Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Butadiene as a Ligand in Open Sandwich Compounds

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Supporting Information

Tables S1 to S23: Atomic coordinates of the optimized structures for the $(C_4H_6)_2M$ (M = Ni, Ti, Co, Fe, Mn, Cr, V) complexes.

Tables S24 to S46: Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the $(C_4H_6)_2M$ (M = Ni, Ti, Co, Fe, Mn, Cr, πV) complexes.

Tables S47 to S53: The distances (in Å) of M-C bonds for the $(C_4H_6)_2M$ (M = Ni, Ti, Co, Fe, Mn, Cr, V) complexes;

Tables S54 to S60. Total energies (E in hartree), relative energies (ΔE in kcal/mol), HOMO and LUMO energies (in hartree), HOMO-LUMO gaps (in eV), the spin expectation $\langle S^2 \rangle$ values, the χ angles for the $(C_4H_6)_2M$ (M = Ni, Ti, Co, Fe, Mn, Cr, V) complexes by all three methods.

Complete Gaussian09 reference (Reference 37).

Table S1. Optimized coordinates for the **$(C_4H_6)_2Ni$** structure **Ni-1S.**

	B3LYP			B3LYP*		
	x	y	z	x	y	z
6	1.468152	-1.532776	0.627141	1.342091	1.630838	-0.627045
6	-0.655474	-1.533717	-1.367385	-0.766449	1.476227	1.371777
6	-0.915334	-1.784066	-0.009107	-1.054691	1.702164	0.011783
6	0.145042	-1.790458	0.982275	0.000000	1.784638	-0.983926
1	-0.140494	-1.826010	2.033478	-0.289623	1.791819	-2.036742
1	-1.944192	-1.822661	0.348040	-2.087079	1.657590	-0.340681
1	-1.496078	-1.390483	-2.042694	-1.590499	1.266545	2.053184
1	0.279208	-1.827631	-1.838824	0.143532	1.852439	1.837950
1	1.862463	-1.773297	-0.356515	1.719044	1.916462	0.353483
1	2.207094	-1.366677	1.408762	2.091658	1.513826	-1.410131
6	0.655473	1.533715	-1.367383	0.766449	-1.476227	1.371777
6	-1.468153	1.532776	0.627143	-1.342091	-1.630838	-0.627045
6	-0.145043	1.790459	0.982276	0.000000	-1.784638	-0.983926
6	0.915333	1.784067	-0.009106	1.054691	-1.702164	0.011783
1	1.944192	1.822666	0.348040	2.087079	-1.657590	-0.340681
1	0.140494	1.826013	2.033479	0.289623	-1.791819	-2.036742
1	-2.207095	1.366677	1.408764	-2.091658	-1.513826	-1.410131
1	-1.862462	1.773291	-0.356515	-1.719044	-1.916462	0.353483
1	-0.279208	1.827629	-1.838823	-0.143532	-1.852439	1.837950
1	1.496077	1.390484	-2.042692	1.590499	-1.266545	2.053184
28	0.000004	-0.000001	-0.058231	0.000000	0.000000	0.064815

	BP86		
	x	y	z
6	1.341929	1.595509	-0.586212
6	-0.781717	1.443324	1.364836
6	-1.072628	1.683442	-0.005879
6	0.000000	1.764991	-0.990177
1	-0.267283	1.777471	-2.055585
1	-2.108868	1.637845	-0.367635
1	-1.612838	1.216377	2.042808
1	0.116660	1.852487	1.842727
1	1.698632	1.925864	0.396093
1	2.115268	1.464453	-1.353250
6	0.781717	-1.443324	1.364836
6	-1.341929	-1.595509	-0.586212
6	0.000000	-1.764991	-0.990177
6	1.072628	-1.683442	-0.005879
1	2.108868	-1.637845	-0.367635
1	0.267283	-1.777471	-2.055585
1	-2.115268	-1.464453	-1.353250
1	-1.698632	-1.925864	0.396093
1	-0.116660	-1.852487	1.842727
1	1.612838	-1.216377	2.042808
28	0.000000	0.000000	0.057102

Table S2. Optimized coordinates for the **$(C_4H_6)_2Co$** structure **Co-1D**.

	B3LYP			B3LYP*		
	x	y	z	x	y	z
6	-0.421133	1.610340	1.414528	0.229979	1.636802	1.410051
6	1.493161	1.315989	-0.787496	1.868510	0.623925	-0.784595
6	0.176706	1.742782	-1.006957	0.820176	1.531768	-1.013897
6	-0.772921	1.877739	0.071131	0.000000	2.025476	0.066794
1	-1.820762	2.013218	-0.195870	-0.917586	2.556199	-0.195364
1	-0.214828	1.769982	-2.024189	0.469885	1.705803	-2.033710
1	2.111259	1.053632	-1.643882	2.337543	0.134623	-1.638625
1	2.035604	1.565736	0.122372	2.472809	0.660858	0.122430
1	0.568961	1.845727	1.802188	1.239805	1.482295	1.793453
1	-1.210286	1.576504	2.162261	-0.510614	1.904141	2.163351
6	-1.493159	-1.315982	-0.787524	-1.868510	-0.623925	-0.784595
6	0.421127	-1.610358	1.414505	-0.229979	-1.636802	1.410051
6	0.772922	-1.877736	0.071105	0.000000	-2.025476	0.066794
6	-0.176701	-1.742768	-1.006985	-0.820176	-1.531768	-1.013897
1	0.214837	-1.769952	-2.024216	-0.469885	-1.705803	-2.033710
1	1.820764	-2.013206	-0.195894	0.917586	-2.556199	-0.195364
1	1.210278	-1.576528	2.162241	0.510614	-1.904141	2.163351
1	-0.568966	-1.845758	1.802159	-1.239805	-1.482295	1.793453
1	-2.035605	-1.565743	0.122338	-2.472809	-0.660858	0.122430
1	-2.111255	-1.053617	-1.643910	-2.337543	-0.134623	-1.638625
27	-0.000004	-0.000001	0.133867	0.000000	0.000000	0.127285

	BP86		
	x	y	z
6	0.259805	1.593771	1.417603
6	1.829176	0.567208	-0.785823
6	0.790380	1.508845	-1.023737
6	0.000000	2.018489	0.077936
1	-0.922161	2.567278	-0.158933
1	0.432962	1.692565	-2.046445
1	2.275519	0.051057	-1.645134
1	2.473300	0.634699	0.101312
1	1.286814	1.450370	1.780573
1	-0.468606	1.850367	2.196172
6	-1.829176	-0.567208	-0.785823
6	-0.259805	-1.593771	1.417603
6	0.000000	-2.018489	0.077936
6	-0.790380	-1.508845	-1.023737
1	-0.432962	-1.692565	-2.046445
1	0.922161	-2.567278	-0.158933
1	0.468606	-1.850367	2.196172
1	-1.286814	-1.450370	1.780573
1	-2.473300	-0.634699	0.101312
1	-2.275519	-0.051057	-1.645134
27	0.000000	0.000000	0.122710

Table S3. Optimized coordinates for the **$(C_4H_6)_2Co$** structure **Co-2D**.

	B3LYP			B3LYP*		
	x	y	z	x	y	z
6	-1.386058	1.496692	0.565350	1.493298	1.385667	0.490765
6	1.386058	1.496692	0.565350	1.493298	-1.385667	0.490765
6	0.709605	1.679100	-0.685761	1.670200	-0.711000	-0.763183
6	-0.709605	1.679100	-0.685761	1.670200	0.711000	-0.763183
1	-1.247361	1.625578	-1.632444	1.613386	1.250339	-1.711173
1	1.247361	1.625578	-1.632444	1.613386	-1.250339	-1.711173
1	2.455046	1.297166	0.535992	1.290717	-2.456181	0.465354
1	1.058709	2.036102	1.453845	2.035148	-1.055233	1.379229
1	-1.058709	2.036102	1.453845	2.035148	1.055233	1.379229
1	-2.455046	1.297166	0.535992	1.290717	2.456181	0.465354
6	-1.386058	-1.496692	0.565350	-1.493298	1.385667	0.490765
6	1.386058	-1.496692	0.565350	-1.493298	-1.385667	0.490765
6	0.709605	-1.679100	-0.685761	-1.670200	-0.711000	-0.763183
6	-0.709605	-1.679100	-0.685761	-1.670200	0.711000	-0.763183
1	-1.247361	-1.625578	-1.632444	-1.613386	1.250339	-1.711173
1	1.247361	-1.625578	-1.632444	-1.613386	-1.250339	-1.711173
1	2.455046	-1.297166	0.535992	-1.290717	-2.456181	0.465354
1	1.058709	-2.036102	1.453845	-2.035148	-1.055233	1.379229
1	-1.058709	-2.036102	1.453845	-2.035148	1.055233	1.379229
1	-2.455046	-1.297166	0.535992	-1.290717	2.456181	0.465354
27	0.000000	0.000000	0.300212	0.000000	0.000000	0.222385

	BP86		
	x	y	z
6	-1.384756	1.484667	0.570598
6	1.384756	1.484667	0.570598
6	0.716375	1.649670	-0.696386
6	-0.716375	1.649670	-0.696386
1	-1.262141	1.587884	-1.648323
1	1.262141	1.587884	-1.648323
1	2.461038	1.275023	0.556513
1	1.046655	2.039150	1.457475
1	-1.046655	2.039150	1.457475
1	-2.461037	1.275023	0.556513
6	-1.384756	-1.484667	0.570598
6	1.384756	-1.484667	0.570598
6	0.716375	-1.649670	-0.696386
6	-0.716375	-1.649670	-0.696386
1	-1.262141	-1.587884	-1.648323
1	1.262141	-1.587884	-1.648323
1	2.461037	-1.275023	0.556513
1	1.046655	-2.039150	1.457475
1	-1.046655	-2.039150	1.457474
1	-2.461037	-1.275023	0.556513
27	0.000000	0.000000	0.288633

Table S4. Optimized coordinates for the **$(C_4H_6)_2Fe$** structure **Fe-1S.**

	B3LYP			B3LYP*		
	x	y	z	x	y	z
6	-0.107936	1.601788	1.475158	0.385489	1.552390	1.474585
6	1.323246	1.038277	-0.988058	1.575049	0.576828	-0.983945
6	0.060726	1.708653	-1.001891	0.575500	1.602730	-1.004604
6	-0.631452	1.978426	0.213288	0.000000	2.074203	0.211959
1	-1.688185	2.239788	0.135079	-0.927257	2.648758	0.134626
1	-0.497037	1.804600	-1.933159	0.073417	1.861386	-1.939032
1	1.713027	0.688141	-1.943781	1.837084	0.113963	-1.937710
1	2.102228	1.324136	-0.276176	2.407195	0.617097	-0.272551
1	0.959359	1.688705	1.688763	1.430910	1.309910	1.687438
1	-0.750850	1.654044	2.350466	-0.209482	1.798899	2.353219
6	-1.323242	-1.038270	-0.988053	-1.575049	-0.576828	-0.983945
6	0.107934	-1.601789	1.475159	-0.385489	-1.552390	1.474585
6	0.631448	-1.978432	0.213289	0.000000	-2.074203	0.211959
6	-0.060726	-1.708653	-1.001889	-0.575500	-1.602730	-1.004604
1	0.497035	-1.804605	-1.933158	-0.073417	-1.861386	-1.939032
1	1.688180	-2.239803	0.135081	0.927257	-2.648758	0.134626
1	0.750847	-1.654050	2.350467	0.209482	-1.798899	2.353219
1	-0.959362	-1.688699	1.688764	-1.430910	-1.309910	1.687438
1	-2.102225	-1.324127	-0.276171	-2.407195	-0.617097	-0.272551
1	-1.713023	-0.688129	-1.943774	-1.837084	-0.113963	-1.937710
26	0.000006	0.000000	0.135807	0.000000	0.000000	0.137388

	BP86		
	x	y	z
6	0.391618	1.522973	1.477148
6	1.572631	0.550804	-0.979649
6	0.571891	1.590605	-1.011437
6	0.000000	2.066735	0.214973
1	-0.929106	2.652698	0.143772
1	0.073076	1.857794	-1.953728
1	1.828032	0.069741	-1.934615
1	2.418012	0.598029	-0.271974
1	1.446668	1.281697	1.684008
1	-0.199925	1.763299	2.368349
6	-1.572631	-0.550804	-0.979649
6	-0.391618	-1.522973	1.477148
6	0.000000	-2.066735	0.214973
6	-0.571891	-1.590605	-1.011437
1	-0.073076	-1.857794	-1.953728
1	0.929106	-2.652698	0.143772
1	0.199925	-1.763299	2.368349
1	-1.446668	-1.281697	1.684008
1	-2.418012	-0.598029	-0.271974
1	-1.828032	-0.069741	-1.934615
26	0.000000	0.000000	0.135229

Table S5. Optimized coordinates for the **$(C_4H_6)_2Fe$** structure **Fe-2S.**

	B3LYP			B3LYP*		
	x	y	z	x	y	z
6	-1.408103	1.529553	0.569824	1.523905	1.408006	0.455169
6	1.408103	1.529553	0.569824	1.523905	-1.408006	0.455169
6	0.714776	1.597321	-0.664018	1.594894	-0.715819	-0.781514
6	-0.714776	1.597321	-0.664018	1.594894	0.715819	-0.781514
1	-1.238417	1.450041	-1.609095	1.450121	1.241279	-1.728530
1	1.238417	1.450041	-1.609095	1.450121	-1.241279	-1.728530
1	2.480823	1.349061	0.549129	1.341397	-2.482419	0.436671
1	1.062869	2.093492	1.438575	2.086776	-1.060760	1.326572
1	-1.062869	2.093492	1.438575	2.086776	1.060760	1.326572
1	-2.480823	1.349061	0.549129	1.341397	2.482419	0.436671
6	-1.408103	-1.529553	0.569824	-1.523905	1.408006	0.455169
6	1.408103	-1.529553	0.569824	-1.523905	-1.408006	0.455169
6	0.714776	-1.597321	-0.664018	-1.594894	-0.715819	-0.781514
6	-0.714776	-1.597321	-0.664018	-1.594894	0.715819	-0.781514
1	-1.238417	-1.450041	-1.609095	-1.450121	1.241279	-1.728530
1	1.238417	-1.450041	-1.609095	-1.450121	-1.241279	-1.728530
1	2.480823	-1.349061	0.549129	-1.341397	-2.482419	0.436671
1	1.062869	-2.093492	1.438575	-2.086776	-1.060760	1.326572
1	-1.062869	-2.093492	1.438575	-2.086776	1.060760	1.326572
1	-2.480823	-1.349061	0.549129	-1.341397	2.482419	0.436671
26	0.000000	0.000000	0.418705	0.000000	0.000000	0.295901

	BP86		
	x	y	z
6	-1.408216	1.508040	0.575546
6	1.408216	1.508040	0.575546
6	0.720507	1.583908	-0.673776
6	-0.720507	1.583908	-0.673776
1	-1.251935	1.442639	-1.626473
1	1.251935	1.442639	-1.626473
1	2.489023	1.321822	0.564561
1	1.055472	2.077554	1.450100
1	-1.055472	2.077554	1.450100
1	-2.489023	1.321822	0.564561
6	-1.408216	-1.508040	0.575546
6	1.408216	-1.508040	0.575546
6	0.720507	-1.583908	-0.673776
6	-0.720507	-1.583908	-0.673776
1	-1.251935	-1.442639	-1.626473
1	1.251935	-1.442639	-1.626473
1	2.489023	-1.321822	0.564561
1	1.055473	-2.077554	1.450100
1	-1.055473	-2.077554	1.450100
1	-2.489023	-1.321822	0.564561
26	0.000000	0.000000	0.396533

Table S6. Optimized coordinates for the **$(C_4H_6)_2Fe$** structure **Fe-1T.**

	B3LYP			B3LYP*		
	x	y	z	x	y	z
6	0.413435	1.541661	1.425715	-1.504702	-1.467205	-0.646574
6	0.413435	1.541661	-1.425715	-1.465054	0.624645	1.408969
6	-0.793638	1.768163	-0.716158	-1.851224	0.905636	0.070875
6	-0.793638	1.768163	0.716159	-1.875539	-0.134162	-0.930661
1	-1.748427	1.753383	1.242013	-1.964136	0.180000	-1.973385
1	-1.748427	1.753384	-1.242013	-1.952198	1.938202	-0.266603
1	0.361222	1.364661	-2.497727	-1.295798	1.461810	2.085797
1	1.364779	1.935482	-1.069001	-1.753923	-0.307217	1.897762
1	1.364781	1.935483	1.068999	-1.719219	-1.927374	0.318677
1	0.361223	1.364660	2.497727	-1.375674	-2.161103	-1.476811
6	-0.413435	-1.541660	-1.425715	1.465058	-0.624757	1.408914
6	-0.413436	-1.541660	1.425715	1.504685	1.467267	-0.646455
6	0.793639	-1.768161	0.716158	1.875540	0.134252	-0.930651
6	0.793640	-1.768160	-0.716158	1.851231	-0.905632	0.070796
1	1.748428	-1.753377	-1.242013	1.952210	-1.938169	-0.266767
1	1.748427	-1.753378	1.242013	1.964149	-0.179820	-1.973402
1	-0.361220	-1.364655	2.497726	1.375659	2.161236	-1.476632
1	-1.364780	-1.935495	1.069008	1.719180	1.927351	0.318842
1	-1.364783	-1.935497	-1.069007	1.753927	0.307060	1.897792
1	-0.361220	-1.364655	-2.497727	1.295810	-1.461981	2.085670
26	-0.000003	-0.000002	0.000000	0.000002	-0.000010	-0.000085

	BP86		
	x	y	z
6	1.409009	1.491817	-0.610497
6	1.413354	-0.626199	1.399365
6	1.838921	-0.890691	0.055176
6	1.852285	0.172170	-0.928442
1	1.953516	-0.118565	-1.983889
1	1.969445	-1.922105	-0.296694
1	1.230168	-1.482282	2.059820
1	1.714915	0.293355	1.919860
1	1.635635	1.953095	0.360449
1	1.253047	2.198751	-1.434190
6	-1.413316	0.626213	1.399379
6	-1.409052	-1.491809	-0.610483
6	-1.852297	-0.172150	-0.928424
6	-1.838896	0.890711	0.055195
1	-1.969394	1.922127	-0.296681
1	-1.953521	0.118594	-1.983869
1	-1.253093	-2.198737	-1.434183
1	-1.635704	-1.953092	0.360456
1	-1.714904	-0.293318	1.919898
1	-1.230082	1.482302	2.059815
26	-0.000003	-0.000019	-0.009169

Table S7. Optimized coordinates for the $(C_4H_6)_2Fe$ structure **Fe-2T.**

	B3LYP			B3LYP*		
	x	y	z	x	y	z
6	0.433299	1.833243	-1.029549	-0.576064	1.862498	0.831862
6	-2.043438	0.735062	0.002547	1.967809	0.732748	0.242240
6	-1.226007	1.555964	0.813383	1.283841	1.475318	-0.766189
6	0.000000	2.086622	0.297595	0.000000	2.024995	-0.470608
1	0.696427	2.532055	1.009221	-0.609788	2.402000	-1.295040
1	-1.388301	1.595458	1.890837	1.604480	1.420677	-1.808826
1	-2.846294	0.174120	0.477843	2.822919	0.129404	-0.063822
1	-2.194500	0.948183	-1.053687	2.012020	1.086482	1.273539
1	-0.284533	1.745211	-1.844426	0.046109	1.942895	1.725884
1	1.430907	2.151949	-1.319385	-1.612439	2.164571	0.971756
6	2.043438	-0.735062	0.002547	-1.967809	-0.732748	0.242240
6	-0.433299	-1.833243	-1.029549	0.576064	-1.862498	0.831862
6	0.000000	-2.086622	0.297595	0.000000	-2.024995	-0.470608
6	1.226007	-1.555964	0.813383	-1.283841	-1.475318	-0.766189
1	1.388301	-1.595458	1.890837	-1.604480	-1.420677	-1.808826
1	-0.696427	-2.532055	1.009221	0.609788	-2.402000	-1.295040
1	-1.430907	-2.151949	-1.319385	1.612439	-2.164571	0.971756
1	0.284533	-1.745211	-1.844426	-0.046109	-1.942895	1.725884
1	2.194500	-0.948183	-1.053687	-2.012020	-1.086482	1.273539
1	2.846294	-0.174120	0.477843	-2.822919	-0.129404	-0.063822
26	0.000000	0.000000	0.025826	0.000000	0.000000	0.013283

