Chemistry–A European Journal

Supporting Information

**New Type of Aromatic π -Systems for Anion Recognition:
Strong Anion- π and C–H...Anion Interactions Between
Halides and Aromatic Ligands in Half-Sandwich
Compounds**

Dušan P. Malenov and Snežana D. Zarić*

SUPPORTING INFORMATION

Estimation of CCSD(T)/CBS interaction energies

The CCSD(T)/CBS interaction energies were estimated by using the energies obtained by the Møller-Plesset perturbation theory of the second order (MP2)¹ at the complete basis set (CBS). The MP2/CBS values were obtained using the procedure of Helgaker² to extrapolate the BSSE corrected MP2 interaction energies calculated with aug-cc-pVDZ³ and aug-cc-pVTZ³ basis sets to the complete basis set. This procedure separately extrapolates the HF and correlation (CORR) energies according to the following formulas:

$$\Delta E(\text{HF/CBS}) = \frac{\Delta E(\text{HF/aug-cc-pVDZ}) \cdot \exp(-1.63 \cdot 3) - \Delta E(\text{HF/aug-cc-pVTZ}) \cdot \exp(-1.63 \cdot 2)}{\exp(-1.63 \cdot 3) - \exp(-1.63 \cdot 2)}$$

$$\Delta E(\text{CORR/CBS}) = \frac{3^3 \cdot \Delta E(\text{CORR/aug-cc-pVTZ}) - 2^3 \cdot \Delta E(\text{CORR/aug-cc-pVDZ})}{3^3 - 2^3}$$

The MP2/CBS energy is then the sum of HF and CORR energies at the complete basis set:

$$\Delta E(\text{MP2/CBS}) = \Delta E(\text{HF/CBS}) + \Delta E(\text{CORR/CBS}).$$

The estimation of CCSD(T)/CBS interaction energies was then done by calculating the BSSE corrected CCSD(T)/aug-cc-pVDZ interaction energies and taking into account the same basis set dependence of CCSD(T) and MP2 methods:⁴

$$\Delta E(\text{CCSD(T)/CBS}) = \Delta E(\text{MP2/CBS}) + \Delta E(\text{CCSD(T)/aug-cc-pVDZ}) - \Delta E(\text{MP2/aug-cc-pVDZ}).$$

Performance of DFT-D3 on anion- π interaction between coordinated Cp and halides

Table S1. Performance of different dispersion corrected DFT methods against the estimated CCSD(T)/CBS interaction energies for anion- π interactions between Cp ligand in half-sandwich compounds and halide anions. All energies are given in kcal/mol. Mean absolute errors (MAE) and mean signed errors (MSE) in kcal/mol for all methods are also given.

	MnCp(CO) ₃			FeCp(CN)(CO) ₂				
	F ⁻	Cl ⁻	Br ⁻	F ⁻	Cl ⁻	Br ⁻		
CCSD(T)/CBS	-14.72	-11.56	-10.87	-21.65	-17.01	-15.99		
<i>with def2-TZVP basis set</i>							MAE	MSE
MP2	-24.92	-20.20	-18.96	-31.67	-25.46	-23.81	8.87	8.87
ω B97xD	-12.75	-9.56	-8.86	-20.44	-15.48	-14.29	1.74	-1.74
B2PLYP-D3	-18.98	-14.45	-13.37	-26.68	-20.43	-18.90	3.50	3.50
B3LYP-D3	-14.56	-10.68	-9.80	-22.27	-16.71	-15.38	0.61	-0.40
B97-D3	-16.00	-11.58	-10.54	-24.01	-17.82	-16.29	0.85	0.74
BLYP-D3	-16.48	-11.83	-10.70	-24.35	-17.99	-16.39	1.05	0.99
PBE-D3	-17.47	-12.17	-10.98	-25.45	-18.33	-16.67	1.55	1.55
B3PW91-D3	-14.35	-10.81	-10.13	-22.11	-16.84	-15.74	0.46	-0.30
<i>with 6-31++G** basis set</i>								
MP2	-24.32	-18.44	-17.95	-30.61	-23.23	-22.49	7.54	7.54
ω B97xD	-12.34	-9.69	-9.21	-19.48	-15.20	-14.36	1.92	-1.92
B2PLYP-D3	-18.07	-13.60	-12.98	-25.26	-19.12	-18.20	2.57	2.57
B3LYP-D3	-13.72	-10.39	-9.79	-20.87	-15.98	-15.06	1.00	-1.00
B97-D3	-14.62	-11.19	-10.53	-22.03	-16.95	-15.97	0.21	-0.09
BLYP-D3	-15.04	-11.24	-10.52	-22.27	-16.87	-15.84	0.32	0.00
PBE-D3	-15.83	-11.62	-10.87	-23.18	-17.27	-16.19	0.53	0.53
B3PW91-D3	-13.38	-10.57	-10.19	-20.58	-16.20	-15.52	0.89	-0.89

SAPT analysis of optimized interactions of aromatic ligands in manganese half-sandwich compounds with anions

Table S2. Decomposition of SAPT0/def2-TZVP interaction energies (in kcal/mol) into electrostatic (ELST), exchange (EXCH), induction (IND) and dispersion component (DISP) for anion- π interactions, C-H $\cdots$ X $^-$ hydrogen bonding and σ -complex interactions between ligands in half-sandwich compounds (Figures 2 and 3 in the main text) and halide anions. The anion- π interactions are obtained by a series of B97-D3/6-31++G** single point calculations in order to determine the optimal d_π distances between anion and center of the aromatic ring (Figure 4 in the main text), while C-H $\cdots$ X $^-$ hydrogen bonds and σ -complex interactions were obtained by optimizing the anion- π interactions at the B97-D3/6-31++G** level of theory. B97-D3/6-31++G** interaction energies (in kcal/mol) are also given for comparison with SAPT0/def2-TZVP interaction energies.

	π -system	anion	B97-D3 6-31++G**	SAPT0 def2-TZVP	ELST	EXCH	IND	DISP
anion- π	Mn-Cp	F $^-$	-14.62	-8.42	-5.87	+18.93	-16.02	-5.45
		Cl $^-$	-11.19	-7.27	-5.66	+12.77	-8.00	-6.38
		Br $^-$	-10.53	-7.04	-6.73	+13.15	-6.48	-6.97
	Mn-Cp*	F $^-$	-19.22	-11.85	-2.37	+11.87	-16.00	-5.34
		Cl $^-$	-16.14	-11.33	-5.42	+11.27	-9.44	-7.74
		Br $^-$	-15.65	-11.38	-6.69	+11.98	-8.01	-8.65
	Mn-Ind	F $^-$	-15.02	-9.89	-1.61	+10.67	-14.51	-4.45
		Cl $^-$	-10.71	-7.94	-3.82	+11.34	-8.57	-6.88
		Br $^-$	-10.14	-7.67	-4.12	+10.43	-6.84	-7.14
C-H $\cdots$ X $^-$ hydrogen bond	Mn-Cp	F $^-$	-32.04	-32.00	-42.20	+54.09	-37.29	-6.61
		Cl $^-$	-16.01	-12.94	-12.23	+11.38	-7.90	-4.18
		Br $^-$	-14.32	-11.68	-13.28	+14.34	-7.42	-5.33
	Mn-Ind	F $^-$	-32.05	-34.40	-43.50	+55.58	-39.67	-6.82
		Cl $^-$	-17.98	-16.60	-14.94	+14.74	-11.15	-5.25
		Br $^-$	-15.68	-15.28	-16.36	+18.77	-10.88	-6.82
	Mn-Cp*	F $^-$	-29.23	-25.38	-25.98	+31.35	-25.13	-5.62
		Cl $^-$	-19.41	-14.84	-10.58	+14.50	-10.55	-8.21
		Br $^-$	-18.34	-14.59	-13.99	+20.48	-9.66	-11.42
σ -complex	Cr-C ₆ H ₆	Br $^-$	-17.71	-17.38	-23.89	+26.23	-11.35	-8.38
	Fe-Cp	Cl $^-$	-23.74	-13.87	-18.86	+24.27	-11.89	-7.39
		Br $^-$	-22.84	-12.09	-23.85	+34.13	-12.48	-9.89
	Fe-Ind	Cl $^-$	-22.61	-14.50	-18.06	+24.68	-13.23	-7.89
		Br $^-$	-21.30	-12.88	-23.17	+34.22	-13.70	-10.23
	Mn-Cp	Cl $^-$	-15.20	-8.60	-8.59	+12.96	-8.56	-4.41
		Br $^-$	-13.97	-5.73	-11.28	+22.20	-9.15	-7.50
	Mn-Ind	Cl $^-$	-14.59	-9.50	-8.49	+13.01	-9.41	-4.62
		Br $^-$	-13.25	-7.11	-11.35	+21.82	-10.02	-7.56

