Beyond the Metal-Metal Triple Bond in Binuclear Cyclopentadienylchromium Carbonyl Chemistry

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Supporting Information

Tables S1-S7. The theoretical harmonic vibrational frequencies for the $Cp_2Cr_2(CO)_n$ (n = 3,2) structures using the BP86 method.

Tables S8-S14. The theoretical Cartesian coordinates for the $Cp_2Cr_2(CO)_n$ (n = 3,2) structures using the BP86 method.

Complete Gaussian03 reference (reference 32).

Appendix. Results from density functional theory studies (B3LYP and BP86) on $(\eta^5\text{-Me}_5C_5)_2Cr_2(CO)_n$ (n = 4, 3, 2) derivatives (**Tables A1-A15** and **Figures A1-A7**).

Table S1. The theoretical harmonic vibrational frequencies (in cm^{-1}) and their infrared intensities (in km/mol) for the triplet $Cp_2Cr_2(CO)_3$ structure **3T-1** using the BP86 method.

	a	a	a	a	a	a	a	a	a
Frequencies	22	23	52	75	80	86	129	135	147
IR Intensities	0	0	1	2	0	0	0	0	2
	a	a	a	a	a	a	a	a	a
Frequencies	149	188	220	326	331	342	348	361	400
IR Intensities	0	1	2	5	5	1	4	1	0
	a	a	a	a	a	a	a	a	a
Frequencies	409	442	452	485	496	519	564	568	573
IR Intensities	9	5	4	3	1	6	77	15	1
	a	a	a	a	a	a	a	a	a
Frequencies	574	580	581	613	785	793	798	801	806
IR Intensities	7	6	1	11	52	34	43	4	23
	a	a	a	a	a	a	a	a	a
Frequencies	814	815	816	816	819	864	869	875	879
IR Intensities	0	0	5	1	3	1	0	2	1
	a	a	a	a	a	a	a	a	a
Frequencies	993	994	995	996	1041	1043	1043	1044	1107
IR Intensities	8	12	9	10	0	0	0	1	5
	a	a	a	a	a	a	a	a	a
Frequencies	1110	1224	1225	1358	1363	1367	1372	1409	1409
IR Intensities	3	0	0	0	0	1	2	2	4
	a	a	a	a	a	a	a	a	a
Frequencies	1410	1413	1796	1831	1872	3161	3163	3168	3169
IR Intensities	2	3	775	789	211	0	0	0	0
	a	a	a	a	a	a			
Frequencies	3173	3179	3181	3183	3188	3192			
IR Intensities	0	0	0	0	0	0			

Table S2. The theoretical harmonic vibrational frequencies (in cm^{-1}) and their infrared intensities (in km/mol) for the triplet $Cp_2Cr_2(CO)_3$ structure **3T-2** using the BP86 method.

	b	a	a	b	b	a	b	a	b
Frequencies	24	32	63	65	69	95	104	128	138
IR Intensities	0	0	0	3	1	0	1	0	1
	a	b	a	b	b	a	a	b	b
Frequencies	162	176	205	270	332	335	349	366	380
IR Intensities	1	0	0	5	3	1	6	0	0
	a	b	a	a	b	b	a	a	b
Frequencies	416	424	445	479	490	523	530	551	560
IR Intensities	0	5	0	6	28	43	16	19	16
	a	b	b	a	b	a	b	a	b
Frequencies	576	576	577	578	788	789	802	803	804
IR Intensities	0	2	1	0	70	0	59	3	6
	a	a	b	a	b	b	a	a	b
Frequencies	805	815	815	816	817	864	864	874	875
IR Intensities	2	0	2	0	2	2	2	0	1
	b	a	b	a	a	b	a	b	a
Frequencies	992	992	993	993	1040	1041	1042	1043	1106
IR Intensities	21	2	1	20	0	1	1	0	0
	b	a	b	b	a	b	a	b	a
Frequencies	1106	1223	1223	1359	1359	1370	1370	1407	1407
IR Intensities	10	0	0	1	0	2	0	1	4
	b	a	a	b	a	a	b	b	a
Frequencies	1411	1411	1785	1830	1861	3166	3166	3166	3167
IR Intensities	4	0	893	877	121	0	0	0	0
	b	a	b	a	b	a			
Frequencies	3178	3178	3181	3181	3190	3190			
IR Intensities	0	0	0	0	0	0			

Table S3. The theoretical harmonic vibrational frequencies (in cm^{-1}) and their infrared intensities (in km/mol) for the singlet $Cp_2Cr_2(CO)_3$ structure **3S-1** using the BP86 method.

	a"	a"	a"	a"	a'	a'	a"	a'	a"
Frequencies	30i	18	35	72	80	105	126	131	133
IR Intensities		0	0	3	1	1	0	0	0
	a'	a'	a'	a"	a"	a'	a'	a'	a"
Frequencies	153	157	215	321	323	332	337	355	406
IR Intensities	0	2	0	8	2	0	4	1	4
	a'	a"	a"	a'	a'	a'	a"	a'	a"
Frequencies	407	427	492	505	513	525	555	569	570
IR Intensities	0	5	0	39	7	0	17	2	1
	a'	a"	a'	a'	a'	a'	a"	a'	a'
Frequencies	574	577	578	609	790	794	799	802	807
IR Intensities	3	0	0	16	63	60	0	20	19
	a"	a"	a'	a'	a"	a"	a"	a'	a'
Frequencies	812	814	815	817	818	863	875	877	878
IR Intensities	0	2	2	5	2	0	0	2	1
	a'	a"	a'	a"	a'	a"	a"	a'	a'
Frequencies	989	991	994	996	1039	1042	1043	1044	1101
IR Intensities	8	15	7	10	0	0	0	1	4
	a'	a"	a"	a'	a"	a"	a'	a"	a'
Frequencies	1110	1223	1224	1342	1365	1367	1370	1406	1407
IR Intensities	3	0	0	2	0	1	1	1	3
	a'	a"	a"	a'	a'	a'	a"	a'	a"
Frequencies	1410	1413	1833	1837	1870	3162	3164	3168	3169
IR Intensities	3	2	670	928	144	0	0	0	0
	a"	a"	a'	a'	a'	a'			
Frequencies	3177	3181	3181	3184	3189	3192			
IR Intensities	0	0	0	0	0	0			

