 1.4) 948.3 (A, 3.0) 1023.7 (A, 5.0) 1042.1 (A, 3.5) 1082.3 (A, 0.4) 1086.9 (A, 1.8) 1148.9 (A, 1.6) 1279.4 (A, 0.0) 1404.3 (A, 2.7) 1407.8 (A, 0.8) 1459.9 (A, 1.8) 1476.6 (A, 3.4) 1636.9 (A, 138.4) 2016.3 (A, 620.7) 2025.8 (A, 1122.5) 2050.2 (A, 547.0) 2068.8 (A, 909.1) 2095.5 (A, 837.8) 2126.8 (A, 611.4) 3230.0 (A, 0.1) 3232.1 (A, 0.1) 3245.4 (A, 0.4) 3248.0 (A, 0.0) 3256.9 (A, 0.1)	829.1 (A, 14.2) 835.0 (A, 3.0) 841.2 (A, 7.3) 905.6 (A, 1.1) 911.6 (A, 2.6) 988.7 (A, 6.0) 1006.3 (A, 5.3) 1051.1 (A, 1.4) 1052.3 (A, 0.5) 1110.8 (A, 0.4) 1245.7 (A, 0.0) 1349.0 (A, 2.1) 1352.4 (A, 1.7) 1407.1 (A, 3.8) 1424.2 (A, 5.9) 1565.3 (A, 132.4) 1948.2 (A, 581.9) 1957.1 (A, 1034.8) 1981.0 (A, 503.3) 1992.0 (A, 861.4) 2022.7 (A, 752.9) 2053.3 (A, 553.1) 3155.0 (A, 0.1) 3160.1 (A, 0.1) 3170.3 (A, 0.1) 3172.2 (A, 0.4) 3181.7 (A, 0.1)
$CpFeMn(CO)_6$ **6CO-1S**	40.8 (A', 0.3) 45.5 (A", 0.0) 64.5 (A", 0.1) 76.9 (A', 0.0) 82.3 (A", 0.1) 83.0 (A', 0.1) 90.1 (A', 0.3) 95.0 (A", 0.1) 98.7 (A", 0.4) 100.8 (A', 2.0) 106.2 (A', 0.7) 133.7 (A", 0.2) 156.4 (A", 0.0) 186.3 (A', 3.0) 213.2 (A', 0.4) 348.5 (A', 5.3) 404.5 (A", 0.6)	34.6 (A, 0.1) 35.5 (A, 0.1) 60.5 (A, 0.0) 68.2 (A, 0.2) 80.9 (A, 0.0) 82.5 (A, 0.0) 93.1 (A, 0.1) 93.3 (A, 0.3) 99.9 (A, 2.0) 102.1 (A, 0.3) 106.0 (A, 0.4) 129.7 (A, 0.3) 161.1 (A, 0.0) 168.1 (A, 3.3) 217.9 (A, 0.2) 328.8 (A, 5.2) 375.7 (A, 2.2)

	418.1 (A", 0.5)	402.8 (A, 1.3)
	425.7 (A', 0.7)	410.5 (A, 0.0)
	429.9 (A', 0.8)	427.3 (A, 1.0)
	435.2 (A', 2.6)	434.3 (A, 0.0)
	435.9 (A", 0.9)	444.2 (A, 1.4)
	457.6 (A", 4.5)	448.1 (A, 0.0)
	473.7 (A", 25.8)	493.7 (A, 0.8)
	497.1 (A', 0.6)	500.3 (A, 23.9)
	499.0 (A", 1.0)	500.4 (A, 1.2)
	506.3 (A', 3.2)	506.6 (A, 2.9)
	509.8 (A', 12.2)	515.6 (A, 13.4)
	549.2 (A', 9.6)	538.9 (A, 8.8)
	586.4 (A", 42.1)	574.4 (A, 0.2)
	593.1 (A", 0.4)	579.2 (A, 9.9)
	602.4 (A', 184.7)	589.8 (A, 24.2)
	607.0 (A", 1.7)	589.8 (A, 140.7)
	636.5 (A', 2.1)	612.5 (A, 0.9)
	648.6 (A', 78.1)	644.5 (A, 85.3)
	655.1 (A", 57.0)	648.1 (A, 57.9)
	658.7 (A', 30.2)	650.6 (A, 27.7)
	697.2 (A', 97.3)	694.0 (A, 97.7)
	814.3 (A", 7.3)	791.9 (A, 9.1)
	829.3 (A', 22.5)	806.3 (A, 36.9)
	840.3 (A', 11.4)	820.8 (A, 8.1)
	851.3 (A", 5.8)	830.1 (A, 3.7)
	878.3 (A', 11.3)	852.2 (A, 9.1)
	911.9 (A", 0.4)	888.2 (A, 2.2)
	947.9 (A", 3.7)	890.6 (A, 1.3)
	1028.7 (A', 0.9)	993.9 (A, 1.2)
	1062.4 (A", 5.6)	1029.1 (A, 7.2)
	1083.4 (A', 2.9)	1052.8 (A, 3.4)
	1134.8 (A', 14.9)	1097.8 (A, 5.6)
	1149.9 (A', 39.0)	1132.5 (A, 40.5)
	1248.0 (A", 0.1)	1210.2 (A, 0.2)
	1374.4 (A", 0.9)	1312.4 (A, 0.7)
	1397.9 (A', 0.0)	1343.1 (A, 0.1)
	1435.2 (A", 2.8)	1384.8 (A, 4.4)
	1460.2 (A', 4.2)	1406.9 (A, 7.3)
	2022.2 (A", 1.3)	1953.1 (A, 0.6)
	2033.4 (A', 262.1)	1966.0 (A, 409.8)
	2049.8 (A', 573.4)	1977.1 (A, 1809.3)
	2052.2 (A", 1914.4)	1981.4 (A, 398.0)
	2057.8 (A', 1358.2)	1988.7 (A, 1232.8)
	2132.4 (A', 462.6)	2059.6 (A, 425.4)

	2741.8 (A', 1.9) 3232.0 (A", 0.2) 3240.3 (A', 0.3) 3247.7 (A", 0.0) 3255.1 (A', 0.4)	2554.4 (A, 0.6) 3156.6 (A, 0.2) 3165.3 (A, 0.2) 3172.2 (A, 0.3) 3178.2 (A, 0.4)
$CpFeMn(CO)_6$ **6CO-2T**	23.9 (A", 0.0) 45.8 (A", 0.0) 60.8 (A', 0.2) 61.0 (A", 0.1) 77.2 (A', 0.6) 78.3 (A", 0.4) 84.7 (A', 0.8) 86.2 (A', 0.2) 86.5 (A", 0.7) 114.2 (A', 0.0) 123.3 (A", 0.1) 175.7 (A', 0.0) 176.2 (A", 0.0) 202.4 (A', 1.9) 246.6 (A', 2.4) 313.8 (A', 0.2) 318.5 (A", 0.1) 345.8 (A", 3.7) 353.8 (A', 3.8) 376.4 (A', 4.4) 392.4 (A", 0.0) 418.5 (A', 30.7) 454.6 (A", 9.2) 455.5 (A', 0.0) 456.1 (A", 3.4) 457.1 (A', 15.5) 463.6 (A', 69.2) 479.8 (A", 0.2) 495.4 (A", 2.8) 499.2 (A', 2.5) 545.4 (A', 66.0) 547.9 (A", 5.0) 550.6 (A', 117.7) 607.7 (A", 2.5) 608.0 (A', 3.1) 634.9 (A", 69.4) 635.3 (A', 70.4) 651.0 (A', 306.1) 829.4 (A', 15.0)	2.4 (A, 0.0) 46.8 (A, 0.0) 59.5 (A, 0.2) 59.6 (A, 0.2) 83.5 (A, 0.1) 84.1 (A, 0.1) 89.1 (A, 0.7) 89.6 (A, 0.3) 90.2 (A, 0.7) 122.0 (A, 0.0) 130.6 (A, 0.0) 180.7 (A, 0.1) 181.6 (A, 0.0) 206.4 (A, 0.4) 243.7 (A, 0.1) 298.0 (A, 1.6) 301.4 (A, 1.0) 338.6 (A, 3.8) 345.9 (A, 4.2) 381.0 (A, 5.1) 389.2 (A, 0.0) 427.8 (A, 21.9) 452.5 (A, 5.7) 455.5 (A, 5.2) 458.0 (A, 0.6) 459.0 (A, 2.0) 464.2 (A, 0.2) 475.2 (A, 55.6) 494.4 (A, 1.5) 497.0 (A, 1.4) 539.0 (A, 5.7) 539.3 (A, 7.9) 554.2 (A, 188.9) 580.4 (A, 0.6) 582.3 (A, 10.0) 629.3 (A, 65.1) 629.7 (A, 65.4) 648.9 (A, 279.1) 808.7 (A, 53.3)

