

Supplementary Information

Coordination Chemistry of Mixed M(Benzene)(Cyclopentadienyl) Sandwich Complexes: Electronic Properties and Bonding Analysis

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Tables S1-S8. Selected parameters obtained for $[M(Bz)Cp]^{+1/0/-1}$ ($M = Sc-Ni$) complexes. The $\Delta(HL)_1$ (BP86) and $\Delta(HL)_2$ (B3LYP) HOMO-LUMO gaps are given in (eV), the E_1 (BP86) and E_2 (B3LYP) total bonding energies are given in (eV) and ΔE_1 (BP86) and ΔE_2 (B3LYP) relative energies between isomers are given in (eV). The M-C bond distances are given in (Å).

Tables S1. Selected parameters (BP86) obtained for $[M(Bz)Cp]^{+1/0/-1}$ ($M = Sc$ and Ti) complexes.

Complex	$[Sc(Bz)Cp]^+$	Sc(Bz)Cp		$[Sc(Bz)Cp]^-$	$[Ti(Bz)Cp]^+$		Ti(Bz)Cp	$[Ti(Bz)Cp]^-$	
TNE	13	14	14	15	14	14	15	16	16
MVE	13	14	14	15	14	14	15	16	16
Coordination mode	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)
Symmetry	(C_s)	(C_s)	(C_s)	(C_s)	(C_i)	(C_i)	(C_i)	(C_i)	(C_i)
Spin state	$S = 1/2$	$S = 0$	$S = 1$	$S = 1/2$	$S = 0$	$S = 1$	$S = 1/2$	$S = 0$	$S = 1$
$\Delta(HL)_1$	-	0.76	-	-	0.78	-	-	0.74	-
ΔE_1	-	5.6	0.0	-	5.2	0.0	-	0.0	4.5
	M-C (C_6 ring)								
M-C(1)	2.594	2.473	2.434	2.412	2.408	2.385	2.324	2.212	2.213
M-C(2)	2.535	2.470	2.435	2.334	2.280	2.386	2.247	2.216	2.216
M-C(3)	2.534	2.473	2.436	2.336	2.290	2.386	2.248	2.221	2.223
M-C(4)	2.589	2.279	2.436	2.414	2.419	2.389	2.327	2.222	2.230
M-C(5)	2.534	2.473	2.436	2.334	2.290	2.389	2.248	2.221	2.222
M-C(6)	2.535	2.470	2.435	2.336	2.280	2.386	2.247	2.216	2.217
	M-C (C_5 ring)								
M-C(7)	2.456	2.443	2.492	2.560	2.397	2.332	2.372	2.370	2.370
M-C(8)	2.437	2.469	2.490	2.543	2.355	2.333	2.356	2.370	2.371
M-C(9)	2.406	2.511	2.488	2.518	2.279	2.336	2.325	2.370	2.370
M-C(10)	2.406	2.511	2.488	2.518	2.279	2.336	2.325	2.370	2.368
M-C(11)	2.437	2.469	2.490	2.543	2.355	2.335	2.356	2.370	2.368
Spin density	0.6668	-	1.0233	0.4378	-	1.6298	0.7163	-	1.8101
$\langle S^2 \rangle$	0.7521	-	2.0027	0.7519	-	2.0081	0.7583	-	2.0149
Hirshfeld charge	0.5413	0.4029	0.3795	0.2559	0.4509	0.4159	0.3059	0.2096	0.1190
E_1	-135.7244	-141.1530	-141.3958	-141.6249	-136.8622	-137.0874	-142.7521	-143.5060	-143.3086

Tables S2. Selected parameters (BP86) obtained for $[M(\text{Bz})\text{Cp}]^{+1/0/-1}$ (M = V and Cr) complexes.