	BP86		
	x	y	z
6	-0.779638	1.870896	0.538628
6	1.837169	0.832915	0.576002
6	1.345155	1.421308	-0.646938
6	0.011506	1.952184	-0.665561
1	-0.451074	2.215991	-1.626686
1	1.886213	1.288455	-1.594089
1	2.771616	0.263568	0.521734
1	1.667213	1.326629	1.543537
1	-0.343837	2.125228	1.515528
1	-1.849631	2.092067	0.454948
6	-1.837169	-0.832915	0.576002
6	0.779638	-1.870896	0.538628
6	-0.011506	-1.952184	-0.665561
6	-1.345155	-1.421308	-0.646938
1	-1.886213	-1.288455	-1.594089
1	0.451074	-2.215991	-1.626686
1	1.849632	-2.092067	0.454948
1	0.343837	-2.125228	1.515528
1	-1.667213	-1.326629	1.543538
1	-2.771616	-0.263568	0.521734
26	0.000000	0.000000	0.031251

Table S8. Optimized coordinates for the **$(C_4H_6)_2Mn$** structure **Mn-1D.**

	B3LYP			B3LYP*		
	x	y	z	x	y	z
6	-1.436169	1.543535	0.563523	1.520329	1.437381	0.506568
6	1.436169	1.543535	0.563523	1.520329	-1.437381	0.506568
6	0.717024	1.775404	-0.639153	1.774914	-0.717567	-0.693872
6	-0.717024	1.775404	-0.639153	1.774914	0.717567	-0.693872
1	-1.232231	1.744218	-1.599141	1.753940	1.233017	-1.656394
1	1.232231	1.744218	-1.599141	1.753940	-1.233017	-1.656394
1	2.508098	1.376504	0.496325	1.354692	-2.511153	0.435722
1	1.100946	1.965025	1.513130	1.933410	-1.104956	1.463733
1	-1.100946	1.965026	1.513130	1.933410	1.104956	1.463733
1	-2.508098	1.376504	0.496325	1.354692	2.511153	0.435722
6	-1.436169	-1.543535	0.563523	-1.520329	1.437381	0.506568
6	1.436169	-1.543535	0.563523	-1.520329	-1.437381	0.506568
6	0.717024	-1.775404	-0.639153	-1.774914	-0.717567	-0.693872
6	-0.717024	-1.775404	-0.639153	-1.774914	0.717567	-0.693872
1	-1.232231	-1.744218	-1.599141	-1.753940	1.233017	-1.656394
1	1.232231	-1.744218	-1.599141	-1.753940	-1.233017	-1.656394
1	2.508098	-1.376504	0.496325	-1.354692	-2.511153	0.435722
1	1.100946	-1.965025	1.513130	-1.933410	-1.104956	1.463733
1	-1.100946	-1.965026	1.513130	-1.933410	1.104956	1.463733
1	-2.508098	-1.376504	0.496325	-1.354692	2.511153	0.435722
25	0.000000	0.000000	0.212238	0.000000	0.000000	0.140922

	BP86		
	x	y	z
6	-1.442242	1.477522	0.562681
6	1.442242	1.477521	0.562681
6	0.721998	1.787842	-0.633710
6	-0.721998	1.787842	-0.633710
1	-1.239756	1.793953	-1.602974
1	1.239756	1.793953	-1.602974
1	2.522434	1.314914	0.485517
1	1.110439	1.859187	1.541801
1	-1.110439	1.859187	1.541801
1	-2.522434	1.314914	0.485517
6	-1.442242	-1.477522	0.562681
6	1.442242	-1.477522	0.562681
6	0.721998	-1.787842	-0.633710
6	-0.721998	-1.787842	-0.633710
1	-1.239756	-1.793954	-1.602974
1	1.239756	-1.793953	-1.602974
1	2.522434	-1.314914	0.485516
1	1.110439	-1.859186	1.541801
1	-1.110439	-1.859187	1.541801
1	-2.522434	-1.314914	0.485517
25	0.000000	0.000000	0.137716

Table S9. Optimized coordinates for the **$(C_4H_6)_2Mn$** structure **Mn-2D.**

	B3LYP			B3LYP*		
	x	y	z	x	y	z
6	0.590600	1.542705	1.438493	0.634583	1.484327	1.442623
6	0.590600	1.542705	-1.438493	0.634583	1.484327	-1.442623
6	-0.590600	1.885045	-0.716809	-0.515194	1.919403	-0.718564
6	-0.590600	1.885045	0.716809	-0.515194	1.919403	0.718564
1	-1.541411	1.975425	1.240965	-1.460277	2.076777	1.241907
1	-1.541411	1.975425	-1.240965	-1.460277	2.076777	-1.241907
1	0.509788	1.375820	-2.510094	0.537046	1.319554	-2.515128
1	1.577592	1.846718	-1.090741	1.645839	1.709408	-1.098191
1	1.577592	1.846718	1.090741	1.645839	1.709408	1.098191
1	0.509788	1.375820	2.510094	0.537046	1.319554	2.515128
6	-0.590600	-1.542705	-1.438493	-0.605243	-1.550089	-1.429921
6	-0.590600	-1.542705	1.438493	-0.605243	-1.550089	1.429921
6	0.590600	-1.885045	0.716809	0.597050	-1.848960	0.717566
6	0.590600	-1.885045	-0.716809	0.597050	-1.848960	-0.717566
1	1.541411	-1.975425	-1.240965	1.549647	-1.907465	-1.246792
1	1.541411	-1.975425	1.240965	1.549647	-1.907465	1.246792
1	-0.509788	-1.375820	2.510094	-0.538176	-1.373989	2.503116
1	-1.577592	-1.846718	1.090741	-1.576159	-1.907651	1.080833
1	-1.577592	-1.846718	-1.090741	-1.576159	-1.907651	-1.080833
1	-0.509788	-1.375820	-2.510094	-0.538176	-1.373989	-2.503116
25	0.000000	0.000000	0.000000	-0.066008	0.004422	0.000000

	BP86		
	x	y	z
6	-0.550225	-1.580776	1.380413
6	-0.550225	-1.580776	-1.380413
6	0.725819	-1.652011	-0.720282
6	0.725819	-1.652011	0.720282
1	1.673134	-1.564847	1.267879
1	1.673134	-1.564847	-1.267879
1	-0.561744	-1.375952	-2.458541
1	-1.397174	-2.185906	-1.025277
1	-1.397174	-2.185906	1.025277
1	-0.561744	-1.375952	2.458541
6	0.670243	1.305667	-1.449397
6	0.670243	1.305667	1.449397
6	-0.379496	1.949712	0.725968
6	-0.379496	1.949712	-0.725968
1	-1.300008	2.248274	-1.248354
1	-1.300008	2.248274	1.248354
1	0.530169	1.141403	2.524370
1	1.717430	1.362198	1.121725
1	1.717430	1.362198	-1.121725
1	0.530169	1.141403	-2.524370
25	-0.276788	0.019142	0.000000

Table S10. Optimized coordinates for the $(C_4H_6)_2Mn$ structure **Mn-1Q.**

	B3LYP			B3LYP*		
	x	y	z	x	y	z
6	-1.358042	1.660996	-0.760473	0.107299	1.646551	1.440204
6	0.658806	1.548108	1.438449	1.948887	0.838245	-0.756927
6	0.975099	1.929564	0.105373	0.896279	1.762574	-0.938005
6	0.000000	1.990219	-0.940597	0.000000	2.147230	0.110037
1	0.378866	2.093782	-1.958565	-0.902495	2.687377	-0.184995
1	2.021736	1.998880	-0.192168	0.607225	2.032569	-1.957059
1	1.475594	1.408809	2.142973	2.491315	0.480736	-1.631450
1	-0.289370	1.838570	1.890622	2.491589	0.781221	0.188720
1	-1.862097	1.846996	0.187524	1.085430	1.485070	1.897832
1	-2.004942	1.597128	-1.632198	-0.690402	1.880867	2.144428
6	-0.658806	-1.548108	1.438449	-1.948887	-0.838245	-0.756927
6	1.358042	-1.660996	-0.760473	-0.107299	-1.646551	1.440204
6	0.000000	-1.990219	-0.940597	0.000000	-2.147230	0.110037
6	-0.975099	-1.929564	0.105373	-0.896279	-1.762574	-0.938005
1	-2.021736	-1.998880	-0.192168	-0.607225	-2.032569	-1.957059
1	-0.378866	-2.093782	-1.958565	0.902495	-2.687377	-0.184995
1	2.004942	-1.597128	-1.632198	0.690402	-1.880867	2.144428
1	1.862097	-1.846996	0.187524	-1.085430	-1.485070	1.897832
1	0.289370	-1.838570	1.890622	-2.491589	-0.781221	0.188720
1	-1.475594	-1.408809	2.142973	-2.491315	-0.480736	-1.631450
25	0.000000	0.000000	0.040424	0.000000	0.000000	0.032854

	BP86		
	x	y	z
6	-0.504083	1.487827	1.455516
6	1.434730	1.479476	-0.775975
6	0.098395	1.948831	-0.937819
6	-0.852933	1.943921	0.138096
1	-1.909763	2.089917	-0.125489
1	-0.295004	2.096185	-1.953963
1	2.057467	1.351967	-1.669100
1	1.986276	1.664863	0.156816
1	0.465432	1.756094	1.898875
1	-1.312430	1.359615	2.185260
6	-1.434730	-1.479476	-0.775975
6	0.504083	-1.487827	1.455516
6	0.852933	-1.943921	0.138096
6	-0.098395	-1.948831	-0.937819
1	0.295004	-2.096185	-1.953963
1	1.909763	-2.089917	-0.125489
1	1.312430	-1.359615	2.185260
1	-0.465432	-1.756094	1.898875
1	-1.986276	-1.664863	0.156816
1	-2.057467	-1.351967	-1.669100
25	0.000000	0.000000	0.015120

Table S11. Optimized coordinates for the $(C_4H_6)_2Mn$ structure **Mn-1X.**

	B3LYP			B3LYP*		
	x	y	z	x	y	z
6	-2.755440	-1.001292	0.537641	-2.719322	-1.011740	0.539217
6	-1.259677	1.669674	0.557517	-1.251646	1.671745	0.561411
6	-1.754008	1.013473	-0.607370	-1.747242	1.018934	-0.606688
6	-2.427790	-0.274947	-0.581938	-2.403368	-0.278564	-0.583021
1	-2.640851	-0.719158	-1.556165	-2.612852	-0.725617	-1.558978
1	-1.637689	1.494349	-1.580048	-1.632241	1.503074	-1.580105
1	-0.837624	2.667123	0.451523	-0.829092	2.671390	0.459077
1	-1.685684	1.454658	1.538060	-1.676884	1.451483	1.543400
1	-2.637177	-0.606376	1.544383	-2.607429	-0.613364	1.547386
1	-3.194851	-1.991133	0.444489	-3.143269	-2.010346	0.446264
6	2.755440	1.001291	-0.537642	2.719327	1.011743	-0.539201
6	1.259676	-1.669674	-0.557517	1.251649	-1.671742	-0.561420
6	1.754008	-1.013473	0.607370	1.747238	-1.018938	0.606685
6	2.427790	0.274946	0.581938	2.403364	0.278559	0.583030
1	2.640852	0.719158	1.556165	2.612843	0.725607	1.558991
1	1.637689	-1.494349	1.580048	1.632230	-1.503083	1.580099
1	0.837622	-2.667123	-0.451522	0.829093	-2.671387	-0.459094
1	1.685683	-1.454658	-1.538060	1.676892	-1.451475	-1.543405
1	2.637177	0.606375	-1.544383	2.607439	0.613373	-1.547374
1	3.194851	1.991132	-0.444489	3.143274	2.010348	-0.446240
25	0.000000	0.000000	0.000000	0.000000	0.000001	-0.000004

	BP86		
	x	y	z
6	-2.640760	1.029143	-0.543946
6	-1.219149	-1.679240	-0.570361
6	-1.723135	-1.036766	0.609009
6	-2.336054	0.285551	0.588698
1	-2.530057	0.743120	1.570236
1	-1.607736	-1.527161	1.586435
1	-0.791491	-2.684534	-0.475970
1	-1.646975	-1.450098	-1.557107
1	-2.552507	0.618432	-1.556792
1	-3.025877	2.050093	-0.451283
6	2.640761	-1.029144	0.543943
6	1.219149	1.679240	0.570363
6	1.723134	1.036767	-0.609008
6	2.336054	-0.285550	-0.588700
1	2.530056	-0.743118	-1.570239
1	1.607735	1.527163	-1.586434
1	0.791490	2.684534	0.475973
1	1.646976	1.450097	1.557108
1	2.552509	-0.618435	1.556790
1	3.025878	-2.050094	0.451278
25	0.000000	0.000000	0.000000

Table S12. Optimized coordinates for the $(C_4H_6)_2Mn$ structure **Mn-2X.**

	B3LYP			B3LYP*		
	x	y	z	x	y	z
6	-1.502583	1.829219	0.513057	-0.275595	-1.820436	1.502839
6	1.502583	1.829219	0.513057	-0.275595	-1.820436	-1.502839
6	0.720396	1.705929	-0.636907	0.878029	-1.706181	-0.720933
6	-0.720396	1.705929	-0.636907	0.878029	-1.706181	0.720933
1	-1.212166	1.444265	-1.573551	1.817874	-1.450565	1.214298
1	1.212165	1.444265	-1.573551	1.817874	-1.450565	-1.214298
1	2.581971	1.721612	0.448620	-0.212107	-1.711317	-2.584052
1	1.131739	2.325807	1.408964	-1.176369	-2.311537	-1.130400
1	-1.131739	2.325807	1.408964	-1.176369	-2.311537	1.130400
1	-2.581971	1.721612	0.448620	-0.212107	-1.711317	2.584052
6	-1.502583	-1.829219	0.513058	-0.275610	1.820425	1.502834
6	1.502583	-1.829220	0.513058	-0.275610	1.820425	-1.502834
6	0.720396	-1.705930	-0.636907	0.878022	1.706179	-0.720933
6	-0.720396	-1.705930	-0.636906	0.878022	1.706179	0.720933
1	-1.212166	-1.444267	-1.573550	1.817870	1.450581	1.214301
1	1.212165	-1.444267	-1.573550	1.817870	1.450581	-1.214301
1	2.581971	-1.721612	0.448621	-0.212121	1.711313	-2.584048
1	1.131739	-2.325806	1.408966	-1.176376	2.311541	-1.130397
1	-1.131739	-2.325806	1.408966	-1.176376	2.311541	1.130397
1	-2.581971	-1.721612	0.448621	-0.212121	1.711313	2.584048
25	0.000000	0.000001	0.910234	-0.647028	0.000004	0.000000

	BP86		
	x	y	z
6	2.474642	-1.273957	0.443701
6	1.554428	1.233503	-1.079270
6	1.657121	1.133596	0.352315
6	2.030338	-0.097189	1.033589
1	1.910667	-0.092379	2.127818
1	1.374085	1.991690	0.976785
1	1.292897	2.208251	-1.510735
1	2.187972	0.606180	-1.725013
1	2.687755	-1.350389	-0.629653
1	2.670618	-2.161546	1.054197
6	-1.553873	-1.233693	-1.079248
6	-2.475864	1.274143	0.442807
6	-2.031110	0.097756	1.033012
6	-1.657243	-1.133126	0.352226
1	-1.374511	-1.991012	0.977126
1	-1.911935	0.093175	2.127298
1	-2.672619	2.161703	1.053095
1	-2.688269	1.350388	-0.630701
1	-2.186797	-0.606348	-1.725575
1	-1.292466	-2.208709	-1.510182
25	0.000437	-0.000349	-0.383201

Table S13. Optimized coordinates for the $(C_4H_6)_2Cr$ structure **Cr-1S**.

	B3LYP			B3LYP*		
	x	y	z	x	y	z
6	-1.452525	1.463683	0.536973	-1.459412	1.451251	-0.560883
6	1.452525	1.463683	0.536973	-1.459412	-1.451251	-0.560883
6	0.717183	1.939508	-0.576492	-1.932984	-0.718328	0.558203
6	-0.717183	1.939508	-0.576492	-1.932984	0.718328	0.558203
1	-1.223639	2.093567	-1.530705	-2.083069	1.227179	1.514067
1	1.223639	2.093567	-1.530705	-2.083069	-1.227179	1.514067
1	2.526241	1.336268	0.427714	-1.328183	-2.526704	-0.454271
1	1.125394	1.671372	1.557851	-1.675752	-1.122771	-1.581921
1	-1.125394	1.671372	1.557851	-1.675752	1.122771	-1.581921
1	-2.526241	1.336268	0.427714	-1.328183	2.526704	-0.454271
6	-1.452525	-1.463683	0.536973	1.459412	1.451251	-0.560883
6	1.452525	-1.463683	0.536973	1.459412	-1.451251	-0.560883
6	0.717183	-1.939508	-0.576492	1.932984	-0.718328	0.558203
6	-0.717183	-1.939508	-0.576492	1.932984	0.718328	0.558203
1	-1.223639	-2.093567	-1.530705	2.083069	1.227179	1.514067
1	1.223639	-2.093567	-1.530705	2.083069	-1.227179	1.514067
1	2.526241	-1.336268	0.427714	1.328183	-2.526704	-0.454271
1	1.125394	-1.671372	1.557851	1.675752	-1.122771	-1.581921
1	-1.125394	-1.671372	1.557851	1.675752	1.122771	-1.581921
1	-2.526241	-1.336268	0.427714	1.328183	2.526704	-0.454271
24	0.000000	0.000000	-0.115904	0.000000	0.000000	0.089700

	BP86		
	x	y	z
6	-1.450317	1.444243	0.545260
6	1.450317	1.444243	0.545260
6	0.723134	1.913395	-0.591991
6	-0.723134	1.913395	-0.591991
1	-1.238395	2.046806	-1.554483
1	1.238395	2.046806	-1.554483
1	2.531830	1.304983	0.444458
1	1.120605	1.691196	1.567305
1	-1.120605	1.691196	1.567305
1	-2.531830	1.304983	0.444458
6	-1.450317	-1.444242	0.545260
6	1.450317	-1.444242	0.545260
6	0.723134	-1.913395	-0.591991
6	-0.723134	-1.913395	-0.591991
1	-1.238395	-2.046806	-1.554483
1	1.238395	-2.046806	-1.554483
1	2.531830	-1.304983	0.444458
1	1.120605	-1.691196	1.567306
1	-1.120605	-1.691196	1.567306
1	-2.531830	-1.304983	0.444458
24	0.000000	0.000000	-0.096741

Table S14. Optimized coordinates for the $(C_4H_6)_2Cr$ structure **Cr-2S**.

