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

Supporting Information

Ligand Stabilization of Manganocene Dianion – In Defiance of the 18-Electron Rule

Monalisa Yadav[1], Hong Fang[2], Santanab Giri[3], and Puru Jena[2]

[1]IISER Kolkata, Haringhata Farm, Nadia, West Bengal- 741252, INDIA

[2]Physics Department, Virginia Commonwealth University, Richmond, VA 23238

[3]Theoretical Chemistry Laboratory, Department of Chemistry, National Institute of Technology Rourkela, Rourkela 769008, INDIA

Table S1. Optimized Energy values in a.u for all possible spin states. "n" denotes neutral state, "a" denotes anionic state, "d" denotes dianionic state, and "t" denotes trianionic state. The most stable spin states have been shown in red.

Structure (central atom,ligand and charged state)	Singlet	Doublet	Triplet	Quartet	Quintet	Sextet
$Mn(C_5H_5)_2$ (n)	-	-1538.0022	-	-1537.9981	-	-1538.0234
$Mn(C_5H_5)_2$ (a)	-1538.0341	-	-1538.0037	-	-1538.0312	-
$Mn(C_5H_5)_2$ (d)	-	-1537.9319	-	-1537.9311	-	-1537.9348
$Mn(C_5H_5)_2$ (t)	-1537.7624	-	-1537.7333	-	-1537.7552	-
$Mn(C_5(CN)_5)_2$(n)	-	-	-	-2460.3187	-	-2460.3513
$Mn(C_5(CN)_5)_2$(a)	-2460.5180	-	-2460.4916	-	-2460.5268	-
$Mn(C_5(CN)_5)_2$(d)	-	-2460.5116		-2460.5524	-	-2460.5374
$Mn(C_5(CN)_5)_2$(t)	-2460.3761	-	-2460.4341	-	-2460.4456	
$Mn(C_5(BO)_5)_2$(n)	-	-	-	-2533.3186	-	-2533.3495
$Mn(C_5(BO)_5)_2$(a)	-2533.5163	-	-2533.4898	-	-2533.5248	-
$Mn(C_5(BO)_5)_2$(d)	-	-2533.5048	-	-2533.5387	-	-2533.5232
$Mn(C_5(BO)_5)_2$ (t)	-2533.3699	-	-2533.4109	-	-2533.4166	

Table S2. Optimized Energy values in Hatree for the most stable spin state. “n” denotes neutral state, “a” denotes anionic state, “d” denotes dianionic state, and “t” denotes trianionic state.

Molecule	Optimized Energy values in (Hartree)	Stable spin state
$Mn(C_5H_5)_2$(n)	-1538.0234	Sextet
$Mn(C_5H_5)_2$(a)	-1538.0341	Singlet
$Mn(C_5H_5)_2$(d)	-1537.9348	Sextet
$Mn(C_5H_5)_2$(t)	-1537.7624	Singlet
$Mn(C_5(CN)_5)_2$(n)	-2460.3513	Sextet
$Mn(C_5(CN)_5)_2$(a)	-2460.5268	Quintet
$Mn(C_5(CN)_5)_2$(d)	-2460.5524	Quartet
$Mn(C_5(CN)_5)_2$(t)	-2460.4456	Quintet
$Mn(C_5(BO)_5)_2$(n)	-2533.3495	Sextet
$Mn(C_5(BO)_5)_2$(a)	-2533.5248	Quintet
$Mn(C_5(BO)_5)_2$(d)	-2533.5387	Quartet
$Mn(C_5(CN)_5)_2$(t)	-2533.4166	Quintet

Figure S1. NBO charge distribution for a) $Mn(C_5H_5)_2$ neutral b) $Mn(C_5H_5)_2$ anion c) $Mn(C_5H_5)_2$dianion d) $Mn(C_5H_5)_2$trianion e) $Mn(C_5(CN)_5)_2$ neutral f) $Mn(C_5(CN)_5)_2$ anion g) $Mn(C_5(CN)_5)_2$dianion h) $Mn(C_5(CN)_5)_2$trianion i) $Mn(C_5(BO)_5)_2$ neutral j) $Mn(C_5(BO)_5)_2$ anion k) $Mn(C_5(BO)_5)_2$dianion l) $Mn(C_5(BO)_5)_2$trianion