Complex	$[\text{V}(\text{Bz})\text{Cp}]^+$	$\text{V}(\text{Bz})\text{Cp}$		$[\text{V}(\text{Bz})\text{Cp}]^-$	$[\text{Cr}(\text{Bz})\text{Cp}]^+$		$\text{Cr}(\text{Bz})\text{Cp}$	$[\text{Cr}(\text{Bz})\text{Cp}]^-$	
TNE	15	16	16	17	16	16	17	18	18
MVE	15	16	16	17	16	16	17	18	18
Coordination mode	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)
Symmetry	(C_s)	(C_s)	(C_s)	(C_s)	(C_s)	(C_s)	(C_s)	(C_s)	(C_s)
Spin state	S = 1/2	S = 0	S = 1	S = 1/2	S = 0	S = 1	S = 1/2	S = 0	S = 1
$\Delta(\text{HL})_1$	-	0.11	-	-	0.56	-	-	1.87	-
ΔE_1	-	18.7	0.0	-	32.2	0.0	-	0.0	27.8
	M-C (C_6 ring)								
M-C(1)	2.304	2.252	2.252 (2.200) ^d	2.168	2.128	2.156	2.124	2.111	2.153
M-C(2)	2.325	2.253	2.253 (2.221) ^d	2.171	2.129	2.243	2.122	2.114	2.143
M-C(3)	2.327	2.255	2.255 (2.223) ^d	2.175	2.132	2.248	2.125	2.118	2.153
M-C(4)	2.309	2.256	2.256 (2.264) ^d	2.177	2.134	2.167	2.128	2.120	2.222
M-C(5)	2.327	2.255	2.255 (2.223) ^d	2.175	2.132	2.248	2.125	2.118	2.153
M-C(6)	2.325	2.253	2.253 (2.221) ^d	2.171	2.129	2.243	2.122	2.114	2.143
		M-C (C_5 ring)							
M-C(7)	2.252	2.224	2.244 (2.252) ^d	2.277	2.175	2.170	2.180	2.163	2.166
M-C(8)	2.260	2.266	2.223 (2.238) ^d	2.277	2.174	2.190	2.182	2.164	2.150
M-C(9)	2.268	2.302	2.221 (2.238) ^d	2.277	2.172	2.229	2.186	2.166	2.120
M-C(10)	2.268	2.302	2.221 (2.238) ^d	2.277	2.172	2.229	2.186	2.166	2.120
M-C(11)	2.260	2.266	2.223 (2.238) ^d	2.277	2.174	2.190	2.182	2.164	2.150
Spin density	1.0239	-	2.0416	1.2884	-	2.2429	1.3100	-	2.3994
$\langle S^2 \rangle$	1.6770	-	2.0358	0.7758	-	2.0484	0.7823	-	2.1393
Hirshfeld charge	0.3050	0.1173	0.1854	0.1025	0.5056	0.4863	0.4046	0.2499	0.3476
E_1	-138.0034	-143.5138	-144.1823	-145.0050	-137.6862	-139.0842	-145.0544	-145.6263	-144.4210

Tables S3. Selected parameters (BP86) obtained for $[\text{M}(\text{Bz})\text{Cp}]^{+1/0/-1}$ (M = Mn and Fe) complexes.