	B3LYP			B3LYP*		
	x	y	z	x	y	z
6	1.573185	1.521040	-0.043087	1.560725	1.517956	-0.058379
6	1.116402	-1.089728	1.222785	1.113867	-1.073292	1.237019
6	1.911732	-0.948432	0.033149	1.915331	-0.948116	0.047367
6	2.100488	0.308580	-0.578523	2.095660	0.301176	-0.584600
1	2.452660	0.301623	-1.612721	2.451507	0.282980	-1.619467
1	2.160292	-1.836842	-0.548782	2.166592	-1.846386	-0.522341
1	0.905132	-2.085669	1.609390	0.904535	-2.063274	1.644968
1	1.213997	-0.327637	2.013103	1.199530	-0.291740	2.012983
1	1.633544	1.715266	1.032854	1.633001	1.726323	1.016591
1	1.645367	2.422867	-0.648034	1.624366	2.415292	-0.674638
6	-1.043451	-1.186579	-1.122975	-1.031919	-1.177826	-1.129368
6	-1.538123	1.542176	0.015604	-1.529453	1.537527	0.026976
6	-2.157470	0.349894	0.495439	-2.158952	0.342437	0.495079
6	-1.972266	-0.933182	-0.068366	-1.976289	-0.935358	-0.083667
1	-2.348203	-1.785498	0.500168	-2.364942	-1.795370	0.469128
1	-2.604165	0.368918	1.492299	-2.614821	0.353504	1.490190
1	-1.654461	2.454917	0.595736	-1.642456	2.447392	0.616151
1	-1.458590	1.722011	-1.062640	-1.452687	1.728172	-1.051861
1	-0.843021	-0.381422	-1.866871	-0.797453	-0.350247	-1.845403
1	-0.906081	-2.185362	-1.532204	-0.901143	-2.165140	-1.572742
24	-0.005811	0.093092	0.012648	-0.005827	0.090478	0.013911

	BP86		
	x	y	z
6	-1.515153	1.514133	0.107658
6	-1.032022	-1.069509	-1.244802
6	-1.948666	-0.948902	-0.136992
6	-2.114768	0.279363	0.553580
1	-2.534873	0.218889	1.569748
1	-2.276119	-1.867147	0.375239
1	-0.878484	-2.014842	-1.780295
1	-0.881380	-0.171644	-1.902977
1	-1.568951	1.790221	-0.961648
1	-1.583358	2.384361	0.772802
6	1.032026	-1.069484	1.244819
6	1.515152	1.514130	-0.107670
6	2.114759	0.279349	-0.553590
6	1.948660	-0.948909	0.136997
1	2.276094	-1.867162	-0.375233
1	2.534864	0.218868	-1.569758
1	1.583351	2.384337	-0.772842
1	1.568998	1.790257	0.961624
1	0.881427	-0.171585	1.902960
1	0.878469	-2.014790	1.780355
24	0.000001	0.084134	0.000001

Table S15. Optimized coordinates for the $(C_4H_6)_2Cr$ structure **Cr-1T**.

	B3LYP			B3LYP*		
	x	y	z	x	y	z
6	0.010678	1.672895	1.538536	1.182629	-1.140189	-1.201239
6	1.182891	1.218172	-1.154748	1.656616	1.537305	0.004104
6	-0.076011	1.887437	-0.952310	2.106884	0.327523	0.604784
6	-0.614088	2.109678	0.339104	1.877258	-0.957072	0.050629
1	-1.666357	2.397771	0.384774	2.045926	-1.819528	0.697554
1	-0.735965	2.047004	-1.803964	2.406902	0.357077	1.656438
1	1.454721	0.962372	-2.177475	1.731790	2.464737	0.569222
1	2.038252	1.465045	-0.518193	1.695505	1.665570	-1.082619
1	1.096772	1.719756	1.648114	1.426873	-0.498023	-2.056486
1	-0.540192	1.742695	2.472636	0.919607	-2.161060	-1.481553
6	-1.182891	-1.218172	-1.154748	-1.656618	1.537303	-0.004103
6	-0.010678	-1.672895	1.538536	-1.182625	-1.140189	1.201240
6	0.614088	-2.109678	0.339104	-1.877257	-0.957074	-0.050627
6	0.076011	-1.887437	-0.952310	-2.106886	0.327520	-0.604781
1	0.735965	-2.047004	-1.803964	-2.406907	0.357073	-1.656435
1	1.666357	-2.397771	0.384774	-2.045926	-1.819531	-0.697551
1	0.540192	-1.742695	2.472636	-0.919600	-2.161060	1.481554
1	-1.096772	-1.719756	1.648114	-1.426868	-0.498023	2.056487
1	-2.038252	-1.465045	-0.518193	-1.695504	1.665569	1.082619
1	-1.454721	-0.962372	-2.177475	-1.731796	2.464735	-0.569222
24	0.000000	0.000000	0.114595	0.000000	0.115488	-0.000002

	BP86		
	x	y	z
6	-0.014708	1.616816	1.540825
6	1.221142	1.133453	-1.128322
6	-0.024714	1.862564	-0.963632
6	-0.595056	2.096180	0.321594
1	-1.649896	2.410244	0.337905
1	-0.660943	2.047401	-1.839267
1	1.507689	0.859275	-2.152003
1	2.084012	1.376016	-0.482288
1	1.077875	1.649054	1.686440
1	-0.592940	1.693063	2.467855
6	-1.221142	-1.133453	-1.128322
6	0.014708	-1.616816	1.540825
6	0.595056	-2.096180	0.321594
6	0.024714	-1.862564	-0.963632
1	0.660943	-2.047401	-1.839267
1	1.649896	-2.410244	0.337905
1	0.592940	-1.693063	2.467855
1	-1.077875	-1.649054	1.686440
1	-2.084012	-1.376016	-0.482288
1	-1.507689	-0.859275	-2.152003
24	0.000000	0.000000	0.112679

Table S16. Optimized coordinates for the $(C_4H_6)_2Cr$ structure **Cr-2T**.

	B3LYP			B3LYP*		
	x	y	z	x	y	z
6	-0.680287	1.970132	0.713501	-0.728297	1.934728	0.684970
6	2.022352	0.922847	0.292225	1.993183	0.914225	0.348998
6	1.315399	1.605712	-0.723666	1.325408	1.620158	-0.681179
6	0.000000	2.108054	-0.531808	0.000000	2.111580	-0.529006
1	-0.554107	2.428015	-1.415059	-0.522816	2.447010	-1.428158
1	1.686705	1.552767	-1.748912	1.736037	1.589553	-1.694482
1	2.956025	0.426729	0.040623	2.939455	0.425699	0.122831
1	1.918782	1.208280	1.340262	1.853322	1.183951	1.399295
1	-0.132611	2.076023	1.653854	-0.219299	2.022974	1.650837
1	-1.725934	2.262507	0.764393	-1.779408	2.218006	0.701810
6	-2.022352	-0.922847	0.292225	-1.993183	-0.914225	0.348998
6	0.680287	-1.970132	0.713501	0.728297	-1.934728	0.684970
6	0.000000	-2.108054	-0.531808	0.000000	-2.111580	-0.529006
6	-1.315399	-1.605712	-0.723666	-1.325408	-1.620158	-0.681179
1	-1.686705	-1.552767	-1.748912	-1.736037	-1.589553	-1.694482
1	0.554107	-2.428015	-1.415059	0.522816	-2.447010	-1.428158
1	1.725934	-2.262507	0.764393	1.779408	-2.218006	0.701810
1	0.132611	-2.076023	1.653854	0.219299	-2.022974	1.650837
1	-1.918782	-1.208280	1.340262	-1.853322	-1.183951	1.399295
1	-2.956025	-0.426729	0.040623	-2.939455	-0.425699	0.122831
24	0.000000	0.000000	0.071944	0.000000	0.000000	0.025431

	BP86		
	x	y	z
6	0.847476	1.900643	-0.568569
6	-1.894599	0.910236	-0.517554
6	-1.342578	1.628048	0.587535
6	0.000000	2.112338	0.563995
1	0.438352	2.444691	1.516605
1	-1.860194	1.611373	1.558124
1	-2.870510	0.429979	-0.390451
1	-1.663766	1.209288	-1.551923
1	0.444213	1.978400	-1.590843
1	1.907305	2.161234	-0.478743
6	1.894599	-0.910236	-0.517554
6	-0.847476	-1.900643	-0.568569
6	0.000000	-2.112338	0.563995
6	1.342578	-1.628048	0.587535
1	1.860194	-1.611373	1.558124
1	-0.438352	-2.444691	1.516605
1	-1.907305	-2.161234	-0.478743
1	-0.444213	-1.978400	-1.590843
1	1.663766	-1.209288	-1.551923
1	2.870510	-0.429979	-0.390451
24	0.000000	0.000000	0.045399

Table S17. Optimized coordinates for the $(C_4H_6)_2Cr$ structure **Cr-1P**.

	B3LYP			B3LYP*		
	x	y	z	x	y	z
6	0.392237	1.657140	1.459240	1.584013	1.458667	0.611730
6	0.392237	1.657140	-1.459240	1.584013	-1.458667	0.611730
6	-0.784354	1.928003	-0.711901	2.012830	-0.712639	-0.520155
6	-0.784354	1.928003	0.711901	2.012830	0.712640	-0.520155
1	-1.747729	1.946738	1.222590	2.162889	1.224811	-1.473513
1	-1.747729	1.946738	-1.222590	2.162889	-1.224811	-1.473513
1	0.305802	1.521681	-2.534598	1.458812	-2.535827	0.509551
1	1.367662	1.997845	-1.111164	1.791646	-1.108215	1.625144
1	1.367662	1.997845	1.111164	1.791646	1.108215	1.625144
1	0.305801	1.521681	2.534598	1.458812	2.535828	0.509551
6	-0.392237	-1.657144	-1.459241	-1.584019	-1.458668	-0.611729
6	-0.392236	-1.657144	1.459241	-1.584019	1.458668	-0.611729
6	0.784354	-1.928001	0.711902	-2.012827	0.712640	0.520158
6	0.784354	-1.928001	-0.711902	-2.012827	-0.712640	0.520158
1	1.747729	-1.946733	-1.222590	-2.162879	-1.224811	1.473517
1	1.747729	-1.946733	1.222590	-2.162879	1.224811	1.473517
1	-0.305802	-1.521685	2.534599	-1.458819	2.535829	-0.509552
1	-1.367662	-1.997845	1.111163	-1.791650	1.108213	-1.625142
1	-1.367663	-1.997846	-1.111162	-1.791651	-1.108213	-1.625142
1	-0.305802	-1.521686	-2.534599	-1.458819	-2.535829	-0.509552
24	-0.000001	0.000001	0.000000	0.000002	0.000000	-0.000002

	BP86		
	x	y	z
6	0.399253	1.633220	1.458307
6	0.399253	1.633220	-1.458307
6	-0.792004	1.909283	-0.716325
6	-0.792004	1.909283	0.716325
1	-1.761198	1.926328	1.234450
1	-1.761198	1.926328	-1.234450
1	0.319146	1.486606	-2.541359
1	1.378167	1.988179	-1.105665
1	1.378167	1.988179	1.105665
1	0.319146	1.486606	2.541359
6	-0.399253	-1.633223	-1.458307
6	-0.399253	-1.633223	1.458307
6	0.792004	-1.909281	0.716326
6	0.792004	-1.909281	-0.716325
1	1.761199	-1.926322	-1.234450
1	1.761199	-1.926322	1.234450
1	-0.319147	-1.486609	2.541360
1	-1.378166	-1.988182	1.105665
1	-1.378166	-1.988183	-1.105664
1	-0.319147	-1.486609	-2.541359
24	-0.000002	0.000000	0.000000

Table S18. Optimized coordinates for the $(C_4H_6)_2Cr$ structure **Cr-2P**.

	B3LYP			B3LYP*		
	x	y	z	x	y	z
6	0.649076	-1.881040	1.462523	1.793188	1.625253	-0.425897
6	-1.325099	-1.808492	-0.804621	1.828153	-0.870918	1.240542
6	0.051954	-1.927714	-0.975003	1.970397	-0.864092	-0.148656
6	1.000760	-1.942168	0.126541	1.930312	0.349368	-0.949003
1	2.058641	-1.921612	-0.136940	1.926066	0.224592	-2.034253
1	0.463767	-1.908321	-1.983190	2.008884	-1.813677	-0.684690
1	-1.973821	-1.716443	-1.671950	1.776141	-1.817065	1.777122
1	-1.816024	-2.028555	0.141780	2.007176	0.017579	1.847474
1	-0.370395	-2.036355	1.808579	1.934936	1.842922	0.632505
1	1.416188	-1.802337	2.228527	1.672588	2.480968	-1.088163
6	-1.335253	1.761708	0.762251	-1.809559	0.538325	1.361633
6	0.612889	1.551441	-1.433624	-1.440998	-1.431678	-0.789801
6	0.999907	1.954962	-0.112571	-1.894708	-0.096984	-1.056688
6	0.060148	2.051330	0.941834	-2.068143	0.852237	-0.016682
1	0.454614	2.143927	1.955763	-2.197295	1.898200	-0.309120
1	2.058931	1.983828	0.149884	-1.903169	0.272138	-2.085916
1	1.407229	1.356555	-2.153220	-1.183288	-2.058103	-1.645344
1	-0.299619	1.956505	-1.876198	-1.851499	-1.984157	0.060716
1	-1.851798	2.131129	-0.126484	-2.149601	-0.417047	1.772485
1	-1.955962	1.738108	1.656782	-1.838309	1.363739	2.074455
24	-0.172412	0.097606	-0.005664	-0.085604	-0.025798	0.182919

	BP86		
	x	y	z
6	-1.497033	-1.581750	-0.595745
6	-1.825904	0.695351	1.270590
6	-1.966679	0.842447	-0.141381
6	-1.807977	-0.279250	-1.039879
1	-1.751766	-0.058687	-2.115651
1	-2.045314	1.843769	-0.585601
1	-1.833491	1.596508	1.895391
1	-2.142612	-0.227633	1.777630
1	-1.794607	-1.939576	0.399249
1	-1.251006	-2.357232	-1.329294
6	1.825908	-0.695350	1.270589
6	1.497031	1.581750	-0.595745
6	1.807978	0.279252	-1.039880
6	1.966681	-0.842445	-0.141382
1	2.045319	-1.843767	-0.585602
1	1.751770	0.058689	-2.115652
1	1.251004	2.357235	-1.329291
1	1.794598	1.939572	0.399253
1	2.142615	0.227633	1.777631
1	1.833497	-1.596508	1.895389
24	-0.000001	-0.000001	0.249731

Table S19. Optimized coordinates for the $(C_4H_6)_2V$ structure **V-1D.**

	B3LYP			B3LYP*		
	x	y	z	x	y	z
6	-1.202697	-1.083355	1.255280	-1.208745	-1.064430	1.273754
6	-1.569438	1.539558	-0.151788	-1.542666	1.536382	-0.182985
6	-2.167779	0.308853	-0.593807	-2.160542	0.304334	-0.604120
6	-2.018291	-0.922420	0.067257	-2.027714	-0.915117	0.084031
1	-2.317211	-1.818081	-0.477884	-2.334515	-1.819750	-0.446239
1	-2.547857	0.261822	-1.616458	-2.542823	0.241980	-1.627125
1	-1.648903	2.404536	-0.806665	-1.606604	2.390966	-0.856403
1	-1.612472	1.803385	0.910168	-1.591748	1.823845	0.874679
1	-1.280955	-0.311898	2.038710	-1.272313	-0.275197	2.043359
1	-1.059031	-2.083550	1.658973	-1.076291	-2.059623	1.698375
6	1.569434	1.539562	0.151784	1.542666	1.536382	0.182985
6	1.202699	-1.083370	-1.255269	1.208745	-1.064431	-1.273754
6	2.018295	-0.922414	-0.067253	2.027715	-0.915117	-0.084031
6	2.167780	0.308863	0.593803	2.160542	0.304334	0.604120
1	2.547869	0.261838	1.616450	2.542824	0.241981	1.627124
1	2.317222	-1.818070	0.477894	2.334516	-1.819749	0.446239
1	1.059040	-2.083569	-1.658953	1.076291	-2.059624	-1.698375
1	1.280934	-0.311912	-2.038702	1.272311	-0.275198	-2.043358
1	1.612439	1.803373	-0.910177	1.591747	1.823844	-0.874679
1	1.648904	2.404548	0.806649	1.606604	2.390966	0.856403
23	0.000000	0.059822	-0.000002	0.000000	0.046153	0.000000

	BP86		
	x	y	z
6	-1.006745	-1.111721	1.313128
6	-1.659533	1.435833	-0.229864
6	-2.184468	0.139271	-0.572175
6	-1.879088	-1.050933	0.154645
1	-2.084235	-1.997199	-0.369586
1	-2.586844	-0.008219	-1.586062
1	-1.779295	2.238892	-0.968237
1	-1.670146	1.784895	0.811568
1	-1.094643	-0.358045	2.112699
1	-0.739290	-2.112498	1.674427
6	1.185544	1.467808	0.706039
6	1.617067	-0.480511	-1.471363
6	2.096031	-0.713592	-0.117478
6	1.867182	0.210816	0.929734
1	2.009519	-0.150437	1.957326
1	2.374119	-1.737691	0.169468
1	1.680040	-1.314654	-2.182538
1	1.793183	0.505026	-1.941930
1	1.458438	2.085443	-0.168043
1	0.918670	2.068269	1.583938
23	-0.021541	-0.016766	-0.233436

Table S20. Optimized coordinates for the $(C_4H_6)_2V$ structure **V-2D.**

	B3LYP			B3LYP*		
	x	y	z	x	y	z
6	-1.459824	1.529406	0.526268	-1.522268	1.458590	-0.552865
6	1.459824	1.529406	0.526268	-1.522268	-1.458590	-0.552865
6	0.709867	2.051386	-0.564414	-2.047791	-0.710755	0.540171
6	-0.709867	2.051386	-0.564414	-2.047791	0.710755	0.540171
1	-1.214947	2.258828	-1.510234	-2.256523	1.217897	1.486921
1	1.214947	2.258828	-1.510234	-2.256523	-1.217897	1.486921
1	2.537014	1.437333	0.412950	-1.427464	-2.537678	-0.441564
1	1.130225	1.706386	1.552837	-1.701431	-1.127240	-1.580815
1	-1.130225	1.706386	1.552837	-1.701431	1.127240	-1.580815
1	-2.537014	1.437333	0.412950	-1.427464	2.537678	-0.441564
6	-1.459824	-1.529406	0.526268	1.522268	1.458590	-0.552865
6	1.459824	-1.529406	0.526268	1.522268	-1.458590	-0.552865
6	0.709867	-2.051386	-0.564414	2.047791	-0.710755	0.540171
6	-0.709867	-2.051386	-0.564414	2.047791	0.710755	0.540171
1	-1.214947	-2.258828	-1.510234	2.256523	1.217897	1.486921
1	1.214947	-2.258828	-1.510234	2.256523	-1.217897	1.486921
1	2.537014	-1.437333	0.412950	1.427464	-2.537678	-0.441564
1	1.130225	-1.706386	1.552837	1.701431	-1.127240	-1.580815
1	-1.130225	-1.706386	1.552837	1.701431	1.127240	-1.580815
1	-2.537014	-1.437333	0.412950	1.427464	2.537678	-0.441564
23	-1.459824	1.529406	0.526268	0.000000	0.000000	0.106369

	BP86		
	x	y	z
6	-1.456627	1.499807	0.529846
6	1.456627	1.499807	0.529846
6	0.714641	2.038497	-0.572216
6	-0.714641	2.038497	-0.572216
1	-1.227775	2.249114	-1.522994
1	1.227775	2.249114	-1.522994
1	2.542112	1.398727	0.423268
1	1.122070	1.690956	1.562579
1	-1.122070	1.690956	1.562579
1	-2.542112	1.398727	0.423268
6	-1.456627	-1.499807	0.529846
6	1.456627	-1.499807	0.529846
6	0.714641	-2.038497	-0.572216
6	-0.714641	-2.038497	-0.572216
1	-1.227775	-2.249114	-1.522994
1	1.227775	-2.249114	-1.522994
1	2.542112	-1.398727	0.423268
1	1.122070	-1.690956	1.562579
1	-1.122070	-1.690956	1.562579
1	-2.542112	-1.398727	0.423268
23	0.000000	0.000000	-0.142126