	836.1 (A', 12.5) 837.1 (A", 0.0) 840.7 (A', 27.0) 850.0 (A", 2.6) 920.9 (A", 1.0) 922.0 (A', 2.9) 1032.5 (A', 7.6) 1034.4 (A", 6.3) 1081.5 (A", 0.2) 1081.7 (A', 0.2) 1151.5 (A', 3.9) 1278.4 (A", 0.0) 1399.5 (A", 0.0) 1401.7 (A', 0.4) 1465.4 (A', 0.5) 1469.7 (A", 1.9) 1932.0 (A", 839.6) 1932.9 (A', 863.1) 1959.7 (A', 54.5) 2062.8 (A", 857.2) 2063.8 (A', 840.1) 2122.5 (A', 1136.2) 3226.3 (A", 0.0) 3226.8 (A', 0.1) 3241.8 (A', 0.1) 3242.7 (A", 0.2) 3253.2 (A', 0.2)	818.1 (A, 3.8) 822.5 (A, 0.0) 823.6 (A, 6.0) 833.0 (A, 3.2) 899.1 (A, 1.2) 901.0 (A, 3.0) 999.3 (A, 8.3) 1001.5 (A, 7.2) 1050.5 (A, 0.3) 1050.8 (A, 0.2) 1115.5 (A, 1.3) 1246.1 (A, 0.0) 1347.1 (A, 0.0) 1348.2 (A, 0.5) 1415.2 (A, 1.6) 1418.5 (A, 3.8) 1860.3 (A, 742.7) 1860.8 (A, 755.2) 1886.0 (A, 50.1) 1989.3 (A, 778.0) 1989.9 (A, 767.1) 2044.7 (A, 1058.9) 3151.8 (A, 0.0) 3151.9 (A, 0.1) 3165.1 (A, 0.0) 3165.6 (A, 0.0) 3176.1 (A, 0.3)
$CpFeMn(CO)_6$ **6CO-3S**	36.7 (A, 0.4) 50.5 (A, 0.1) 70.0 (A, 0.0) 72.3 (A, 0.1) 77.8 (A, 0.2) 84.3 (A, 0.3) 92.9 (A, 0.1) 99.0 (A, 0.4) 104.2 (A, 0.3) 108.2 (A, 0.3) 122.6 (A, 0.4) 130.3 (A, 1.7) 146.6 (A, 0.0) 182.8 (A, 1.2) 247.2 (A, 1.5) 361.1 (A, 2.1) 400.2 (A, 2.8)	35.3 (A, 0.2) 37.7 (A, 0.2) 47.8 (A, 0.2) 67.5 (A, 0.1) 71.6 (A, 0.2) 83.0 (A, 0.2) 86.3 (A, 0.0) 99.0 (A, 0.1) 100.4 (A, 0.2) 103.6 (A, 0.5) 116.7 (A, 0.7) 121.8 (A, 0.7) 141.7 (A, 0.0) 167.0 (A, 0.4) 224.4 (A, 2.2) 339.1 (A, 4.1) 374.8 (A, 4.6)

	406.3 (A, 1.5)	376.2 (A, 2.3)
	415.4 (A, 3.7)	408.6 (A, 0.7)
	422.5 (A, 2.4)	412.3 (A, 0.8)
	426.3 (A, 3.3)	427.8 (A, 0.2)
	435.9 (A, 1.0)	439.5 (A, 2.1)
	456.3 (A, 30.1)	455.2 (A, 5.0)
	473.7 (A, 9.0)	482.9 (A, 12.6)
	487.2 (A, 3.9)	489.2 (A, 9.2)
	506.9 (A, 9.1)	504.7 (A, 16.9)
	508.9 (A, 5.1)	507.9 (A, 6.8)
	518.1 (A, 7.4)	520.0 (A, 7.0)
	545.6 (A, 6.6)	534.9 (A, 3.4)
	586.3 (A, 75.2)	573.8 (A, 61.3)
	599.6 (A, 17.9)	580.7 (A, 33.7)
	603.5 (A, 14.1)	581.8 (A, 14.7)
	614.1 (A, 10.0)	587.9 (A, 7.0)
	630.2 (A, 60.1)	615.0 (A, 56.3)
	650.0 (A, 76.7)	641.9 (A, 62.2)
	650.9 (A, 34.7)	642.3 (A, 22.6)
	661.4 (A, 158.8)	656.8 (A, 138.5)
	693.9 (A, 93.0)	688.1 (A, 111.4)
	835.5 (A, 4.7)	816.9 (A, 29.9)
	836.2 (A, 0.6)	821.6 (A, 1.3)
	850.8 (A, 15.5)	822.8 (A, 6.4)
	855.0 (A, 21.7)	828.5 (A, 14.6)
	866.3 (A, 8.3)	844.2 (A, 7.0)
	920.0 (A, 2.0)	896.9 (A, 2.0)
	933.0 (A, 2.2)	899.7 (A, 1.2)
	1022.7 (A, 4.4)	986.0 (A, 5.1)
	1038.3 (A, 2.9)	1004.2 (A, 4.4)
	1080.1 (A, 1.2)	1048.2 (A, 0.8)
	1082.5 (A, 0.9)	1049.2 (A, 1.2)
	1146.8 (A, 4.5)	1108.6 (A, 2.1)
	1275.6 (A, 0.0)	1242.8 (A, 0.0)
	1403.1 (A, 1.0)	1347.6 (A, 0.8)
	1406.9 (A, 0.2)	1351.2 (A, 0.0)
	1453.4 (A, 1.6)	1401.1 (A, 3.8)
	1470.2 (A, 2.5)	1419.2 (A, 4.3)
	1834.6 (A, 346.5)	1777.7 (A, 307.8)
	2020.3 (A, 572.6)	1954.3 (A, 511.9)
	2036.7 (A, 541.3)	1964.6 (A, 539.8)
	2048.8 (A, 494.5)	1976.4 (A, 575.9)
	2060.9 (A, 1656.8)	1986.8 (A, 1408.5)
	2132.2 (A, 546.4)	2058.5 (A, 519.2)

	3228.4 (A, 0.1) 3229.5 (A, 0.2) 3243.1 (A, 1.1) 3246.2 (A, 0.7) 3254.8 (A, 0.4)	3154.3 (A, 0.1) 3155.3 (A, 0.1) 3166.9 (A, 0.6) 3170.4 (A, 0.3) 3178.7 (A, 0.5)
$CpFeMn(CO)_6$ **6CO-4S**	32.8 (A", 0.0) 41.1 (A", 0.3) 63.8 (A", 0.0) 65.5 (A', 1.9) 81.2 (A', 0.2) 81.8 (A", 0.5) 84.4 (A', 2.6) 92.8 (A', 0.6) 94.3 (A", 0.3) 110.3 (A', 1.1) 122.3 (A", 0.0) 135.7 (A", 0.1) 148.1 (A', 1.2) 173.4 (A', 1.2) 193.1 (A', 0.4) 354.2 (A', 4.3) 378.5 (A", 1.0) 402.2 (A', 1.2) 402.8 (A", 0.2) 407.6 (A', 12.1) 423.8 (A", 2.5) 433.3 (A', 6.5) 435.2 (A", 0.5) 487.4 (A", 14.3) 491.6 (A', 15.2) 494.9 (A', 65.8) 512.5 (A", 3.2) 519.7 (A', 48.2) 562.3 (A', 110.1) 576.3 (A", 21.7) 579.5 (A", 3.2) 586.6 (A', 38.5) 614.5 (A', 15.8) 615.6 (A", 1.5) 626.0 (A", 43.9) 627.2 (A', 19.4) 650.1 (A', 46.5) 702.8 (A', 97.3) 831.0 (A', 7.7)	30.9 (A", 0.0) 45.0 (A", 0.2) 50.8 (A', 3.9) 57.0 (A", 0.0) 78.1 (A", 0.5) 79.5 (A', 0.5) 84.5 (A', 1.7) 89.7 (A", 0.0) 95.3 (A', 0.4) 104.4 (A", 0.1) 108.5 (A', 0.8) 135.6 (A", 0.1) 148.0 (A', 1.3) 166.3 (A', 1.9) 189.5 (A', 0.2) 325.7 (A', 6.2) 340.8 (A", 1.2) 378.8 (A', 0.6) 393.8 (A", 2.3) 402.8 (A', 16.2) 412.9 (A", 3.2) 428.9 (A", 0.9) 441.2 (A', 5.0) 463.9 (A", 13.2) 488.8 (A', 109.2) 504.9 (A', 12.6) 514.5 (A", 1.0) 523.4 (A', 19.0) 551.3 (A', 59.5) 563.3 (A", 1.8) 568.6 (A', 35.2) 573.4 (A", 14.0) 583.8 (A", 0.7) 590.2 (A', 30.6) 612.6 (A', 13.2) 620.3 (A", 42.7) 642.8 (A', 46.9) 695.3 (A', 98.3) 810.3 (A', 11.0)

	833.2 (A", 0.1) 843.1 (A', 2.5) 846.3 (A', 29.2) 881.3 (A", 4.3) 931.7 (A", 0.5) 931.8 (A', 5.5) 1028.0 (A", 4.5) 1039.0 (A', 3.5) 1082.0 (A', 1.5) 1083.6 (A", 0.1) 1151.5 (A', 2.5) 1277.3 (A", 0.0) 1407.6 (A', 3.8) 1409.1 (A", 0.0) 1455.0 (A", 3.9) 1472.6 (A', 1.0) 1991.0 (A", 446.4) 2005.6 (A', 877.6) 2013.6 (A', 97.8) 2039.4 (A", 1149.7) 2052.9 (A', 904.8) 2122.7 (A', 818.6) 3227.2 (A', 0.1) 3228.8 (A", 0.3) 3243.0 (A", 0.5) 3250.1 (A', 0.4) 3256.9 (A', 0.4)	814.7 (A', 41.7) 818.3 (A", 0.0) 825.3 (A', 0.2) 860.6 (A", 3.6) 907.3 (A", 0.7) 908.4 (A', 5.1) 992.0 (A", 5.7) 1006.8 (A', 4.9) 1051.1 (A', 1.0) 1051.6 (A", 0.1) 1114.0 (A', 0.5) 1244.6 (A", 0.0) 1352.1 (A", 0.1) 1352.5 (A', 3.7) 1403.6 (A", 6.6) 1424.3 (A', 2.1) 1923.9 (A', 763.3) 1923.9 (A", 366.3) 1946.0 (A', 103.0) 1963.4 (A", 1074.4) 1976.6 (A', 867.2) 2043.5 (A', 752.4) 3152.9 (A', 0.1) 3155.0 (A", 0.1) 3168.0 (A", 0.0) 3173.1 (A', 0.4) 3181.0 (A', 0.2)
$CpFeMn(CO)_6$ **6CO-5S**	31.1 (A', 0.1) 36.4 (A", 0.2) 48.6 (A", 0.0) 72.1 (A", 0.1) 78.2 (A', 0.5) 82.3 (A", 0.4) 82.6 (A', 0.8) 87.1 (A', 1.2) 92.6 (A", 0.1) 98.3 (A', 0.0) 116.7 (A", 0.2) 125.8 (A', 0.2) 201.3 (A", 1.2) 226.6 (A', 0.2) 245.3 (A', 0.1) 315.6 (A", 0.7) 360.6 (A', 0.3)	24.3 (A", 0.1) 35.9 (A', 0.1) 50.0 (A", 0.0) 70.7 (A", 0.0) 82.1 (A', 2.0) 84.5 (A', 0.2) 84.6 (A", 0.5) 88.6 (A', 0.7) 98.9 (A", 0.1) 104.8 (A', 0.2) 128.9 (A", 0.0) 138.2 (A', 0.5) 225.9 (A', 0.6) 228.2 (A", 1.4) 235.8 (A', 0.0) 307.6 (A", 1.3) 340.8 (A", 9.0)