Complex	$[\text{Mn}(\text{Bz})\text{Cp}]^+$	$\text{Mn}(\text{Bz})\text{Cp}$		$[\text{Mn}(\text{Bz})\text{Cp}]^-$	$[\text{Fe}(\text{Bz})\text{Cp}]^+$		$\text{Fe}(\text{Bz})\text{Cp}$	$[\text{Fe}(\text{Bz})\text{Cp}]^-$	
TNE	17	18	18	19	18		19	20	
MVE	17	18	18	19	18	18	19	20	16
Coordination mode	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)	(η^5, η^5)	(η^6, η^2)
Symmetry	(C_s)	(C_s)	(C_s)	(C_s)	(C_s)	(C_s)	(C_s)	(C_s)	(C_s)
Spin state	S = 1/2	S = 0	S = 1	S = 1/2	S = 0	S = 1	S = 1/2	S = 0	S = 1
$\Delta(\text{HL})_1$	-	2.59	-	-	2.83	-	-	0.33	-
ΔE_1	-	0.0	9.0	-	0.0	38.2	-	18.4	0.0
M-C (C_6 ring)									
M-C(1)	2.125	2.101	2.219	2.124	2.106	2.222	2.162	1.989	2.095
M-C(2)	2.125	2.101	2.216	2.097	2.111	2.255	2.109	2.090	2.119
M-C(3)	2.126	2.100	2.212	2.115	2.115	2.250	2.122	2.320	2.159
M-C(4)	2.127	2.097	2.206	2.177	2.117	2.214	2.193	2.763	2.175
M-C(5)	2.126	2.100	2.212	2.115	2.115	2.250	2.122	2.320	2.195
M-C(6)	2.125	2.101	2.216	2.097	2.111	2.255	2.109	2.090	2.119
M-C (C_5 ring)									
M-C(7)	2.129	2.133	2.297	2.318	2.085	2.182	2.225	2.125	2.820
M-C(8)	2.130	2.131	2.238	2.220	2.087	2.231	2.155	2.109	2.618
M-C(9)	2.129	2.133	2.286	2.290	2.091	2.161	2.203	2.141	2.258
M-C(10)	2.129	2.133	2.286	2.290	2.091	2.161	2.203	2.141	2.258
M-C(11)	2.130	2.131	2.238	2.220	2.087	2.231	2.155	2.109	2.618
Spin density	1.2814	-	2.2541	1.0293	-	1.9306	0.9536	-	2.1090
$\langle S^2 \rangle$	0.7797	-	2.1150	0.7819	-	2.0632	0.7755	-	2.1320
Hirshfeld charge	0.1704	0.0550	0.1369	-0.0173	0.0978	0.1838	0.0533	-0.0123	0.0257
E_1	-139.0794	-145.4287	-145.0363	-145.8487	-139.2260	-137.5657	-144.0271	-143.5351	-144.3332

Tables S4. Selected parameters (BP86) obtained for $[\text{M}(\text{Bz})\text{Cp}]^{+1/0/-1}$ (M = Co and Ni) complexes.

Complex	$[\text{Co}(\text{Bz})\text{Cp}]^+$	Co(Bz)Cp		$[\text{Co}(\text{Bz})\text{Cp}]^-$	$[\text{Ni}(\text{Bz})\text{Cp}]^+$		Ni(Bz)Cp	$[\text{Ni}(\text{Bz})\text{Cp}]^-$	
TNE	19	20		21	20	20	21	22	22
MVE	19	18	18	19	18	18	17	18	18
Coordination mode	(η^6, η^5)	(η^4, η^5)	(η^4, η^5)	(η^3, η^5)	(η^4, η^5)	(η^4, η^5)	(η^2, η^5)	(η^2, η^5)	(η^2, η^5)
Symmetry	(C_I)	(C_I)	(C_I)	(C_I)	(C_s)	(C_s)	(C_s)	(C_s)	(C_s)
Spin state	S = 1/2	S = 0	S = 1	S = 1/2	S = 0	S = 1	S = 1/2	S = 0	S = 1
$\Delta(\text{HL})_1$	-	1.45	-	-	0.05	-	-	1.72	-
ΔE_1	-	0.0	3.0	-	2.3	0.0	-	0.0	40.3
	M-C (C_6 ring)								
M-C(1)	2.195	1.987 (1.971) ^c	1.985	1.931	2.226	2.299	2.045	2.045	2.120
M-C(2)	2.192	2.079 (2.019) ^c	2.077	2.154	2.291	2.305	2.870	2.870	3.038
M-C(3)	2.136	2.847 (2.822) ^c	2.847	3.000	2.313	2.313	3.468	3.468	3.624
M-C(4)	2.206	2.847 (2.889) ^c	2.847	3.234	2.313	2.313	3.468	3.468	3.624
M-C(5)	2.206	2.081 (2.038) ^c	2.081	2.769	2.291	2.305	2.870	2.870	3.038
M-C(6)	2.139	1.987 (1.986) ^c	1.987	2.138	2.269	2.299	2.045	2.045	2.120
	M-C (C_5 ring)								
M-C(7)	2.165	2.162 (2.036) ^c	2.161	2.240	2.203	2.205	2.151	2.151	2.175
M-C(8)	2.164	2.067 (2.040) ^c	2.069	2.151	2.209	2.207	2.181	2.181	2.236
M-C(9)	2.112	2.078 (2.032) ^c	2.079	2.114	2.206	2.205	2.172	2.172	2.271
M-C(10)	2.138	2.068 (2.078) ^c	2.067	2.169	2.206	2.205	2.172	2.172	2.271
M-C(11)	2.119	2.154 (2.070) ^c	2.152	2.268	2.209	2.207	2.181	2.181	2.236
Spin Density	0.7639	-	1.6276	0.9368	-	1.0407	0.7353	-	1.1268
$\langle S^2 \rangle$	0.7643	-	2.0474	0.7772	-	2.0065	0.7567	-	2.0089
Hirshfeld Charge	0.1118	0.0406	0.0865	-0.0080	0.3937	0.4244	0.3361	0.2026	0.2332
E_1	-137.437	-142.963	-142.832	-143.658	-133.383	-133.482	-140.015	-141.289	-139.543