Table S21. Optimized coordinates for the $(C_4H_6)_2V$ structure **V-1Q.**

	B3LYP			B3LYP*		
	x	y	z	x	y	z
6	-1.491927	1.690902	0.544646	-1.681652	1.493224	-0.422553
6	1.491927	1.690902	0.544646	-1.681653	-1.493224	-0.422553
6	0.712595	1.830349	-0.631576	-1.834523	-0.713425	0.753703
6	-0.712595	1.830349	-0.631576	-1.834523	0.713425	0.753703
1	-1.208604	1.749412	-1.599474	-1.763157	1.210467	1.724167
1	1.208604	1.749412	-1.599474	-1.763157	-1.210467	1.724167
1	2.571377	1.605648	0.455482	-1.597203	-2.574654	-0.334037
1	1.143745	2.107037	1.494416	-2.085116	-1.142884	-1.379531
1	-1.143745	2.107037	1.494416	-2.085116	1.142884	-1.379530
1	-2.571377	1.605648	0.455482	-1.597203	2.574654	-0.334037
6	-1.491926	-1.690903	0.544646	1.681652	1.493224	-0.422553
6	1.491926	-1.690903	0.544646	1.681652	-1.493224	-0.422553
6	0.712595	-1.830349	-0.631576	1.834523	-0.713425	0.753703
6	-0.712595	-1.830349	-0.631576	1.834523	0.713425	0.753703
1	-1.208604	-1.749411	-1.599473	1.763157	1.210467	1.724167
1	1.208604	-1.749411	-1.599473	1.763158	-1.210466	1.724167
1	2.571377	-1.605649	0.455483	1.597203	-2.574654	-0.334036
1	1.143745	-2.107037	1.494416	2.085116	-1.142885	-1.379530
1	-1.143745	-2.107037	1.494416	2.085116	1.142885	-1.379530
1	-2.571377	-1.605648	0.455483	1.597202	2.574654	-0.334037
23	0.000000	0.000001	0.485827	0.000000	0.000000	-0.347391

	BP86		
	x	y	z
6	-1.521679	1.544789	0.509970
6	1.521677	1.544774	0.509969
6	0.718273	2.070242	-0.543482
6	-0.718269	2.070248	-0.543481
1	-1.206288	2.291503	-1.503423
1	1.206292	2.291490	-1.503425
1	2.606691	1.497710	0.374929
1	1.190634	1.601294	1.559651
1	-1.190632	1.601299	1.559652
1	-2.606693	1.497737	0.374932
6	-1.521687	-1.544755	0.509941
6	1.521684	-1.544741	0.509942
6	0.718271	-2.070251	-0.543491
6	-0.718267	-2.070258	-0.543491
1	-1.206284	-2.291544	-1.503428
1	1.206290	-2.291532	-1.503428
1	2.606700	-1.497711	0.374902
1	1.190655	-1.601269	1.559631
1	-1.190656	-1.601276	1.559630
1	-2.606703	-1.497738	0.374901
23	-0.000008	-0.000010	-0.050594

Table S22. Optimized coordinates for the $(C_4H_6)_2V$ structure **V-2Q.**

	B3LYP			B3LYP*		
	x	y	z	x	y	z
6	-1.535485	-1.205723	1.155870	-1.533196	-1.231904	1.096233
6	-1.765949	1.558398	0.001267	-1.634041	1.591836	0.029687
6	-2.129316	0.389195	-0.677317	-2.116015	0.458773	-0.665066
6	-2.029639	-0.935644	-0.132107	-2.068956	-0.879788	-0.167715
1	-2.187040	-1.768202	-0.817574	-2.276536	-1.677950	-0.884515
1	-2.354914	0.464341	-1.742571	-2.355461	0.575940	-1.725758
1	-1.766342	2.510976	-0.520705	-1.614999	2.559236	-0.468352
1	-1.750903	1.615778	1.089097	-1.651781	1.635053	1.123060
1	-1.636164	-0.487242	1.969943	-1.643108	-0.568743	1.959873
1	-1.373967	-2.237952	1.458070	-1.424659	-2.288573	1.340776
6	1.581402	1.606043	0.011727	1.634001	1.591849	-0.029688
6	1.519781	-1.208325	-1.096905	1.533186	-1.231922	-1.096208
6	2.089163	-0.854672	0.164529	2.068972	-0.879768	0.167723
6	2.122166	0.466162	0.679180	2.116027	0.458799	0.665057
1	2.367078	0.568330	1.738116	2.355513	0.575981	1.725738
1	2.311898	-1.656481	0.870445	2.276566	-1.677913	0.884538
1	1.444345	-2.266826	-1.339844	1.424640	-2.288602	-1.340702
1	1.675594	-0.563132	-1.967538	1.643115	-0.568812	-1.959886
1	1.662015	1.690079	-1.077613	1.651687	1.635033	-1.123065
1	1.571033	2.561334	0.529927	1.614973	2.559260	0.468329
23	0.040201	0.029408	-0.035966	0.000008	0.011428	-0.000007

	BP86		
	x	y	z
6	-1.518729	-1.232313	1.098350
6	-1.592691	1.595189	0.037418
6	-2.103690	0.468956	-0.664332
6	-2.066858	-0.878221	-0.168714
1	-2.287591	-1.678535	-0.889440
1	-2.350587	0.594875	-1.729130
1	-1.564705	2.572630	-0.454905
1	-1.602473	1.629777	1.138928
1	-1.628539	-0.568280	1.970276
1	-1.407334	-2.295927	1.341941
6	1.592690	1.595189	-0.037418
6	1.518730	-1.232313	-1.098350
6	2.066858	-0.878221	0.168714
6	2.103690	0.468956	0.664333
1	2.350587	0.594876	1.729130
1	2.287590	-1.678535	0.889441
1	1.407335	-2.295927	-1.341941
1	1.628540	-0.568280	-1.970276
1	1.602473	1.629776	-1.138928
1	1.564705	2.572630	0.454904
23	0.000000	0.002069	0.000000

Table S23. Optimized coordinates for the **$(C_4H_6)_2Ti$** structure **Ti-1S.**

	B3LYP			B3LYP*		
	x	y	z	x	y	z
6	-0.581808	1.498918	1.454611	0.132086	1.601071	-1.450534
6	1.468458	1.315877	-0.846109	-1.793114	0.825168	0.840308
6	0.258962	2.131644	-0.842344	-0.878040	1.961977	0.839939
6	-0.673748	2.209854	0.200219	0.000000	2.310250	-0.197606
1	-1.646521	2.625050	-0.069738	0.806286	2.995712	0.077854
1	-0.084664	2.493343	-1.812885	-0.662448	2.410576	1.813396
1	2.035906	1.290167	-1.774645	-2.341354	0.636246	1.763619
1	2.112836	1.349230	0.043996	-2.405225	0.657299	-0.059958
1	0.382570	1.484213	1.974341	-0.782855	1.294157	-1.974034
1	-1.427629	1.564275	2.135679	0.924507	1.912838	-2.130586
6	-1.468458	-1.315877	-0.846109	1.793114	-0.825168	0.840308
6	0.581808	-1.498918	1.454611	-0.132086	-1.601071	-1.450534
6	0.673748	-2.209854	0.200219	0.000000	-2.310250	-0.197606
6	-0.258962	-2.131644	-0.842344	0.878040	-1.961977	0.839939
1	0.084664	-2.493343	-1.812885	0.662448	-2.410576	1.813396
1	1.646521	-2.625050	-0.069738	-0.806286	-2.995712	0.077854
1	1.427629	-1.564275	2.135679	-0.924507	-1.912838	-2.130586
1	-0.382570	-1.484213	1.974341	0.782855	-1.294157	-1.974034
1	-2.112836	-1.349230	0.043996	2.405225	-0.657299	-0.059958
1	-2.035906	-1.290167	-1.774645	2.341354	-0.636246	1.763619
22	0.000000	0.000000	-0.027391	0.000000	0.000000	0.028825

	BP86		
	x	y	z
6	-0.618709	1.475342	1.448124
6	1.478227	1.304531	-0.843051
6	0.271079	2.133459	-0.840188
6	-0.684970	2.205419	0.195509
1	-1.658992	2.629630	-0.089714
1	-0.063515	2.504339	-1.820204
1	2.071454	1.290427	-1.765131
1	2.105629	1.298991	0.071478
1	0.350296	1.432853	1.978637
1	-1.473963	1.542188	2.130287
6	-1.478227	-1.304531	-0.843051
6	0.618709	-1.475342	1.448124
6	0.684970	-2.205419	0.195509
6	-0.271079	-2.133459	-0.840188
1	0.063515	-2.504339	-1.820204
1	1.658992	-2.629630	-0.089714
1	1.473963	-1.542188	2.130287
1	-0.350296	-1.432853	1.978637
1	-2.105629	-1.298991	0.071478
1	-2.071454	-1.290427	-1.765131
22	0.000000	0.000000	-0.032636

Table S24. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the **$(C_4H_6)_2Ni$** structure Ni-1S.

B3LYP		B3LYP*		BP86	
81	(1)	78	(1)	82	(1)
129	(2)	127	(2)	134	(2)
133	(1)	131	(1)	139	(2)
173	(3)	185	(3)	230	(1)
199	(3)	205	(2)	230	(2)
258	(5)	260	(5)	277	(5)
287	(1)	282	(1)	284	(1)
302	(0)	297	(0)	301	(1)
387	(1)	388	(0)	399	(1)
402	(5)	401	(5)	404	(5)
414	(3)	409	(2)	410	(1)
446	(0)	442	(0)	439	(1)
462	(12)	461	(13)	465	(13)
607	(9)	602	(8)	595	(7)
622	(0)	617	(0)	609	(0)
674	(0)	668	(0)	654	(0)
701	(15)	694	(13)	680	(7)
725	(0)	713	(0)	697	(0)
744	(5)	732	(6)	718	(6)
845	(29)	837	(0)	814	(1)
850	(0)	838	(26)	816	(14)
858	(10)	844	(14)	822	(27)
879	(7)	868	(7)	845	(6)
927	(0)	917	(0)	877	(0)
928	(1)	920	(1)	887	(1)
934	(0)	923	(0)	901	(1)
945	(3)	932	(4)	901	(0)
954	(0)	944	(0)	902	(0)
956	(0)	945	(0)	903	(3)
1059	(2)	1051	(3)	1025	(5)
1059	(0)	1051	(0)	1026	(0)
1078	(11)	1069	(10)	1037	(9)
1080	(6)	1070	(6)	1038	(5)
1225	(6)	1213	(6)	1175	(5)
1226	(5)	1214	(5)	1176	(4)
1268	(0)	1256	(0)	1215	(0)
1278	(29)	1266	(24)	1227	(16)
1410	(1)	1396	(1)	1354	(1)
1411	(0)	1398	(0)	1355	(0)
1458	(1)	1445	(2)	1406	(1)
1461	(24)	1449	(19)	1414	(11)
1538	(19)	1522	(18)	1472	(17)
1544	(28)	1529	(24)	1481	(8)
1563	(31)	1545	(28)	1493	(1)
1563	(2)	1545	(2)	1494	(23)
3157	(1)	3135	(1)	3074	(15)
3158	(9)	3136	(9)	3074	(2)
3159	(2)	3137	(2)	3077	(12)
3159	(7)	3137	(7)	3077	(0)
3174	(6)	3152	(5)	3095	(6)
3174	(2)	3153	(2)	3095	(2)
3188	(9)	3166	(9)	3108	(13)
3188	(9)	3166	(9)	3108	(12)
3246	(12)	3224	(12)	3162	(13)
3246	(2)	3224	(2)	3163	(1)
3250	(0)	3228	(0)	3166	(1)
3250	(11)	3228	(11)	3167	(15)

Table S25. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the **$(C_4H_6)_2Co$** structure Co-1D.

B3LYP		B3LYP*		BP86	
98	(3)	97	(2)	95	(2)
134	(0)	132	(0)	134	(0)
144	(1)	143	(1)	156	(1)
219	(1)	229	(1)	236	(4)
231	(3)	238	(3)	249	(0)
275	(4)	283	(4)	316	(0)
291	(6)	299	(5)	319	(3)
305	(1)	310	(2)	336	(5)
411	(0)	415	(0)	422	(4)
423	(7)	426	(7)	425	(2)
425	(9)	427	(8)	432	(8)
455	(0)	455	(0)	445	(0)
460	(17)	459	(19)	455	(22)
604	(9)	602	(9)	590	(8)
625	(1)	624	(1)	618	(0)
689	(0)	686	(0)	667	(10)
704	(27)	698	(23)	673	(0)
714	(1)	706	(1)	677	(4)
717	(0)	712	(0)	690	(1)
836	(16)	834	(21)	814	(11)
848	(18)	842	(15)	823	(30)
856	(0)	849	(0)	837	(0)
877	(9)	873	(8)	852	(7)
918	(1)	910	(0)	877	(0)
929	(3)	918	(3)	886	(1)
931	(4)	925	(4)	900	(2)
931	(0)	925	(0)	903	(0)
961	(2)	945	(1)	907	(4)
963	(0)	947	(0)	909	(0)
1062	(6)	1054	(6)	1029	(7)
1064	(0)	1055	(0)	1031	(0)
1077	(9)	1066	(9)	1034	(7)
1079	(7)	1069	(7)	1036	(6)
1215	(8)	1204	(7)	1166	(5)
1217	(6)	1205	(6)	1167	(5)
1266	(0)	1251	(0)	1211	(0)
1269	(46)	1257	(36)	1218	(21)
1409	(0)	1396	(0)	1353	(0)
1410	(0)	1397	(0)	1353	(0)
1462	(25)	1451	(17)	1416	(1)
1465	(2)	1453	(2)	1416	(6)
1527	(14)	1512	(15)	1465	(14)
1528	(42)	1514	(31)	1469	(12)
1549	(38)	1533	(2)	1478	(1)
1550	(3)	1533	(35)	1480	(25)
3146	(0)	3124	(1)	3059	(10)
3146	(8)	3125	(3)	3060	(0)
3149	(7)	3126	(6)	3061	(5)
3149	(1)	3126	(7)	3062	(12)
3170	(2)	3148	(2)	3089	(4)
3170	(3)	3149	(2)	3090	(2)
3185	(13)	3162	(13)	3103	(19)
3185	(7)	3162	(8)	3103	(11)
3235	(10)	3213	(6)	3148	(1)
3235	(6)	3213	(14)	3149	(22)
3237	(1)	3214	(5)	3150	(11)
3238	(11)	3215	(3)	3151	(0)

Table S26. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the **$(C_4H_6)_2Co$** structure Co-2D.

B3LYP		B3LYP*		BP86	
18	(0)	36	(0)	49	(0)
153	(1)	150	(1)	156	(1)
190	(1)	185	(1)	198	(2)
298	(2)	293	(2)	287	(2)
315	(1)	313	(1)	317	(0)
351	(0)	352	(0)	357	(0)
366	(1)	370	(1)	378	(2)
385	(8)	388	(10)	389	(7)
389	(10)	393	(3)	412	(0)
447	(9)	441	(10)	435	(8)
454	(0)	452	(0)	437	(0)
458	(6)	454	(6)	443	(11)
476	(8)	473	(8)	471	(9)
627	(0)	623	(0)	611	(0)
649	(1)	641	(1)	621	(1)
703	(52)	696	(36)	690	(15)
719	(22)	707	(19)	693	(12)
740	(0)	725	(0)	700	(0)
748	(0)	737	(0)	730	(0)
841	(3)	833	(5)	818	(11)
868	(0)	856	(0)	837	(0)
876	(14)	865	(12)	852	(8)
904	(3)	890	(1)	870	(0)
909	(3)	896	(2)	878	(0)
936	(19)	922	(19)	899	(0)
951	(13)	936	(0)	902	(15)
952	(0)	939	(0)	905	(0)
955	(0)	941	(11)	915	(8)
956	(2)	946	(1)	921	(3)
1056	(0)	1046	(0)	1018	(0)
1062	(13)	1053	(13)	1026	(11)
1069	(22)	1061	(19)	1035	(14)
1072	(0)	1064	(0)	1039	(0)
1176	(0)	1166	(0)	1136	(0)
1181	(12)	1171	(11)	1142	(9)
1203	(65)	1197	(54)	1171	(32)
1222	(0)	1215	(0)	1189	(0)
1393	(0)	1380	(0)	1341	(0)
1396	(0)	1383	(0)	1344	(0)
1471	(36)	1459	(25)	1420	(8)
1483	(1)	1471	(2)	1433	(4)
1507	(0)	1493	(0)	1452	(0)
1509	(26)	1493	(24)	1455	(6)
1510	(7)	1496	(7)	1456	(15)
1520	(15)	1506	(14)	1470	(11)
3135	(0)	3112	(0)	3053	(13)
3135	(10)	3113	(10)	3053	(0)
3137	(4)	3114	(4)	3054	(8)
3137	(19)	3115	(19)	3054	(24)
3167	(0)	3143	(0)	3085	(0)
3168	(1)	3145	(1)	3086	(3)
3183	(4)	3159	(4)	3100	(6)
3184	(24)	3161	(24)	3101	(33)
3223	(0)	3201	(0)	3144	(0)
3226	(0)	3203	(0)	3146	(0)
3226	(29)	3204	(28)	3146	(35)
3229	(8)	3207	(8)	3148	(8)

Table S27. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the **$(C_4H_6)_2Fe$** structure Fe-1S.

B3LYP		B3LYP*		BP86	
99	(4)	100	(4)	106	(3)
141	(4)	137	(3)	141	(2)
191	(1)	187	(1)	199	(1)
229	(12)	220	(10)	211	(6)
276	(0)	271	(0)	277	(0)
333	(0)	332	(0)	338	(0)
362	(0)	365	(0)	373	(1)
417	(14)	417	(11)	421	(8)
421	(0)	425	(3)	425	(20)
438	(28)	432	(26)	440	(4)
473	(13)	471	(15)	465	(6)
480	(3)	476	(4)	467	(18)
483	(7)	485	(6)	499	(6)
601	(4)	595	(3)	575	(1)
633	(2)	628	(2)	613	(1)
654	(21)	644	(18)	622	(12)
711	(0)	703	(0)	681	(22)
719	(27)	704	(24)	687	(0)
772	(9)	761	(9)	753	(9)
829	(12)	821	(14)	808	(14)
877	(3)	867	(3)	846	(3)
877	(22)	872	(21)	849	(19)
906	(2)	897	(3)	865	(3)
937	(0)	928	(0)	908	(7)
941	(6)	930	(6)	908	(1)
951	(0)	941	(11)	909	(3)
952	(13)	941	(0)	921	(1)
975	(0)	957	(0)	926	(5)
981	(0)	964	(0)	930	(0)
1066	(11)	1057	(9)	1030	(4)
1069	(5)	1059	(6)	1030	(6)
1075	(6)	1065	(7)	1037	(10)
1075	(4)	1066	(3)	1037	(0)
1197	(5)	1186	(4)	1152	(3)
1199	(5)	1188	(5)	1155	(4)
1250	(36)	1239	(28)	1206	(15)
1255	(1)	1243	(1)	1210	(1)
1405	(2)	1392	(1)	1351	(1)
1406	(0)	1393	(0)	1352	(1)
1474	(12)	1461	(8)	1424	(3)
1478	(1)	1465	(1)	1428	(2)
1518	(25)	1502	(19)	1459	(7)
1522	(2)	1506	(2)	1463	(3)
1526	(23)	1512	(21)	1472	(13)
1530	(17)	1515	(17)	1475	(13)
3100	(20)	3075	(21)	3006	(33)
3100	(0)	3075	(0)	3007	(0)
3128	(4)	3105	(4)	3040	(4)
3129	(3)	3106	(3)	3042	(4)
3157	(8)	3133	(9)	3069	(13)
3158	(0)	3134	(0)	3070	(1)
3175	(1)	3152	(1)	3087	(28)
3176	(20)	3153	(19)	3088	(3)
3194	(0)	3171	(0)	3105	(1)
3197	(34)	3173	(35)	3107	(44)
3228	(7)	3205	(6)	3144	(8)
3228	(4)	3206	(4)	3144	(6)

Table S28. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the **$(C_4H_6)_2Fe$** structure Fe-2S.