xyz coordinates of the most stable gas phase anion- π systems

For all the systems of this half-sandwich compound the coordinates of atoms of half-sandwich compound are the same, and the coordinates of halide anions are different.

anion- π Cr-C₆H₆-X

C	1.633561	-0.246186	1.395850
C	1.634800	1.331298	-0.485009
C	1.633863	-1.086178	-0.910840
C	1.634310	1.075972	0.922040
C	1.634217	0.260021	-1.393197
C	1.633687	-1.336981	0.471084
H	1.567635	-0.442366	2.457975
H	1.569623	2.349257	-0.846187
H	1.568143	-1.907896	-1.611821
H	1.568856	1.902114	1.617827
H	1.568704	0.449695	-2.456535
H	1.567861	-2.352633	0.838553
Cr	-0.007182	0.000083	-0.000017
C	-1.152618	-0.884355	1.042788
C	-1.151924	1.346014	0.244541
C	-1.152770	-0.460860	-1.287321
O	-1.971873	-1.437984	1.695655
O	-1.970977	2.188440	0.397319
O	-1.972300	-0.749537	-2.092852
F	4.284043	-0.001761	0.001006
Cl	4.934043	-0.002068	0.001176
Br	5.084043	-0.002139	0.001216

xyz coordinates of the most stable gas phase anion- π systems

For all the systems of this half-sandwich compound the coordinates of atoms of half-sandwich compound are the same, and the coordinates of halide anions are different.

anion- π Mn-Cp-X⁻

Mn	-0.034856	0.001119	-0.000765
C	-1.671966	1.206002	-0.221449
C	-1.682028	-1.084618	-0.546049
C	-1.677923	0.178006	-1.216295
C	1.004125	0.267081	-1.309215
C	-1.692158	-0.837212	0.865445
C	-1.690076	0.577002	1.065278
C	0.968322	-1.289404	0.430297
C	0.984083	1.008162	0.897466
O	1.714863	-2.171375	0.723834
O	1.777887	0.448325	-2.197100
O	1.742430	1.696045	1.507938
H	-1.628617	2.267545	-0.406943
H	-1.647070	-2.053502	-1.018717
H	-1.649131	0.328570	-2.284041
H	-1.671992	-1.586974	1.640627
H	-1.667512	1.082303	2.017954
F	-4.232671	0.029192	-0.017742
Cl	-4.882645	0.034731	-0.019574
Br	-5.032639	0.036010	-0.019996

anion- π Fe-Cp-X⁻

Fe	0.012039	0.051016	-0.000042
C	-1.589981	-0.221506	-1.161513
C	-1.590334	-0.218633	1.161821
C	-1.645011	-1.058347	0.001191
C	0.707097	-1.583464	0.001794
C	-1.451440	1.136092	0.718240
C	-1.451234	1.134323	-0.721298
C	1.039522	0.544994	1.150940
C	1.039793	0.542509	-1.151834
O	1.794239	0.942785	1.979250
N	1.170933	-2.681742	0.002932
O	1.794662	0.938224	-1.981000
H	-1.569518	-0.567619	-2.183192
H	-1.570125	-0.562207	2.184364
H	-1.722133	-2.133167	0.002514
H	-1.354896	2.004105	1.351848
H	-1.354552	2.000768	-1.357025
F	-4.037050	0.358862	0.028752
Cl	-4.684832	0.411974	0.036320
Br	-4.834320	0.424231	0.038066

xyz coordinates of the most stable gas phase anion- π systems

For all the systems of this half-sandwich compound the coordinates of atoms of half-sandwich compound are the same, and the coordinates of halide anions are different.

anion- π Mn-Cp*-X⁻

Mn	-0.013464	-0.052084	0.617811
O	-2.338106	0.935829	2.163156
O	2.055407	1.201356	2.327373
C	-1.398863	0.533488	1.587343
C	1.219132	0.695569	1.679216
C	-1.162053	-0.191959	-1.215804
C	-0.068901	-1.118764	-1.276720
C	1.161530	-0.376426	-1.170473
C	-2.622217	-0.527268	-1.362998
C	-0.185419	-2.602493	-1.504580
C	2.551928	-0.946765	-1.252964
H	-2.924228	-0.482509	-2.422330
H	-3.253114	0.175374	-0.804533
H	-0.213854	-2.816801	-2.584866
H	-1.100125	-3.007814	-1.055192
H	0.665273	-3.144538	-1.074702
H	2.886686	-1.015472	-2.301402
H	2.595375	-1.953358	-0.818441
H	3.271763	-0.320951	-0.710795
C	0.072603	-1.625665	1.467874
C	-0.608100	1.139600	-1.095454
C	0.820396	1.023629	-1.077128
H	-2.840443	-1.536677	-0.992716
O	0.136043	-2.679350	1.978781
C	-1.397773	2.421063	-1.094835
C	1.797804	2.168983	-1.061011
H	-1.569761	2.767934	-2.126852
H	-2.376548	2.287782	-0.617821
H	-0.870071	3.216512	-0.554520
H	2.029444	2.482689	-2.091484
H	1.391467	3.036488	-0.526610
H	2.739473	1.890051	-0.573405
F	0.118917	0.330350	-3.855422
Cl	0.137286	0.378278	-4.403022
Br	0.142296	0.391349	-4.552368

anion- π Fe-Cp*-X⁻

Fe	-0.131175	0.014549	-0.465255
O	-1.479950	2.019859	-1.891310
O	-1.507851	-1.890655	-1.999649
C	-0.880872	1.176324	-1.285172
C	-0.896045	-1.090321	-1.349545
C	0.597009	1.122884	1.032139
C	1.387206	-0.075224	0.862913
C	0.507487	-1.214752	0.984427
C	1.142532	2.513719	0.985783
C	2.880258	-0.135103	0.816430
C	0.943906	-2.640883	0.883557
H	1.600940	2.758859	1.946929
H	0.355661	3.235304	0.778791
H	3.243099	-0.193494	1.846503
H	3.296854	0.746647	0.337667
H	3.223820	-1.005940	0.264850
H	1.368299	-2.960908	1.838301
H	1.699720	-2.750232	0.107920
H	0.106727	-3.290017	0.637745
C	1.296466	0.040377	-1.511801
C	-0.769633	0.726476	1.243636
C	-0.823849	-0.724757	1.212973
H	1.895779	2.596396	0.204089
N	2.235902	0.066144	-2.250297
C	-1.919464	1.632194	1.555171
C	-2.041952	-1.552950	1.476582
H	-2.022332	1.727563	2.638529
H	-1.767425	2.621940	1.130431
H	-2.845880	1.231922	1.148790
H	-2.157779	-1.694939	2.553549
H	-2.931755	-1.060745	1.089956
H	-1.965333	-2.528567	1.001850
F	0.635937	-0.115385	3.777893
Cl	0.710530	-0.128840	4.221463
Br	0.735394	-0.133325	4.369320

xyz coordinates of the most stable gas phase anion- π systems

For all the systems of this half-sandwich compound the coordinates of atoms of half-sandwich compound are the same, and the coordinates of halide anions are different.