Tables S5. Selected parameters (B3LYP) obtained for $[\text{M}(\text{Bz})\text{Cp}]^{+1/0/-1}$ (M = Sc and Ti) complexes.

	$[\text{Sc}(\text{Bz})\text{Cp}]^+$	$\text{Sc}(\text{Bz})\text{Cp}$		$[\text{Sc}(\text{Bz})\text{Cp}]^-$	$[\text{Ti}(\text{Bz})\text{Cp}]^+$		$\text{Ti}(\text{Bz})\text{Cp}$	$[\text{Ti}(\text{Bz})\text{Cp}]^-$	
NTE	13	14	14	15	14	14	15	16	16
MVE	13	14	14	15	14	14	15	16	16
Coordination mode Symmetry	(η^6, η^5) (C_s)	(η^6, η^5) (C_s)	(η^6, η^5) (C_s)	(η^6, η^5) (C_s)	(η^6, η^5) (C_I)	(η^6, η^5) (C_I)	(η^6, η^5) (C_I)	(η^6, η^5) (C_I)	(η^6, η^5) (C_I)
Spin state	S = 1/2	S = 0	S = 1	S = 1/2	S = 0	S = 1	S = 1/2	S = 0	S = 1
$\Delta(\text{HL})_2$	-	2.14	-	-	2.58	-	-	2.39	-
ΔE_2	-	0.0	1.5	-	6.3	0.0	-	0.0	0.2
M-C (C_6 ring)									
M-C(1)	2.598	2.482	2.431	2.414	2.393	2.414	2.327	2.234	2.225
M-C(2)	2.549	2.355	2.431	2.336	2.389	2.413	2.299	2.215	2.222
M-C(3)	2.546	2.355	2.428	2.334	2.252	2.415	2.213	2.221	2.247
M-C(4)	2.594	2.482	2.427	2.412	2.391	2.419	2.327	2.224	2.227
M-C(5)	2.546	2.355	2.428	2.334	2.384	2.420	2.299	2.222	2.228
M-C(6)	2.549	2.355	2.431	2.336	2.250	2.416	2.214	2.246	2.238
M-C (C_5 ring)									
M-C(7)	2.465	2.536	2.496	2.560	2.380	2.339	2.388	2.392	2.372
M-C(8)	2.446	2.510	2.496	2.543	2.386	2.340	2.388	2.393	2.374
M-C(9)	2.417	2.467	2.496	2.518	2.326	2.344	2.367	2.394	2.376
M-C(10)	2.417	2.467	2.496	2.518	2.279	2.346	2.353	2.393	2.376
M-C(11)	2.446	2.510	2.496	2.543	2.317	2.343	2.369	2.392	2.374
E_2	-154.6370	-159.7573	-159.6908	-159.8505	-156.4646	-156.7384	-161.9973	-162.3898	-162.3728

Tables S6. Selected parameters (B3LYP) obtained for $[M(\text{Bz})\text{Cp}]^{+1/0/-1}$ (M = V and Cr) complexes.