B3LYP		B3LYP*		BP86	
102	(0)	108	(0)	103	(0)
159	(0)	162	(0)	152	(0)
193	(0)	194	(0)	200	(1)
236	(23)	235	(21)	217	(16)
307	(0)	308	(0)	311	(0)
326	(0)	331	(0)	339	(0)
367	(15)	369	(12)	369	(1)
389	(0)	392	(0)	392	(0)
415	(5)	420	(3)	412	(34)
427	(27)	424	(29)	425	(0)
441	(0)	440	(0)	426	(0)
445	(31)	443	(31)	443	(38)
517	(14)	517	(15)	517	(16)
621	(13)	614	(13)	589	(12)
636	(0)	631	(0)	610	(0)
695	(32)	690	(20)	675	(4)
726	(0)	717	(0)	687	(0)
727	(14)	719	(13)	689	(11)
738	(0)	737	(0)	715	(1)
846	(3)	847	(7)	823	(12)
854	(0)	849	(0)	828	(0)
886	(5)	887	(3)	855	(14)
892	(33)	891	(33)	858	(1)
903	(1)	899	(0)	862	(2)
920	(8)	919	(5)	883	(14)
941	(2)	935	(2)	885	(0)
942	(2)	939	(0)	887	(0)
946	(0)	942	(2)	907	(2)
947	(1)	942	(0)	913	(2)
1067	(0)	1058	(0)	1026	(0)
1068	(7)	1061	(7)	1032	(11)
1072	(0)	1063	(14)	1032	(6)
1073	(14)	1065	(0)	1036	(0)
1192	(0)	1182	(0)	1149	(0)
1194	(15)	1184	(13)	1151	(9)
1232	(53)	1224	(42)	1194	(22)
1246	(0)	1236	(0)	1204	(0)
1397	(0)	1385	(0)	1342	(0)
1401	(0)	1390	(0)	1346	(0)
1471	(14)	1461	(6)	1421	(0)
1477	(2)	1467	(3)	1427	(5)
1524	(0)	1510	(0)	1465	(0)
1525	(54)	1513	(43)	1469	(12)
1529	(16)	1515	(15)	1474	(19)
1533	(17)	1521	(16)	1482	(12)
3115	(2)	3093	(2)	3030	(4)
3116	(0)	3093	(0)	3031	(0)
3121	(2)	3099	(2)	3035	(7)
3124	(26)	3101	(25)	3038	(29)
3156	(0)	3134	(0)	3067	(0)
3159	(3)	3136	(3)	3069	(7)
3171	(3)	3148	(3)	3080	(6)
3175	(29)	3151	(31)	3083	(45)
3212	(0)	3191	(0)	3132	(0)
3216	(1)	3194	(37)	3134	(0)
3216	(38)	3195	(0)	3134	(47)
3220	(11)	3199	(11)	3137	(11)

Table S29. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the **$(C_4H_6)_2Fe$** structure Fe-1T.

B3LYP		B3LYP*		BP86	
4	(0)	88	(2)	86	(2)
138	(1)	91	(1)	98	(1)
164	(0)	125	(2)	140	(2)
277	(0)	216	(0)	221	(0)
278	(7)	260	(0)	247	(1)
304	(0)	267	(3)	305	(1)
318	(17)	288	(2)	311	(1)
334	(1)	307	(2)	342	(2)
336	(0)	397	(1)	405	(2)
423	(0)	414	(4)	422	(5)
436	(22)	430	(8)	430	(9)
438	(0)	455	(0)	448	(1)
476	(14)	460	(5)	456	(10)
604	(12)	600	(11)	585	(9)
612	(0)	617	(0)	610	(0)
669	(9)	666	(0)	650	(0)
688	(0)	689	(10)	661	(4)
696	(0)	706	(0)	681	(1)
712	(14)	707	(17)	685	(11)
822	(0)	825	(1)	808	(32)
827	(31)	828	(30)	812	(1)
860	(2)	836	(5)	818	(4)
862	(0)	862	(5)	836	(2)
888	(2)	875	(0)	844	(1)
897	(0)	883	(1)	861	(1)
931	(0)	917	(0)	878	(0)
934	(1)	922	(0)	888	(0)
940	(7)	923	(7)	900	(0)
940	(0)	929	(0)	903	(7)
1063	(10)	1047	(0)	1020	(12)
1064	(21)	1048	(9)	1020	(1)
1065	(0)	1066	(14)	1035	(12)
1069	(0)	1067	(7)	1036	(5)
1190	(0)	1197	(8)	1161	(6)
1196	(14)	1199	(8)	1162	(7)
1239	(52)	1247	(0)	1209	(0)
1250	(0)	1251	(39)	1214	(24)
1397	(0)	1391	(0)	1348	(0)
1398	(0)	1391	(0)	1348	(0)
1464	(31)	1445	(2)	1408	(3)
1466	(0)	1446	(15)	1411	(6)
1520	(0)	1505	(16)	1454	(14)
1520	(55)	1507	(17)	1456	(3)
1521	(15)	1518	(38)	1467	(1)
1526	(0)	1518	(3)	1469	(30)
3135	(3)	3124	(1)	3058	(2)
3135	(0)	3124	(9)	3059	(13)
3141	(21)	3129	(4)	3063	(7)
3141	(0)	3129	(3)	3063	(3)
3168	(2)	3148	(2)	3090	(4)
3168	(0)	3149	(0)	3090	(0)
3183	(22)	3170	(4)	3112	(10)
3184	(0)	3170	(7)	3112	(5)
3228	(0)	3213	(1)	3149	(1)
3230	(26)	3213	(10)	3149	(13)
3232	(7)	3218	(1)	3154	(0)
3234	(0)	3219	(10)	3154	(12)

Table S30. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the **$(C_4H_6)_2Fe$** structure Fe-2T.

B3LYP		B3LYP*		BP86	
30	(0)	43	(0)	39	(0)
103	(5)	132	(1)	134	(1)
132	(0)	132	(1)	157	(2)
219	(0)	266	(2)	268	(1)
232	(7)	282	(0)	302	(0)
253	(27)	318	(1)	345	(0)
267	(3)	328	(1)	346	(1)
302	(0)	339	(18)	386	(4)
332	(20)	399	(4)	421	(2)
374	(1)	403	(1)	437	(7)
410	(9)	429	(7)	440	(8)
437	(9)	448	(8)	445	(0)
453	(1)	462	(1)	446	(2)
604	(11)	616	(8)	600	(0)
623	(1)	625	(0)	613	(0)
684	(3)	697	(12)	689	(18)
697	(14)	699	(4)	699	(16)
702	(23)	708	(30)	704	(0)
708	(1)	726	(0)	719	(0)
787	(9)	814	(11)	782	(16)
821	(7)	840	(5)	817	(1)
859	(0)	846	(1)	825	(0)
863	(1)	848	(2)	826	(0)
891	(4)	892	(1)	859	(1)
893	(0)	909	(5)	876	(0)
937	(5)	918	(0)	887	(0)
938	(0)	925	(0)	896	(10)
939	(7)	937	(13)	911	(12)
949	(0)	939	(0)	917	(0)
1060	(18)	1049	(21)	1022	(0)
1061	(0)	1051	(0)	1022	(20)
1077	(13)	1060	(4)	1027	(2)
1079	(6)	1062	(13)	1030	(12)
1200	(17)	1176	(15)	1138	(0)
1203	(7)	1176	(2)	1140	(10)
1246	(1)	1219	(47)	1178	(33)
1250	(57)	1221	(0)	1188	(0)
1402	(1)	1383	(1)	1338	(0)
1403	(0)	1384	(0)	1340	(0)
1463	(0)	1457	(23)	1416	(7)
1467	(36)	1458	(1)	1429	(2)
1516	(30)	1492	(14)	1447	(0)
1520	(26)	1493	(14)	1449	(8)
1528	(18)	1501	(15)	1452	(8)
1529	(0)	1503	(6)	1463	(14)
3145	(2)	3118	(7)	3054	(0)
3146	(2)	3118	(0)	3054	(9)
3147	(8)	3119	(4)	3055	(7)
3147	(7)	3119	(17)	3055	(29)
3164	(4)	3144	(2)	3088	(1)
3164	(0)	3145	(0)	3089	(0)
3181	(12)	3161	(13)	3104	(4)
3181	(2)	3161	(3)	3104	(18)
3234	(5)	3206	(7)	3149	(0)
3234	(8)	3206	(7)	3150	(3)
3241	(12)	3216	(14)	3153	(26)
3242	(0)	3217	(1)	3154	(6)

Table S31. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the **$(C_4H_6)_2Mn$** structure Mn-1D.

B3LYP		B3LYP*		BP86	
86	(0)	81	(0)	88	(0)
99	(0)	106	(0)	100	(0)
152	(1)	157	(1)	174	(2)
235	(6)	221	(6)	201	(5)
261	(0)	276	(0)	301	(0)
311	(0)	321	(0)	334	(0)
336	(8)	352	(7)	367	(0)
363	(0)	368	(0)	372	(0)
370	(15)	393	(16)	408	(24)
421	(18)	418	(20)	417	(4)
423	(14)	428	(17)	437	(36)
437	(2)	444	(1)	443	(0)
449	(0)	449	(0)	448	(1)
596	(7)	592	(7)	565	(6)
616	(0)	613	(0)	589	(0)
689	(22)	688	(10)	681	(4)
691	(13)	694	(21)	682	(21)
699	(0)	701	(0)	688	(0)
710	(0)	713	(0)	703	(1)
827	(22)	823	(22)	805	(25)
835	(0)	838	(0)	825	(1)
855	(5)	854	(3)	830	(0)
872	(0)	863	(1)	842	(0)
873	(0)	866	(0)	849	(3)
888	(19)	892	(16)	876	(0)
908	(0)	903	(0)	880	(0)
928	(0)	916	(0)	880	(10)
932	(5)	925	(5)	899	(4)
936	(0)	929	(0)	904	(0)
1054	(10)	1047	(11)	1021	(13)
1055	(1)	1049	(1)	1025	(2)
1070	(0)	1061	(0)	1034	(0)
1074	(17)	1066	(16)	1040	(12)
1190	(0)	1181	(0)	1153	(0)
1191	(15)	1182	(14)	1153	(11)
1240	(31)	1231	(30)	1205	(20)
1247	(0)	1238	(0)	1210	(0)
1395	(0)	1382	(0)	1344	(0)
1397	(0)	1386	(0)	1347	(0)
1461	(5)	1451	(3)	1416	(0)
1466	(3)	1457	(3)	1422	(4)
1515	(20)	1501	(0)	1460	(0)
1515	(0)	1501	(20)	1464	(14)
1519	(17)	1505	(16)	1466	(9)
1523	(16)	1511	(16)	1476	(13)
3120	(1)	3095	(0)	3030	(1)
3120	(0)	3096	(0)	3031	(0)
3127	(2)	3103	(2)	3038	(4)
3129	(23)	3104	(24)	3040	(31)
3168	(1)	3146	(1)	3087	(2)
3168	(0)	3146	(0)	3088	(0)
3183	(1)	3161	(1)	3102	(2)
3184	(14)	3162	(14)	3103	(18)
3225	(0)	3204	(0)	3149	(0)
3228	(0)	3207	(0)	3151	(0)
3228	(25)	3207	(25)	3152	(31)
3232	(6)	3211	(6)	3156	(5)

Table S32. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the **$(C_4H_6)_2Mn$** structure Mn-2D.

B3LYP		B3LYP*		BP86	
52	(1)	39	(1)	51	(0)
73	(1)	72	(1)	141	(1)
144	(0)	145	(0)	152	(0)
251	(0)	242	(0)	201	(1)
261	(0)	267	(0)	292	(1)
281	(4)	284	(3)	310	(0)
282	(0)	292	(1)	331	(6)
317	(0)	323	(0)	343	(0)
329	(2)	330	(3)	350	(13)
405	(0)	409	(4)	418	(1)
415	(12)	419	(9)	422	(2)
433	(0)	432	(0)	425	(7)
449	(11)	443	(12)	480	(17)
593	(0)	590	(1)	573	(0)
599	(6)	598	(6)	619	(10)
650	(13)	647	(14)	656	(10)
653	(0)	653	(1)	663	(6)
658	(3)	654	(3)	666	(1)
664	(0)	666	(0)	681	(2)
796	(0)	796	(0)	791	(14)
808	(52)	800	(38)	802	(1)
832	(4)	826	(4)	805	(7)
836	(24)	831	(27)	831	(12)
845	(0)	838	(1)	841	(3)
846	(0)	845	(1)	850	(17)
876	(0)	868	(0)	850	(0)
904	(1)	892	(1)	875	(0)
932	(0)	924	(4)	904	(3)
932	(7)	926	(4)	914	(4)
1048	(10)	1040	(11)	1013	(10)
1050	(0)	1043	(1)	1020	(13)
1059	(0)	1051	(10)	1028	(2)
1061	(24)	1055	(13)	1036	(5)
1180	(0)	1172	(0)	1142	(3)
1190	(13)	1181	(13)	1159	(10)
1239	(12)	1227	(12)	1185	(11)
1242	(0)	1233	(3)	1209	(11)
1386	(0)	1375	(0)	1336	(0)
1390	(0)	1379	(0)	1343	(0)
1457	(0)	1446	(0)	1410	(6)
1460	(3)	1447	(3)	1414	(2)
1502	(0)	1489	(1)	1450	(5)
1507	(17)	1495	(16)	1460	(11)
1508	(20)	1495	(18)	1464	(10)
1509	(0)	1499	(3)	1467	(8)
3135	(0)	3113	(1)	3043	(3)
3135	(2)	3116	(1)	3047	(19)
3141	(18)	3119	(12)	3057	(3)
3142	(0)	3121	(6)	3060	(15)
3175	(0)	3152	(0)	3080	(0)
3176	(1)	3156	(0)	3095	(6)
3190	(9)	3167	(4)	3096	(1)
3191	(0)	3171	(5)	3109	(17)
3232	(0)	3210	(6)	3136	(15)
3233	(17)	3213	(11)	3139	(6)
3235	(4)	3213	(3)	3152	(9)
3237	(0)	3216	(1)	3154	(3)

Table S33. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the **$(C_4H_6)_2Mn$** structure Mn-1Q.

B3LYP		B3LYP*		BP86	
55	(1)	55	(1)	58	(1)
87	(0)	79	(0)	60	(0)
114	(1)	116	(1)	130	(3)
181	(5)	192	(5)	215	(1)
187	(1)	196	(1)	227	(5)
236	(8)	239	(7)	244	(7)
246	(5)	259	(5)	283	(2)
258	(0)	267	(0)	293	(3)
366	(8)	371	(8)	381	(12)
371	(3)	377	(4)	387	(6)
430	(1)	436	(3)	432	(4)
440	(2)	443	(2)	443	(1)
442	(4)	450	(2)	460	(1)
599	(7)	597	(7)	587	(7)
604	(2)	603	(2)	593	(1)
646	(1)	642	(1)	637	(0)
677	(20)	673	(18)	650	(4)
679	(0)	676	(0)	663	(1)
686	(13)	681	(13)	670	(18)
798	(7)	795	(39)	768	(40)
799	(40)	796	(5)	776	(2)
814	(45)	809	(37)	805	(31)
848	(10)	842	(8)	820	(2)
882	(0)	870	(0)	841	(1)
889	(8)	875	(6)	858	(1)
926	(0)	922	(0)	904	(0)
927	(8)	923	(9)	905	(4)
956	(2)	942	(2)	906	(8)
960	(0)	945	(0)	911	(0)
1059	(6)	1052	(8)	1027	(10)
1059	(0)	1052	(0)	1028	(0)
1080	(16)	1070	(15)	1040	(13)
1080	(12)	1071	(10)	1042	(8)
1203	(15)	1193	(14)	1159	(11)
1204	(16)	1194	(14)	1160	(11)
1267	(0)	1255	(0)	1218	(0)
1270	(29)	1258	(28)	1222	(21)
1405	(0)	1392	(0)	1351	(0)
1406	(1)	1394	(0)	1352	(0)
1470	(7)	1459	(7)	1424	(4)
1472	(4)	1461	(5)	1426	(4)
1520	(18)	1505	(17)	1461	(4)
1521	(11)	1505	(9)	1463	(15)
1533	(70)	1520	(69)	1475	(0)
1536	(2)	1522	(1)	1477	(54)
3140	(6)	3119	(7)	3058	(9)
3141	(1)	3120	(1)	3058	(5)
3143	(2)	3122	(2)	3061	(1)
3143	(3)	3123	(1)	3061	(4)
3163	(0)	3142	(0)	3087	(0)
3164	(2)	3142	(1)	3088	(2)
3181	(8)	3159	(8)	3103	(12)
3181	(7)	3159	(7)	3103	(8)
3232	(8)	3211	(8)	3150	(2)
3232	(2)	3211	(2)	3150	(9)
3238	(1)	3216	(2)	3155	(2)
3238	(10)	3217	(11)	3155	(13)

Table S34. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the **$(C_4H_6)_2Mn$** structure Mn-1X.

B3LYP		B3LYP*		BP86	
21	(1)	19	(0)	21	(0)
63	(1)	66	(1)	68	(0)
68	(0)	71	(0)	84	(0)
90	(1)	91	(1)	90	(1)
115	(2)	114	(2)	114	(2)
222	(0)	223	(0)	217	(0)
248	(3)	249	(3)	247	(2)
274	(0)	273	(0)	263	(0)
308	(4)	308	(2)	297	(1)
313	(23)	325	(0)	326	(0)
324	(0)	332	(22)	354	(13)
423	(0)	420	(0)	416	(0)
444	(0)	443	(0)	436	(2)
570	(0)	566	(0)	553	(0)
583	(2)	578	(2)	563	(2)
615	(0)	611	(0)	588	(0)
628	(41)	624	(43)	602	(41)
676	(0)	671	(0)	646	(0)
680	(22)	676	(21)	655	(18)
791	(33)	786	(23)	747	(0)
809	(0)	797	(0)	747	(66)
815	(91)	803	(88)	771	(30)
831	(0)	824	(0)	793	(0)
843	(0)	835	(0)	807	(0)
852	(6)	846	(6)	817	(2)
898	(0)	893	(0)	876	(0)
898	(9)	894	(8)	876	(7)
975	(13)	962	(0)	924	(0)
975	(0)	962	(13)	925	(15)
1049	(0)	1042	(0)	1017	(0)
1049	(6)	1042	(6)	1017	(6)
1082	(0)	1073	(0)	1043	(0)
1083	(18)	1074	(18)	1045	(16)
1208	(102)	1198	(84)	1169	(50)
1211	(0)	1200	(0)	1169	(0)
1284	(124)	1275	(103)	1244	(57)
1298	(0)	1287	(0)	1253	(0)
1401	(33)	1389	(25)	1349	(12)
1403	(0)	1390	(0)	1351	(0)
1442	(167)	1433	(141)	1404	(71)
1456	(0)	1445	(0)	1410	(0)
1502	(133)	1491	(124)	1452	(93)
1510	(0)	1498	(0)	1457	(0)
1567	(126)	1555	(127)	1514	(110)
1580	(0)	1567	(0)	1521	(0)
3131	(0)	3111	(0)	3054	(0)
3132	(8)	3112	(8)	3054	(10)
3154	(4)	3134	(4)	3081	(4)
3155	(0)	3135	(0)	3082	(0)
3162	(0)	3142	(0)	3088	(0)
3162	(17)	3142	(17)	3088	(15)
3172	(0)	3152	(0)	3097	(0)
3172	(11)	3152	(10)	3098	(12)
3225	(0)	3206	(0)	3151	(0)
3226	(7)	3206	(6)	3151	(7)
3257	(0)	3238	(0)	3185	(0)
3257	(17)	3238	(16)	3185	(17)

Table S35. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the **$(C_4H_6)_2Mn$** structure Mn-2X.