	361.3 (A", 8.9)	346.8 (A', 2.1)
	410.7 (A", 0.2)	380.1 (A', 1.1)
	411.7 (A', 0.8)	401.3 (A", 0.0)
	416.1 (A', 4.5)	422.0 (A', 7.1)
	428.2 (A", 0.7)	434.9 (A", 0.1)
	455.5 (A', 5.1)	445.2 (A', 4.4)
	471.9 (A", 6.5)	464.3 (A", 5.2)
	476.2 (A', 23.5)	483.0 (A', 17.0)
	509.6 (A", 0.3)	496.7 (A", 0.8)
	509.9 (A', 6.9)	510.3 (A', 2.7)
	532.0 (A", 22.9)	528.6 (A", 9.5)
	538.7 (A', 2.5)	532.6 (A', 2.4)
	552.5 (A', 9.5)	550.1 (A', 15.1)
	587.7 (A', 40.7)	576.2 (A", 3.2)
	595.9 (A', 187.0)	580.7 (A', 3.8)
	596.2 (A", 15.9)	584.2 (A", 17.1)
	606.8 (A", 6.9)	590.2 (A', 45.5)
	612.8 (A', 4.1)	601.3 (A', 105.9)
	646.9 (A', 324.4)	644.0 (A", 39.6)
	652.1 (A", 39.0)	647.0 (A', 343.1)
	689.0 (A', 95.6)	685.9 (A', 114.3)
	823.7 (A', 8.7)	811.1 (A', 25.7)
	829.1 (A", 2.3)	818.1 (A", 3.1)
	840.3 (A", 2.7)	820.3 (A", 2.2)
	845.9 (A', 42.9)	825.1 (A', 30.6)
	853.2 (A', 1.5)	843.8 (A', 4.6)
	919.6 (A", 2.0)	899.5 (A", 1.5)
	923.2 (A', 1.6)	903.9 (A', 0.5)
	1010.3 (A', 5.4)	980.3 (A', 4.4)
	1026.1 (A", 1.9)	1004.7 (A", 4.6)
	1076.0 (A", 3.3)	1049.0 (A", 1.2)
	1077.4 (A', 0.2)	1049.2 (A', 0.6)
	1137.8 (A', 2.1)	1107.3 (A', 0.5)
	1270.0 (A", 0.0)	1245.1 (A", 0.0)
	1385.4 (A", 0.6)	1341.0 (A", 0.4)
	1400.9 (A', 3.1)	1349.4 (A', 3.1)
	1445.0 (A', 0.8)	1399.9 (A', 3.7)
	1475.9 (A", 0.9)	1428.5 (A", 2.4)
	1894.8 (A", 813.1)	1814.9 (A", 762.2)
	1927.1 (A', 106.4)	1839.7 (A', 49.4)
	2038.3 (A', 744.0)	1961.8 (A', 644.4)
	2042.1 (A", 976.5)	1974.2 (A", 818.6)
	2071.4 (A', 1401.3)	1999.4 (A', 1225.4)
	2113.1 (A', 619.8)	2037.3 (A', 612.3)

	3187.1 (A', 2.6) 3230.8 (A", 0.1) 3236.9 (A', 0.1) 3245.7 (A", 0.0) 3254.6 (A', 0.2)	3148.6 (A', 0.1) 3157.0 (A", 0.1) 3165.8 (A', 0.1) 3171.9 (A", 0.4) 3179.4 (A', 0.2)
$CpFeMn(CO)_5$ **5CO-1S**	29.5 (A", 0.0) 41.3 (A', 0.2) 47.6 (A", 0.2) 63.9 (A', 0.0) 80.6 (A", 0.9) 85.9 (A", 0.3) 97.0 (A', 0.3) 101.5 (A', 1.0) 136.5 (A", 0.0) 137.0 (A', 0.4) 196.3 (A', 0.6) 216.9 (A", 0.0) 239.3 (A', 0.7) 367.7 (A', 11.2) 379.7 (A", 0.0) 411.2 (A", 6.1) 411.5 (A', 9.4) 419.1 (A", 0.8) 432.2 (A', 16.5) 448.6 (A", 1.3) 460.1 (A', 41.5) 473.8 (A', 8.6) 476.3 (A", 1.9) 518.1 (A', 67.3) 530.4 (A', 6.8) 538.5 (A", 5.5) 551.7 (A", 9.8) 594.8 (A', 24.3) 598.7 (A", 5.4) 609.9 (A", 34.4) 612.5 (A', 9.3) 653.2 (A', 27.3) 681.3 (A', 67.9) 828.8 (A', 3.3) 833.8 (A", 0.0) 841.3 (A', 7.4) 845.8 (A', 16.7) 879.1 (A", 3.6) 922.0 (A', 1.4)	14.1 (A, 0.0) 40.3 (A, 0.2) 44.9 (A, 0.3) 65.7 (A, 0.0) 80.4 (A, 0.9) 85.4 (A, 0.1) 99.7 (A, 0.5) 101.3 (A, 0.7) 132.2 (A, 0.5) 136.3 (A, 0.0) 190.4 (A, 0.9) 202.2 (A, 0.1) 235.9 (A, 1.1) 339.0 (A, 3.2) 350.0 (A, 0.6) 392.9 (A, 7.2) 398.4 (A, 6.7) 412.1 (A, 0.7) 423.2 (A, 22.7) 440.1 (A, 1.6) 452.7 (A, 57.9) 474.7 (A, 0.4) 476.1 (A, 1.3) 518.6 (A, 56.5) 526.0 (A, 2.3) 535.1 (A, 3.7) 544.1 (A, 9.7) 571.7 (A, 0.0) 582.0 (A, 18.4) 586.0 (A, 18.0) 605.1 (A, 33.2) 643.4 (A, 25.0) 673.8 (A, 52.7) 810.2 (A, 1.0) 813.5 (A, 38.0) 819.4 (A, 0.4) 822.5 (A, 1.6) 854.4 (A, 3.2) 894.0 (A, 0.9)

	922.3 (A", 0.0) 1021.0 (A", 4.1) 1041.3 (A', 7.0) 1079.2 (A", 0.1) 1082.5 (A', 1.1) 1149.1 (A', 7.1) 1275.1 (A", 0.0) 1400.1 (A", 0.0) 1412.3 (A', 0.1) 1446.6 (A", 2.6) 1478.4 (A', 1.8) 1954.8 (A", 697.4) 1966.8 (A', 425.3) 2026.1 (A', 988.0) 2038.9 (A", 968.7) 2101.3 (A', 958.7) 3225.9 (A', 0.1) 3226.6 (A", 0.0) 3239.6 (A", 0.1) 3246.1 (A', 0.4) 3253.5 (A', 0.0)	897.1 (A, 0.3) 985.9 (A, 5.1) 1006.9 (A, 8.2) 1048.0 (A, 0.1) 1050.6 (A, 1.1) 1111.1 (A, 2.9) 1243.4 (A, 0.0) 1343.9 (A, 0.1) 1357.0 (A, 0.0) 1396.3 (A, 4.7) 1428.9 (A, 3.4) 1884.4 (A, 595.7) 1898.6 (A, 382.8) 1952.4 (A, 908.8) 1963.7 (A, 868.8) 2024.5 (A, 865.8) 3153.1 (A, 0.1) 3153.2 (A, 0.0) 3164.2 (A, 0.0) 3171.2 (A, 0.3) 3178.5 (A, 0.0)
$CpFeMn(CO)_5$ **5CO-2T**	21.3 (A", 0.1) 24.7 (A', 0.3) 30.7 (A", 0.1) 77.3 (A', 0.3) 78.0 (A", 0.0) 87.9 (A", 0.3) 89.0 (A', 2.3) 97.6 (A', 0.1) 108.2 (A', 0.9) 131.3 (A", 0.7) 199.9 (A', 3.2) 226.4 (A", 2.3) 232.9 (A', 1.5) 288.9 (A", 4.8) 329.3 (A', 0.9) 362.3 (A', 6.2) 366.8 (A", 2.0) 409.6 (A", 0.1) 419.2 (A', 21.2) 425.1 (A", 0.0) 429.1 (A', 0.6) 466.3 (A', 15.0) 469.5 (A", 2.0)	20.6 (A", 0.1) 23.5 (A', 0.5) 37.2 (A", 0.0) 78.1 (A", 0.0) 82.1 (A', 0.3) 87.3 (A", 0.1) 93.3 (A', 1.1) 98.7 (A', 0.9) 124.3 (A', 0.2) 138.1 (A", 0.2) 204.3 (A', 0.0) 237.3 (A', 0.5) 247.6 (A", 0.1) 313.8 (A", 4.8) 327.9 (A', 4.0) 351.5 (A', 1.1) 373.8 (A", 3.5) 401.9 (A", 1.3) 411.0 (A', 0.6) 420.8 (A", 0.0) 425.1 (A', 15.0) 463.9 (A", 0.6) 470.1 (A', 5.5)