anion- π Mn-Ind- X^-

Mn	0.683357	0.116956	-0.005681
O	0.993489	-1.823623	2.105894
O	0.951624	-2.035084	-1.908090
O	3.551388	0.171079	-0.036596
C	0.845322	-1.009172	1.248331
C	0.821280	-1.134843	-1.138202
C	2.355203	0.174666	-0.025212
C	-1.170004	0.743243	-0.756796
C	-0.071996	1.548327	-1.229787
H	0.211184	1.689720	-2.261910
C	0.556949	2.154037	-0.095714
H	1.406508	2.819299	-0.125643
C	-0.070657	1.651205	1.088192
H	0.213420	1.883536	2.103477
C	-1.168688	0.806703	0.689531
C	-2.161234	0.100439	1.439388
H	-2.157194	0.139495	2.521753
C	-3.117683	-0.599014	0.745438
H	-3.888626	-1.129725	1.290127
C	-3.119254	-0.661318	-0.686534
H	-3.891435	-1.237120	-1.181398
C	-2.163858	-0.025528	-1.440600
H	-2.162052	-0.080555	-2.522264
F	-2.130317	3.499584	-0.224418
Cl	-2.447679	3.884807	-0.254161
Br	-2.574624	4.038896	-0.266058

anion- π Fe-Ind- X^-

Fe	-0.729845	-0.003615	-0.058841
N	0.296470	-0.773528	2.615025
O	-1.732590	2.433931	0.898763
O	-3.216451	-1.183392	0.431912
C	-0.134549	-0.478049	1.541120
C	-1.277525	1.405245	0.505426
C	-2.141565	-0.708601	0.237605
C	1.023044	0.598960	-0.921380
C	-0.166002	0.878881	-1.692713
H	-0.478471	1.851088	-2.044435
C	-0.822938	-0.373072	-1.971204
H	-1.727496	-0.500791	-2.546273
C	-0.090613	-1.417669	-1.311714
H	-0.360218	-2.462970	-1.283229
C	1.063008	-0.832755	-0.686159
C	2.152245	-1.418168	0.030853
H	2.183076	-2.486197	0.202158
C	3.130251	-0.580648	0.500900
H	3.967039	-0.993314	1.049663
C	3.066363	0.839506	0.310014
H	3.855941	1.453233	0.725375
C	2.040746	1.441259	-0.377065
H	1.998341	2.513985	-0.518072
F	1.647578	-0.497794	-3.520937
Cl	1.947745	-0.553535	-3.978422
Br	2.029609	-0.568737	-4.103191

xyz coordinates of gas phase optimized C-H...X hydrogen bonding systems

hydrogen bonding C₆H₆-F⁻

C	-0.686154	0.000170	-0.000039
C	1.452962	-1.215239	0.000008
C	1.453202	1.215079	0.000012
C	0.045016	-1.206161	-0.000015
C	2.164074	-0.000161	0.000019
C	0.045268	1.206337	-0.000019
H	-1.823053	0.000128	-0.000078
H	1.999067	-2.164274	0.000016
H	1.999611	2.163938	0.000019
H	-0.503217	-2.152601	-0.000022
H	3.257886	-0.000194	0.000031
H	-0.502770	2.152894	-0.000023
F	-3.474860	-0.000004	0.000029

hydrogen bonding C₆H₆-Br⁻

C	0.947380	-0.702968	0.000028
C	2.165781	-1.402794	0.000004
C	3.388441	-0.703390	-0.000017
C	3.388765	0.702823	-0.000018
C	2.166430	1.402800	0.000007
C	0.947710	0.703526	0.000027
H	-0.023114	-1.204710	0.000046
H	2.166129	-2.495974	0.000003
H	4.334923	-1.250833	-0.000033
H	4.335499	1.249832	-0.000037
H	2.167306	2.495980	0.000005
H	-0.022538	1.205737	0.000039
Br	-2.599579	0.000000	-0.000006

hydrogen bonding C₆H₆-Cl⁻

C	0.136971	-0.703352	0.000001
C	1.355474	-1.404145	0.000002
C	2.577418	-0.703174	-0.000002
C	2.577432	0.703139	0.000000
C	1.355506	1.404146	0.000001
C	0.136986	0.703389	-0.000001
H	-0.835238	-1.202755	0.000000
H	1.357170	-2.497356	0.000001
H	3.524579	-1.249607	-0.000003
H	3.524601	1.249560	-0.000001
H	1.357254	2.497357	0.000001
H	-0.835219	1.202798	0.000000
Cl	-3.348934	-0.000001	0.000000

xyz coordinates of gas phase optimized C-H...X hydrogen bonding systems

hydrogen bonding Cr-C₆H₆-F⁻

C	-1.884678	-0.357226	0.003777
C	-0.222585	-1.789403	1.178032
C	-0.234855	-1.717909	-1.276738
C	-1.315728	-0.864271	1.195634
C	0.30986	-2.229122	-0.057176
C	-1.303297	-0.78999	-1.232829
H	-2.850863	0.335266	0.019253
H	0.224639	-2.132483	2.111901
H	0.211201	-2.008362	-2.228693
H	-1.699372	-0.512803	2.154336
H	1.162303	-2.90717	-0.080229
H	-1.689035	-0.372105	-2.163691
Cr	0.434012	0.009844	0.000559
C	0.171877	1.701102	-0.673318
C	1.180969	0.727773	1.507153
C	2.08048	-0.023334	-0.77559
O	0.030639	2.77948	-1.119849
O	1.667602	1.166334	2.489946
O	3.149264	-0.076274	-1.282429
F	-4.138607	0.939929	0.028744

hydrogen bonding Cr-C₆H₆-Br⁻

C	0.684966	0.79982	-0.705053
C	-0.37284	1.441204	1.41701
C	-1.413691	2.095297	-0.7149
C	0.685138	0.799751	0.704757
C	-1.413565	2.095319	0.715108
C	-0.373033	1.441439	-1.417141
H	1.508755	0.286303	-1.204354
H	-0.396768	1.397998	2.505203
H	-2.240504	2.552811	-1.256937
H	1.509073	0.286284	1.203858
H	-2.240264	2.552795	1.257342
H	-0.397134	1.39835	-2.505329
Cr	-1.329654	-0.035555	-0.000031
C	-1.263262	-1.342459	-1.287972
C	-1.26682	-1.339932	1.29059
C	-3.152078	-0.139776	-0.002511
O	-1.230632	-2.168129	-2.125269
O	-1.236304	-2.163877	2.12969
O	-4.333233	-0.175669	-0.004105
Br	3.882315	-0.190394	-0.000025

hydrogen bonding Cr-C₆H₆-Cl⁻

C	1.356211	0.450404	-0.698933
C	0.411683	1.265943	1.416656
C	-0.487648	2.087343	-0.721445
C	1.351367	0.455688	0.709978
C	-0.492652	2.092964	0.707819
C	0.421969	1.255964	-1.418221
H	2.096742	-0.176775	-1.195987
H	0.37544	1.230894	2.504669
H	-1.217182	2.68387	-1.267928
H	2.087371	-0.168118	1.2175
H	-1.225765	2.693737	1.244714
H	0.393475	1.213103	-2.506156
Cr	-0.793803	-0.019323	0.0001
C	-0.962818	-1.319076	-1.28422
C	-0.988239	-1.294884	1.304534
C	-2.60331	0.207657	-0.019402
O	-1.078686	-2.137803	-2.122226
O	-1.120073	-2.097842	2.155502
O	-3.772163	0.38173	-0.032054
Cl	4.486422	-0.434922	0.000613