Table S4. The theoretical harmonic vibrational frequencies (in cm^{-1}) and their infrared intensities (in km/mol) for the triplet $Cp_2Cr_2(CO)_2$ structure **2T-1** using the BP86 method.

	a"	a"	a'	a"	a'	a'	a"	a'	a'
Frequencies	6	27	37	66	80	87	103	142	167
IR Intensities	0	0	1	0	0	0	0	1	0
	a"	a'	a"	a'	a"	a'	a'	a"	a'
Frequencies	176	281	300	312	330	339	381	397	463
IR Intensities	0	1	3	2	1	2	30	0	5
	a"	a'	a"	a'	a"	a"	a'	a'	a'
Frequencies	479	493	554	563	573	576	576	583	762
IR Intensities	4	10	16	1	1	0	4	7	4
	a'	a'	a"	a'	a"	a"	a'	a'	a"
Frequencies	768	773	779	781	793	813	813	815	816
IR Intensities	41	88	1	53	5	1	0	0	0
	a"	a"	a'	a'	a"	a"	a'	a'	a'
Frequencies	849	851	857	861	985	990	994	996	1038
IR Intensities	0	1	2	1	6	15	8	20	1
	a"	a"	a'	a'	a'	a"	a"	a"	a'
Frequencies	1040	1040	1041	1104	1106	1221	1224	1353	1355
IR Intensities	0	0	0	6	3	0	0	1	2
	a"	a'	a"	a"	a'	a'	a"	a'	a'
Frequencies	1358	1363	1401	1407	1414	1415	1805	1838	3159
IR Intensities	0	1	3	3	1	2	998	257	0
	a"	a'	a"	a'	a"	a'	a"	a'	a'
Frequencies	3161	3163	3165	3174	3174	3177	3180	3186	3189
IR Intensities	0	0	0	0	0	1	1	0	0

Table S5. The theoretical harmonic vibrational frequencies (in cm^{-1}) and their infrared intensities (in km/mol) for the quintet $Cp_2Cr_2(CO)_2$ structure **2Q-1** using the BP86 method

	a"	a"	a'	a"	a'	a'	a"	a'	a"
Frequencies	17i	10	45	59	70	100	120	148	167
IR Intensities		0	1	0	2	0	0	2	0
	a'	a'	a"	a"	a'	a'	a"	a'	a'
Frequencies	175	304	304	325	334	345	402	406	474
IR Intensities	0	3	3	2	6	4	0	18	10
	a"	a'	a'	a"	a"	a'	a"	a'	a'
Frequencies	496	507	567	567	571	577	578	596	768
IR Intensities	6	16	1	7	8	2	0	4	25
	a'	a'	a"	a'	a"	a'	a"	a'	a"
Frequencies	769	772	778	780	790	812	813	814	816
IR Intensities	0	90	2	47	2	6	0	2	1
	a"	a"	a'	a'	a'	a"	a"	a'	a'
Frequencies	852	858	859	866	990	991	991	995	1038
IR Intensities	1	2	1	4	17	4	18	16	0
	a'	a"	a"	a'	a'	a"	a"	a"	a'
Frequencies	1040	1040	1042	1104	1106	1222	1224	1353	1355
IR Intensities	0	0	0	7	3	0	0	0	1
	a'	a"	a"	a'	a"	a'	a"	a'	a"
Frequencies	1362	1363	1404	1407	1408	1411	1797	1833	3158
IR Intensities	1	0	2	2	3	2	865	283	0
	a"	a'	a'	a'	a"	a'	a"	a'	a'
Frequencies	3159	3162	3165	3174	3175	3175	3178	3186	3189
IR Intensities	0	0	1	0	0	0	1	0	0

Table S6. The theoretical harmonic vibrational frequencies (in cm^{-1}) and their infrared intensities (in km/mol) for the septet Cp$_2$Cr$_2$(CO)$_2$ **2H-1** using the BP86 method

	a"	a"	a"	a'	a"	a'	a'	a'	a"
Frequencies	44i	26i	22	24	67	74	120	143	153
IR Intensities			5	1	3	1	0	0	0

	a'	a"	a'	a"	a'	a'	a"	a'	a"
Frequencies	154	266	292	312	342	352	371	380	435
IR Intensities	1	4	1	1	25	2	5	24	14

	a'	a'	a"	a'	a"	a"	a'	a'	a"
Frequencies	440	483	553	556	563	570	572	583	752
IR Intensities	5	10	54	26	0	1	0	60	8

	a'	a'	a'	a"	a'	a"	a"	a'	a'
Frequencies	766	778	781	790	791	805	809	814	816
IR Intensities	106	1	15	0	21	6	0	15	2

	a'	a"	a"	a'	a'	a"	a'	a"	a"
Frequencies	849	849	852	863	985	987	988	996	1036
IR Intensities	0	3	0	0	17	11	16	11	0

	a'	a'	a"	a'	a'	a"	a"	a"	a'
Frequencies	1037	1039	1040	1100	1105	1221	1223	1347	1354
IR Intensities	2	1	0	12	4	0	0	0	10

	a'	a"	a'	a"	a'	a"	a"	a'	a'
Frequencies	1355	1363	1402	1402	1404	1417	1723	1791	3156
IR Intensities	1	11	2	3	2	2	2028	0	0

	a"	a'	a"	a'	a'	a"	a"	a'	a'
Frequencies	3156	3158	3162	3168	3174	3175	3180	3184	3188
IR Intensities	0	0	2	1	1	0	0	0	0

Table S7. The theoretical harmonic vibrational frequencies (in cm^{-1}) and their infrared intensities (in km/mol) for the singlet $Cp_2Cr_2(CO)_2$ structure **2S-1** using the BP86 method.