	478.3 (A", 5.7) 500.0 (A', 7.7) 518.2 (A', 1.2) 540.2 (A", 0.0) 554.7 (A', 25.8) 599.7 (A', 3.3) 600.7 (A", 0.7) 629.7 (A", 47.5) 634.0 (A', 33.4) 675.3 (A', 121.5) 816.5 (A', 36.9) 818.1 (A", 2.1) 830.4 (A', 20.9) 831.7 (A", 0.0) 837.5 (A', 8.7) 899.4 (A", 0.0) 911.1 (A', 0.1) 1027.9 (A', 11.8) 1033.2 (A", 7.2) 1076.3 (A', 2.0) 1078.1 (A", 0.4) 1147.2 (A', 4.8) 1275.7 (A", 0.0) 1388.2 (A', 9.1) 1393.8 (A", 0.1) 1461.8 (A', 2.1) 1463.0 (A", 0.9) 1908.1 (A", 908.4) 1914.2 (A', 135.1) 2031.7 (A', 943.5) 2054.2 (A", 815.7) 2106.2 (A', 1276.6) 3222.7 (A', 0.1) 3226.5 (A", 0.0) 3240.0 (A', 0.0) 3245.0 (A", 0.0) 3253.5 (A', 0.0)	491.8 (A", 4.5) 512.5 (A", 0.0) 514.0 (A', 22.8) 519.1 (A', 0.7) 554.3 (A', 13.8) 568.1 (A", 1.0) 575.4 (A', 1.8) 613.5 (A", 42.1) 613.8 (A', 27.2) 659.4 (A', 94.2) 806.4 (A', 52.0) 812.9 (A", 0.9) 815.5 (A", 1.8) 821.5 (A', 4.7) 829.4 (A', 1.5) 889.7 (A', 0.6) 892.7 (A", 0.4) 996.0 (A', 9.6) 998.5 (A", 6.8) 1044.0 (A", 0.6) 1049.0 (A', 1.9) 1109.4 (A', 1.6) 1243.0 (A", 0.0) 1338.5 (A", 0.5) 1340.4 (A', 1.6) 1410.0 (A", 2.2) 1410.2 (A', 4.5) 1824.1 (A", 761.9) 1835.3 (A', 168.6) 1955.4 (A', 804.1) 1980.5 (A", 772.8) 2026.5 (A', 1215.0) 3145.7 (A', 0.2) 3155.8 (A", 0.0) 3165.6 (A', 0.0) 3169.5 (A", 0.3) 3178.3 (A', 0.1)
$CpFeMn(CO)_5$ **5CO-3S**	35.7 (A, 0.2) 49.2 (A, 0.6) 61.1 (A, 0.1) 72.2 (A, 0.2) 76.8 (A, 1.0) 93.8 (A, 0.2) 98.6 (A, 0.3)	16.0 (A, 0.0) 24.5 (A, 0.2) 47.4 (A, 0.6) 69.6 (A, 0.4) 79.0 (A, 0.9) 87.3 (A, 0.9) 91.7 (A, 0.6)

	100.9 (A, 0.9)	100.4 (A, 0.3)
	104.8 (A, 0.6)	106.7 (A, 0.5)
	119.7 (A, 0.9)	114.1 (A, 0.4)
	126.7 (A, 1.2)	119.6 (A, 0.9)
	191.0 (A, 3.6)	154.9 (A, 0.2)
	283.7 (A, 3.2)	228.9 (A, 5.8)
	363.4 (A, 2.7)	348.2 (A, 3.8)
	395.7 (A, 3.3)	358.1 (A, 3.8)
	406.5 (A, 2.2)	376.7 (A, 6.4)
	429.4 (A, 1.2)	411.2 (A, 0.2)
	438.9 (A, 10.7)	422.5 (A, 11.0)
	447.8 (A, 0.2)	439.1 (A, 2.0)
	474.9 (A, 5.6)	450.8 (A, 4.2)
	490.9 (A, 6.4)	489.1 (A, 3.7)
	508.8 (A, 5.5)	502.5 (A, 1.0)
	534.9 (A, 14.8)	528.0 (A, 9.3)
	539.3 (A, 7.9)	543.4 (A, 3.4)
	548.6 (A, 3.3)	556.4 (A, 4.9)
	598.5 (A, 82.4)	571.7 (A, 68.1)
	604.8 (A, 4.2)	585.7 (A, 6.0)
	612.9 (A, 8.0)	587.3 (A, 68.2)
	628.0 (A, 28.4)	621.1 (A, 27.5)
	639.3 (A, 42.5)	627.9 (A, 42.9)
	648.0 (A, 28.5)	645.1 (A, 42.5)
	676.7 (A, 113.6)	649.8 (A, 12.4)
	716.4 (A, 53.0)	707.1 (A, 82.9)
	835.8 (A, 1.8)	813.6 (A, 27.8)
	837.2 (A, 5.6)	821.2 (A, 0.4)
	848.0 (A, 17.4)	824.0 (A, 22.4)
	861.4 (A, 21.2)	826.1 (A, 1.5)
	866.4 (A, 8.4)	847.6 (A, 6.3)
	915.7 (A, 1.3)	895.0 (A, 2.6)
	934.4 (A, 1.3)	901.5 (A, 0.2)
	1020.9 (A, 4.0)	985.2 (A, 5.4)
	1041.0 (A, 3.1)	1005.1 (A, 4.8)
	1080.5 (A, 0.7)	1049.1 (A, 0.8)
	1081.8 (A, 1.2)	1049.6 (A, 0.3)
	1146.3 (A, 4.0)	1109.0 (A, 1.3)
	1276.0 (A, 0.0)	1242.8 (A, 0.0)
	1401.9 (A, 0.6)	1346.0 (A, 0.7)
	1407.3 (A, 0.5)	1352.2 (A, 0.2)
	1450.0 (A, 1.5)	1398.1 (A, 4.5)
	1472.6 (A, 2.1)	1421.6 (A, 3.3)
	1780.0 (A, 325.3)	1774.6 (A, 295.5)

	1998.6 (A, 604.0) 2018.0 (A, 829.8) 2046.1 (A, 1105.7) 2091.8 (A, 727.6) 3229.6 (A, 0.1) 3230.3 (A, 0.0) 3243.8 (A, 0.6) 3246.5 (A, 0.8) 3255.3 (A, 0.4)	1925.6 (A, 642.8) 1941.1 (A, 710.7) 1974.7 (A, 971.1) 2012.3 (A, 638.4) 3154.8 (A, 0.1) 3158.0 (A, 0.1) 3169.1 (A, 0.0) 3172.9 (A, 0.3) 3181.5 (A, 0.3)
$CpFeMn(CO)_5$ **5CO-4S**	26.4 (A, 0.2) 40.5 (A, 0.2) 47.2 (A, 0.5) 60.7 (A, 0.9) 76.6 (A, 0.3) 80.6 (A, 0.4) 84.8 (A, 0.3) 92.8 (A, 0.4) 103.2 (A, 0.1) 124.6 (A, 0.7) 167.0 (A, 0.2) 217.5 (A, 0.9) 252.7 (A, 1.4) 366.7 (A, 0.4) 379.0 (A, 3.4) 382.2 (A, 2.1) 407.3 (A, 1.6) 420.3 (A, 0.5) 441.8 (A, 3.5) 452.2 (A, 3.7) 476.7 (A, 3.9) 485.9 (A, 0.9) 512.6 (A, 28.9) 524.5 (A, 26.9) 530.8 (A, 0.5) 558.1 (A, 24.9) 565.5 (A, 17.1) 598.8 (A, 4.3) 607.1 (A, 35.0) 613.0 (A, 10.9) 622.9 (A, 84.0) 691.9 (A, 132.0) 702.9 (A, 35.2) 825.5 (A, 11.1) 829.5 (A, 1.9)	22.2 (A, 0.1) 31.4 (A, 0.2) 42.2 (A, 0.5) 49.0 (A, 0.6) 68.2 (A, 0.2) 79.1 (A, 0.2) 84.3 (A, 0.6) 94.6 (A, 0.5) 104.4 (A, 0.2) 118.6 (A, 0.4) 163.5 (A, 0.3) 204.6 (A, 0.9) 232.3 (A, 2.7) 346.9 (A, 2.8) 357.6 (A, 5.1) 366.8 (A, 1.5) 387.1 (A, 1.6) 416.4 (A, 0.1) 437.3 (A, 4.0) 453.6 (A, 5.3) 478.8 (A, 8.0) 484.4 (A, 0.7) 515.2 (A, 24.2) 518.6 (A, 5.7) 527.8 (A, 8.5) 547.3 (A, 23.3) 560.4 (A, 6.3) 570.9 (A, 2.8) 582.0 (A, 6.0) 606.8 (A, 99.1) 608.7 (A, 53.1) 684.0 (A, 115.3) 699.4 (A, 26.0) 804.3 (A, 32.0) 814.1 (A, 4.4)