	$[\text{V}(\text{Bz})\text{Cp}]^+$	$\text{V}(\text{Bz})\text{Cp}$		$[\text{V}(\text{Bz})\text{Cp}]^-$	$[\text{Cr}(\text{Bz})\text{Cp}]^+$		$\text{Cr}(\text{Bz})\text{Cp}$	$[\text{Cr}(\text{Bz})\text{Cp}]^-$	
NTE	15	16	16	17	16	16	17	18	18
MVE	15	16	16	17	16	16	17	18	18
Coordination mode	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)	(η^6, η^5)
Symmetry	(C_s)	(C_s)	(C_s)	(C_s)	(C_s)	(C_s)	(C_s)	(C_s)	(C_s)
Spin state	S = 1/2	S = 0	S = 1	S = 1/2	S = 0	S = 1	S = 1/2	S = 0	S = 1
$\Delta(\text{HL})_2$	-	2.10	-	-	1.57	-	-	3.03	-
ΔE_2	-	21.2	0.0	-	25.7	0.0	-	0.0	3.1
M-C (C_5 ring)									
M-C(1)	2.370	2.158	2.179	2.177	2.192	2.191	2.141	2.127	2.140
M-C(2)	2.383	2.161	2.278	2.179	2.242	2.271	2.142	2.129	2.135
M-C(3)	2.385	2.165	2.281	2.184	2.249	2.274	2.145	2.134	2.149
M-C(4)	2.376	2.167	2.188	2.185	2.206	2.199	2.146	2.137	2.149
M-C(5)	2.385	2.165	2.281	2.184	2.249	2.274	2.145	2.134	2.149
M-C(6)	2.383	2.161	2.278	2.179	2.242	2.271	2.142	2.129	2.135
M-C (C_5 ring)									
M-C(7)	2.275	2.257	2.289	2.315	2.169	2.179	2.209	2.230	2.245
M-C(8)	2.277	2.256	2.301	2.316	2.178	2.197	2.208	2.230	2.245
M-C(9)	2.280	2.255	2.322	2.317	2.214	2.236	2.207	2.231	2.250
M-C(10)	2.280	2.255	2.322	2.317	2.214	2.236	2.207	2.231	2.250
M-C(11)	2.277	2.256	2.301	2.316	2.178	2.197	2.208	2.230	2.245
E_2	-158.5272	-163.4803	-164.3981	-164.7039	-159.1879	-160.3012	-165.7806	-166.0516	-164.6166

Tables S7. Selected parameters (B3LYP) obtained for $[\text{M}(\text{Bz})\text{Cp}]^{+1/0/-1}$ (M = Mn and Fe) complexes.

	$[\text{Mn}(\text{Bz})\text{Cp}]^+$	$\text{Mn}(\text{Bz})\text{Cp}$		$[\text{Mn}(\text{Bz})\text{Cp}]^-$	$[\text{Fe}(\text{Bz})\text{Cp}]^+$		$\text{Fe}(\text{Bz})\text{Cp}$	$[\text{Fe}(\text{Bz})\text{Cp}]^-$	
NTE	17	18	18	19	18		19	20	
MVE	17	18	18	19	18	18	19	20	16
Coordination mode Symmetry	(η^6, η^5) (C_s)	(η^6, η^5) (C_s)	(η^6, η^5) (C_s)	(η^6, η^5) (C_s)	(η^6, η^5) (C_s)	(η^6, η^5) (C_s)	(η^6, η^5) (C_s)	(η^5, η^5) (C_s)	(η^6, η^2) (C_s)
Spin state	S = 1/2	S = 0	S = 1	S = 1/2	S = 0	S = 1	S = 1/2	S = 0	S = 1
$\Delta(\text{HL})_2$	-	4.46	-	-	5.12	-	-	1.90	-
ΔE_2	-	0.0	11.3	-	0.0	19.2	-	8.4	0.0
M-C (C_6 ring)									
M-C(1)	2.252	2.262	2.330	2.332	2.138	2.352	2.117	1.935	2.250
M-C(2)	2.253	2.268	2.325	2.353	2.140	2.365	2.144	2.257	2.242
M-C(3)	2.255	2.270	2.320	2.340	2.141	2.361	2.154	2.324	2.235
M-C(4)	2.256	2.275	2.305	2.326	2.141	2.344	2.196	3.285	2.120
M-C(5)	2.255	2.270	2.320	2.340	2.141	2.361	2.154	2.324	2.235
M-C(6)	2.253	2.268	2.325	2.335	2.140	2.365	2.144	2.257	2.242
M-C (C_5 ring)									
M-C(7)	2.120	2.135	2.248	2.302	2.097	2.213	2.249	2.224	2.915
M-C(8)	2.145	2.134	2.299	2.345	2.098	2.253	2.190	2.182	2.771
M-C(9)	2.188	2.133	2.260	2.307	2.098	2.184	2.235	2.128	2.243
M-C(10)	2.188	2.133	2.260	2.307	2.098	2.184	2.235	2.128	2.243
M-C(11)	2.145	2.134	2.299	2.345	2.098	2.253	2.190	2.182	2.771
E_2	-160.3122	-166.0695	-165.5806	-166.3195	-160.4071	-159.5728	-165.2854	-165.1502	-165.5167