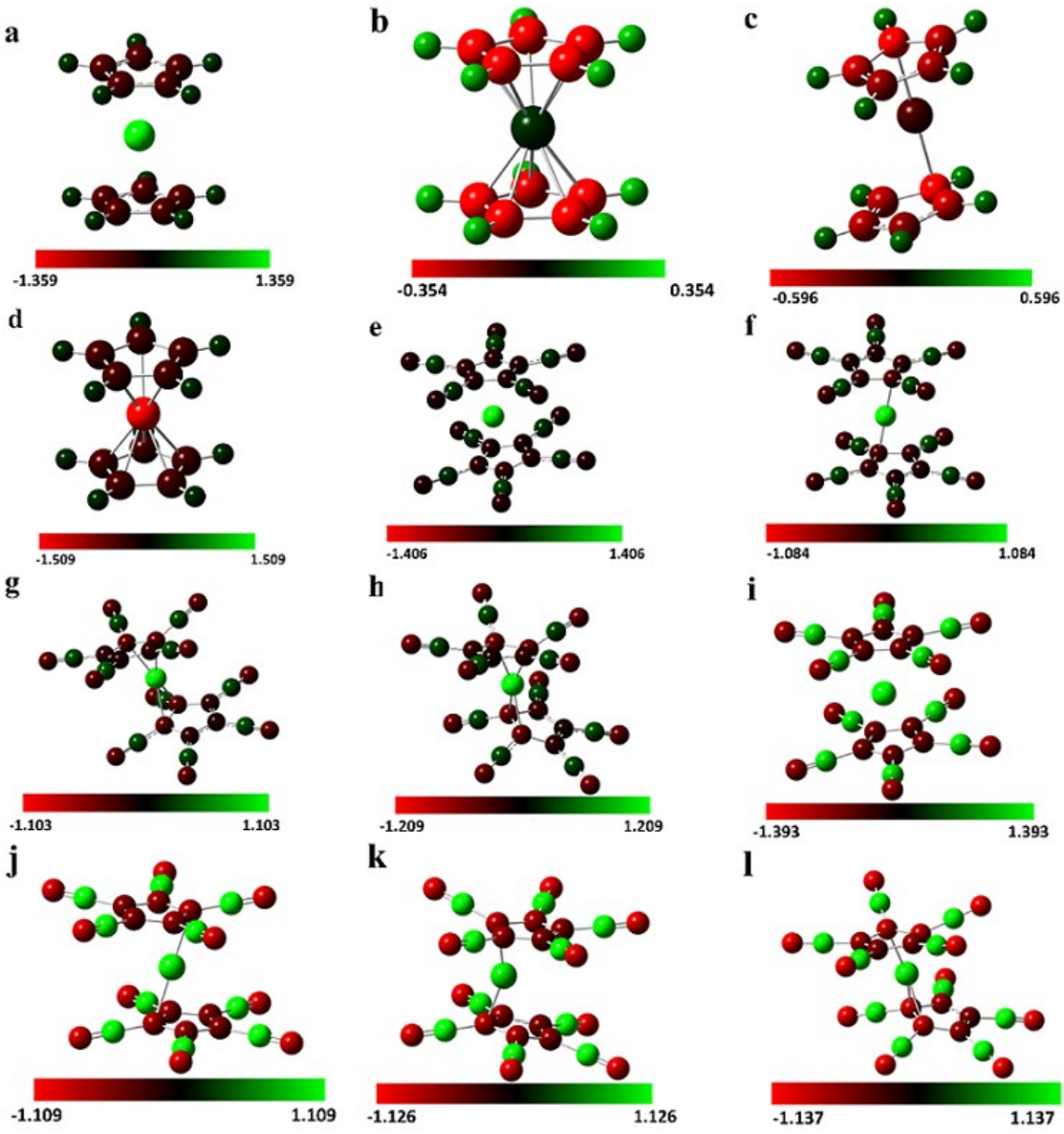

Figure S2.Molecular Orbital Energy diagram a)$Mn(C_5(H)_5)_2$dianion with up spin b) $Mn(C_5(BO)_5)_2$dianion with up spin c) $Mn(C_5(CN)_5)_2$dianion with up spin d) $Mn(C_5(H)_5)_2$dianion with down spin e) $Mn(C_5(BO)_5)_2$dianion with down spin f) $Mn(C_5(CN)_5)_2$dianion with down spin.