	836.1 (A, 9.5)	816.4 (A, 9.0)
	839.5 (A, 16.0)	821.3 (A, 5.4)
	869.1 (A, 9.3)	848.0 (A, 6.8)
	908.1 (A, 1.4)	887.4 (A, 1.0)
	918.7 (A, 0.9)	894.2 (A, 0.2)
	1016.2 (A, 6.3)	980.1 (A, 6.5)
	1038.7 (A, 3.4)	1005.1 (A, 4.9)
	1077.4 (A, 0.6)	1046.4 (A, 0.7)
	1080.0 (A, 1.1)	1049.0 (A, 0.8)
	1144.8 (A, 4.6)	1106.3 (A, 2.1)
	1273.5 (A, 0.0)	1242.0 (A, 0.0)
	1396.6 (A, 1.3)	1341.5 (A, 1.1)
	1405.6 (A, 0.7)	1350.2 (A, 0.2)
	1445.1 (A, 1.8)	1393.1 (A, 4.1)
	1477.1 (A, 1.3)	1425.9 (A, 2.5)
	1800.3 (A, 499.2)	1735.5 (A, 461.8)
	2010.8 (A, 321.0)	1941.1 (A, 379.4)
	2020.1 (A, 651.5)	1947.2 (A, 831.6)
	2029.1 (A, 1461.5)	1963.0 (A, 1124.9)
	2091.3 (A, 780.0)	2016.1 (A, 666.2)
	3225.7 (A, 0.0)	3150.3 (A, 0.0)
	3228.8 (A, 0.0)	3156.5 (A, 0.0)
	3240.4 (A, 0.2)	3164.3 (A, 0.0)
	3245.6 (A, 0.3)	3171.1 (A, 0.2)
	3253.5 (A, 0.2)	3180.3 (A, 0.2)

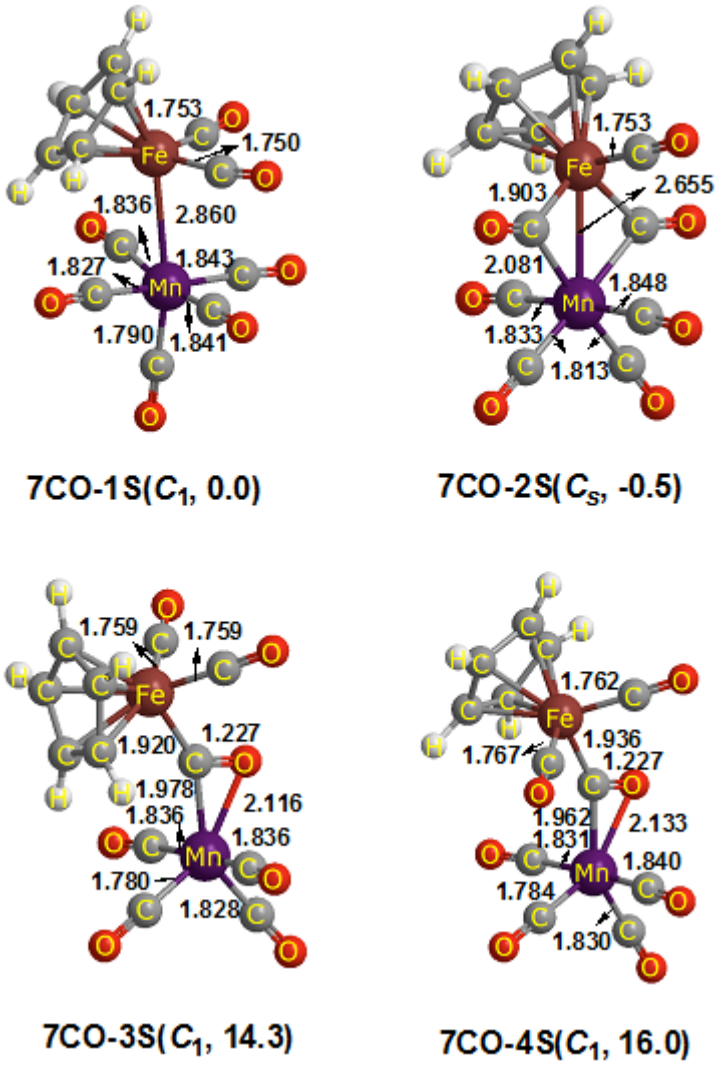
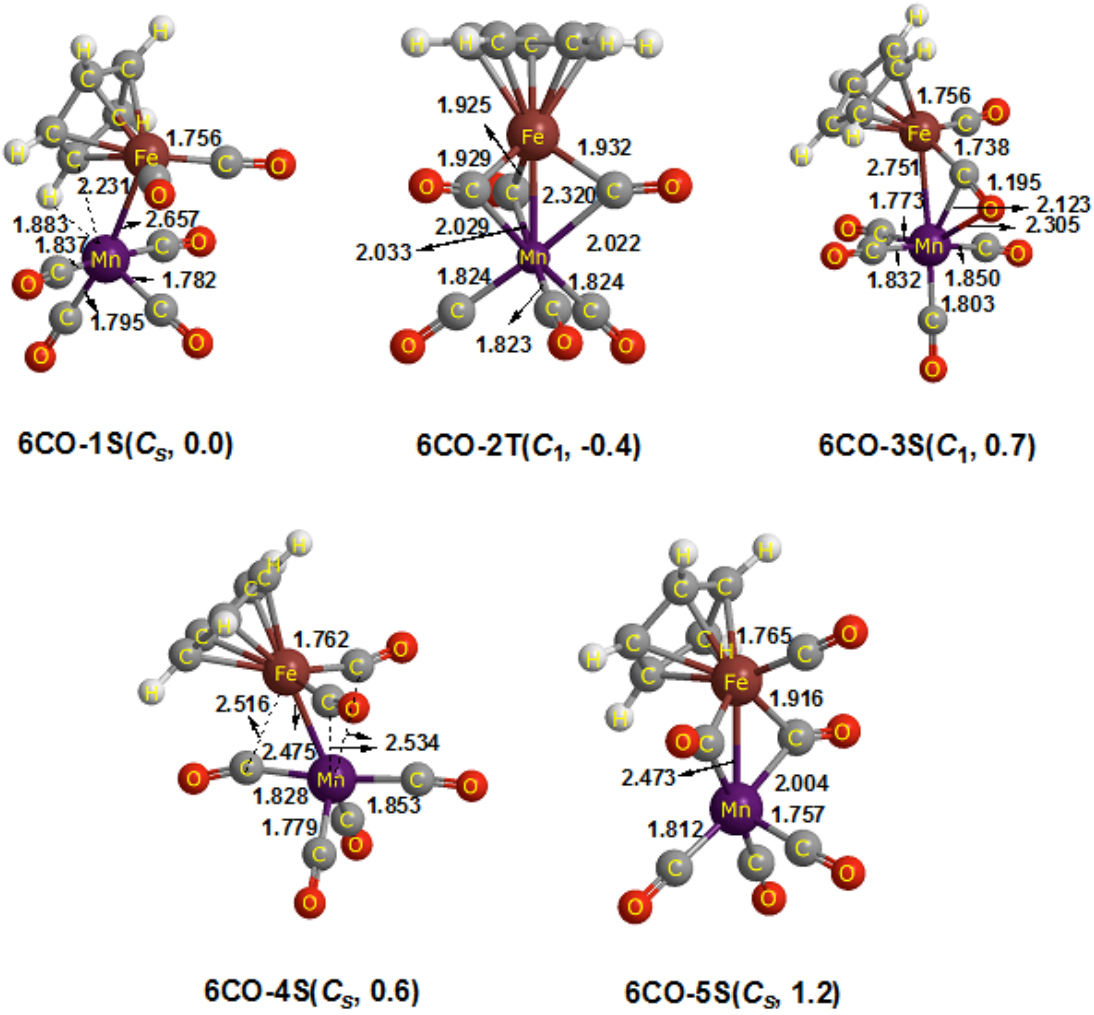


Figure S1. Four optimized geometries (bond lengths in Å) for $CpFeMn(CO)_7$ at the BP86 level of theory. The numbers in parentheses are the relative energies (ΔE in kcal·mol^{-1}). The subsequent figures have the same arrangement.

Table S15 The total energies (E, in Hartree), relative energies (ΔE, in kcal·mol^{-1}), Fe-Mn bond distances (Å), the number of imaginary vibrational frequencies (N_{imag}) and spin expectation values $\langle S^2 \rangle$ for the $CpFeMn(CO)_7$ structures.

Structures	E	ΔE	Fe-Mn	N_{imag}	$\langle S^2 \rangle$
7CO-1S (C_1)	-3402.433502	0.0	2.860	0	0.00
7CO-2S (C_s)	-3402.434350	-0.5	2.655	0	0.00
7CO-3S (C_1)	-3402.410767	14.3	3.763	0	0.00
7CO-4S (C_1)	-3402.407940	16.0	3.782	0	0.00



6CO-1S(C_S, 0.0) **6CO-2T(C_1, -0.4)** **6CO-3S(C_1, 0.7)**

6CO-4S(C_S, 0.6) **6CO-5S(C_S, 1.2)**

Figure S2. Optimized geometries for the five $CpFeMn(CO)_6$ structures at the BP86 level of theory.

Table S16 The total energies (E, in Hartree), relative energies (ΔE, in kcal·mol^{-1}), Fe-Mn bond distances (Å), the number of imaginary vibrational frequencies (N_{imag}) and spin expectation values $\langle S^2 \rangle$ for the $CpFeMn(CO)_6$ structures.