xyz coordinates of gas phase optimized C-H...X hydrogen bonding systems

hydrogen bonding Fe-Cp-F⁻

Fe	-0.373918	-0.000638	0.023227
C	-0.121953	-2.007749	0.622911
C	0.962353	-1.101883	-1.204029
C	-0.130183	-1.938208	-0.803566
C	-1.968033	0.094147	-1.032730
C	1.697527	-0.657069	-0.037275
C	1.001235	-1.216505	1.079842
C	0.143325	1.618704	-0.471854
C	-1.225699	0.523734	1.465859
O	0.474696	2.685579	-0.799597
N	-2.950779	0.106597	-1.690138
O	-1.773130	0.847165	2.449079
H	-0.845348	-2.535123	1.238863
H	1.190168	-0.822665	-2.228810
H	-0.883140	-2.372963	-1.453747
H	2.710110	0.015522	0.000883
H	1.262254	-1.047957	2.121549
F	3.908812	0.653402	0.070837

hydrogen bonding Fe-Cp-Br⁻

Fe	1.242580	-0.016825	-0.000057
C	0.711504	1.682595	1.155572
C	0.707746	1.678261	-1.160535
C	1.436338	2.101025	-0.004429
C	3.154697	-0.050020	-0.006097
C	-0.486391	1.007200	-0.709668
C	-0.484160	1.009913	0.711028
C	1.161223	-1.211647	-1.295116
C	1.168372	-1.202483	1.303568
O	1.100099	-1.984240	-2.165698
N	4.336052	-0.019359	-0.010069
O	1.111415	-1.968262	2.180503
H	1.026954	1.822195	2.184247
H	1.019996	1.813643	-2.190744
H	2.409856	2.580078	-0.006929
H	-1.283217	0.549415	-1.291752
H	-1.278557	0.553888	1.297686
Br	-3.613216	-0.149008	-0.000140

hydrogen bonding Fe-Cp-Cl⁻

Fe	0.699563	-0.014589	-0.000083
C	0.027896	1.630932	1.157601
C	0.027709	1.630150	-1.158722
C	0.717133	2.109764	-0.000756
C	2.609052	0.116816	-0.000912
C	-1.112055	0.867306	-0.710402
C	-1.111947	0.867767	0.709952
C	0.720371	-1.207255	-1.298810
C	0.720976	-1.205105	1.300597
O	0.723046	-1.980107	-2.171839
N	3.783546	0.247764	-0.001483
O	0.723799	-1.976303	2.175090
H	0.329532	1.795343	2.186940
H	0.329203	1.793904	-2.188204
H	1.647657	2.667490	-0.001014
H	-1.876166	0.354835	-1.290549
H	-1.875908	0.355677	1.290622
Cl	-4.141022	-0.325485	-0.000150

xyz coordinates of gas phase optimized C-H...X hydrogen bonding systems

hydrogen bonding Mn-Cp-F⁻

Mn	0.410672	0.018429	0.000012
C	-1.053574	1.137319	1.145504
C	0.013563	2.005394	-0.712342
C	0.013210	2.004258	0.715292
C	1.620835	-0.241931	1.279786
C	-1.054270	1.139095	-1.143309
C	-1.737109	0.606204	0.000367
C	1.579148	-0.273786	-1.311402
C	-0.159706	-1.690439	0.030130
O	2.347236	-0.427695	-2.192764
O	2.417083	-0.374165	2.139543
O	-0.505792	-2.807290	0.050344
H	-1.298960	0.909397	2.179161
H	0.711486	2.543667	-1.349115
H	0.711308	2.541396	1.352911
H	-1.299766	0.912544	-2.177264
H	-2.713370	-0.076052	-0.000094
F	-3.975365	-0.726128	-0.000782

hydrogen bonding Mn-Cp-Br⁻

Mn	1.317695	0.002658	0.000045
C	0.629411	1.700358	1.15158
C	0.599527	1.676949	-1.167861
C	1.314241	2.155425	-0.021721
C	3.098963	0.01448	-0.030993
C	-0.535363	0.933828	-0.696308
C	-0.516878	0.94787	0.723814
C	1.206831	-1.239533	-1.285765
C	1.251312	-1.205184	1.32041
O	1.138435	-2.029716	-2.149127
O	4.275612	0.058959	-0.051847
O	1.210934	-1.972031	2.206601
H	0.932489	1.882756	2.17769
H	0.875895	1.83871	-2.204885
H	2.231071	2.738543	-0.039341
H	-1.31256	0.430947	-1.266698
H	-1.276162	0.455352	1.325615
Br	-3.705178	-0.165018	0.000073

hydrogen bonding Mn-Cp-Cl⁻

Mn	0.760376	0.006533	-0.000987
C	-0.08442	1.613078	1.177581
C	-0.077379	1.642375	-1.141416
C	0.579036	2.149954	0.023979
C	2.524273	0.159082	0.195178
C	-1.156956	0.797922	-0.706428
C	-1.161056	0.784198	0.714289
C	0.907369	-1.093989	-1.404182
C	0.647903	-1.333093	1.185153
O	1.00048	-1.78721	-2.346499
O	3.686169	0.298454	0.327902
O	0.577125	-2.189035	1.9827
H	0.18656	1.798426	2.212127
H	0.202093	1.848969	-2.169907
H	1.444898	2.806286	0.033802
H	-1.889264	0.256471	-1.299296
H	-1.897028	0.227678	1.289195
Cl	-4.24938	-0.352706	-0.001117

xyz coordinates of gas phase optimized C-H...X hydrogen bonding systems

hydrogen bonding Fe-Cp*-F⁻

Fe	-0.735714	-0.008670	0.424980
O	-0.588376	1.648542	2.841439
O	-1.800808	-2.412477	1.717754
C	-0.663765	0.987600	1.878654
C	-1.398443	-1.436017	1.207696
C	0.334805	1.125088	-1.022049
C	-0.248598	-0.043877	-1.642447
C	0.306999	-1.200667	-1.002538
C	0.056517	2.548113	-1.414638
C	-1.187772	-0.039628	-2.815695
C	0.050979	-2.632679	-1.385803
H	0.644078	2.828418	-2.304847
H	0.326113	3.233163	-0.600955
H	-0.609761	-0.029802	-3.755309
H	-1.843676	0.837453	-2.791799
H	-1.831710	-0.927733	-2.814939
H	0.790509	-2.955545	-2.136551
H	-0.951889	-2.761416	-1.812338
H	0.140056	-3.297943	-0.518112
C	-2.452109	0.675362	-0.079511
C	1.309614	0.679856	-0.052799
C	1.247100	-0.756369	0.002039
H	-1.009382	2.687078	-1.637283
N	-3.483112	1.124729	-0.446501
C	2.331298	1.477005	0.663702
C	2.196369	-1.590003	0.806796
H	3.334631	1.091781	0.239289
H	2.192559	2.558376	0.536084
H	2.358383	1.237922	1.736044
H	3.218748	-1.341509	0.440505
H	2.156226	-1.315857	1.870702
H	1.982656	-2.663438	0.714572
F	4.492035	0.057793	-0.269224