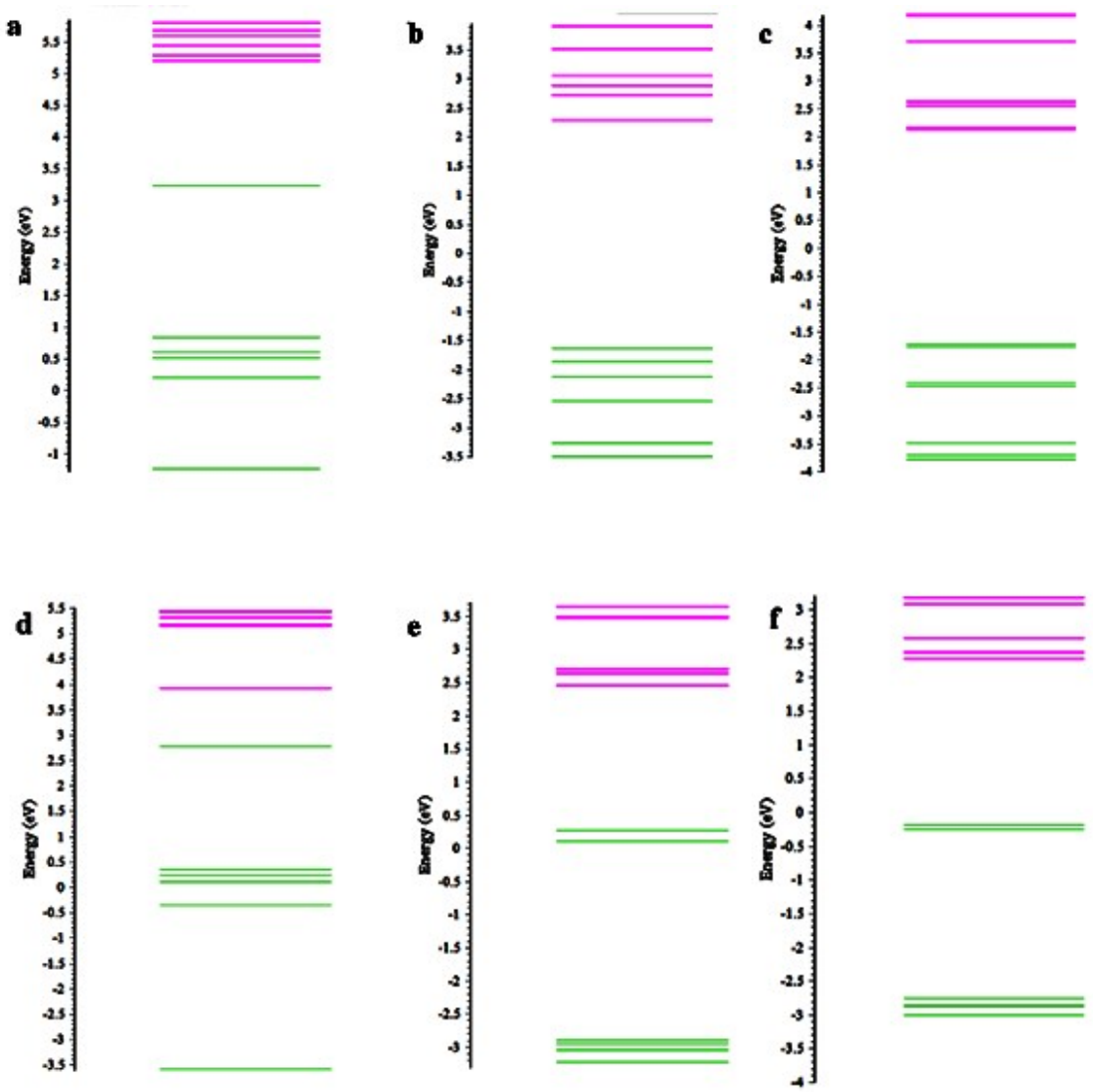
a
b
c
d
e
f
Energy (eV)

Table S3: The fragment which contributes the most to the various energy levels have been mentioned. The values are given in percentage. The Carbon atom of the ring is denoted by C_1.