	a	a	a	a	a	a	a	a	a
Frequencies	37	39	40	57	96	111	119	139	197
IR Intensities	0	0	0	1	1	0	0	1	1
	a	a	a	a	a	a	a	a	a
Frequencies	224	298	302	320	332	352	374	413	449
IR Intensities	0	2	1	2	4	1	2	1	3
	a	a	a	a	a	a	a	a	a
Frequencies	493	528	550	561	568	571	576	580	757
IR Intensities	7	4	4	7	4	4	4	4	4
	a	a	a	a	a	a	a	a	a
Frequencies	764	772	776	789	795	810	812	814	815
IR Intensities	31	55	62	6	1	1	1	0	1
	a	a	a	a	a	a	a	a	a
Frequencies	842	848	862	868	982	983	994	995	1035
IR Intensities	2	3	1	0	11	9	4	21	1
	a	a	a	a	a	a	a	a	a
Frequencies	1038	1040	1042	1101	1102	1219	1221	1352	1353
IR Intensities	1	0	1	5	6	0	0	4	1
	a	a	a	a	a	a	a	a	a
Frequencies	1353	1357	1397	1400	1418	1419	1802	1817	3150
IR Intensities	0	0	3	3	1	1	1039	206	0
	a	a	a	a	a	a	a	a	a
Frequencies	3156	3158	3169	3173	3175	3179	3182	3187	3193
IR Intensities	0	0	0	1	0	0	0	0	1

Table S8 The theoretical Cartesian coordinates (in Å) for the triplet $Cp_2Cr_2(CO)_3$ structure **3T-1** using the BP86 method

Standard orientation:

Center Number	atomic Number	atomic type	Coordinates (angstroms)		
			X	Y	Z
1	24	0	-1.181695	0.060582	-0.005251
2	24	0	1.109634	-0.077332	0.000056
3	6	0	3.015164	-0.225899	1.135274
4	6	0	2.813869	1.141342	0.753619
5	6	0	2.793199	1.202706	-0.682489
6	1	0	3.068104	-0.605325	2.159144
7	1	0	2.662645	1.985559	1.431023
8	1	0	2.623967	2.102648	-1.278790
9	6	0	-3.022586	0.253452	1.208124
10	6	0	-3.022854	1.278668	0.198455
11	1	0	-2.967671	0.415728	2.288555
12	1	0	-2.994148	2.357534	0.370740
13	6	0	-0.069281	1.636439	-0.017078
14	8	0	0.092625	2.827981	-0.026882
15	6	0	0.345145	-1.051945	1.365835
16	8	0	0.033870	-1.730034	2.298888
17	6	0	3.114765	-1.017871	-0.061733
18	6	0	2.980821	-0.125888	-1.185973
19	1	0	3.262342	-2.099540	-0.109609
20	1	0	3.007814	-0.416107	-2.239509
21	6	0	-3.042076	-1.024932	0.548987
22	6	0	-3.066715	-0.790449	-0.867335
23	1	0	-3.008714	-2.002115	1.038814
24	1	0	-3.038677	-1.559478	-1.644638
25	6	0	0.346875	-1.100268	-1.328583
26	8	0	0.043272	-1.813141	-2.238385
27	6	0	-3.055950	0.627295	-1.084396
28	1	0	-3.026587	1.128736	-2.056244

Table S9 The theoretical Cartesian coordinates (in Å) for the triplet $Cp_2Cr_2(CO)_3$ structure **3T-2** using the BP86 method

Standard orientation:

Center Number	Atomic Number	Atomic Type	X	Y	Z
1	24	0	-0.000000	1.135579	-0.020228
2	24	0	-0.000000	-1.135579	-0.020228
3	6	0	0.945924	-2.815562	1.088870
4	6	0	1.432295	-2.784093	-0.260746
5	6	0	0.314020	-2.985412	-1.146889
6	6	0	-0.864844	-3.149906	-0.331491
7	6	0	-0.472239	-3.042193	1.043420
8	1	0	1.537785	-2.658444	1.994096
9	1	0	2.464603	-2.594440	-0.567255
10	1	0	0.348245	-3.008836	-2.239283
11	1	0	-1.881382	-3.309467	-0.700319
12	1	0	-1.140250	-3.071745	1.908734
13	6	0	0.472239	3.042193	1.043420
14	6	0	-0.945924	2.815562	1.088870
15	6	0	-1.432295	2.784093	-0.260746
16	6	0	-0.314020	2.985412	-1.146889
17	6	0	0.864844	3.149906	-0.331491
18	1	0	1.140250	3.071745	1.908734
19	1	0	-1.537785	2.658444	1.994096
20	1	0	-2.464603	2.594440	-0.567255
21	1	0	-0.348245	3.008836	-2.239283
22	1	0	1.881382	3.309467	-0.700319
23	6	0	1.430117	0.389419	-0.944087
24	8	0	2.410412	0.159570	-1.586719
25	6	0	-1.430117	-0.389419	-0.944087
26	8	0	-2.410412	-0.159570	-1.586719
27	6	0	0.000000	-0.000000	1.611049
28	8	0	0.000000	-0.000000	2.813912

Table S10 The theoretical Cartesian coordinates (in Å) for the singlet $Cp_2Cr_2(CO)_3$ structure **3S-1** using the BP86 method

Standard orientation:

Center number	atomic number	atomic type	Coordinates (angstroms)		
			X	Y	Z
1	24	0	-0.076586	-1.075658	0.000000
2	24	0	0.169598	1.101756	0.000000
3	6	0	1.026484	2.974927	0.726072
4	6	0	-0.344078	2.933873	1.159400
5	6	0	-1.187763	2.897844	0.000000
6	1	0	1.911508	3.023653	1.365353
7	1	0	-0.690485	2.868803	2.195303
8	1	0	-2.277692	2.812323	0.000000
9	6	0	1.187800	-2.744184	0.719470
10	6	0	-0.992897	-3.130718	0.000000
11	6	0	-0.156182	-2.982520	1.160185
12	1	0	2.055008	-2.557644	1.357926
13	1	0	-2.071994	-3.302956	0.000000
14	1	0	-0.494552	-3.019385	2.199260
15	6	0	-1.162752	-0.264560	1.260140
16	8	0	-1.949785	0.034640	2.108628
17	6	0	1.781568	0.247684	0.000000
18	8	0	2.941285	-0.052513	0.000000
19	6	0	1.026484	2.974927	-0.726072
20	6	0	-0.344078	2.933873	-1.159400
21	1	0	1.911508	3.023653	-1.365353
22	1	0	-0.690485	2.868803	-2.195303
23	6	0	1.187800	-2.744184	-0.719470
24	6	0	-0.156182	-2.982520	-1.160185
25	1	0	2.055008	-2.557644	-1.357926
26	1	0	-0.494552	-3.019385	-2.199260
27	6	0	-1.162752	-0.264560	-1.260140
28	8	0	-1.949785	0.034640	-2.108628