hydrogen bonding Fe-Cp*-Cl⁻

Fe	-1.058858	0.052690	-0.181364
O	-2.261409	-1.657684	-2.232171
O	-2.293555	2.576293	-1.015533
C	-1.796403	-0.970909	-1.404002
C	-1.829829	1.554980	-0.673886
C	0.487887	-1.225507	0.535121
C	0.357229	-0.120711	1.445688
C	0.604496	1.083645	0.719448
C	0.395477	-2.676085	0.904952
C	0.108003	-0.224204	2.921321
C	0.696359	2.465455	1.296621
H	1.370705	-3.019460	1.286080
H	0.129902	-3.293169	0.037303
H	1.077882	-0.303952	3.438654
H	-0.502801	-1.100601	3.162383
H	-0.422764	0.657173	3.299963
H	1.748157	2.662705	1.558310
H	0.081864	2.568249	2.199741
H	0.374520	3.227344	0.575052
C	-2.404437	-0.384166	1.113772
C	0.882819	-0.694116	-0.746077
C	0.923538	0.728297	-0.644796
H	-0.366036	-2.836727	1.678498
N	-3.204081	-0.677298	1.934279
C	1.313907	-1.489475	-1.940680
C	1.405195	1.670292	-1.706258
H	2.410145	-1.574495	-1.873233
H	0.865748	-2.490970	-1.953121
H	1.053397	-0.981944	-2.878502
H	2.503280	1.707417	-1.622613
H	1.137361	1.317085	-2.710742
H	0.991220	2.678410	-1.573795
Cl	3.945917	-0.088222	0.094459

xyz coordinates of gas phase optimized C-H...X hydrogen bonding systems

hydrogen bonding Fe-Cp*-Br⁻

Fe	-1.469163	-0.024437	0.143058
O	-2.803652	2.001806	1.784310
O	-2.754651	-2.396603	1.285820
C	-2.292827	1.184620	1.116631
C	-2.267967	-1.438010	0.817959
C	0.164574	1.199430	-0.502110
C	0.070340	0.077909	-1.388968
C	0.219009	-1.115942	-0.616608
C	0.172560	2.642498	-0.909119
C	-0.060458	0.148322	-2.880924
C	0.312853	-2.511495	-1.156791
H	1.196332	2.918295	-1.210143
H	-0.127373	3.293555	-0.078211
H	0.952062	0.190708	-3.314313
H	-0.623223	1.034787	-3.192731
H	-0.583056	-0.728493	-3.279380
H	1.370591	-2.720949	-1.384913
H	-0.280228	-2.629764	-2.072191
H	-0.034457	-3.251963	-0.424759
C	-2.717230	0.144783	-1.303247
C	0.435263	0.692629	0.822442
C	0.458786	-0.730527	0.755421
H	-0.508404	2.824686	-1.750122
N	-3.464888	0.257898	-2.212484
C	0.798914	1.516335	2.020934
C	0.849312	-1.653826	1.870136
H	1.891902	1.649934	1.992613
H	0.308814	2.498283	2.010218
H	0.530701	1.007465	2.955883
H	1.949980	-1.702303	1.871364
H	0.505557	-1.281112	2.844055
H	0.441292	-2.662352	1.725520
Br	3.516275	0.017352	-0.038874

hydrogen bonding Mn-Cp*-F⁻

Mn	0.771147	-0.000098	-0.416512
O	2.790647	2.164439	-0.493229
O	0.165899	0.002208	-3.319728
C	1.992428	1.295901	-0.488304
C	0.432675	0.001275	-2.174314
C	0.248168	0.000763	1.657373
C	-0.345507	-1.163132	1.041165
C	-1.277475	-0.723545	0.045974
C	1.196661	0.001616	2.826240
C	-0.120055	-2.592528	1.456747
C	-2.263649	-1.539663	-0.727549
H	0.644947	0.002044	3.782880
H	1.845829	0.887328	2.811441
H	-0.863589	-2.885158	2.216207
H	0.881695	-2.738455	1.881347
H	-0.225767	-3.271901	0.601540
H	-3.279555	-1.207318	-0.374721
H	-2.111579	-2.618027	-0.580302
H	-2.208076	-1.319936	-1.803487
C	1.990836	-1.297515	-0.490027
C	-0.346264	1.163758	1.040032
C	-1.278047	0.722627	0.045382
H	1.846194	-0.883850	2.812427
O	2.788078	-2.166929	-0.496160
C	-0.121798	2.593673	1.454273
C	-2.264627	1.537535	-0.728782
H	-0.866142	2.886817	2.212740
H	0.879523	2.740521	1.879573
H	-0.227082	3.272075	0.598231
H	-3.280399	1.204895	-0.375404
H	-2.113064	2.616101	-0.582521
H	-2.209200	1.316815	-1.804523
F	-4.556610	-0.000202	0.206782

xyz coordinates of gas phase optimized C-H...X hydrogen bonding systems

hydrogen bonding Mn-Cp*-Cl⁻

Mn	1.104115	-0.008264	-0.150928
O	2.240185	2.065338	-1.937637
O	2.287960	-2.359615	-1.511578
C	1.810124	1.226697	-1.230307
C	1.842841	-1.409091	-0.975481
C	-0.556448	1.178920	0.596967
C	-0.375981	0.037964	1.448512
C	-0.566027	-1.142224	0.659927
C	-0.578380	2.617239	1.028725
C	-0.164042	0.076282	2.936692
C	-0.607178	-2.556019	1.165594
H	-1.612314	2.904767	1.280138
H	-0.223450	3.279664	0.228184
H	-1.143850	0.085207	3.440702
H	0.389687	0.972669	3.243712
H	0.396534	-0.799781	3.287484
H	-1.650096	-2.822855	1.401831
H	-0.000277	-2.679793	2.072266
H	-0.235003	-3.262424	0.411741
C	2.389812	0.137138	1.077811
C	-0.901905	0.696636	-0.713601
C	-0.901763	-0.728367	-0.678073
H	0.055629	2.784530	1.909622
O	3.214815	0.237249	1.914800
C	-1.363320	1.536566	-1.866499
C	-1.371376	-1.628341	-1.781331
H	-2.461577	1.592470	-1.793181
H	-0.938800	2.548418	-1.833071
H	-1.092896	1.083300	-2.829318
H	-2.469524	-1.679549	-1.699805
H	-1.107152	-1.229946	-2.769877
H	-0.947407	-2.637272	-1.693832
Cl	-4.026129	0.015472	0.081077

hydrogen bonding Mn-Cp*-Br⁻

Mn	1.513912	0.1012	-0.001004
O	2.608318	2.845403	-0.236266
O	3.241643	-1.148937	-2.058473
C	2.201442	1.743355	-0.1414
C	2.574329	-0.637442	-1.231702
C	-0.431344	0.856078	0.656257
C	-0.244759	-0.459231	1.178443
C	-0.087104	-1.363613	0.074586
C	-0.80176	2.074469	1.447682
C	-0.377333	-0.850427	2.621331
C	0.024603	-2.859073	0.165001
H	-1.897355	2.063442	1.567334
H	-0.514176	2.995506	0.92381
H	-1.437591	-1.085775	2.807363
H	-0.083531	-0.030411	3.28883
H	0.232401	-1.728848	2.869051
H	-0.982803	-3.307294	0.143709
H	0.518345	-3.167057	1.096172
H	0.603139	-3.269148	-0.67355
C	2.539971	-0.393863	1.372815
C	-0.419945	0.768065	-0.780051
C	-0.221772	-0.59956	-1.135395
H	-0.324499	2.080622	2.436927
O	3.185398	-0.739716	2.297002
C	-0.780876	1.886288	-1.712063
C	-0.320574	-1.162762	-2.523664
H	-1.88116	1.949688	-1.730108
H	-0.371298	2.847482	-1.373332
H	-0.416692	1.699756	-2.731086
H	-1.386461	-1.338683	-2.74091
H	0.078071	-0.46714	-3.27334
H	0.221513	-2.112219	-2.618713
Br	-3.554796	-0.037932	0.001823