B3LYP		B3LYP*		BP86	
37	(0)	28	(0)	14	(0)
67	(0)	63	(0)	55	(0)
90	(0)	87	(0)	64	(0)
91	(0)	96	(0)	89	(0)
112	(59)	131	(44)	126	(0)
176	(0)	170	(0)	216	(0)
207	(0)	207	(0)	231	(1)
252	(1)	249	(1)	273	(0)
256	(1)	252	(1)	279	(0)
331	(23)	327	(20)	342	(0)
345	(0)	340	(0)	357	(18)
402	(5)	400	(5)	425	(3)
413	(0)	409	(0)	439	(0)
580	(1)	573	(1)	551	(2)
585	(0)	578	(0)	564	(0)
633	(179)	624	(163)	585	(27)
637	(2)	628	(2)	603	(2)
664	(6)	652	(5)	656	(0)
676	(0)	667	(0)	659	(36)
739	(23)	732	(14)	744	(62)
788	(0)	776	(0)	745	(1)
809	(18)	800	(15)	775	(8)
821	(17)	811	(17)	813	(17)
891	(0)	875	(0)	824	(5)
893	(15)	879	(15)	839	(25)
917	(0)	909	(0)	876	(7)
918	(1)	910	(2)	879	(0)
945	(1)	932	(0)	935	(14)
948	(0)	932	(1)	942	(1)
1060	(5)	1052	(4)	1017	(9)
1062	(1)	1055	(2)	1019	(0)
1086	(0)	1076	(0)	1046	(11)
1088	(15)	1078	(16)	1048	(3)
1227	(29)	1216	(28)	1168	(48)
1227	(0)	1216	(0)	1172	(1)
1266	(258)	1258	(220)	1243	(67)
1292	(3)	1281	(3)	1254	(1)
1410	(0)	1396	(0)	1351	(17)
1412	(0)	1398	(0)	1353	(0)
1453	(245)	1442	(204)	1399	(81)
1468	(20)	1455	(20)	1410	(8)
1529	(323)	1514	(315)	1446	(81)
1552	(3)	1538	(3)	1452	(12)
1557	(0)	1542	(0)	1510	(104)
1562	(32)	1547	(31)	1524	(0)
3151	(0)	3129	(0)	3041	(1)
3151	(2)	3130	(3)	3042	(9)
3154	(9)	3133	(8)	3080	(3)
3155	(4)	3134	(4)	3081	(14)
3171	(0)	3149	(0)	3086	(1)
3175	(1)	3153	(1)	3087	(5)
3188	(0)	3166	(0)	3106	(1)
3192	(16)	3170	(16)	3106	(10)
3247	(0)	3226	(0)	3139	(9)
3247	(14)	3227	(12)	3139	(0)
3249	(3)	3229	(2)	3183	(4)
3250	(1)	3229	(1)	3184	(11)

Table S36. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the **$(C_4H_6)_2Cr$** structure Cr-1S.

B3LYP		B3LYP*		BP86	
93	(0)	90	(0)	101	(0)
154	(0)	151	(0)	165	(0)
160	(3)	170	(3)	169	(2)
241	(0)	223	(0)	238	(0)
295	(1)	295	(1)	316	(1)
311	(0)	323	(0)	351	(0)
345	(0)	346	(0)	373	(0)
368	(7)	372	(1)	412	(1)
396	(12)	404	(9)	444	(13)
430	(13)	415	(14)	447	(17)
456	(0)	444	(0)	468	(0)
460	(20)	451	(22)	489	(22)
481	(0)	485	(0)	535	(0)
585	(4)	557	(2)	568	(12)
627	(0)	610	(0)	638	(0)
720	(18)	693	(20)	725	(1)
723	(3)	695	(0)	726	(22)
724	(0)	701	(3)	726	(0)
725	(6)	701	(2)	732	(2)
827	(22)	792	(27)	822	(11)
846	(0)	805	(1)	834	(4)
861	(3)	825	(0)	843	(0)
863	(0)	835	(0)	856	(0)
874	(1)	838	(3)	867	(0)
897	(0)	867	(0)	889	(1)
906	(2)	869	(0)	898	(0)
911	(0)	882	(2)	903	(2)
926	(9)	901	(9)	935	(13)
932	(0)	908	(0)	941	(0)
1045	(14)	1016	(19)	1054	(23)
1050	(3)	1022	(3)	1058	(3)
1064	(0)	1035	(0)	1070	(0)
1072	(12)	1043	(10)	1078	(10)
1186	(0)	1152	(0)	1193	(0)
1188	(15)	1154	(13)	1194	(14)
1239	(35)	1207	(25)	1247	(33)
1243	(0)	1211	(0)	1250	(0)
1385	(0)	1342	(0)	1381	(0)
1389	(0)	1346	(0)	1385	(1)
1452	(8)	1412	(1)	1456	(1)
1460	(2)	1420	(4)	1462	(2)
1504	(0)	1456	(0)	1502	(0)
1504	(21)	1461	(9)	1507	(17)
1509	(15)	1462	(14)	1510	(19)
1516	(15)	1473	(11)	1522	(11)
3097	(1)	3031	(2)	3108	(9)
3098	(0)	3032	(0)	3109	(0)
3104	(2)	3038	(4)	3114	(12)
3106	(31)	3040	(38)	3115	(79)
3132	(1)	3077	(1)	3155	(6)
3134	(0)	3079	(0)	3157	(0)
3149	(1)	3094	(1)	3172	(5)
3150	(16)	3095	(19)	3173	(45)
3205	(0)	3149	(0)	3232	(0)
3207	(0)	3151	(0)	3234	(71)
3208	(26)	3152	(30)	3235	(0)
3212	(5)	3156	(4)	3237	(11)

Table S37. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the **$(C_4H_6)_2Cr$** structure Cr-2S.

B3LYP		B3LYP*		BP86	
76	(27)	84	(19)	68	(29)
104	(4)	110	(6)	108	(1)
158	(5)	158	(5)	156	(5)
221	(20)	227	(19)	232	(19)
279	(0)	282	(0)	281	(1)
301	(1)	300	(1)	300	(1)
361	(12)	362	(12)	316	(5)
379	(14)	382	(13)	395	(7)
389	(1)	393	(1)	400	(0)
423	(1)	424	(2)	429	(1)
440	(33)	441	(28)	442	(32)
483	(1)	484	(1)	480	(2)
492	(3)	490	(3)	485	(1)
544	(24)	540	(17)	521	(7)
587	(4)	580	(3)	579	(2)
615	(9)	613	(9)	599	(7)
663	(1)	657	(1)	640	(2)
683	(4)	676	(4)	650	(4)
700	(5)	694	(5)	675	(5)
817	(8)	815	(14)	801	(24)
847	(2)	839	(3)	813	(13)
866	(5)	856	(5)	819	(5)
883	(10)	873	(9)	838	(3)
898	(5)	890	(3)	863	(7)
904	(12)	893	(13)	874	(2)
940	(0)	934	(0)	906	(6)
945	(13)	939	(13)	911	(0)
967	(0)	951	(0)	916	(1)
973	(1)	961	(1)	918	(15)
1061	(19)	1054	(14)	1026	(6)
1064	(6)	1056	(11)	1028	(6)
1070	(4)	1061	(2)	1031	(11)
1072	(5)	1062	(4)	1033	(0)
1177	(6)	1166	(5)	1127	(6)
1186	(7)	1175	(7)	1137	(6)
1243	(23)	1231	(19)	1197	(16)
1251	(13)	1239	(11)	1200	(1)
1399	(0)	1386	(0)	1344	(2)
1404	(1)	1391	(1)	1345	(0)
1464	(14)	1453	(16)	1412	(15)
1473	(4)	1458	(4)	1416	(4)
1500	(5)	1486	(4)	1441	(0)
1506	(2)	1493	(2)	1443	(4)
1528	(38)	1517	(28)	1481	(13)
1531	(19)	1519	(16)	1481	(4)
2908	(11)	2861	(11)	2840	(9)
3027	(7)	3004	(7)	2843	(9)
3085	(4)	3062	(4)	2998	(11)
3093	(9)	3068	(9)	2998	(9)
3142	(9)	3119	(7)	3057	(7)
3142	(6)	3120	(7)	3057	(4)
3164	(19)	3139	(22)	3071	(55)
3167	(17)	3144	(18)	3072	(14)
3191	(15)	3170	(14)	3113	(13)
3199	(9)	3177	(8)	3113	(6)
3204	(12)	3182	(12)	3119	(11)
3211	(9)	3189	(9)	3120	(16)

Table S38. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the **$(C_4H_6)_2Cr$** structure Cr-1T.

B3LYP		B3LYP*		BP86	
87	(3)	92	(3)	100	(3)
102	(0)	104	(0)	109	(0)
136	(2)	140	(2)	145	(3)
207	(14)	196	(15)	184	(13)
218	(0)	223	(0)	235	(0)
298	(0)	301	(0)	306	(0)
325	(2)	332	(3)	344	(6)
369	(12)	379	(9)	390	(4)
381	(0)	389	(2)	406	(20)
404	(17)	405	(20)	409	(3)
414	(6)	434	(4)	439	(8)
453	(3)	451	(4)	458	(1)
472	(4)	470	(3)	463	(2)
588	(5)	581	(8)	560	(7)
600	(37)	591	(30)	572	(21)
608	(5)	607	(5)	596	(4)
652	(1)	648	(1)	636	(1)
676	(3)	669	(3)	653	(2)
677	(3)	672	(2)	658	(3)
779	(22)	778	(23)	761	(21)
817	(34)	817	(33)	790	(34)
835	(9)	831	(7)	807	(3)
848	(0)	846	(0)	816	(1)
870	(2)	871	(1)	863	(12)
878	(12)	879	(12)	865	(0)
934	(15)	927	(0)	904	(0)
934	(0)	927	(16)	905	(15)
965	(3)	955	(2)	915	(4)
966	(0)	957	(0)	919	(0)
1052	(9)	1043	(10)	1018	(11)
1055	(4)	1047	(4)	1021	(3)
1074	(7)	1066	(7)	1038	(7)
1074	(13)	1066	(12)	1038	(9)
1184	(4)	1175	(4)	1144	(4)
1188	(12)	1179	(11)	1148	(8)
1255	(23)	1246	(20)	1216	(13)
1259	(3)	1249	(3)	1219	(2)
1400	(1)	1388	(1)	1348	(1)
1402	(0)	1389	(0)	1349	(0)
1474	(8)	1461	(9)	1420	(11)
1476	(1)	1463	(1)	1423	(2)
1496	(14)	1482	(12)	1438	(6)
1500	(3)	1486	(3)	1442	(5)
1526	(32)	1515	(29)	1478	(17)
1530	(26)	1518	(24)	1481	(18)
3096	(13)	3070	(13)	3004	(17)
3097	(0)	3070	(0)	3004	(0)
3122	(7)	3098	(7)	3036	(6)
3123	(1)	3099	(1)	3037	(1)
3154	(10)	3132	(10)	3075	(12)
3155	(0)	3133	(0)	3075	(0)
3185	(1)	3162	(1)	3102	(1)
3185	(11)	3163	(11)	3103	(15)
3207	(0)	3183	(0)	3122	(0)
3208	(18)	3185	(18)	3124	(22)
3232	(5)	3210	(5)	3153	(5)
3232	(4)	3211	(4)	3154	(5)

Table S39. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the **$(C_4H_6)_2Cr$** structure Cr-2T.

B3LYP		B3LYP*		BP86	
38	(1)	34	(0)	37	(0)
59	(0)	70	(0)	98	(0)
132	(1)	142	(1)	162	(3)
189	(10)	181	(9)	172	(5)
227	(0)	243	(0)	244	(0)
254	(0)	255	(0)	281	(0)
293	(19)	305	(22)	325	(0)
318	(0)	322	(0)	329	(26)
367	(7)	371	(8)	375	(8)
373	(0)	377	(0)	387	(0)
388	(10)	413	(9)	399	(0)
420	(16)	417	(0)	419	(10)
420	(0)	423	(13)	451	(6)
593	(0)	590	(0)	574	(0)
593	(10)	592	(8)	580	(5)
639	(10)	639	(6)	636	(1)
660	(1)	657	(2)	647	(0)
674	(17)	676	(15)	663	(10)
678	(4)	680	(5)	665	(7)
780	(0)	784	(0)	778	(0)
794	(49)	798	(49)	797	(54)
832	(9)	836	(5)	832	(1)
845	(11)	845	(6)	833	(5)
862	(6)	860	(6)	836	(1)
871	(1)	873	(1)	857	(1)
932	(6)	926	(7)	891	(0)
934	(0)	928	(0)	896	(1)
943	(0)	935	(0)	904	(6)
947	(3)	938	(3)	910	(0)
1062	(7)	1055	(8)	1034	(8)
1062	(0)	1056	(0)	1035	(1)
1075	(1)	1067	(1)	1038	(0)
1077	(23)	1070	(21)	1045	(17)
1187	(0)	1178	(0)	1149	(0)
1191	(25)	1183	(23)	1156	(18)
1255	(22)	1245	(20)	1215	(12)
1257	(1)	1248	(1)	1218	(1)
1399	(0)	1387	(0)	1348	(0)
1401	(0)	1390	(0)	1353	(0)
1476	(1)	1465	(0)	1428	(0)
1477	(7)	1467	(8)	1432	(11)
1513	(5)	1501	(3)	1461	(0)
1515	(14)	1504	(15)	1467	(18)
1533	(41)	1521	(33)	1485	(9)
1534	(15)	1525	(18)	1493	(17)
3109	(1)	3089	(1)	3040	(1)
3110	(11)	3090	(10)	3041	(10)
3133	(1)	3111	(0)	3045	(1)
3133	(7)	3111	(6)	3046	(9)
3156	(2)	3133	(2)	3076	(0)
3156	(2)	3133	(2)	3076	(2)
3175	(3)	3152	(3)	3092	(6)
3175	(16)	3152	(16)	3092	(21)
3225	(13)	3206	(13)	3152	(0)
3225	(0)	3206	(0)	3153	(5)
3234	(10)	3213	(11)	3155	(25)
3235	(4)	3214	(3)	3157	(3)

Table S40. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the **$(C_4H_6)_2Cr$** structure Cr-1P.

B3LYP		B3LYP*		BP86	
22	(2)	39	(1)	6	(1)
123	(0)	122	(0)	125	(1)
140	(2)	139	(2)	138	(2)
242	(46)	250	(0)	249	(0)
250	(0)	264	(31)	276	(0)
265	(0)	268	(0)	283	(0)
269	(0)	272	(0)	285	(10)
305	(0)	304	(0)	305	(0)
321	(7)	323	(9)	321	(10)
379	(0)	382	(0)	376	(0)
434	(6)	432	(0)	425	(0)
438	(0)	434	(7)	433	(10)
452	(9)	448	(8)	439	(6)
596	(7)	592	(7)	574	(6)
601	(0)	598	(0)	578	(0)
657	(0)	652	(3)	631	(2)
659	(3)	653	(0)	633	(0)
676	(0)	669	(0)	647	(0)
679	(55)	676	(47)	659	(29)
766	(26)	762	(26)	749	(27)
779	(0)	771	(0)	752	(0)
829	(6)	820	(5)	797	(3)
830	(0)	822	(0)	799	(0)
871	(0)	859	(0)	829	(0)
881	(3)	869	(3)	841	(3)
934	(13)	923	(0)	891	(0)
935	(0)	927	(12)	899	(0)
938	(0)	928	(0)	904	(11)
947	(1)	932	(1)	904	(0)
1061	(12)	1053	(12)	1028	(11)
1064	(0)	1057	(0)	1031	(0)
1072	(28)	1063	(27)	1034	(23)
1075	(0)	1065	(0)	1037	(0)
1189	(0)	1180	(0)	1150	(0)
1198	(18)	1189	(17)	1159	(14)
1245	(98)	1236	(85)	1207	(55)
1258	(0)	1248	(0)	1219	(0)
1397	(0)	1385	(0)	1345	(0)
1399	(0)	1387	(0)	1347	(1)
1470	(57)	1460	(46)	1423	(23)
1475	(0)	1464	(0)	1426	(0)
1516	(147)	1502	(0)	1460	(0)
1516	(0)	1503	(20)	1461	(17)
1517	(21)	1504	(136)	1466	(101)
1525	(0)	1514	(0)	1477	(0)
3136	(0)	3117	(0)	3058	(0)
3136	(1)	3117	(1)	3058	(18)
3138	(0)	3118	(15)	3058	(0)
3138	(15)	3118	(0)	3059	(2)
3165	(1)	3143	(2)	3088	(2)
3165	(0)	3144	(0)	3088	(0)
3182	(0)	3160	(17)	3103	(0)
3182	(18)	3160	(0)	3104	(22)
3233	(0)	3214	(0)	3157	(0)
3234	(16)	3215	(15)	3158	(19)
3236	(4)	3216	(3)	3159	(4)
3236	(0)	3217	(0)	3159	(0)

Table S41. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the **$(C_4H_6)_2Cr$** structure Cr-2P.

B3LYP		B3LYP*		BP86	
43	(1)	50	(1)	22	(42)
78	(0)	81	(0)	68	(1)
91	(1)	95	(2)	114	(45)
149	(1)	155	(1)	124	(1)
205	(1)	209	(2)	209	(0)
237	(2)	240	(2)	255	(4)
269	(0)	272	(0)	279	(1)
303	(6)	302	(6)	295	(1)
328	(0)	325	(1)	302	(35)
357	(2)	361	(1)	361	(15)
390	(11)	392	(8)	373	(5)
418	(2)	414	(2)	415	(20)
460	(6)	458	(5)	424	(0)
579	(2)	574	(2)	569	(5)
592	(6)	590	(7)	576	(0)
615	(9)	613	(7)	613	(0)
642	(20)	637	(25)	619	(35)
666	(7)	659	(8)	643	(28)
671	(0)	668	(0)	644	(1)
798	(30)	784	(26)	714	(4)
809	(9)	796	(14)	751	(0)
817	(55)	811	(37)	757	(11)
829	(20)	822	(21)	800	(20)
858	(6)	851	(7)	838	(1)
907	(1)	902	(1)	846	(1)
921	(2)	910	(1)	891	(4)
939	(14)	932	(13)	892	(0)
945	(1)	934	(1)	902	(2)
959	(2)	947	(3)	912	(0)
1054	(10)	1048	(10)	1025	(4)
1057	(0)	1049	(0)	1026	(0)
1066	(18)	1059	(17)	1040	(13)
1087	(9)	1077	(9)	1042	(6)
1182	(17)	1174	(16)	1166	(21)
1236	(8)	1224	(9)	1171	(5)
1243	(11)	1234	(14)	1224	(94)
1293	(36)	1281	(30)	1227	(0)
1397	(1)	1385	(1)	1351	(2)
1412	(1)	1398	(1)	1352	(0)
1454	(42)	1443	(36)	1401	(116)
1475	(3)	1463	(4)	1418	(8)
1500	(13)	1488	(14)	1461	(101)
1512	(29)	1498	(39)	1468	(13)
1551	(86)	1537	(71)	1487	(82)
1572	(19)	1557	(22)	1493	(1)
3113	(10)	3094	(9)	3054	(1)
3115	(3)	3097	(2)	3054	(9)
3149	(1)	3129	(1)	3071	(3)
3158	(1)	3135	(1)	3071	(3)
3166	(4)	3146	(4)	3089	(0)
3167	(13)	3147	(13)	3090	(5)
3176	(2)	3155	(2)	3108	(8)
3195	(3)	3174	(3)	3108	(11)
3205	(13)	3186	(13)	3151	(0)
3207	(6)	3188	(5)	3151	(13)
3252	(4)	3230	(3)	3167	(2)
3259	(3)	3239	(3)	3168	(9)

Table S42. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the $(C_4H_6)_2V$ structure V-1D.