Table S11 The theoretical Cartesian coordinates (in Å) for the triplet $Cp_2Cr_2(CO)_2$ structure **2T-1** using the BP86 method

Standard orientation:

Center Number	atomic number	atomic type	X	Y	Z
1	24	0	-0.127017	1.143674	0.000000
2	24	0	-0.210361	-1.165604	-0.000000
3	6	0	0.292977	-3.007432	1.161962
4	6	0	1.512575	-2.376890	0.716223
5	1	0	-0.005813	-3.161966	2.201878
6	1	0	2.288142	-1.956894	1.362127
7	6	0	1.442406	2.587893	0.718441
8	6	0	0.174212	3.107350	1.159745
9	1	0	2.256857	2.246079	1.363308
10	1	0	-0.148581	3.207681	2.200071
11	6	0	-0.907146	-0.320428	1.518568
12	8	0	-1.344484	-0.007518	2.590129
13	6	0	0.292977	-3.007432	-1.161962
14	6	0	1.512575	-2.376890	-0.716223
15	1	0	-0.005813	-3.161966	-2.201878
16	1	0	2.288142	-1.956894	-1.362127
17	6	0	1.442406	2.587893	-0.718441
18	6	0	0.174212	3.107350	-1.159745
19	1	0	2.256857	2.246079	-1.363308
20	1	0	-0.148581	3.207681	-2.200071
21	6	0	-0.907146	-0.320428	-1.518568
22	8	0	-1.344484	-0.007518	-2.590129
23	6	0	-0.601892	3.434629	0.000000
24	1	0	-1.622895	3.827254	0.000000
25	6	0	-0.447912	-3.409254	-0.000000
26	1	0	-1.430973	-3.888608	-0.000000

Table S12 The theoretical Cartesian coordinates (in Å) for the quintet $Cp_2Cr_2(CO)_2$ structure **2Q-1** using the BP86 method

Standard orientation:

Center Number	Atomic number	Atomic Type	Coordinates (angstroms)		
			X	Y	Z
1	24	0	0.117462	1.196833	0.000000
2	24	0	0.113774	-1.156493	-0.000000
3	6	0	0.030034	-3.052170	1.161142
4	6	0	1.378381	-2.818459	0.719593
5	1	0	-0.304803	-3.099093	2.200712
6	1	0	2.243732	-2.649112	1.366918
7	6	0	1.316448	2.961184	0.719018
8	6	0	-0.038776	3.156496	1.160444
9	1	0	2.188976	2.823030	1.364151
10	1	0	-0.378607	3.167905	2.200051
11	6	0	-0.764172	-0.343959	1.403079
12	8	0	-1.387116	-0.051709	2.387965
13	6	0	0.030034	-3.052170	-1.161142
14	6	0	1.378381	-2.818459	-0.719593
15	1	0	-0.304803	-3.099093	-2.200712
16	1	0	2.243732	-2.649112	-1.366918
17	6	0	1.316448	2.961184	-0.719018
18	6	0	-0.038776	3.156496	-1.160444
19	1	0	2.188976	2.823030	-1.364151
20	1	0	-0.378607	3.167905	-2.200051
21	6	0	-0.764172	-0.343959	-1.403079
22	8	0	-1.387116	-0.051709	-2.387965
23	6	0	-0.873414	3.283301	0.000000
24	1	0	-1.959638	3.411853	0.000000
25	6	0	-0.805396	-3.200593	-0.000000
26	1	0	-1.884879	-3.371473	-0.000000

Table S13 The theoretical Cartesian coordinates (in Å) for the septet $Cp_2Cr_2(CO)_2$ structure **2H-1** using the BP86 method

Standard orientation:

Center Number	atomic number	atomic type	X	Y	Z
1	24	0	-0.001101	1.301315	-0.000000
2	24	0	-0.005282	-1.314145	0.000000
3	6	0	-0.387817	-3.143947	1.164751
4	6	0	0.984713	-3.099264	0.721711
5	1	0	-0.727913	-3.140736	2.203208
6	1	0	1.864866	-3.065144	1.369775
7	6	0	0.965019	3.249187	0.722937
8	6	0	-0.394303	3.253129	1.167337
9	1	0	1.851570	3.243114	1.364340
10	1	0	-0.732133	3.224593	2.206903
11	6	0	0.020835	-0.320763	1.586673
12	8	0	0.049895	0.011049	2.744090
13	6	0	-0.387817	-3.143947	-1.164751
14	6	0	0.984713	-3.099264	-0.721711
15	1	0	-0.727913	-3.140736	-2.203208
16	1	0	1.864866	-3.065144	-1.369775
17	6	0	0.965019	3.249187	-0.722937
18	6	0	-0.394303	3.253129	-1.167337
19	1	0	1.851570	3.243114	-1.364340
20	1	0	-0.732133	3.224593	-2.206903
21	6	0	0.020835	-0.320763	-1.586673
22	8	0	0.049895	0.011049	-2.744090
23	6	0	-1.236342	3.217120	-0.000000
24	1	0	-2.330677	3.194475	-0.000000
25	6	0	-1.225206	-3.167548	0.000000
26	1	0	-2.319317	-3.144544	0.000000

Table S14 The theoretical Cartesian coordinates (in Å) for the septet $Cp_2Cr_2(CO)_2$ structure **2S-1** using the BP86 method

Standard orientation:

Center Number	atomic Number	atomic Type	Coordinates (angstroms) X	Y	Z
1	24	0	-0.985678	0.076685	-0.215322
2	24	0	1.100418	0.026417	-0.415801
3	6	0	3.302007	0.595977	-0.084102
4	6	0	3.179870	-0.820554	-0.002025
5	6	0	2.234881	-1.117129	1.051249
6	6	0	1.802999	0.129638	1.634572
7	6	0	2.449110	1.195094	0.907541
8	1	0	3.885911	1.145347	-0.830412
9	1	0	3.667049	-1.554992	-0.648530
10	1	0	1.929915	-2.117614	1.368234
11	1	0	1.132981	0.246754	2.488426
12	1	0	2.320612	2.266663	1.080912
13	6	0	-3.215828	-0.548635	-0.408143
14	6	0	-3.149940	0.825316	-0.037554
15	6	0	-2.422007	0.919827	1.210161
16	6	0	-2.050547	-0.415535	1.602244
17	6	0	-2.521020	-1.323887	0.582638
18	1	0	-3.651979	-0.942694	-1.331472
19	1	0	-3.551609	1.668022	-0.606236
20	1	0	-2.225643	1.840393	1.766044
21	1	0	-1.507558	-0.696821	2.509084
22	1	0	-2.386165	-2.408379	0.571229
23	6	0	0.254652	-1.540055	-0.952059
24	8	0	0.037091	-2.691171	-1.220827
25	6	0	-0.314735	1.671541	-0.828955
26	8	0	0.004917	2.772331	-1.188391

Complete Gaussian 03 reference
(Reference 31)

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; 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.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. Gaussian 03, Revision C.02; Gaussian, Inc., Wallingford CT, **2004**.

Appendix

Results from density functional theory studies on $(\eta^5\text{-}Me_5C_5)_2Cr_2(CO)_n$ ($n = 4, 3, 2$) derivatives (B3LYP and BP86 methods).

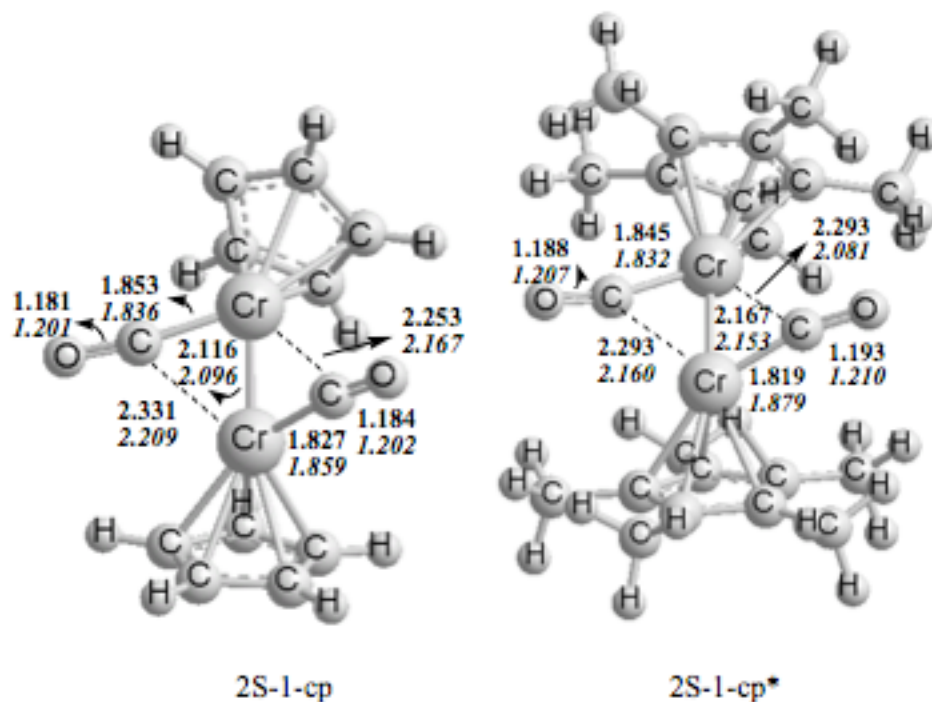2S-1-cp   2S-1-cp*

Figure A1. Comparison of the structures 2S-1-cp and 2S-1-cp*.

Table A1: The Cr-Cr bond length and the number of imaginary vibrational frequencies (Nimg) for 2S-1-cp and 2S-1-cp*.

		2S-1-cp *(C_s)	2S-1-cp (C_1)
B3LYP	Cr-Cr (Å)	2.167	2.116
	Nimg	0	0
BP86	Cr-Cr (Å)	2.153	2.096
	Nimg	0	0

Table A2 Infrared active $\nu(CO)$ vibrational frequencies (cm^{-1}) predicted for 2S-1-cp and 2S-1-cp* (infrared intensities in parentheses are in km/mol).

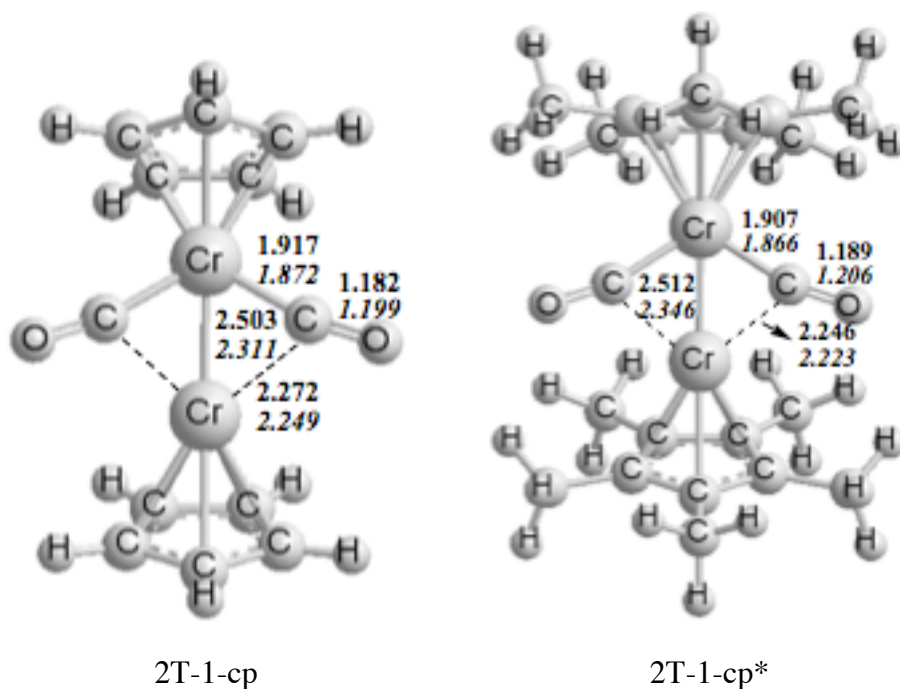|	BP86
2S-1-cp	1802 (1040), 1817 (206)
2S-1-cp*	1757(802), 1778(175)

2T-1-cp   2T-1-cp*

Figure A2. The structures of 2T-1-cp and 2T-1-cp*.