xyz coordinates of gas phase optimized C-H...X hydrogen bonding systems

hydrogen bonding Fe-Ind-F⁻

Fe	0.453464	0.450293	0.040705
N	-0.585011	2.537076	-2.00145
O	0.087065	2.170065	2.389831
O	3.211194	1.285074	-0.423855
C	-0.171414	1.753371	-1.218868
C	0.230725	1.503588	1.438496
C	2.117505	0.93243	-0.240174
C	-1.03501	-1.061308	0.680438
C	0.324949	-1.379197	1.084809
H	0.654314	-1.50354	2.113175
C	1.145079	-1.583522	-0.072641
H	2.30282	-1.96674	-0.070049
C	0.317406	-1.248314	-1.207689
H	0.644915	-1.241666	-2.243269
C	-1.037502	-0.989442	-0.768466
C	-2.246177	-0.679445	-1.462368
H	-2.239712	-0.587284	-2.547945
C	-3.404425	-0.4864	-0.728709
H	-4.337782	-0.252869	-1.244254
C	-3.404225	-0.561755	0.701596
H	-4.338637	-0.39153	1.240158
C	-2.242017	-0.827963	1.408211
H	-2.238847	-0.875075	2.498297
F	3.544723	-2.502424	-0.023322

hydrogen bonding Fe-Ind-Cl⁻

Fe	0.941799	-0.460149	-0.015063
N	3.229496	1.23532	1.204508
O	-0.063677	-1.408286	2.585869
O	2.752432	-2.708502	-0.373857
C	2.354668	0.575819	0.761647
C	0.324957	-1.033721	1.556509
C	2.027195	-1.803903	-0.218179
C	-0.950017	0.65822	-0.5165
C	-0.892107	-0.67363	-1.08847
H	-1.655957	-1.43207	-0.903127
C	0.230123	-0.703969	-1.967414
H	0.530447	-1.553332	-2.574741
C	0.954016	0.537894	-1.861869
H	1.87306	0.79671	-2.377277
C	0.186901	1.415241	-1.001753
C	0.375303	2.762764	-0.575979
H	1.247547	3.326321	-0.904791
C	-0.566727	3.312911	0.277944
H	-0.444015	4.344274	0.614715
C	-1.69574	2.562936	0.745534
H	-2.410548	3.050099	1.411235
C	-1.899961	1.244061	0.374071
H	-2.759661	0.639325	0.679403
Cl	-3.980931	-1.532243	-0.034981

xyz coordinates of gas phase optimized C-H...X hydrogen bonding systems

hydrogen bonding Fe-Ind-Br⁻

Fe	1.180934	-0.654247	-0.024142
N	3.765296	0.147399	1.481403
O	-0.300853	-1.341637	2.429668
O	2.204684	-3.352223	-0.380414
C	2.768943	-0.168222	0.929971
C	0.265322	-1.061487	1.455889
C	1.793208	-2.268148	-0.225648
C	-0.172775	1.050364	-0.593227
C	-0.513961	-0.214603	-1.216302
H	-1.487975	-0.694377	-1.098883
C	0.592597	-0.593941	-2.030169
H	0.638517	-1.481793	-2.654784
C	1.678892	0.328984	-1.817411
H	2.669473	0.274295	-2.256989
C	1.18509	1.393083	-0.967971
C	1.776441	2.58936	-0.467147
H	2.80826	2.837602	-0.713071
C	1.0098	3.401857	0.352865
H	1.442075	4.325032	0.744032
C	-0.332583	3.057703	0.718914
H	-0.890103	3.733549	1.369862
C	-0.931175	1.889352	0.276601
H	-1.954056	1.588128	0.520522
Br	-3.721057	-0.385107	-0.015572

hydrogen bonding Mn-Ind-F⁻

Mn	0.437117	0.477331	-0.000105
O	-0.214407	2.353118	-2.202213
O	-0.215013	2.353257	2.201644
O	3.285447	1.275439	0.000608
C	0.053128	1.620858	-1.320084
C	0.052749	1.620905	1.319656
C	2.165247	0.939552	0.000285
C	-1.031835	-1.041784	0.726617
C	0.319595	-1.347508	1.149457
H	0.647916	-1.426375	2.18235
C	1.137213	-1.612014	0.000024
H	2.263848	-2.009531	0.000056
C	0.319564	-1.34772	-1.149385
H	0.647448	-1.427147	-2.182382
C	-1.031866	-1.041922	-0.726513
C	-2.244259	-0.770262	-1.43475
H	-2.243978	-0.761562	-2.52598
C	-3.407558	-0.542615	-0.715953
H	-4.342786	-0.349198	-1.245659
C	-3.407513	-0.542504	0.716133
H	-4.342708	-0.349014	1.245876
C	-2.244184	-0.770042	1.434895
H	-2.243816	-0.761097	2.526121
F	3.528472	-2.632613	-0.00004

xyz coordinates of gas phase optimized C-H...X hydrogen bonding systems

hydrogen bonding Mn-Ind-Cl⁻

Mn	0.987358	-0.419957	-0.012212
O	3.281339	1.125736	1.054466
O	-0.000857	-1.330186	2.641121
O	2.627934	-2.839896	-0.395077
C	2.370076	0.500635	0.653091
C	0.377238	-0.978549	1.592815
C	1.973642	-1.877097	-0.224185
C	-0.966212	0.631289	-0.500964
C	-0.889812	-0.687967	-1.088868
H	-1.630468	-1.46673	-0.901637
C	0.213007	-0.68005	-1.99416
H	0.521352	-1.516182	-2.615694
C	0.894947	0.58098	-1.90966
H	1.776093	0.876548	-2.470935
C	0.135386	1.425387	-1.010545
C	0.286388	2.781452	-0.585651
H	1.115879	3.385499	-0.956493
C	-0.651862	3.302501	0.291846
H	-0.560052	4.340814	0.618801
C	-1.743043	2.514296	0.78509
H	-2.460947	2.977138	1.46494
C	-1.911673	1.190344	0.413632
H	-2.75059	0.562771	0.731061
Cl	-4.028884	-1.560323	-0.029616

hydrogen bonding Mn-Ind-Br⁻

Mn	1.242068	-0.624601	-0.018211
O	3.749894	0.080616	1.396908
O	-0.246628	-1.364588	2.450642
O	2.137693	-3.398509	-0.453476
C	2.747730	-0.210441	0.855311
C	0.314878	-1.068570	1.471545
C	1.775615	-2.295363	-0.262209
C	-0.195144	1.035969	-0.579385
C	-0.511741	-0.220782	-1.222474
H	-1.468321	-0.730770	-1.102645
C	0.592673	-0.553764	-2.060053
H	0.653947	-1.430693	-2.698679
C	1.646482	0.402937	-1.866840
H	2.617233	0.399890	-2.353221
C	1.142597	1.430306	-0.979431
C	1.698560	2.647898	-0.479390
H	2.705750	2.952633	-0.767891
C	0.923094	3.426468	0.366417
H	1.327840	4.366365	0.748739
C	-0.396261	3.028531	0.759811
H	-0.966138	3.678792	1.426207
C	-0.961925	1.845254	0.313300
H	-1.972930	1.512892	0.567564
Br	-3.763888	-0.413854	-0.011914

xyz coordinates of gas phase optimized σ -complex geometries

σ -complex Cr-C₆H₆-Br⁻

C	0.559948	-0.11522	1.22828
C	0.560625	-0.118408	-1.226778
C	-0.391868	-2.033456	0.002979
C	0.939027	0.489014	0.00008
C	-0.084045	-1.379899	-1.221608
C	-0.084884	-1.376662	1.226016
H	0.789652	0.382287	2.166925
H	0.790672	0.376707	-2.1666
H	-0.908939	-2.991124	0.004094
H	1.376845	1.480423	-0.000984
H	-0.374736	-1.841416	-2.164763
H	-0.376135	-1.835954	2.170088
Cr	-1.382745	-0.004889	0.000154
C	-2.667093	-0.198813	1.282891
C	-1.640633	1.810269	-0.003362
C	-2.666417	-0.204338	-1.282405
O	-3.48868	-0.346738	2.119911
O	-1.803575	2.978553	-0.005636
O	-3.487397	-0.356024	-2.119359
Br	3.856507	0.145862	-0.000239