Structures	E	ΔE	Fe-Mn	N_{imag}	$\langle S^2 \rangle$
6CO-1S (C_s)	-3289.032220	0.0	2.657	0	0.00
6CO-2T (C_1)	-3289.032806	-0.4	2.320	0	2.03
6CO-3S (C_1)	-3289.031110	0.7	2.751	0	0.00
6CO-4S (C_s)	-3289.031230	0.6	2.475	0	0.00
6CO-5S (C_s)	-3289.030379	1.2	2.473	0	0.00

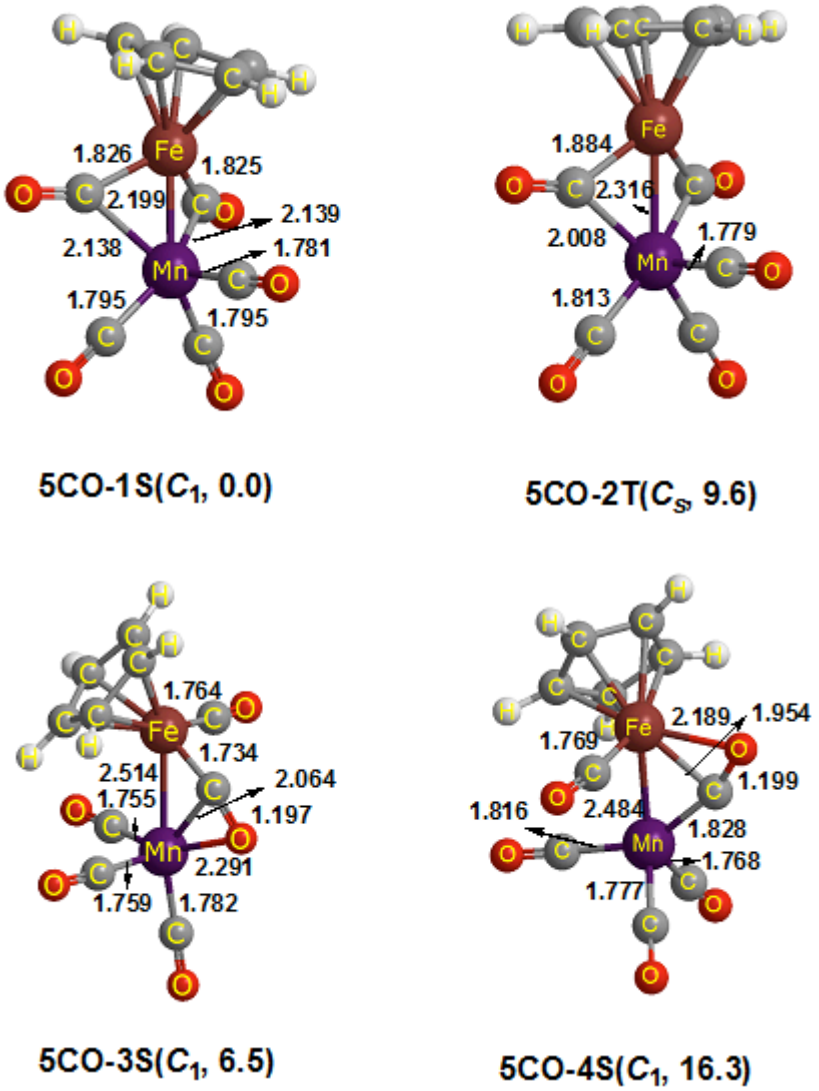
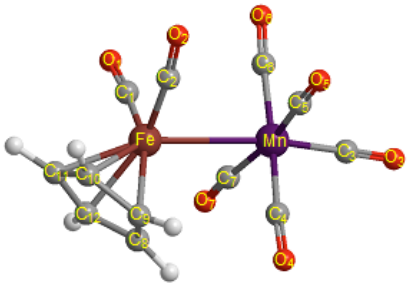


Figure S3. Four optimized structures for the CpFeMn(CO)$_5$ structure at the BP86 level of theory.

Table S17 The total energies (E, in Hartree), relative energies (ΔE, in kcal·mol^{-1}), Fe-Mn bond distances (Å), the number of imaginary vibrational frequencies (N_{imag}) and spin expectation values $\langle S^2 \rangle$ for the CpFeMn(CO)$_5$ structures

Structures	E	ΔE	Fe-Mn	N_{imag}	$\langle S^2 \rangle$
5CO-1S (C_1)	-3175.640899	0.0	2.199	0	0.00
5CO-2T (C_s)	-3175.625594	9.6	2.316	0	2.03
5CO-3S (C_1)	-3175.630508	6.5	2.514	0	0.00
5CO-4S (C_1)	-3175.614982	16.3	2.484	0	0.00



$CpFe(CO)_2Mn(CO)_5$

Figure S4. The structure of $CpFe(CO)_2Mn(CO)_5$.

Table S18 Comparison of theoretical intramolecular distances (in Å) and angles (deg) of $CpFe(CO)_2Mn(CO)_5$ with the experimental X-ray structural data (ref. 24).

7CO-1S	M06-L	BP86	Exp[22]
Fe-Mn	2.843	2.860	2.840, 2.845 with the average 2.843
Fe-C(1)	1.759	1.753	1.676, 1.726
Fe-C(2)	1.759	1.750	1.754, 1.709
Fe-C average	1.759	1.752	the average 1.716
Mn-C(3)	1.793	1.790	1.748, 1.750
$Mn\text{-}C_{axial\ carbonyl}$	1.793	1.790	with the average 1.749
Mn-C(4)	1.826	1.827	1.841, 1.815
Mn-C(5)	1.840	1.841	1.809, 1.819
Mn-C(6)	1.851	1.843	1.823, 1.833
Mn-C(7)	1.840	1.836	1.827,1.833
$Mn\text{-}C_{equatorial\ carbonyl}$	1.839	1.837	the average 1.825
C(1)-O(1)	1.150	1.161	1.217, 1.158
C(2)-O(2)	1.150	1.163	1.129, 1.170
C-O (Fe)	1.150	1.162	the average 1.169
C(3)-O(3)	1.148	1.159	1.194, 1.195
C-O (Mn, axial)	1.148	1.159	the average 1.195
C(4)-O(4)	1.148	1.158	1.146, 1.159
C(5)-O(5)	1.147	1.154	1.148, 1.160
C(6)-O(6)	1.144	1.153	1.152, 1.153
C(7)-O(7)	1.147	1.159	1.180, 1.150
C-O (Mn,equatorial)	1.147	1.156	the average 1.156
Fe-C(1)-O(1)	176.8	175.0	169.5, 173.5
Fe-C(2)-O(2)	176.8	173.4	173.1, 173.9
Mn-C(3)-O(3)	179.9	179.0	177.9, 178.6
Mn-C(4)-O(4)	178.7	176.4	177.1, 178.6
Mn-C(5)-O(5)	177.1	177.3	177.8, 177.6
Mn-C(6)-O(6)	179.2	176.9	179.6, 177.2
Mn-C(7)-O(7)	177.1	174.5	178.5, 179.1

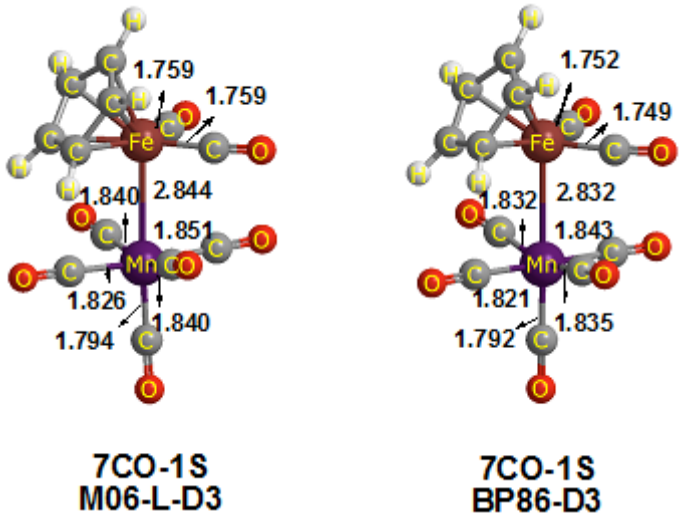


Figure S5. Optimized geometries (bond lengths in Å) for the experimentally known heterobimetallic compound $CpFeMn(CO)_7$ at the M06-L and BP86 level of theory using the the empirical dispersion correction by Grimme's DFT-D3 method.

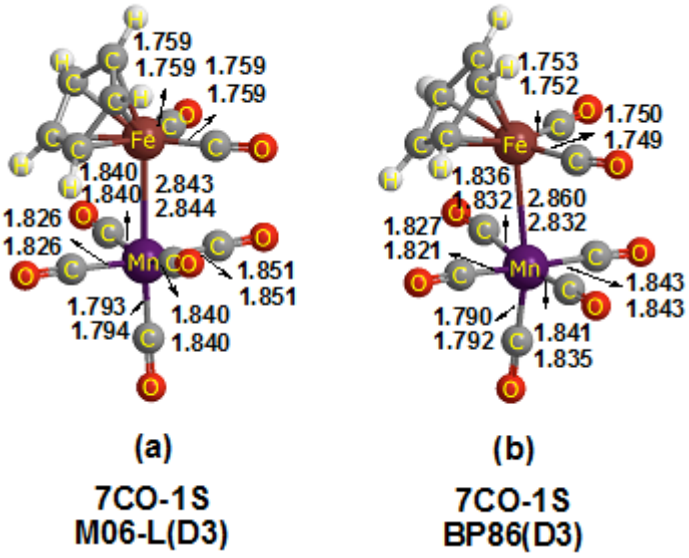


Figure S6. Optimized geometries (bond lengths in Å) for the experimentally known heterobimetallic compound $CpFeMn(CO)_7$ using the DFT methods: (a) M06-L (up) and M06-L-D3 (below), (b) BP86 (up) and BP86-D3 (below).