Table A3. The Cr-Cr bond length and the number of imaginary vibrational frequencies (Nimg) for 2T-1-cp and 2T-1-cp*.

		2T-1-cp *(C_s)	2T-1-cp (C_s)
B3LYP	Cr-Cr (Å)	2.512	2.503
	Nimg	0	0
BP86	Cr-Cr (Å)	2.346	2.311
	Nimg	1(13i)	0

Table A4. Infrared active ν(CO) vibrational frequencies (cm^{-1}) predicted for 2T-1-cp and 2T-1-cp* (infrared intensities in parentheses are in km/mol).

	BP86
2T-1-cp	1805 (998), 1838 (257)
2T-1-cp*	1766(839), 1799(183)

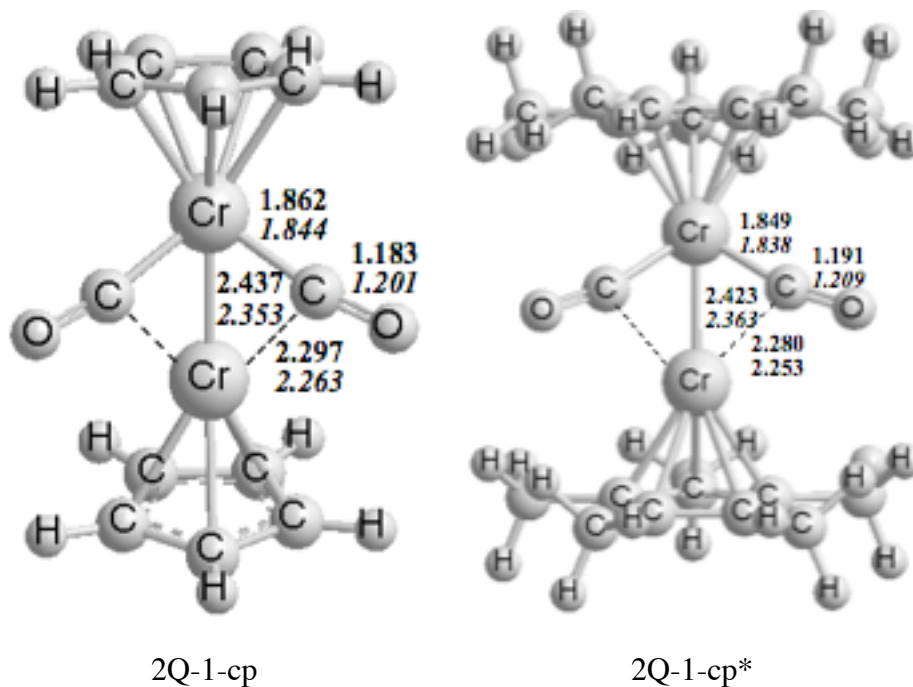2Q-1-cp   2Q-1-cp*

Figure A3. The structures of 2Q-1-cp and 2Q-1-cp*.

Table A5. The Cr-Cr bond length and the number of imaginary vibrational frequencies (Nimg) for 2Q-1-cp and 2Q-1-cp*.

		2Q-1-cp *(C_s)	2Q-1-cp (C_s)
B3LYP	Cr-Cr (Å)	2.423	2.437
		1 (7i)	
	Nimg	This small imaginary frequency disappears with a finer grid (120, 974).	1 (14i)
BP86	Cr-Cr (Å)	2.363	2.353
	Nimg	0	1 (17i)

Table A6. Infrared active ν(CO) vibrational frequencies (cm^{-1}) predicted for 2Q-1-cp and 2Q-1-cp* (infrared intensities in parentheses are in km/mol).

	BP86
2Q-1-cp	1797 (865), 1833 (283)
2Q-1-cp*	1756(12), 1793(12)

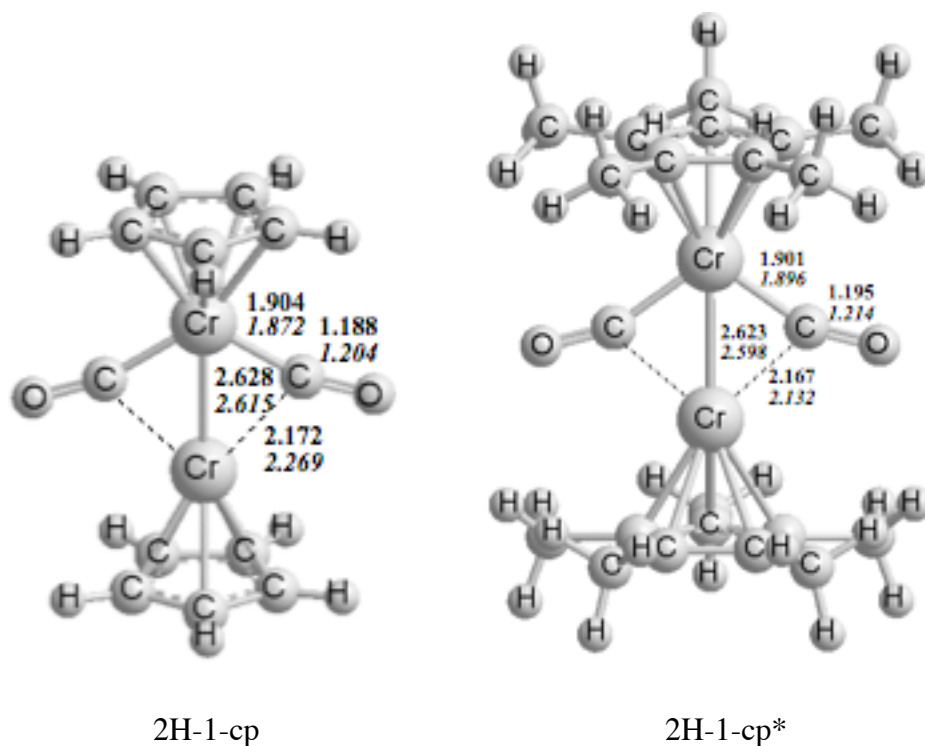2H-1-cp   2H-1-cp*

Figure A4. The structures of 2H-1-cp and 2H-1-cp*.