B3LYP		B3LYP*		BP86	
76	(1)	69	(0)	65	(1)
80	(7)	81	(4)	93	(1)
135	(6)	136	(6)	149	(0)
197	(21)	206	(18)	211	(1)
243	(0)	247	(0)	242	(3)
288	(1)	280	(1)	298	(0)
349	(14)	348	(16)	350	(5)
387	(0)	394	(0)	377	(3)
403	(19)	400	(1)	398	(6)
410	(3)	402	(12)	407	(5)
411	(1)	407	(5)	438	(8)
478	(4)	472	(3)	457	(4)
478	(0)	484	(2)	471	(0)
500	(14)	494	(7)	516	(9)
526	(1)	509	(0)	561	(4)
560	(13)	552	(13)	565	(9)
618	(3)	609	(3)	608	(4)
663	(2)	654	(2)	634	(9)
669	(0)	663	(0)	642	(3)
794	(32)	792	(46)	782	(66)
825	(10)	819	(9)	794	(12)
832	(0)	822	(0)	797	(5)
857	(12)	846	(11)	812	(12)
872	(14)	862	(9)	831	(2)
876	(2)	874	(2)	851	(4)
933	(0)	926	(0)	886	(1)
935	(27)	929	(26)	901	(1)
967	(1)	954	(0)	902	(1)
967	(1)	955	(1)	907	(13)
1043	(15)	1036	(14)	1009	(12)
1047	(1)	1039	(1)	1020	(6)
1063	(8)	1054	(8)	1030	(12)
1066	(15)	1057	(15)	1042	(11)
1172	(4)	1162	(4)	1137	(8)
1175	(8)	1165	(8)	1152	(12)
1251	(19)	1241	(15)	1210	(5)
1251	(2)	1242	(2)	1230	(6)
1394	(1)	1381	(1)	1341	(0)
1396	(0)	1382	(0)	1347	(0)
1458	(20)	1444	(23)	1406	(12)
1460	(1)	1446	(1)	1417	(5)
1485	(2)	1471	(1)	1432	(7)
1487	(10)	1473	(11)	1440	(11)
1526	(34)	1515	(25)	1470	(9)
1526	(8)	1517	(6)	1479	(9)
3027	(4)	3008	(5)	2997	(4)
3028	(7)	3010	(5)	3012	(7)
3094	(3)	3074	(6)	3030	(5)
3094	(7)	3074	(4)	3062	(5)
3150	(1)	3129	(9)	3065	(1)
3150	(11)	3129	(0)	3084	(8)
3176	(5)	3153	(17)	3085	(2)
3176	(16)	3153	(6)	3103	(13)
3205	(1)	3185	(1)	3123	(6)
3205	(11)	3185	(9)	3133	(7)
3212	(4)	3191	(3)	3134	(7)
3212	(10)	3191	(9)	3145	(4)

Table S43. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the **$(C_4H_6)_2V$** structure V-2D.

B3LYP		B3LYP*		BP86	
52	(0)	58	(0)	71	(0)
130	(0)	127	(0)	130	(0)
143	(2)	150	(3)	152	(3)
205	(1)	204	(1)	191	(2)
217	(0)	224	(0)	243	(0)
281	(1)	286	(1)	284	(1)
314	(24)	315	(23)	322	(0)
323	(1)	326	(1)	324	(19)
375	(2)	375	(3)	375	(6)
428	(0)	428	(0)	417	(0)
435	(0)	429	(0)	425	(11)
446	(11)	440	(11)	434	(0)
464	(2)	465	(2)	462	(2)
606	(8)	601	(7)	576	(6)
620	(0)	617	(0)	597	(0)
673	(4)	670	(3)	643	(1)
686	(0)	680	(0)	658	(0)
690	(10)	688	(10)	662	(8)
698	(10)	692	(11)	664	(11)
793	(0)	789	(0)	765	(0)
809	(29)	807	(38)	786	(51)
854	(7)	850	(5)	815	(11)
860	(2)	851	(14)	822	(0)
863	(17)	853	(1)	823	(3)
885	(2)	877	(2)	845	(2)
929	(2)	916	(2)	868	(1)
930	(0)	918	(0)	875	(0)
935	(12)	929	(12)	903	(12)
941	(0)	934	(0)	910	(0)
1060	(11)	1051	(11)	1025	(13)
1063	(1)	1055	(1)	1029	(2)
1071	(0)	1063	(0)	1034	(0)
1078	(21)	1069	(20)	1042	(17)
1184	(0)	1174	(0)	1142	(0)
1191	(24)	1180	(23)	1149	(21)
1247	(29)	1237	(24)	1206	(16)
1250	(2)	1240	(2)	1208	(1)
1395	(0)	1383	(0)	1340	(0)
1400	(1)	1387	(0)	1346	(0)
1476	(1)	1465	(1)	1422	(0)
1480	(4)	1469	(4)	1427	(7)
1508	(0)	1495	(0)	1449	(0)
1514	(20)	1500	(20)	1455	(20)
1520	(34)	1508	(26)	1472	(8)
1532	(27)	1520	(26)	1483	(20)
3116	(0)	3095	(0)	3032	(1)
3117	(0)	3096	(0)	3033	(1)
3117	(1)	3096	(1)	3033	(0)
3119	(25)	3098	(24)	3034	(29)
3144	(1)	3123	(1)	3068	(1)
3145	(0)	3124	(0)	3069	(0)
3163	(4)	3141	(3)	3085	(4)
3163	(23)	3142	(22)	3086	(26)
3222	(0)	3203	(0)	3146	(0)
3223	(0)	3204	(0)	3148	(1)
3224	(29)	3205	(28)	3149	(31)
3226	(4)	3207	(4)	3151	(3)

Table S44. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the **$(C_4H_6)_2V$** structure V-1Q.

B3LYP		B3LYP*		BP86	
73	(1)	51	(0)	50	(0)
87	(0)	86	(0)	75	(0)
108	(0)	103	(0)	109	(2)
135	(112)	170	(46)	207	(7)
244	(0)	241	(0)	245	(0)
279	(124)	288	(130)	302	(0)
290	(0)	292	(0)	303	(0)
345	(0)	342	(0)	334	(68)
346	(3)	345	(2)	361	(1)
375	(10)	371	(12)	371	(2)
417	(1)	412	(31)	384	(40)
421	(30)	413	(1)	409	(15)
454	(0)	450	(0)	450	(0)
579	(12)	572	(12)	543	(4)
592	(0)	585	(0)	548	(0)
621	(132)	612	(103)	611	(30)
653	(1)	643	(1)	624	(4)
667	(0)	656	(0)	639	(0)
672	(20)	662	(19)	645	(25)
733	(17)	730	(9)	734	(0)
791	(0)	780	(0)	772	(0)
823	(24)	811	(20)	798	(4)
834	(30)	822	(25)	811	(0)
862	(8)	855	(9)	825	(19)
867	(0)	856	(0)	839	(0)
927	(10)	918	(9)	889	(0)
927	(1)	919	(1)	890	(8)
942	(0)	928	(2)	894	(1)
942	(2)	932	(0)	902	(0)
1059	(15)	1050	(13)	1022	(16)
1062	(0)	1053	(1)	1023	(1)
1075	(0)	1065	(0)	1041	(0)
1078	(20)	1069	(19)	1047	(12)
1194	(27)	1185	(25)	1164	(15)
1196	(0)	1187	(0)	1168	(0)
1249	(157)	1240	(130)	1229	(67)
1263	(1)	1252	(1)	1236	(1)
1400	(0)	1387	(0)	1352	(0)
1401	(0)	1389	(0)	1353	(0)
1463	(115)	1451	(79)	1411	(37)
1471	(4)	1459	(5)	1420	(13)
1513	(215)	1500	(205)	1466	(109)
1517	(0)	1503	(0)	1467	(0)
1520	(21)	1507	(21)	1469	(13)
1527	(23)	1515	(22)	1488	(17)
3107	(2)	3085	(3)	3040	(0)
3108	(0)	3086	(0)	3041	(0)
3112	(1)	3090	(1)	3042	(14)
3113	(18)	3091	(18)	3043	(1)
3162	(0)	3140	(0)	3084	(2)
3163	(1)	3141	(1)	3084	(0)
3179	(3)	3156	(3)	3099	(7)
3179	(21)	3157	(21)	3099	(16)
3231	(0)	3212	(0)	3162	(0)
3232	(21)	3212	(19)	3163	(2)
3233	(2)	3213	(1)	3164	(21)
3234	(5)	3215	(4)	3166	(1)

Table S45. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the $(C_4H_6)_2V$ structure V-2Q.

B3LYP		B3LYP*		BP86	
46	(17)	63	(42)	78	(1)
94	(2)	77	(1)	87	(1)
96	(5)	101	(14)	116	(4)
172	(15)	116	(3)	134	(7)
220	(1)	220	(0)	219	(0)
260	(1)	280	(0)	279	(0)
279	(15)	287	(55)	302	(5)
324	(31)	299	(41)	320	(46)
347	(16)	335	(6)	339	(5)
368	(5)	366	(3)	369	(3)
390	(11)	391	(32)	382	(24)
417	(12)	422	(9)	414	(16)
452	(5)	443	(1)	433	(1)
578	(5)	573	(15)	553	(12)
585	(5)	586	(2)	569	(1)
612	(78)	609	(80)	590	(52)
628	(7)	629	(1)	613	(1)
665	(2)	666	(1)	645	(1)
672	(3)	667	(4)	647	(4)
751	(16)	733	(22)	729	(4)
795	(20)	785	(22)	763	(18)
824	(16)	817	(8)	794	(6)
835	(1)	824	(0)	800	(0)
861	(10)	867	(0)	830	(0)
891	(5)	869	(12)	834	(12)
918	(2)	916	(10)	893	(8)
930	(12)	917	(0)	894	(0)
948	(0)	937	(1)	898	(2)
957	(0)	945	(0)	909	(1)
1053	(14)	1050	(12)	1025	(10)
1060	(2)	1051	(1)	1026	(0)
1075	(12)	1071	(3)	1042	(2)
1082	(8)	1071	(13)	1043	(11)
1190	(14)	1196	(4)	1167	(4)
1219	(8)	1200	(13)	1171	(11)
1258	(90)	1253	(147)	1226	(84)
1277	(40)	1264	(0)	1233	(0)
1402	(1)	1394	(0)	1354	(0)
1409	(1)	1394	(0)	1354	(0)
1459	(104)	1448	(127)	1414	(63)
1471	(4)	1458	(2)	1421	(2)
1508	(10)	1502	(230)	1468	(159)
1514	(167)	1513	(4)	1472	(11)
1533	(36)	1514	(9)	1473	(10)
1545	(16)	1521	(5)	1485	(2)
3093	(0)	3096	(5)	3038	(7)
3094	(9)	3097	(0)	3039	(0)
3136	(2)	3105	(6)	3042	(4)
3150	(2)	3106	(1)	3044	(1)
3154	(7)	3133	(3)	3077	(3)
3161	(3)	3134	(1)	3077	(2)
3168	(14)	3153	(2)	3094	(3)
3184	(7)	3153	(20)	3094	(24)
3205	(11)	3200	(1)	3140	(1)
3225	(6)	3201	(14)	3141	(16)
3235	(5)	3219	(2)	3162	(3)
3252	(3)	3220	(4)	3163	(6)

Table S46. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the **$(C_4H_6)_2Ti$** structure Ti-1S.

B3LYP		B3LYP*		BP86	
35	(1)	31	(1)	29	(1)
66	(0)	69	(0)	65	(0)
134	(0)	135	(0)	133	(0)
211	(1)	212	(1)	207	(0)
220	(4)	219	(4)	216	(3)
295	(0)	295	(0)	290	(0)
328	(11)	325	(11)	315	(11)
382	(1)	382	(1)	384	(1)
400	(0)	399	(1)	388	(5)
404	(0)	402	(0)	400	(2)
457	(23)	448	(23)	430	(18)
469	(9)	464	(10)	450	(10)
503	(18)	497	(14)	484	(6)
514	(6)	511	(5)	494	(2)
529	(7)	523	(6)	502	(6)
537	(8)	537	(10)	524	(1)
545	(0)	541	(1)	527	(14)
641	(13)	636	(12)	613	(9)
667	(2)	662	(2)	638	(1)
787	(107)	780	(117)	754	(121)
811	(0)	802	(0)	777	(1)
825	(35)	816	(36)	786	(55)
838	(23)	828	(22)	792	(21)
878	(1)	868	(11)	834	(1)
878	(12)	868	(1)	835	(8)
927	(0)	921	(0)	897	(0)
929	(31)	922	(28)	899	(23)
974	(1)	960	(2)	926	(2)
977	(2)	963	(2)	929	(3)
1033	(10)	1026	(10)	1002	(8)
1036	(1)	1028	(1)	1004	(1)
1065	(19)	1058	(18)	1034	(17)
1067	(18)	1059	(17)	1036	(15)
1174	(13)	1165	(13)	1136	(14)
1174	(10)	1165	(10)	1137	(11)
1270	(2)	1262	(2)	1236	(2)
1271	(10)	1262	(9)	1236	(5)
1397	(0)	1385	(0)	1345	(0)
1398	(0)	1385	(0)	1345	(0)
1453	(23)	1441	(24)	1398	(26)
1454	(6)	1442	(8)	1399	(8)
1476	(4)	1463	(4)	1422	(4)
1479	(12)	1466	(12)	1426	(13)
1532	(21)	1522	(18)	1490	(9)
1535	(11)	1524	(10)	1492	(10)
3054	(6)	3034	(7)	2974	(7)
3054	(3)	3034	(3)	2974	(3)
3093	(0)	3070	(0)	3009	(0)
3094	(2)	3072	(2)	3011	(2)
3150	(2)	3129	(2)	3074	(2)
3150	(1)	3130	(1)	3075	(2)
3169	(18)	3148	(17)	3092	(21)
3169	(8)	3148	(8)	3092	(9)
3202	(9)	3184	(7)	3133	(6)
3202	(1)	3184	(1)	3134	(2)
3213	(3)	3194	(2)	3142	(3)
3213	(4)	3194	(4)	3142	(3)

Table S47. Nickel–carbon distances (in Å) for the **$(C_4H_6)_2Ni$** structures. The **bold** face indicates the existence of Ni-C bonds.

	Ni-1S		
	B3LYP	B3LYP*	BP86
NiC1	**2.076**	**2.070**	**2.052**
NiC2	**2.006**	**2.003**	**1.997**
NiC3	**2.120**	**2.115**	**2.099**
NiC4	**2.006**	**2.003**	**1.997**
NiC5	**2.076**	**2.070**	**2.052**
NiC6	**2.230**	**2.223**	**2.182**
NiC7	**2.230**	**2.223**	**2.182**
NiC8	**2.120**	**2.115**	**2.099**

Table S48. Cobalt–carbon distances (in Å) for the **$(C_4H_6)_2Co$** structures. The **bold** face indicates the existence of Co-C bonds.

	Co-1D			Co-2D		
	B3LYP	B3LYP*	BP86	B3LYP	B3LYP*	BP86
CoC1	**2.032**	**2.026**	**2.019**	**2.072**	**2.066**	**2.051**
CoC2	**2.090**	**2.079**	**2.053**	**2.072**	**2.066**	**2.051**
CoC3	**2.193**	**2.171**	**2.120**	**2.057**	**2.055**	**2.050**
CoC4	**2.090**	**2.079**	**2.053**	**2.072**	**2.066**	**2.051**
CoC5	**2.032**	**2.026**	**2.019**	**2.072**	**2.066**	**2.051**
CoC6	**2.100**	**2.092**	**2.070**	**2.057**	**2.055**	**2.050**
CoC7	**2.100**	**2.092**	**2.070**	**2.057**	**2.055**	**2.050**
CoC8	**2.193**	**2.171**	**2.120**	**2.057**	**2.055**	**2.050**

Table S49. Iron–carbon distances (in Å) for the **$(C_4H_6)_2Fe$** structures. The **bold** face indicates the existence of Fe-C bonds.

	Fe-1S			Fe-2S		
	B3LYP	B3LYP*	BP86	B3LYP	B3LYP*	BP86
FeC1	**2.078**	**2.076**	**2.068**	**2.058**	**2.054**	**2.043**
FeC2	**2.054**	**2.050**	**2.043**	**2.058**	**2.054**	**2.043**
FeC3	**2.023**	**2.018**	**2.005**	**2.084**	**2.081**	**2.071**
FeC4	**2.054**	**2.050**	**2.043**	**2.058**	**2.054**	**2.043**
FeC5	**2.078**	**2.076**	**2.068**	**2.058**	**2.054**	**2.043**
FeC6	**2.091**	**2.085**	**2.067**	**2.084**	**2.081**	**2.071**
FeC7	**2.091**	**2.085**	**2.067**	**2.084**	**2.081**	**2.071**
FeC8	**2.023**	**2.018**	**2.005**	**2.084**	**2.081**	**2.071**
	Fe-1T			Fe-2T		
	B3LYP	B3LYP*	BP86	B3LYP	B3LYP*	BP86
FeC1	**2.066**	**2.098**	**2.075**	**2.104**	**2.082**	**2.073**
FeC2	**2.066**	**2.062**	**2.044**	**2.132**	**2.105**	**2.071**
FeC3	**2.140**	**2.127**	**2.091**	**2.172**	**2.112**	**2.089**
FeC4	**2.066**	**2.062**	**2.044**	**2.132**	**2.105**	**2.071**
FeC5	**2.066**	**2.098**	**2.075**	**2.104**	**2.082**	**2.073**
FeC6	**2.140**	**2.199**	**2.138**	**2.159**	**2.114**	**2.089**
FeC7	**2.140**	**2.199**	**2.138**	**2.159**	**2.114**	**2.089**
FeC8	**2.140**	**2.126**	**2.091**	**2.172**	**2.112**	**2.089**

Table S50. Manganese–carbon distances (in Å) for the **$(C_4H_6)_2$Mn** structures. The **bold** face indicates the existence of Mn-C bonds..

	Mn-1D			Mn-2D		
	B3LYP	B3LYP*	BP86	B3LYP	B3LYP*	BP86
MnC1	**2.095**	**2.089**	**2.077**	**2.101**	**2.094**	**2.078**
MnC2	**2.095**	**2.089**	**2.077**	**2.101**	**2.094**	**2.078**
MnC3	**2.137**	**2.124**	**2.108**	**2.190**	**2.182**	**2.131**
MnC4	**2.095**	**2.089**	**2.077**	**2.101**	**2.095**	**2.065**
MnC5	**2.095**	**2.089**	**2.077**	**2.101**	**2.095**	**2.065**
MnC6	**2.137**	**2.124**	**2.108**	**2.190**	**2.180**	**2.157**
MnC7	**2.137**	**2.124**	**2.108**	**2.190**	**2.182**	**2.131**
MnC8	**2.137**	**2.124**	**2.108**	**2.190**	**2.180**	**2.157**
	Mn-1Q			**Mn-1X**		
	B3LYP	**B3LYP***	**BP86**	**B3LYP**	**B3LYP***	**BP86**
MnC1	**2.219**	**2.149**	**2.126**	**2.512**	**2.489**	**2.426**
MnC2	**2.163**	**2.203**	**2.172**	**2.115**	**2.112**	**2.101**
MnC3	**2.187**	**2.264**	**2.208**	**2.165**	**2.163**	**2.152**
MnC4	**2.163**	**2.203**	**2.172**	**2.512**	**2.489**	**2.426**
MnC5	**2.219**	**2.149**	**2.126**	**2.115**	**2.112**	**2.101**
MnC6	**2.290**	**2.169**	**2.131**	**2.165**	**2.163**	**2.152**
MnC7	**2.290**	**2.169**	**2.131**	**2.981**	**2.951**	**2.886**
MnC8	**2.187**	**2.264**	**2.208**	**2.981**	**2.951**	**2.886**
	Mn-2X					
	B3LYP	B3LYP*	BP86			
MnC1	**2.413**	**2.399**	**2.477**			
MnC2	**2.413**	**2.399**	**2.138**			
MnC3	**2.400**	**2.390**	**2.103**			
MnC4	**2.413**	**2.399**	**2.138**			
MnC5	**2.413**	**2.399**	**2.478**			
MnC6	**2.400**	**2.390**	**2.905**			
MnC7	**2.400**	**2.390**	**2.903**			
MnC8	**2.400**	**2.390**	**2.103**			

Table S51. Chromium–carbon distances (in Å) for the **$(C_4H_6)_2Cr$** structures. The **bold** face indicates the existence of Cr-C bonds..