For presenting clearly the bond distances (in Å) with and without considering the dispersion effectsare shown in Figure S6. It indicates that the results optimized by the M06-L method are in excellent agreement with those obtained by the M06-L-D3 method. Thus the difference between the Fe-Mn bond length with and without dispersion is only 0.001 Å. However, the difference between the BP86 and BP86-D3 results is larger than that in M06-L and M06-L-D3, especially the difference in the Fe-Mn bond length of 0.028 Å between the BP86 and BP86-D3 methods. This

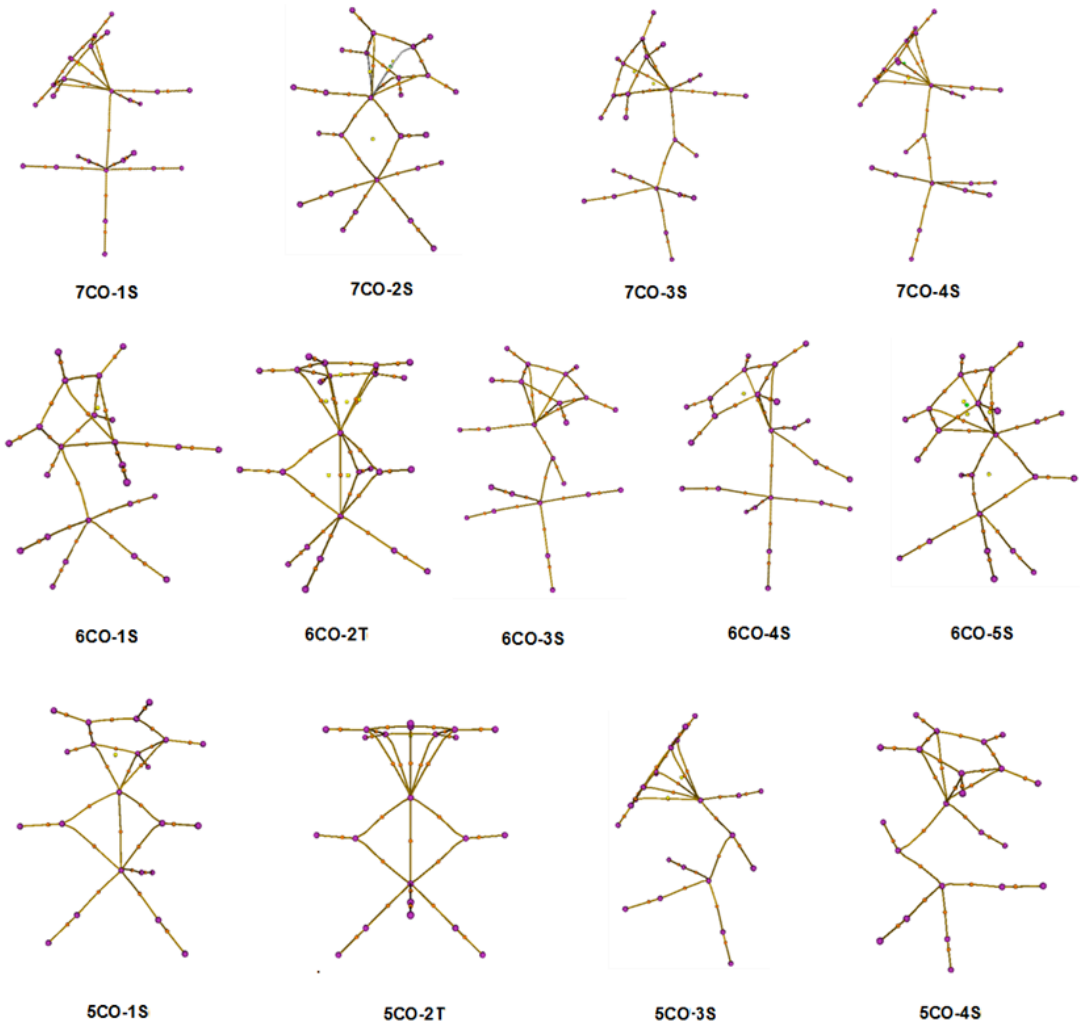


Figure S7. Bond paths for optimized CpFeMn(CO)$_n$ (n = 7, 6, 5) structures at the M06-L level of theory. Red dots are bond critical points, yellow dots are ring critical points, and green dots are cage critical points.

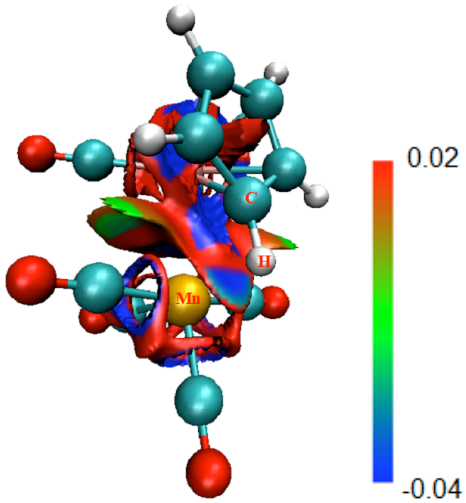


Figure S8. NCI isosurfaces of **6CO-1S** at the M06-L level of theory. The cutoff value is 0.09 au. The surfaces describe the reduced density gradient at an isovalue of 0.4 au. The surfaces are colored on a blue-green-red scale ranging from -0.04 to +0.02 au.

Table S19 Topological data at the bond critical point for Mn-C_{cp} segment in 6CO-1S at the M06-L level of theory. All values are in au.

Structures	ρ_h	$\nabla^2\rho_h$	G_h	V_h	H_h	G_h/ρ_h
6CO-1S (C_s)	0.056	0.133	0.048	-0.063	-0.015	0.857

Table S20. Wiberg Bond Indices (WBI) of the Fe-Mn, Fe-Mn bond lengths and the natural charges on the Fe and Mn atoms in the $CpFeMn(CO)_n$ (n = 7, 6, 5) structures from NBO analysis using the BP86 method.

Structures (symmetry)	Fe-Mn WBI	formal bond order	Fe-Mn distance, Å	Bridging groups	Natural charges	
					Fe	Mn
7CO-1S (C_1)	0.34	1	2.860	none	-0.37	-1.15
7CO-2S (C_s)	0.28	1	2.655	2 μ-CO	-0.42	-1.15
7CO-3S (C_1)	0.12	0	3.763	η^2-μ-CO	-0.54	-0.83
7CO-4S (C_1)	0.12	0	3.782	η^2-μ-CO	-0.55	-0.83
6CO-1S (C_s)	0.42	1	2.657	Mn-H-C	-0.45	-0.82
6CO-2T (C_1)	0.32	2	2.320	3 μ-CO	-0.10	-1.03
6CO-3S (C_1)	0.36	1	2.751	η^2-μ-CO	-0.35	-0.76
6CO-4S (C_s)	0.52	2	2.475	none	-0.35	-0.70
6CO-5S (C_s)	0.40	1	2.473	2 μ-CO	-0.45	-0.59
5CO-1S (C_1)	0.82	3	2.199	2 μ-CO	-0.21	-0.61
5CO-2T (C_s)	0.57	2	2.316	2 μ-CO	0.19	-0.73
5CO-3S (C_1)	0.49	2	2.514	η^2-μ-CO	-0.40	-0.27
5**CO-4S** (C_1)	0.54	2	2.484	η^2-μ-CO	-0.14	-0.57

Table S21 The ADCH atomic charges on the Fe and Mn atoms in the $CpFeMn(CO)_n$ (n = 7, 6, 5) structures at the M06-L level of theory.

Structures (symmetry)	ADCH charges	
	Fe	Mn
7CO-1S (C_1)	-0.205	-0.171
7CO-2S (C_s)	-0.169	-0.130
7CO-3S (C_1)	-0.166	-0.099
7CO-4S (C_1)	-0.154	-0.085
6CO-1S (C_s)	-0.252	-0.077
6CO-2T (C_1)	-0.101	-0.108
6CO-3S (C_1)	-0.208	-0.098
6CO-4S (C_s)	-0.200	-0.098
6CO-5S (C_s)	-0.180	-0.012
5CO-1S (C_1)	-0.188	-0.091
5CO-2T (C_s)	0.001	-0.092
5CO-3S (C_1)	-0.209	0.067
5**CO-4S** (C_1)	-0.170	-0.118

Table S22 The CDA results of the $CpFeMn(CO)_n$ (n = 7, 6, 5) structures at the M06-L/DZP level of theory: calculated donation d(A→B), back-donation b(A←B), repulsive polarization r(A↔B), and the donation/back-donation (d/b) ratio.