Table A7. The Cr-Cr bond length and the number of imaginary vibrational frequencies (Nimg) for 2H-1-cp and 2H-1-cp*.

		2H-1-cp* (C_s)	2H-1-cp (C_s)
B3LYP	Cr-Cr (Å)	2.623	2.628
	Nimg	2(24*i*,10*i*)	2(22*i*,18*i*)
BP86	Cr-Cr (Å)	2.598	2.615
	Nimg	0	2(44*i*,26*i*)

Table A8. Infrared active ν(CO) vibrational frequencies (cm^{-1}) predicted for 2H-1-cp and 2H-1-cp* (infrared intensities in parentheses are in km/mol).

	BP86
	BP86
2H-1-cp	1723 (2030), 1791 (0)
2H-1-cp*	1687(1110), 1738(3)

Table A9. The total energies (E, in hartree) and relative energies (ΔE, in kcal/mol) for the Cp*$_2$Cr$_2$(CO)$_2$ structures. The number of imaginary vibrational frequencies (Nimg) for each structure is also reported.

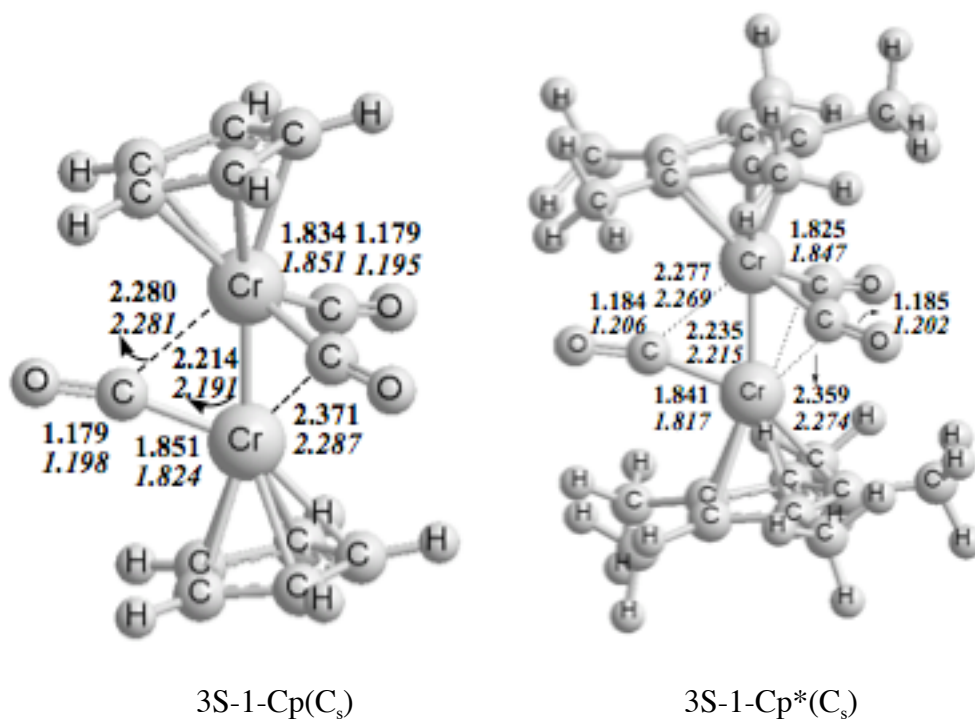|		2S-1-cp * (C$_1$)	2T-1-cp * (C$_s$)	2Q-1-cp * (C$_s$)	2H-1-cp* (C$_s$)
B3LYP	E	-3096.02410	-3096.09806	-3096.08255	-3096.08078
	ΔE	36.7	-9.7	0.0	1.1
	$\langle S^2 \rangle$	0.0	3.31	6.52	12.15
	Cr-Cr (Å)	2.167	2.512	2.423	2.623
	Nimg	0	0	1 (7i)	2(24i,10i)
BP86	E	-3096.38620	-3096.41206	-3096.40772	-3096.39298
	ΔE	13.5	-2.7	0.0	9.2
	$\langle S^2 \rangle$	0.0	4.33	6.16	12.09
	Cr-Cr (Å)	2.153	2.346	2.363	2.598
	Nimg	0	1(13i)	0	0

3S-1-Cp(C$_s$)   3S-1-Cp*(C$_s$)

Figure A5. The structures of 3S-1 and Cp*$_2$Cr$_2$(CO)$_3$.

Table A10. The Cr-Cr bond length and the number of imaginary vibrational frequencies (Nimg) for 3S-1-Cp and 3S-1-Cp*.

		3S-1-Cp*(C$_s$)	3S-1-Cp(C$_s$)
B3LYP	Cr-Cr (Å)	2.235	2.214
	Nimg	0	0
BP86	Cr-Cr (Å)	2.215	2.191
	Nimg	0	1(30i)

Table A11. Infrared active ν(CO) vibrational frequencies (cm^{-1}) predicted for 3S-1-Cp and 3S-1-Cp* (infrared intensities in parentheses are in km/mol).

	BP86
3S-1-Cp*	1792(733), 1795(545), 1833(188)
3S-1-Cp(C$_s$)	1833(670), 1837(928), 1870(144)