	Spin up		Spin down	
Molecule	HOMO	LUMO	HOMO	LUMO
$Mn(C_5H_5)_2$(n)	C_1: 74	Mn: 82	C_1: 77	C_1: 81
$Mn(C_5H_5)_2$(a)	C_1: 76	Mn: 96	-	-
$Mn(C_5H_5)_2$(d)	Mn: 82	C_1: 51	C_1: 71	Mn: 81
$Mn(C_5(CN)_5)_2$(n)	C_1: 58	C_1: 52	CN: 47	CN: 49
$Mn(C_5(CN)_5)_2$(a)	C_1: 74	C_1: 68	C_1: 81	C_1: 56
$Mn(C_5(CN)_5)_2$(d)	C_1: 44	C_1: 52	CN: 51	CN: 48
$Mn(C_5(BO)_5)_2$(n)	C_1: 66	C_1: 79	C_1: 51	C_1: 40
$Mn(C_5(BO)_5)_2$(a)	C_1: 77	C_1: 78	C_1: 58	C_1: 67
$Mn(C_5(BO)_5)_2$(d)	C_1: 94	Mn: 50	C_1: 73	C_1: 62

Table S4: The table gives the contribution of the various ligands (H, CN, BO) to the various spin up MO for the molecules $Mn(C_5H_5)_2$(n,a,d), $Mn(C_5(CN)_5)_2$(n,a,d) and $Mn(C_5(BO)_5)_2$(n,a,d) respectively in the various charged states (n: neutral; a: mono-anion; d: dianion)

MO energy levels	$Mn(C_5H_5)_2$ (n)	$Mn(C_5H_5)_2$ (a)	$Mn(C_5H_5)_2$ (d)	$Mn(C_5(CN)_5)_2$ (n)	$Mn(C_5(CN)_5)_2$ (a)	$Mn(C_5(CN)_5)$ (d)	$Mn(C_5(BO)_5)_2$ (n)	$Mn(C_5(BO)_5)_2$ (a)	$Mn(C_5(BO)_5)_2$ (d)
LUMO+5	-	-	-	24	14	44	6	6	16
LUMO+4	-	-	-	31	12	20	1	9	15
LUMO+3	-	-	-	24	20	51	13	14	6
LUMO+2	-	-	-	25	30	37	13	16	8
LUMO+1	-	-	-	42	26	30	17	8	8
LUMO	-	-	-	42	21	45	17	21	4
HOMO	-	-	-	32	20	19	22	13	3
HOMO-1	-	2	-	30	48	27	21	21	19
HOMO-2	-	-	-	42	12	31	10	18	16
HOMO-3	-	-	-	48	28	55	10	25	17
HOMO-4	-	2	-	30	20	52	46	17	5
HOMO-5	-	2	-	50	35	10	2	11	9

Table S5: The table gives the contribution of the various ligands (H, CN, BO) to the various spin down MO for the molecules $Mn(C_5H_5)_2$(n,a,d), $Mn(C_5(CN)_5)_2$(n,a,d) and $Mn(C_5(BO)_5)_2$(n,a,d) respectively in the various charged states (n: neutral; a: mono-anion; d: dianion)

MO energy levels	$Mn(C_5H_5)_2$ (n)	$Mn(C_5H_5)_2$ (d)	$Mn(C_5(CN)_5)_2$ (n)	$Mn(C_5(CN)_5)_2$ (a)	$Mn(C_5(CN)_5)$ (d)	$Mn(C_5(BO)_5)_2$ (n)	$Mn(C_5(BO)_5)_2$ (a)	$Mn(C_5(BO)_5)_2$ (d)
LUMO+5	-	-	33	55	37	12	16	11
LUMO+4	-	-	32	54	17	12	13	7
LUMO+3	2	-	32	22	17	11	8	12
LUMO+2	2	-	30	23	19	3	6	9
LUMO+1	-	-	45	22	43	28	14	5
LUMO	-	-	49	23	48	28	16	14
HOMO	-	-	47	7	51	6	15	10
HOMO-1	-	-	42	30	19	7	15	12
HOMO-2	-	-	40	23	32	27	8	14
HOMO-3	1	-	38	13	22	29	22	19
HOMO-4	4	-	30	27	22	47	34	18
HOMO-5	5	2	44	35	38	2	30	26

Figure S3: HOMO for a) Spin up $Mn(C_5(BO)_5)_2^{2-}$ b) Spin down $Mn(C_5(BO)_5)_2^{2-}$