σ -complex Fe-Cp-Cl⁻

Fe	0.768216	-0.000829	0.028932
C	-0.471015	1.703067	0.193959
C	-1.026956	-0.098028	-1.142628
C	-0.502120	1.229747	-1.150917
C	2.112422	0.353922	-1.294300
C	-1.408567	-0.421650	0.205538
C	-0.995057	0.657118	1.036445
C	1.125327	-1.730120	0.063215
C	1.856948	0.441744	1.335255
O	1.359741	-2.876163	0.091923
N	2.916980	0.599452	-2.124980
O	2.549015	0.743583	2.230614
H	-0.104208	2.669757	0.522556
H	-1.168733	-0.734038	-2.007860
H	-0.127312	1.758775	-2.019768
H	-1.785854	-1.375832	0.543535
H	-1.113618	0.705271	2.112795
Cl	-4.206393	-0.173688	0.053628

σ -complex Fe-Cp-Br⁻

Fe	1.331550	0.006045	0.027775
C	0.077600	1.651424	0.470628
C	-0.429688	0.120069	-1.182953
C	0.090307	1.430038	-0.936609
C	2.641055	0.393458	-1.321084
C	-0.877510	-0.425668	0.069526
C	-0.457314	0.470692	1.097733
C	1.642147	-1.732817	-0.023270
C	2.466608	0.353205	1.323706
O	1.857156	-2.883255	-0.041693
N	3.424793	0.658655	-2.165719
O	3.190159	0.584710	2.215900
H	0.432507	2.541642	0.979538
H	-0.537107	-0.349237	-2.153177
H	0.488821	2.105852	-1.684752
H	-1.217085	-1.439687	0.223304
H	-0.608903	0.325548	2.160828
Br	-3.669995	-0.089312	0.015212

σ -complex Mn-Cp-Cl⁻

Mn	0.826353	-0.015806	0.000017
C	-0.936676	-0.581856	-1.153401
C	-0.231171	-1.749645	0.715847
C	-0.230454	-1.752103	-0.710878
C	2.038435	-0.168532	-1.30046
C	-0.937647	-0.577845	1.153674
C	-1.39925	0.12081	-0.001324
C	2.038408	-0.166031	1.300783
C	0.878085	1.778308	-0.001777
O	2.817252	-0.292912	2.174318
O	2.817308	-0.297479	-2.173657
O	0.908076	2.951451	-0.002604
H	-1.12084	-0.295187	-2.182455
H	0.233871	-2.493678	1.355297
H	0.235097	-2.498304	-1.347426
H	-1.123637	-0.287736	2.181427
H	-1.993732	1.026015	-0.002882
Cl	-4.502887	0.272761	-0.000214

xyz coordinates of gas phase optimized σ -complex geometries **σ -complex Mn-Cp-Br⁻**

Mn	-1.394116	-0.023048	-0.000112
C	0.425375	-0.378153	1.151412
C	-0.134271	-1.614938	-0.721362
C	-0.134055	-1.622302	0.704487
C	-2.573243	-0.297602	1.311402
C	0.42451	-0.366592	-1.156171
C	0.824593	0.364661	0.001443
C	-2.588013	-0.313488	-1.29465
C	-1.626743	1.7549	-0.01014
O	-3.352201	-0.523861	-2.166054
O	-3.32708	-0.49722	2.194232
O	-1.779908	2.920295	-0.017414
H	0.579032	-0.078768	2.181407
H	-0.504329	-2.407286	-1.364333
H	-0.503801	-2.421179	1.339469
H	0.578084	-0.056921	-2.183124
H	1.25002	1.358152	0.006367
Br	3.811957	0.109417	0.000525

 σ -complex Fe-Ind-Cl⁻

Fe	0.796547	-0.595871	0.035130
N	2.803956	0.182796	-2.201182
O	2.668842	-0.147276	2.254281
O	1.431483	-3.433647	-0.236721
C	2.051694	-0.122976	-1.342045
C	1.942268	-0.318862	1.352830
C	1.166971	-2.297832	-0.132892
C	-0.624660	0.973186	0.712496
C	-1.000348	-0.353970	1.151410
H	-1.152865	-0.661748	2.179313
C	-1.348633	-1.116194	-0.004081
H	-1.667962	-2.148672	-0.000346
C	-0.948950	-0.374178	-1.163585
H	-1.034386	-0.707530	-2.190675
C	-0.595411	0.958881	-0.736278
C	-0.235152	2.137556	-1.454047
H	-0.186361	2.116230	-2.541731
C	0.052628	3.286249	-0.738455
H	0.324056	4.199411	-1.270597
C	0.016403	3.303981	0.693236
H	0.252171	4.232737	1.216057
C	-0.303053	2.170137	1.421198
H	-0.332348	2.182827	2.511208
Cl	-4.140316	-0.931097	-0.006325

 σ -complex Fe-Ind-Br⁻

Fe	1.14501	-0.696966	0.034418
N	3.216769	-0.417537	-2.260947
O	3.121547	-0.595398	2.206131
O	1.16796	-3.613263	-0.142079
C	2.438192	-0.533242	-1.378823
C	2.353188	-0.631024	1.323595
C	1.143379	-2.444295	-0.077536
C	0.057816	1.113745	0.715469
C	-0.569253	-0.114145	1.153858
H	-0.777881	-0.388825	2.181295
C	-1.076623	-0.784221	-0.003339
H	-1.548447	-1.755591	0.000912
C	-0.522703	-0.144707	-1.162066
H	-0.66497	-0.45931	-2.18879
C	0.087495	1.092757	-0.734253
C	0.683537	2.172295	-1.450932
H	0.73385	2.138242	-2.538259
C	1.194267	3.240999	-0.735207
H	1.649137	4.078364	-1.266847
C	1.156857	3.267566	0.696177
H	1.575681	4.12912	1.219583
C	0.61362	2.222092	1.423956
H	0.587555	2.240627	2.513997
Br	-3.814779	-0.171897	-0.003656

xzy coordinates of gas phase optimized σ -complex geometries **σ -complex Mn-Ind-Cl⁻**

Mn	0.534469	-0.791845	-0.000022
O	2.491393	-1.132170	-2.204776
O	2.482702	-1.133650	2.212200
O	-0.185801	-3.658085	-0.002247
C	1.724805	-1.007870	-1.322323
C	1.719583	-1.008719	1.326842
C	0.098587	-2.518695	-0.001324
C	-0.070045	1.241794	0.724846
C	-0.996996	0.219816	1.156417
H	-1.260660	-0.009238	2.182709
C	-1.621879	-0.328686	-0.003283
H	-2.418334	-1.062538	-0.004150
C	-0.993490	0.219498	-1.161287
H	-1.253745	-0.009635	-2.188445
C	-0.067876	1.241637	-0.727158
C	0.766240	2.160363	-1.436299
H	0.766703	2.161517	-2.526940
C	1.542070	3.052815	-0.715066
H	2.172176	3.770844	-1.243320
C	1.540057	3.052888	0.717021
H	2.168695	3.770942	1.246982
C	0.762150	2.160557	1.436179
H	0.759578	2.161900	2.526817
Cl	-4.648337	0.323011	-0.000113