	Cr-1S			Cr-2S		
	B3LYP	B3LYP*	BP86	B3LYP	B3LYP*	BP86
CrC1	**2.119**	**2.115**	**2.105**	**2.198**	**2.195**	**2.195**
CrC2	**2.119**	**2.115**	**2.105**	**2.182**	**2.184**	**2.210**
CrC3	**2.163**	**2.159**	**2.145**	**2.030**	**2.026**	**1.986**
CrC4	**2.119**	**2.115**	**2.105**	**2.220**	**2.224**	**2.210**
CrC5	**2.119**	**2.115**	**2.105**	**2.220**	**2.221**	**2.195**
CrC6	**2.163**	**2.159**	**2.145**	**2.109**	**2.101**	**2.086**
CrC7	**2.163**	**2.159**	**2.145**	**2.130**	**2.121**	**2.086**
CrC8	**2.163**	**2.159**	**2.145**	**2.001**	**1.992**	**1.986**
	Cr-1T			Cr-2T		
	B3LYP	B3LYP*	BP86	B3LYP	B3LYP*	BP86
CrC1	**2.200**	**2.198**	**2.188**	**2.357**	**2.342**	**2.238**
CrC2	**2.200**	**2.198**	**2.188**	**2.257**	**2.245**	**2.175**
CrC3	**2.243**	**2.239**	**2.226**	**2.366**	**2.344**	**2.204**
CrC4	**2.200**	**2.198**	**2.188**	**2.184**	**2.177**	**2.175**
CrC5	**2.200**	**2.198**	**2.188**	**2.199**	**2.194**	**2.238**
CrC6	**2.243**	**2.239**	**2.226**	**2.184**	**2.182**	**2.336**
CrC7	**2.243**	**2.239**	**2.226**	**2.597**	**2.574**	**2.336**
CrC8	**2.243**	**2.239**	**2.226**	**2.171**	**2.163**	**2.204**
	Cr-1P			Cr-2P		
	B3LYP	B3LYP*	BP86	B3LYP	B3LYP*	BP86
CrC1	**2.209**	**2.163**	**2.189**	**2.193**	**2.183**	**2.175**
CrC2	**2.169**	**2.202**	**2.151**	**2.223**	**2.209**	**2.179**
CrC3	**2.120**	**2.183**	**2.077**	**2.234**	**2.217**	**2.176**
CrC4	**2.169**	**2.202**	**2.151**	**2.223**	**2.209**	**2.179**
CrC5	**2.209**	**2.163**	**2.189**	**2.193**	**2.183**	**2.175**
CrC6	**2.197**	**2.102**	**2.157**	**2.181**	**2.170**	**2.170**
CrC7	**2.197**	**2.102**	**2.157**	**2.181**	**2.170**	**2.170**
CrC8	**2.120**	**2.183**	**2.077**	**2.234**	**2.217**	**2.176**

Table S52. Vanadium–carbon distances (in Å) for the **$(C_4H_6)_2V$** structures. The **bold** face indicates the existence of V-C bonds.

	V-1D			V-2D		
	B3LYP	B3LYP*	BP86	B3LYP	B3LYP*	BP86
VC1	**2.246**	**2.246**	**2.161**	**2.214**	**2.211**	**2.203**
VC2	**2.261**	**2.258**	**2.195**	**2.214**	**2.211**	**2.203**
VC3	**2.162**	**2.153**	**2.189**	**2.214**	**2.209**	**2.196**
VC4	**2.261**	**2.258**	**2.230**	**2.214**	**2.211**	**2.203**
VC5	**2.246**	**2.246**	**2.232**	**2.214**	**2.211**	**2.203**
VC6	**2.081**	**2.078**	**2.105**	**2.214**	**2.209**	**2.196**
VC7	**2.081**	**2.078**	**2.136**	**2.214**	**2.209**	**2.196**
VC8	**2.162**	**2.153**	**2.132**	**2.214**	**2.209**	**2.196**
	V-1Q			V-2Q		
	B3LYP	B3LYP*	BP86	B3LYP	B3LYP*	BP86
VC1	**2.260**	**2.255**	**2.246**	**2.286**	**2.259**	**2.253**
VC2	**2.260**	**2.255**	**2.246**	**2.291**	**2.263**	**2.255**
VC3	**2.256**	**2.250**	**2.240**	**2.367**	**2.273**	**2.253**
VC4	**2.260**	**2.255**	**2.246**	**2.244**	**2.263**	**2.255**
VC5	**2.260**	**2.255**	**2.246**	**2.241**	**2.259**	**2.253**
VC6	**2.256**	**2.250**	**2.240**	**2.202**	**2.258**	**2.244**
VC7	**2.256**	**2.250**	**2.240**	**2.330**	**2.258**	**2.244**
VC8	**2.256**	**2.250**	**2.240**	**2.205**	**2.273**	**2.253**

Table S53. Titanium–carbon distances (in Å) for the **$(C_4H_6)_2Ti$** structures. The **bold** face indicates the existence of Ti-C bonds.

	Ti-1S		
	B3LYP	B3LYP*	BP86
TiC1	**2.321**	**2.321**	**2.321**
TiC2	**2.297**	**2.297**	**2.297**
TiC3	**2.135**	**2.134**	**2.132**
TiC4	**2.297**	**2.297**	**2.297**
TiC5	**2.321**	**2.321**	**2.321**
TiC6	**2.187**	**2.184**	**2.180**
TiC7	**2.187**	**2.184**	**2.180**
TiC8	**2.135**	**2.134**	**2.132**

Table S54. Total energies (E in hartree), total free energies (G, in hartree), HOMO and LUMO energies (in hartree), HOMO-LUMO gaps (in eV), and the χ angles for the $(C_4H_6)_2Ni$ structures by all three methods.

Ni-1S			
	B3LYP(***C*$_2$**)	B3LYP*(***C*$_2$**)	BP86(***C*$_2$**)
–HOMO(α)	0.19189	0.18230	0.15833
–LUMO(α)	0.03841	0.04524	0.06964
gap/eV	4.18	3.73	2.41
E+1820	-0.42877	-0.03655	-0.66271
G+1820	-0.28967	0.10176	-0.52750
χ	80.1°	80.4°	78.0°

Table S55. Total energies (E in hartree), total free energies (G, in hartree),relative energies (ΔE in kcal/mol), HOMO and LUMO energies (in hartree), HOMO-LUMO gaps (in eV), the spin expectation $\langle S^2 \rangle$ values, and the χ angles for the $(C_4H_6)_2Co$ structures by all three methods.

Co-1D			
	B3LYP(***C*$_2$**)	B3LYP*(***C*$_2$**)	BP86(***C*$_2$**)
–HOMO(α)	0.19992	0.19083	0.16456
–LUMO(α)	0.03976	0.04322	0.06176
gap/eV	4.36	4.01	2.80
E+1694	-0.87711	-0.49087	-1.09527
ΔE	0.0	0.0	0.0
G+1694	-0.73820	-0.35246	-0.96043
ΔG	0.0	0.0	0.0
$\langle S^2 \rangle$	0.85	0.80	0.76
χ	88.9°	88.7°	89.6°
Co-2D			
	B3LYP(***C*$_{2v}$**)	B3LYP*(***C*$_{2v}$**)	BP86(***C*$_{2v}$**)
–HOMO(α)	0.16693	0.15894	0.14233
–LUMO(α)	0.04216	0.04791	0.07199
gap/eV	3.40	3.02	1.91
E+1694	-0.85920	-0.47549	-1.08659
ΔE	11.2	9.7	5.4
G+1694	-0.72021	-0.33670	-0.95163
ΔG	11.3	9.9	5.5
$\langle S^2 \rangle$	0.77	0.76	0.75
χ	0.0°	0.0°	0.0°

Table S56. Total energies (E in hartree), total free energies (G, in hartree),relative energies (ΔE in kcal/mol), HOMO and LUMO energies (in hartree), HOMO-LUMO gaps (in eV), the spin expectation $\langle S^2 \rangle$ values, and the χ angles for the $(C_4H_6)_2Fe$ structures by all three methods.

Fe-1S			
	B3LYP(***C*$_2$**)	B3LYP*(***C*$_2$**)	BP86(***C*$_2$**)
–HOMO(α)	0.19424	0.18477	0.15327
–LUMO(α)	0.06341	0.07378	0.10768
gap/eV	3.56	3.02	1.24
E+1575	-0.79048	-0.41421	-1.00252
ΔE	0.0	0.0	0.0
G+1575	-0.64945	-0.27410	-0.86612
ΔG	3.0	8.9	-5.0
χ	103.0°	102.8°	102.8°
Fe-2S			
	B3LYP(***C*$_{2v}$**)	B3LYP*(***C*$_{2v}$**)	BP86(***C*$_{2v}$**)
–HOMO(α)	0.20242	0.19113	0.14872
–LUMO(α)	0.07299	0.08190	0.11086
gap/eV	3.52	2.97	1.03
E+1575	-0.78598	-0.41063	-1.00132
ΔE	2.8	2.2	0.8
G+1575	-0.64510	-0.27013	-0.86590
ΔG	5.7	11.4	-4.8
χ	0.0°	0.0°	0.0°
Fe-1T			
	B3LYP(***C*$_2$**)	B3LYP*(***C*$_1$**)	BP86(***C*$_2$**)
–HOMO(α)	0.16987	0.19737	0.13867
–LUMO(α)	0.05047	0.04550	0.07192
gap/eV	3.25	4.13	1.82
E+1575	-0.79029	-0.42419	-0.99132
ΔE	0.1	-6.3	7.0
G+1575	-0.65416	-0.28825	-0.85821
ΔG	0.0	0.0	0.0
$\langle S^2 \rangle$	2.17	2.18	2.03
χ	36.6°	82.7°	1.3°
Fe-2T			
	B3LYP(***C*$_{2h}$**)	B3LYP*(***C*$_2$**)	BP86(***C*$_2$**)
–HOMO(α)	0.15435	0.15710	0.17593
–LUMO(α)	0.01981	0.05111	0.05954
gap/eV	3.66	2.88	3.17
E+1575	-0.78221	-0.40997	-1.00069
E	5.2	2.7	1.1
G+1575	-0.64706	-0.27306	-0.86823
ΔG	4.5	9.5	-6.3
$\langle S^2 \rangle$	2.02	2.17	2.06
χ	180.0°	20.3°	79.8°

Table S57. Total energies (E in hartree), total free energies (G, in hartree),relative energies (ΔE in kcal/mol), HOMO and LUMO energies (in hartree), HOMO-LUMO gaps (in eV), the spin expectation $\langle S^2 \rangle$ values, and the χ angles for the $(C_4H_6)_2Mn$ structures by all three methods.

	Mn-1D		
	B3LYP(***C*****$_{2v}$**)	B3LYP*(***C*****$_{2v}$**)	BP86(***C*****$_{2v}$**)
–HOMO(α)	0.21790	0.20222	0.16334
–LUMO(α)	0.08587	0.08901	0.10833
gap/eV	3.59	3.08	1.50
E+1462	-1.06180	-0.68943	-1.24974
ΔE	18.8	14.4	2.7
G+1462	-0.92416	-0.55200	-1.11620
ΔG	20.8	16.5	4.8
$\langle S^2 \rangle$	1.18	1.02	0.82
χ	0.0°	0.0°	0.0°
	Mn-2D		
	B3LYP(***C*****$_{2h}$**)	B3LYP*(***C*****$_{s}$**)	BP86(***C*****$_{s}$**)
–HOMO(α)	0.22567	0.20969	0.16301
–LUMO(α)	0.09213	0.09929	0.11809
gap/eV	3.63	3.00	1.22
E+1462	-1.05688	-0.68058	-1.23365
ΔE	21.9	20.0	12.8
G+1462	-0.92115	-0.54680	-1.10151
ΔG	22.7	19.8	14.0
$\langle S^2 \rangle$	1.96	1.89	1.06
χ	180.0°	180.0°	180.0°
	Mn-1Q		
	B3LYP(***C*****$_{2}$**)	B3LYP*(***C*****$_{2}$**)	BP86(***C*****$_{2}$**)
–HOMO(α)	0.19816	0.18833	0.16011
–LUMO(α)	0.04916	0.05145	0.06441
gap/eV	4.05	3.72	2.60
E+1462	-1.09183	-0.71245	-1.25405
ΔE	0.0	0.0	0.0
G+1462	-0.95737	-0.57837	-1.12378
ΔG	0.0	0.0	0.0
$\langle S^2 \rangle$	4.23	4.08	3.87
χ	87.8°	87.6°	89.9°
	Mn-1X		
	B3LYP(***C*****$_{i}$**)	B3LYP*(***C*****$_{i}$**)	BP86(***C*****$_{i}$**)
–HOMO(α)	0.14371	0.13922	0.13261
–LUMO(α)	0.04206	0.04585	0.06134
gap/eV	2.77	2.54	1.94
E+1462	-1.06168	-0.67913	-1.20913
ΔE	18.9	20.9	28.2

G+1462	-0.93197	-0.55056	-1.08413
ΔG	15.9	17.5	24.9
$\langle S^2 \rangle$	8.83	8.83	8.80
χ	180.0°	180.0°	180.0°
Mn-2X			
	B3LYP(***C*$_{2v}$**)	B3LYP*(***C*$_{2v}$**)	BP86(***C*$_1$**)
–HOMO(α)	0.15092	0.14554	0.12908
–LUMO(α)	0.06318	0.06727	0.06141
gap/eV	2.39	2.13	1.84
E+1462	-1.05757	-0.67318	-1.20991
ΔE	21.5	24.6	27.7
G+1462	-0.92707	-0.54432	-1.08553
ΔG	19.0	21.4	24.0
$\langle S^2 \rangle$	8.79	8.79	8.81
χ	0.0°	0.0°	58.3°

Table S58. Total energies (E in hartree), total free energies (G, in hartree),relative energies (ΔE in kcal/mol), HOMO and LUMO energies (in hartree), HOMO-LUMO gaps (in eV), the spin expectation $\langle S^2 \rangle$ values, and the χ angles for the $(C_4H_6)_2Cr$ structures by all three methods.

Cr-1S			
	B3LYP(***C*****$_{2v}$**)	B3LYP*(***C*****$_{2v}$**)	BP86(***C*****$_{2v}$**)
–HOMO(α)	0.18211	0.17068	0.14420
–LUMO(α)	0.06104	0.07546	0.12484
gap/eV	3.29	2.59	0.53
E+1356	-0.52054	-0.15373	-0.68416
ΔE	24.5	22.3	18.4
G+1356	-0.38008	-0.01439	-0.54964
ΔG	26.8	25.0	19.8
χ	0.0°	0.0°	0.0°
Cr-2S			
	B3LYP(***C*****$_1$**)	B3LYP*(***C*****$_1$**)	BP86(***C*****$_2$**)
–HOMO(α)	0.17340	0.15781	0.11894
–LUMO(α)	0.06161	0.07216	0.10683
gap/eV	3.04	2.33	0.33
E+1356	-0.51028	-0.14341	-0.67359
ΔE	30.9	28.8	25.1
G+1356	-0.37293	-0.00722	-0.54190
ΔG	31.3	29.5	24.6
χ	110.4°	109.0°	102.6°
Cr-1T			
	B3LYP(***C*****$_2$**)	B3LYP*(***C*****$_2$**)	BP86(***C*****$_2$**)
–HOMO(α)	0.20368	0.19306	0.16237
–LUMO(α)	0.07350	0.07692	0.09709
gap/eV	3.54	3.16	1.78
E+1356	-0.55957	-0.18934	-0.71353
ΔE	0.0	0.0	0.0
G+1356	-0.42284	-0.05424	-0.58118
ΔG	0.0	0.0	0.0
$\langle S^2 \rangle$	2.39	2.26	2.10
χ	118.3°	116.0°	113.8°
Cr-2T			
	B3LYP(***C*****$_2$**)	B3LYP*(***C*****$_2$**)	BP86(***C*****$_2$**)
–HOMO(α)	0.20785	0.19594	0.15328
–LUMO(α)	0.08086	0.08183	0.09724
gap/eV	3.46	3.10	1.52
E+1356	-0.55136	-0.18093	-0.70624
ΔE	5.2	5.3	4.6
G+1356	-0.41679	-0.04701	-0.57485
ΔG	3.8	4.5	4.0
$\langle S^2 \rangle$	2.55	2.37	2.13
χ	15.1°	12.1°	1.8°

Cr-1P			
	B3LYP(***C*****$_{2h}$**)	B3LYP*(***C*****$_{2h}$**)	BP86(***C*****$_{2h}$**)
–HOMO(α)	0.14823	0.14258	0.13306
–LUMO(α)	0.01949	0.02829	0.05593
gap/eV	3.50	3.11	2.10
E+1356	-0.54644	-0.17408	-0.69179
ΔE	8.2	9.6	13.6
G+1356	-0.41219	-0.04043	-0.56348
ΔG	6.7	8.7	11.1
$\langle S^2 \rangle$	6.04	6.04	6.04
χ	180.0°	180.0°	180.0°
Cr-2P			
	B3LYP(***C*****$_{1}$**)	B3LYP*(***C*****$_{1}$**)	BP86(***C*****$_{2}$**)
–HOMO(α)	0.17267	0.16603	0.13800
–LUMO(α)	0.03418	0.03919	0.05974
gap/eV	3.77	3.45	2.13
E+1356	-0.54411	-0.17022	-0.68525
ΔE	9.7	12.0	17.7
G+1356	-0.41105	-0.03809	-0.55808
ΔG	7.4	10.1	14.5
$\langle S^2 \rangle$	6.16	6.12	6.05
χ	76.3°	74.9°	72.7°

Table S59. Total energies (E in hartree), total free energies (G, in hartree),relative energies (ΔE in kcal/mol), HOMO and LUMO energies (in hartree), HOMO-LUMO gaps (in eV), the spin expectation $\langle S^2 \rangle$ values, and the χ angles for the $(C_4H_6)_2V$ structures by all three methods.

	V-1D		
	B3LYP(***C*$_2$**)	B3LYP*(***C*$_2$**)	BP86(***C*$_1$**)
–HOMO(α)	0.20002	0.18523	0.14529
–LUMO(α)	0.07737	0.08635	0.10808
gap/eV	3.34	2.69	1.01
E+1255	-1.07924	-0.71570	-1.21698
ΔE	0.0	0.0	0.0
G+1255	-0.94439	-0.58223	-1.08610
ΔG	0.0	0.0	0.0
$\langle S^2 \rangle$	0.83	0.80	0.77
χ	106.8°	105.4°	89.4°
	V-2D		
	B3LYP(***C*$_{2v}$**)	B3LYP*(***C*$_{2v}$**)	BP86(***C*$_{2v}$**)
–HOMO(α)	0.19864	0.18729	0.15406
–LUMO(α)	0.06645	0.07838	0.11789
gap/eV	3.60	2.96	0.98
E+1255	-1.07682	-0.71282	-1.21076
ΔE	1.5	1.8	3.9
G+1255	-0.94043	-0.57679	-1.07920
ΔG	2.5	3.4	4.3
$\langle S^2 \rangle$	0.81	0.79	0.77
χ	0.0°	0.0°	0.0°
	V-1Q		
	B3LYP(***C*$_{2v}$**)	B3LYP*(***C*$_{2v}$**)	BP86(***C*$_{2v}$**)
–HOMO(α)	0.17735	0.16905	0.12466
–LUMO(α)	0.04918	0.05632	0.06947
gap/eV	3.49	3.06	1.50
E+1255	-1.07006	-0.70428	-1.19924
ΔE	5.8	7.2	11.1
G+1255	-0.93603	-0.57182	-1.06985
ΔG	5.2	6.5	10.2
$\langle S^2 \rangle$	3.78	3.77	3.78
χ	0.0°	0.0°	0.0°
	V-2Q		
	B3LYP(***C*$_1$**)	B3LYP*(***C*$_2$**)	BP86(***C*$_2$**)
–HOMO(α)	0.17427	0.16105	0.12373
–LUMO(α)	0.05419	0.06265	0.08842
gap/eV	3.28	2.67	0.96
E+1255	-1.06912	-0.70296	-1.19620
ΔE	6.4	8.0	13.0

G+1255	-0.93556	-0.57084	-1.06715
ΔG	5.5	7.1	11.9
$\langle S^2 \rangle$	3.79	3.78	3.77
χ	127.7°	131.2°	131.7°

Table S60. Total energies (E in hartree), total free energies (G, in hartree),HOMO and LUMO energies (in hartree), HOMO-LUMO gaps (in eV), and the χ angles for the $(C_4H_6)_2Ti$ structures by all three methods.

	Ti-1S		
	B3LYP(***C*$_2$**)	B3LYP*(***C*$_2$**)	BP86(***C*$_2$**)
–HOMO(α)	0.18919	0.18138	0.16454
–LUMO(α)	0.06354	0.07201	0.10263
gap/eV	3.42	2.97	1.68
E+1161	-0.56080	-0.20171	-0.66910
G+1161	-0.42578	-0.06803	-0.54016
χ	85.2°	84.5°	83.7°

Complete Gaussian 09 reference (Reference 37)

Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.