Tables S8. Selected parameters (B3LYP) obtained for $[\text{M}(\text{Bz})\text{Cp}]^{+1/0/-1}$ (M = Co and Ni) complexes.

	$[\text{Co}(\text{Bz})\text{Cp}]^+$	$\text{Co}(\text{Bz})\text{Cp}$		$[\text{Co}(\text{Bz})\text{Cp}]^-$	$[\text{Ni}(\text{Bz})\text{Cp}]^+$		$\text{Ni}(\text{Bz})\text{Cp}$	$[\text{Ni}(\text{Bz})\text{Cp}]^-$	
NTE	19	20		21	20	20	21	22	22
MVE	19	18	18	19	18	18	17	18	18
Coordination mode	(η^6, η^5)	(η^4, η^5)	(η^4, η^5)	(η^3, η^5)	(η^4, η^5)	(η^4, η^5)	(η^2, η^5)	(η^2, η^5)	(η^2, η^5)
Symmetry	(C_I)	(C_I)	(C_I)	(C_I)	(C_s)	(C_s)	(C_s)	(C_s)	(C_s)
Spin state	S = 1/2	S = 0	S = 1	S = 1/2	S = 0	S = 1	S = 1/2	S = 0	S = 1
$\Delta(\text{HL})_2$	-	3.25	-	-	1.25	-	-	3.01	-
ΔE_2	-	0.0	5.0	-	0.0	2.9		0.0	20.7
M-C (C_6 ring)									
M-C(1)	2.246	2.004	2.069	2.011	2.250	2.280	2.219	1.895	2.066
M-C(2)	2.199	2.113	2.220	2.346	2.352	2.370	3.366	3.046	3.766
M-C(3)	2.261	2.832	2.894	3.176	2.377	2.480	3.048	3.022	2.864
M-C(4)	2.260	2.832	2.889	3.168	2.377	2.480	3.048	3.022	2.864
M-C(5)	2.202	2.113	2.220	2.527	2.352	2.370	3.366	3.406	3.766
M-C(6)	2.250	2.005	2.065	2.005	2.298	2.350	2.245	2.221	2.143
M-C (C_5 ring)									
M-C(7)	2.191	2.214	2.297	2.298	2.094	2.144	2.359	2.553	2.868
M-C(8)	2.123	2.106	2.293	2.296	2.245	2.276	2.263	2.423	2.616
M-C(9)	2.185	2.105	2.289	2.171	2.224	2.243	2.158	2.187	2.178
M-C(10)	2.127	2.104	2.291	2.296	2.224	2.243	2.158	2.187	2.178
M-C(11)	2.187	2.201	2.297	2.307	2.245	2.276	2.263	2.423	2.616
E_2	-158.700	164.721	-164.502	-165.081	-153.759	-153.655	-159.506	-159.941	-159.042