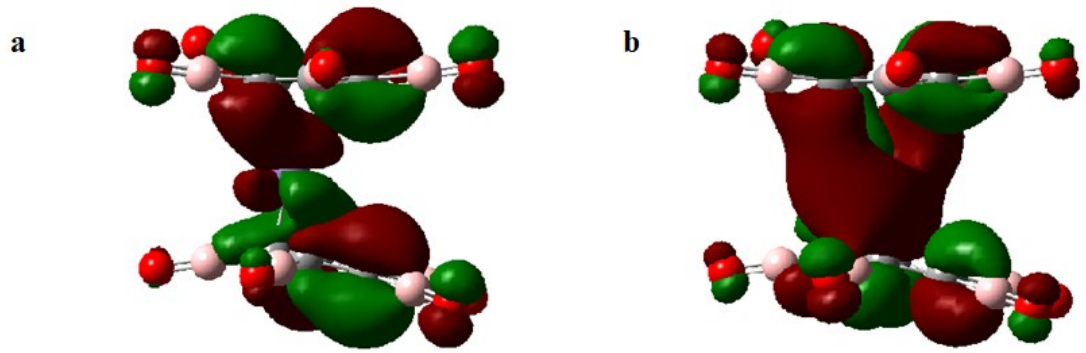

Table S6.NICS values in ppm

dis from centre(Å)	C_6H_6	$C_5BO_5^-$	$C_5CN_5^-$	$C_5H_5^-$
0	-8.0379	-12.9864	-12.6854	-15.7059
0.1	-8.1467	-13.025	-12.6631	-15.6271
0.2	-8.4554	-13.1236	-12.5934	-15.3955
0.3	-8.9059	-13.2389	-12.4685	-15.0248
0.4	-9.417	-13.315	-12.2781	-14.5341
0.5	-9.9025	-13.2997	-12.0123	-13.9445
0.6	-10.2883	-13.1557	-11.6644	-13.2763
0.7	-10.5227	-12.8665	-11.2329	-12.5468
0.8	-10.5804	-12.4352	-10.7227	-11.7715
0.9	-10.4604	-11.8798	-10.1453	-10.965
1	-10.1801	-11.2278	-9.5172	-10.1424
1.1	-9.7685	-10.5101	-8.8579	-9.3193
1.2	-9.2594	-9.7572	-8.1876	-8.511
1.3	-8.6866	-8.996	-7.5249	-7.7315
1.4	-8.0804	-8.2484	-6.8851	-6.9926
1.5	-7.4658	-7.531	-6.2799	-6.3026
1.6	-6.8621	-6.8549	-5.7167	-5.6671
1.7	-6.2832	-6.2268	-5.1998	-5.0881
1.8	-5.7379	-5.6496	-4.7302	-4.5655
1.9	-5.2314	-5.1237	-4.3068	-4.0971
2	-4.7657	-4.6472	-3.9269	-3.6794
2.1	-4.3408	-4.2173	-3.5869	-3.3081
2.2	-3.9551	-3.8304	-3.283	-2.9787
2.3	-3.6063	-3.4827	-3.0112	-2.6866
2.4	-3.2916	-3.1703	-2.7677	-2.4274
2.5	-3.0081	-2.8897	-2.549	-2.1973
2.6	-2.7526	-2.6375	-2.352	-1.9927
2.7	-2.5226	-2.4107	-2.1742	-1.8104
2.8	-2.3152	-2.2066	-2.0131	-1.6478
2.9	-2.1281	-2.0227	-1.8667	-1.5025

3	-1.9592	-1.8568	-1.7333	-1.3724
3.1	-1.8065	-1.7069	-1.6114	-1.2557
3.2	-1.6682	-1.5714	-1.4997	-1.1508
3.3	-1.5428	-1.4487	-1.3972	-1.0564
3.4	-1.429	-1.3374	-1.3027	-0.9713
3.5	-1.3254	-1.2363	-1.2156	-0.8945
3.6	-1.2311	-1.1444	-1.1351	-0.8249
3.7	-1.1451	-1.0608	-1.0606	-0.7619
3.8	-1.0665	-0.9844	-0.9915	-0.7047
3.9	-0.9945	-0.9148	-0.9274	-0.6527
4	-0.9286	-0.8511	-0.8679	-0.6053
4.1	-0.8681	-0.7928	-0.8126	-0.562
4.2	-0.8126	-0.7394	-0.7612	-0.5226
4.3	-0.7614	-0.6904	-0.7134	-0.4864
4.4	-0.7143	-0.6455	-0.669	-0.4533
4.5	-0.6709	-0.6041	-0.6277	-0.423
4.6	-0.6308	-0.5661	-0.5894	-0.3951
4.7	-0.5937	-0.531	-0.5537	-0.3695
4.8	-0.5593	-0.4987	-0.5206	-0.3459
4.9		-0.4689	-0.4898	-0.3241