	A-B	*d*	*b*	*d-b*	*r*	*d/b*
7CO-1S	CO-$CpFe(CO)_2Mn(CO)_4$	0.189	0.114	0.075	-0.360	1.66
7CO-2S	CO-$CpFe(CO)(\mu\text{-}CO)_2Mn(CO)_3$	0.164	0.113	0.051	-0.420	1.45
7CO-3S	CO-$CpFe(CO)_2(\eta^2\text{-}\mu\text{-}CO)Mn(CO)_3$	0.154	0.103	0.051	-0.308	1.50
7CO-4S	CO-$CpFe(CO)_2(\eta^2\text{-}\mu\text{-}CO)Mn(CO)_3$	0.187	0.137	0.050	-0.412	1.36
6CO-1S	CO-$CpFe(CO)_2Mn(CO)_3$	0.172	0.130	0.042	-0.402	1.32
6CO-2T	CO-$CpFe(\mu\text{-}CO)_3Mn(CO)_2$	0.141	0.103	0.038	-0.350	1.37
6CO-3S	CO-$CpFe(CO)(\eta^2\text{-}\mu\text{-}CO)Mn(CO)_3$	0.179	0.115	0.064	-0.364	1.56
6CO-4S	CO-$CpFe(CO)_2Mn(CO)_3$	0.152	0.127	0.025	-0.383	1.20
6CO-5S	CO-$CpFe(CO)(\mu\text{-}CO)_2Mn(CO)_2$	0.137	0.117	0.020	-0.434	1.17
5CO-1S	CO-$CpFe(\mu\text{-}CO)_2Mn(CO)_2$	0.141	0.131	0.010	-0.414	1.08
5CO-2T	CO-$CpFe(\mu\text{-}CO)_2Mn(CO)_2$	0.104	0.113	-0.009	-0.322	0.92
5CO-3S	CO-$CpFe(CO)(\eta^2\text{-}\mu\text{-}CO)Mn(CO)_2$	0.160	0.105	0.055	-0.352	1.52
5**CO-4S**	CO-$CpFe(CO)(\eta^2\text{-}\mu\text{-}CO)Mn(CO)_2$	0.140	0.120	0.020	-0.354	1.17
$Ni(CO)_4$ (DZP)	CO-$Ni(CO)_3$	0.218	0.155	0.063	-0.123	1.41
$Ni(CO)_4$ (TZP)	CO-$Ni(CO)_3$	0.126	0.179	-0.053	-0.120	0.70

However, as has recently been demonstrated[1,2] that the charge decomposition analysis (CDA) could give reasonable estimates of donation and back-donation between the metal fragment and the ligand fragment if their electronic polarization is sufficiently small or absent. And, we also calculated the donation and π-back-donation of $Ni(CO)_4$ using the M06-L method with DZP and TZP basis sets, respectively. The results show that the amount of CO→Ni donation is greater than that of the Mn→CO back-donation with DZP basis set which consisting with the previous report[3], while the result of TZP is opposite. Thus, the CDA for the $CpFeMn(CO)_n$ (n = 7, 6, 5) structures are calculated at the M06-L/DZP level of theory.

The CDA results given in Table S22 show the amount of CO→Mn charge donation (d), Mn→CO back-donation (b), the CO↔Mn repulsive polarization (r) and the donation/back-donation ratio (d/b). The CDA results show that the CO→Mn σ forward bonding is stronger than the concurrent Mn→CO back-bonding, corresponding to the observation of the natrure charge on Mn atom. This term r is negative, because electronic charge is depleted from the overlapping area of the occupied orbitals, thus reflecting an electron repulsive effect.

The CDA results for the structures of 7CO-1S and 6CO-4S with no bridging CO

groups show that the amount of π-back-donation for 6CO-4S is larger than that in 7CO-1S, which is in agreement with that the *v*(CO) vibrational frequencies of 6CO-4S is lower than that in 7CO-1S (Table S23). However, other structures with bridging CO groups or an agostic bond, have no such obvious variation of the CO frequencies. But, the amount of *d*-*b* decreases generally as CO groups are lost, and the CO frequencies decrease with the decreasing of the amount of *d*-*b*.

Table S23 The ν(CO) vibrational frequencies (cm^{-1}) for the $CpFeMn(CO)_n$ (n = 7, 6, 5) structures by M06-L and BP86 methods (infrared intensities in parentheses are in $kcal \cdot mol^{-1}$).

	M06-L	BP86
7CO-1S	2023(33),2035 (179),2043(762) 2055(1767),2064 (279),2069(1431) 2142(437)	1948(13),1968(368),1973(793) 1980(930),1993(1429),2005(487) 2072(478)
7CO-2S	1893(860),1917(20),2042(650) 2061(516),2063(951), 2075 (1204) 2142 (649)	1822 (780),18448(12),1971(631) 1988(626),1992(851),2002(934) 2068(623)
7CO-3S	1643(140),2005(714),2027(1110) 2050(587),2072(954),2100(1240) 2126(307)	1571(138),1938(657),1958(1064) 1981(515),1996(907),2027(1092) 2052(292)
7CO-4S	1637(138),2016(621),2026(1123) 2050(547),2069(909),2096(838) 2127(611)	1565(132),1948(582),1957(1035) 1981(503),1992(861),2023(753) 2053(553)
6CO-1S	2022(1),2033(262),2050(573) 2052(1914),2058(1358), 2132(463)	1953(1),1966(410),1977(1809) 1981(398),1989(1233),2060(425)
6CO-2T	1932(840),1933(863),1960(55) 2063(857),2064(840),2123(1136)	1860(743),1861(755),1886(50) 1989(778),1990(767),2045(1059)
6CO-3S	1835(347),2020(573),2037(541) 2049(495),2061(1657), 2132(546)	1778(308),1954(512),1965(540) 1976(575.9),1987(1409),2059(519)
6CO-4S	1991(446),2006(878),201(98) 2039(1150),2053(905),2123(819)	1924(763),1924(366),1946(103) 1963(1074),1977(867),2043.5(752)
6CO-5S	1895(813),1927(106),2038(744) 2042(977),2071(1401), 2113 (620)	1815(762),1840(49),1962(644) 1974(819),1999(1225),2037 (612)
5CO-1S	1955(697),1967(425),2026(988) 2039(969),2101(959)	1884(596),1899(383),1952(909) 1964(869),2025 (866)
5CO-2T	1908(908),1914(135),2032(944) 2054(816),2106 (1277)	1824(762),1835(169),1955(804) 1981(779),2027 (1215)
5CO-3S	1780(325),1999(604),2018(830) 2046(1106),2092(728)	1775(296),1926(643),1941(711) 1975 (971),2012 (638)
5CO-4S	1800(499),2011(321),2020(652) 2029(1461),2091 (780)	1736(462),1941(379),1947(832) 1963 (1125),2016(666)

Table S24 Energies (ΔE, in kcal·mol^{-1}) for reactions of CpFeMn(CO)$_n$ using the BP86 method.

	ΔE
$CpFeMn(CO)_7$ (**7CO-1S**) → $CpFeMn(CO)_6$ (**6CO-1S**) + CO	32.4
$CpFeMn(CO)_6$ (**6CO-1 S**) → $CpFeMn(CO)_5$ (**5CO-1S**) + CO	26.1
$CpFeMn(CO)_7 \rightarrow CpFe(CO)_2\cdot + Mn(CO)_5\cdot$	26.1
$CpFeMn(CO)_6 \rightarrow CpFe(CO)_2\cdot + Mn(CO)_4\cdot$	41.0
$CpFeMn(CO)_6 \rightarrow CpFeCO\cdot + Mn(CO)_5\cdot$	53.0
$2CpFeMn(CO)_6 \rightarrow CpFeMn(CO)_7 + CpFeMn(CO)_5$	-6.3
$2CpFeMn(CO)_7 \rightarrow Cp_2Fe_2(CO)_4 + Mn_2(CO)_{10}$	-9.6

Table S25 Energies (ΔE, in kcal·mol^{-1}) for reactions of $CpFeMn(CO)_n$ at the M06-L level of theory using the empirical dispersion correction by Grimme's DFT-D3 method.

Structures	ΔE
$CpFeMn(CO)_7$ **(7CO-1S)** → $CpFeMn(CO)_6$ **(6CO-1S)** + CO	33.5
$CpFeMn(CO)_6$ **(6CO-1S)** → $CpFeMn(CO)_5$ **(5CO-1S)** + CO	30.7
$CpFeMn(CO)_7 \rightarrow CpFe(CO)_2\cdot + Mn(CO)_5\cdot$	32.2
$CpFeMn(CO)_6 \rightarrow CpFe(CO)_2\cdot + Mn(CO)_4\cdot$	43.5
$CpFeMn(CO)_6 \rightarrow CpFeCO\cdot + Mn(CO)_5\cdot$	53.1
$2CpFeMn(CO)_6 \rightarrow CpFeMn(CO)_7 + CpFeMn(CO)_5$	-2.8
$2CpFeMn(CO)_7 \rightarrow Cp_2Fe_2(CO)_4 + Mn_2(CO)_{10}$	-5.2

Table S26 Energies (ΔE, in kcal·mol^{-1}) for reactions of $CpFeMn(CO)_n$ at the BP86 level of theory using the empirical dispersion correction by Grimme's DFT-D3 method.

Structures	ΔE
$CpFeMn(CO)_7$ **(7CO-1S)** → $CpFeMn(CO)_6$ **(6CO-1S)** + CO	37.5
$CpFeMn(CO)_6$ **(6CO-1S)** → $CpFeMn(CO)_5$ **(5CO-1S)** + CO	31.5
$CpFeMn(CO)_7 \rightarrow CpFe(CO)_2\cdot + Mn(CO)_5\cdot$	40.6
$CpFeMn(CO)_6 \rightarrow CpFe(CO)_2\cdot + Mn(CO)_4\cdot$	52.6
$CpFeMn(CO)_6 \rightarrow CpFeCO\cdot + Mn(CO)_5\cdot$	64.8
$2CpFeMn(CO)_6 \rightarrow CpFeMn(CO)_7 + CpFeMn(CO)_5$	-6.1
$2CpFeMn(CO)_7 \rightarrow Cp_2Fe_2(CO)_4 + Mn_2(CO)_{10}$	-9.0

The description of the DZP basis set

The double-ζ plus polarization (DZP) basis sets were used for all computations. For carbon and oxygen, these DZP basis sets were obtained by adding one set of pure spherical harmonic d functions with orbital exponents α_d(C) = 0.75 and α_d(O) = 0.85, respectively, to the Huzinaga−Dunning standard contracted DZ sets, designated as (9s5p1d/4s2p1d)[4,5] For iron and manganese, our loosely contracted DZP basis set (14s11p6d/10s8p3d) uses the Wachters primitive set[6] augmented by two sets of p functions and one set of d functions, and contracted following Hood, Pitzer, and Schaefer.[7] For hydrogen, a set of p polarization functions (α_p (H) = 0.75) was added to the Huzinaga−Dunning DZ sets.

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