 σ -complex Mn-Ind-Br⁻

Mn	1.169147	-0.714784	0.000007
O	3.142161	-0.693458	-2.217590
O	3.140984	-0.695724	2.218661
O	0.976736	-3.663978	-0.001567
C	2.372481	-0.706191	-1.328377
C	2.371727	-0.707379	1.329066
C	1.051419	-2.490611	-0.000870
C	0.171798	1.158499	0.726094
C	-0.531881	-0.026437	1.159262
H	-0.744437	-0.301605	2.185792
C	-1.052181	-0.675406	0.000181
H	-1.638524	-1.582921	0.000211
C	-0.532075	-0.026396	-1.158987
H	-0.744832	-0.301540	-2.185482
C	0.171643	1.158528	-0.725911
C	0.807145	2.223122	-1.436080
H	0.805120	2.224675	-2.526724
C	1.389973	3.252907	-0.715920
H	1.863899	4.081749	-1.245164
C	1.390161	3.252858	0.715942
H	1.864230	4.081658	1.245123
C	0.807491	2.223029	1.436174
H	0.805723	2.224515	2.526819
Br	-4.000717	-0.112880	-0.000006

SUMMARY

Table S3. B97-D3/6-31++G** interaction energies and SAPT0/def2-TZVP interaction energies decomposed into electrostatic (ELST), exchange (EXCH), induction (IND) and dispersion (DISP) contributions (all in kcal/mol), for all gas phase anion- π , C-H $\cdots$ X $^-$ and σ -complex interactions between aromatic ligands in half-sandwich compounds and halide anions found in this study.

interaction	π -system	anion	B97-D3 6-31++G**	SAPT0 def2-TZVP	ELST	EXCH	IND	DISP
anion- π	C ₆ F ₆	F $^-$	-18.32	-22.82	-22.19	+15.64	-11.83	-4.45
		Cl $^-$	-12.70	-16.80	-17.44	+12.88	-6.26	-5.99
		Br $^-$	-12.45	-15.44	-16.91	+13.41	-5.28	-6.66
	Cr-C ₆ H ₆	F $^-$	-16.48	-18.50	-12.80	+13.67	-14.69	-4.67
		Cl $^-$	-12.93	-15.05	-11.62	+10.16	-7.80	-5.80
		Br $^-$	-12.25	-14.41	-12.05	+10.68	-6.59	-6.45
	Mn-Cp	F $^-$	-14.62	-8.42	-5.87	+18.93	-16.02	-5.45
		Cl $^-$	-11.19	-7.27	-5.66	+12.77	-8.00	-6.38
		Br $^-$	-10.53	-7.04	-6.73	+13.15	-6.48	-6.97
	Fe-Cp	F $^-$	-22.03	-15.97	-15.33	+21.86	-16.60	-5.90
		Cl $^-$	-16.95	-13.31	-12.96	+14.73	-8.26	-6.81
		Br $^-$	-15.97	-12.64	-13.60	+15.15	-6.77	-7.41
	Mn-Cp*	F $^-$	-19.22	-11.85	-2.37	+11.87	-16.00	-5.34
		Cl $^-$	-16.14	-11.33	-5.42	+11.27	-9.44	-7.74
		Br $^-$	-15.65	-11.38	-6.69	+11.98	-8.01	-8.65
	Fe-Cp*	F $^-$	-24.98	-22.12	-12.65	+10.64	-15.17	-4.94
		Cl $^-$	-21.19	-20.20	-15.56	+13.35	-9.73	-8.26
		Br $^-$	-20.48	-19.71	-16.40	+14.16	-8.29	-9.18
	Mn-Ind	F $^-$	-15.02	-9.89	-1.61	+10.67	-14.51	-4.45
		Cl $^-$	-10.71	-7.94	-3.82	+11.34	-8.57	-6.88
		Br $^-$	-10.14	-7.67	-4.12	+10.43	-6.84	-7.14
	Fe-Ind	F $^-$	-21.24	-16.42	-9.54	+14.08	-15.77	-5.19
		Cl $^-$	-15.64	-13.17	-9.89	+12.94	-8.90	-7.32
		Br $^-$	-14.80	-12.58	-10.55	+13.46	-7.41	-8.08
C-H $\cdots$ X $^-$ hydrogen bond	C ₆ H ₆	F $^-$	-15.32	-18.71	-21.36	+27.28	-20.89	-3.74
		Cl $^-$	-8.11	-9.19	-7.69	+8.17	-6.64	-3.03
		Br $^-$	-7.05	-8.00	-8.23	+10.38	-6.26	-3.89
	Cr-C ₆ H ₆	F $^-$	-34.37	-40.37	-49.10	+53.52	-38.23	-6.56
		Cl $^-$	-19.23	-20.82	-20.23	+13.11	-9.26	-4.44
		Br $^-$	-17.03	-18.80	-20.62	+16.62	-9.14	-5.67
	Mn-Cp	F $^-$	-32.04	-32.00	-42.20	+54.09	-37.29	-6.61
		Cl $^-$	-16.01	-12.94	-12.23	+11.38	-7.90	-4.18
		Br $^-$	-14.32	-11.68	-13.28	+14.34	-7.42	-5.33
	Fe-Cp	F $^-$	-41.93	-44.93	-57.42	+63.93	-43.89	-7.55
		Cl $^-$	-22.82	-22.15	-22.38	+13.06	-8.34	-4.50
		Br $^-$	-20.86	-20.68	-23.17	+15.95	-7.85	-5.62
	Mn-Cp*	F $^-$	-29.23	-25.38	-25.98	+31.35	-25.13	-5.62
		Cl $^-$	-19.41	-14.84	-10.58	+14.50	-10.55	-8.21
		Br $^-$	-18.34	-14.59	-13.99	+20.48	-9.66	-11.42

interaction	π -system	anion	B97-D3 6-31++G**	SAPT0 def2-TZVP	ELST	EXCH	IND	DISP
C-H...X ⁻ hydrogen bond	Fe-Cp*	F ⁻	-37.35	-33.64	-37.99	+39.91	-29.04	-6.53
		Cl ⁻	-25.21	-20.64	-17.63	+16.93	-11.03	-8.92
		Br ⁻	-23.72	-19.84	-20.98	+23.17	-10.09	-11.94
	Mn-Ind	F ⁻	-32.05	-34.40	-43.50	+55.58	-39.67	-6.82
		Cl ⁻	-17.98	-16.60	-14.94	+14.74	-11.15	-5.25
		Br ⁻	-15.68	-15.28	-16.36	+18.77	-10.88	-6.82
	Fe-Ind	F ⁻	-41.06	-46.73	-57.68	+65.02	-46.33	-7.74
		Cl ⁻	-23.80	-24.07	-23.15	+16.39	-11.77	-5.55
		Br ⁻	-21.28	-22.77	-24.81	+20.68	-11.51	-7.13
σ -complex	Cr-C ₆ H ₆	Br ⁻	-17.71	-17.38	-23.89	+26.23	-11.35	-8.38
	Mn-Cp	Cl ⁻	-15.20	-8.60	-8.59	+12.96	-8.56	-4.41
		Br ⁻	-13.97	-5.73	-11.28	+22.20	-9.15	-7.50
	Fe-Cp	Cl ⁻	-23.74	-13.87	-18.86	+24.27	-11.89	-7.39
		Br ⁻	-22.84	-12.09	-23.85	+34.13	-12.48	-9.89
	Mn-Ind	Cl ⁻	-14.59	-9.50	-8.49	+13.01	-9.41	-4.62
		Br ⁻	-13.25	-7.11	-11.35	+21.82	-10.02	-7.56
	Fe-Ind	Cl ⁻	-22.61	-14.50	-18.06	+24.68	-13.23	-7.89
		Br ⁻	-21.30	-12.88	-23.17	+34.22	-13.70	-10.23

REFERENCES

- 1 C. Møller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618–622.
- 2 T. Helgaker, W. Klopper, H. Koch and J. Noga, *J. Chem. Phys.*, 1997, **106**, 9639.
- 3 T. H. Dunning Jr, *J. Chem. Phys.*, 1989, **90**, 1007.
- 4 M. O. Sinnokrot and C. D. Sherrill, *J. Phys. Chem. A*, 2004, **108**, 10200–10207.