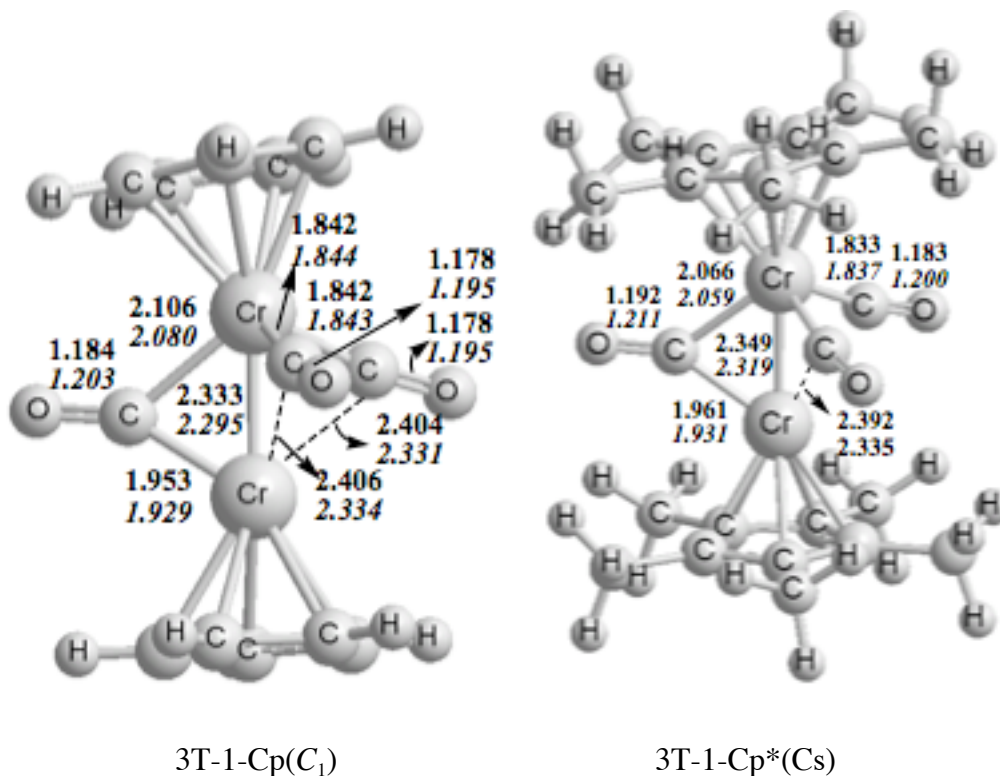3T-1-Cp(C_1)   3T-1-Cp*(Cs)

Figure A6. The structures of the triplets 3T-1-Cp and 3T-1-Cp*.

Table A12. The Cr-Cr bond lengths and the number of imaginary vibrational frequencies (Nimg) for 3T-1-Cp and the triplet 3T-1-Cp*

		3T-1-Cp*(Cs)	3T-1-Cp (C_1)
B3LYP	Cr-Cr (Å)	2.349	2.333
	Nimg	2(44i,11i)	0
BP86	Cr-Cr (Å)	2.319	2.295
		1(10i)	
	Nimg	This small imaginary frequency disappears with a finer grid (120974).	0

Table A13. Infrared active ν(CO) vibrational frequencies (cm^{-1}) predicted for the 3T-1-Cp and the triplet 3T-1-Cp* (infrared intensities in parentheses are in km/mol).

	BP86
3T-1-Cp* (triplet, Cs)	1747(639), 1801(657), 1842(205)
3T-1 (C_1)	1796(775),1831(789), 1872(211)

Table A14. The total energies (E, in hartree) and relative energies (ΔE, in kcal/mol) for the Cp*$_2$Cr$_2$(CO)$_3$ structures. The number of imaginary vibrational frequencies (Nimg) for each structure is also reported.

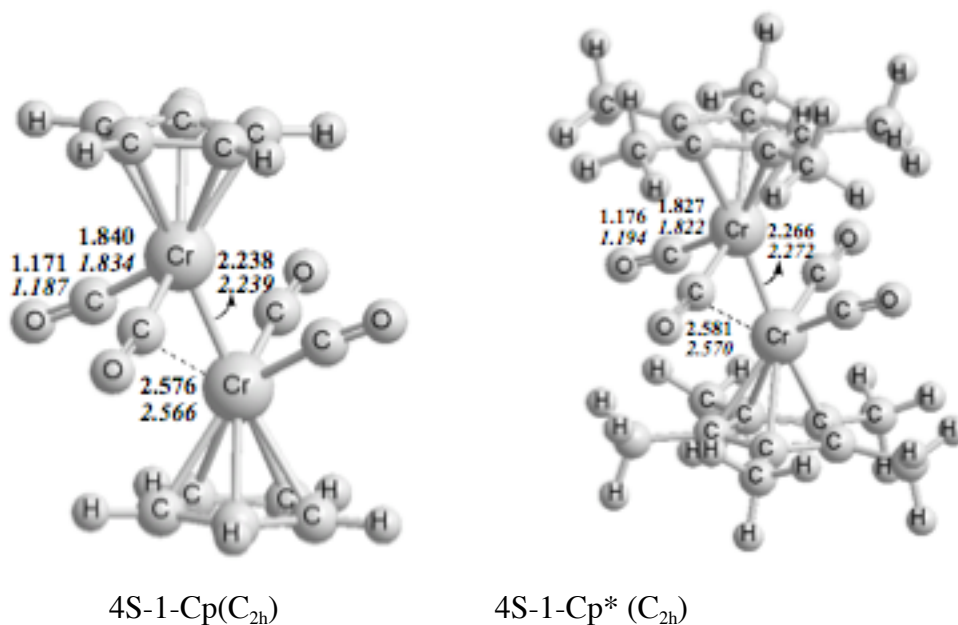|		3S-1-Cp*	3T-1-Cp*
B3LYP	E	-3209.44350	-3209.47802
	ΔE	21.7	0.0
	$\langle S^2 \rangle$	0.00	2.36
	Cr-Cr (Å)	2.235	2.349
	Nimg	0	2(44i,11i)
BP86	E	-3209.81066	-3209.82934
	ΔE	11.7	0.0
	$\langle S^2 \rangle$	0.00	2.11
	Cr-Cr (Å)	2.215	2.319
			1(10i)
	Nimg	0	This small imaginary frequency disappears with a finer grid (120,974).

4S-1-Cp(C$_{2h}$)   4S-1-Cp* (C$_{2h}$)

Figure A7. The structures of 4S-1-Cp and the triplet 4S-1-Cp *.

Table A15. Infrared active ν(CO) vibrational frequencies (cm^{-1}) predicted for the 4S-1-Cp and the triplet 4S-1-Cp* (infrared intensities in parentheses are in km/mol).

	BP86
4S-1-Cp (*C$_{2h}$*)	1876 (0), 1890 (1332), 1904 (1146), 1940 (0)
4S-1-Cp* (*C$_{2h}$*)	1838(0), 1852 (1109), 1869 (950), 1903 (0)