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

Supplementary Information

Low energy electron-induced decomposition of (η^5-Cp)$Fe(CO)_2Mn(CO)_5$, a potential bimetallic precursor for focused electron beam induced deposition of alloy structures

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Optimized geometries used in quantum chemical calculations

CO

6	-1.664731000	1.072138000	0.080799000
8	-0.770328000	1.610416000	-0.368701000

$CpFe(CO)_2$

6	-3.321146000	-0.471629000	1.105948000
6	-2.176827000	-1.339810000	1.269103000
6	-1.734912000	-1.733425000	-0.025980000
6	-2.554483000	-1.079915000	-0.989792000
6	-3.553669000	-0.312644000	-0.281487000
1	-3.886749000	-0.010505000	1.909432000
1	-1.748957000	-1.655159000	2.215654000
1	-0.877832000	-2.365269000	-0.242153000
1	-2.463912000	-1.162029000	-2.068498000
1	-4.329848000	0.293072000	-0.738287000
26	-1.602204000	0.400992000	0.198043000

8	-1.455667000	2.543898000	-1.778151000
8	-0.803063000	2.098274000	2.433802000
6	-1.086911000	1.420669000	1.532593000
6	-1.478420000	1.688229000	-0.991265000

$[CpFe(CO)_2]^-$

6	-3.447599000	-0.585206000	1.120182000
6	-2.205345000	-1.301278000	1.273810000
6	-1.674262000	-1.593531000	-0.023858000
6	-2.590499000	-1.040200000	-0.977738000
6	-3.686513000	-0.423884000	-0.272011000
1	-4.076607000	-0.218657000	1.926713000
1	-1.734331000	-1.547670000	2.222028000
1	-0.772042000	-2.157069000	-0.243278000
1	-2.464871000	-1.052189000	-2.057448000
1	-4.533293000	0.084338000	-0.724818000
26	-1.841922000	0.495919000	0.243296000
8	-1.094980000	2.478704000	-1.750972000
8	-0.503557000	2.069442000	2.292901000
6	-1.049916000	1.432412000	1.453600000
6	-1.398862000	1.673619000	-0.933445000

$[CpFe(CO)_2Mn(CO)_4]^-$

6	-2.725504000	-0.711614000	-1.540662000
6	-1.411627000	-1.154369000	-1.927031000
6	-0.605506000	-0.000007000	-2.171538000
6	-1.411631000	1.154352000	-1.927038000
6	-2.725507000	0.711594000	-1.540667000
1	-3.560841000	-1.353704000	-1.277492000
1	-1.076080000	-2.185095000	-1.982577000

1	0.436057000	-0.000006000	-2.475713000
1	-1.076089000	2.185080000	-1.982591000
1	-3.560846000	1.353682000	-1.277500000
26	-1.308273000	-0.000003000	-0.159982000
25	1.343589000	0.000003000	0.283179000
6	1.773013000	0.000009000	2.026460000
6	3.006821000	0.000005000	-0.335397000
6	1.203419000	1.802796000	0.027604000
6	1.203425000	-1.802791000	0.027613000
8	4.116622000	0.000006000	-0.724388000
8	2.107142000	0.000012000	3.149328000
8	1.159633000	2.955657000	-0.173058000
8	1.159642000	-2.955653000	-0.173044000
8	-1.523570000	2.066479000	1.871446000
8	-1.523562000	-2.066473000	1.871458000
6	-1.386207000	-1.235934000	1.058265000
6	-1.386212000	1.235936000	1.058258000

$[CpFe(CO)Mn(CO)_5]^-$

6	-2.806064000	-0.698170000	1.099255000
6	-1.958931000	-1.821620000	0.874522000
6	-1.957371000	-2.111088000	-0.531683000
6	-2.798281000	-1.182991000	-1.188813000
6	-3.295711000	-0.271229000	-0.187250000
1	-3.046156000	-0.250133000	2.058865000
1	-1.383313000	-2.352515000	1.627608000
1	-1.356850000	-2.878829000	-1.012362000
1	-2.975050000	-1.118708000	-2.258091000
1	-4.001516000	0.536688000	-0.360907000
26	-1.199641000	0.150288000	-0.142364000

25	1.520027000	-0.156247000	-0.208717000
6	1.339853000	-1.952060000	0.059719000
6	1.833368000	1.624447000	-0.529811000
6	3.284136000	-0.423948000	-0.359097000
6	0.641265000	-0.298803000	-1.837304000
6	0.997368000	0.192977000	1.504327000
8	1.275967000	-3.103268000	0.226958000
8	4.438727000	-0.601141000	-0.445244000
8	2.084797000	2.738781000	-0.735344000
8	0.338661000	-0.447231000	-2.959555000
8	0.712455000	0.403865000	2.618632000
8	-1.492085000	2.919748000	-0.904601000
6	-1.326822000	1.792694000	-0.589232000

$[CpFe(CO)_2Mn(CO)_5]^-$

6	-3.313782000	-0.480746000	1.109084000
6	-2.179351000	-1.363054000	1.263744000
6	-1.757899000	-1.774387000	-0.030280000
6	-2.560873000	-1.093680000	-0.986745000
6	-3.550311000	-0.316830000	-0.276580000
1	-3.860766000	-0.001879000	1.915788000
1	-1.731432000	-1.665783000	2.205248000
1	-0.924356000	-2.429650000	-0.250418000
1	-2.454331000	-1.157106000	-2.065430000
1	-4.310961000	0.311686000	-0.729886000
26	-1.587140000	0.401424000	0.200532000
25	1.698923000	-0.327666000	-0.329335000
6	1.615682000	-2.134842000	-0.479600000
6	1.703527000	1.500760000	-0.160998000
6	3.472173000	-0.338712000	-0.587471000

6	0.825564000	-0.225374000	-1.926515000
6	1.313140000	-0.530520000	1.440607000
8	1.562635000	-3.298166000	-0.575859000
8	4.630024000	-0.355480000	-0.757543000
8	1.747896000	2.657327000	-0.057688000
8	0.318610000	-0.225378000	-2.979553000
8	1.124810000	-0.723099000	2.577815000
8	-1.452369000	2.571728000	-1.735855000
8	-0.861902000	2.165947000	2.400055000
6	-1.102651000	1.447800000	1.509044000
6	-1.456646000	1.691898000	-0.965455000

$CpFe(CO)_2Mn(CO)_5$

6	-3.025814000	-0.708657000	1.036679000
6	-2.014713000	-1.701815000	0.822498000
6	-1.814385000	-1.820571000	-0.588532000
6	-2.671084000	-0.894591000	-1.240006000
6	-3.428503000	-0.200194000	-0.231052000
1	-3.400183000	-0.380623000	2.001715000
1	-1.507128000	-2.273561000	1.591776000
1	-1.128561000	-2.499579000	-1.082270000
1	-2.733139000	-0.731497000	-2.311437000
1	-4.170495000	0.572250000	-0.406647000
26	-1.392884000	0.183359000	0.063406000
25	1.391103000	-0.141705000	-0.057646000
6	1.096365000	-1.917313000	0.283351000
6	1.562261000	1.688163000	-0.268707000
6	3.101235000	-0.433957000	-0.526702000
6	0.683770000	-0.319226000	-1.750314000
6	1.707482000	0.057677000	1.749966000

8	0.969303000	-3.042860000	0.519176000
8	4.196577000	-0.630301000	-0.845042000
8	1.712866000	2.824768000	-0.382183000
8	0.340347000	-0.465851000	-2.847106000
8	1.943959000	0.150604000	2.875028000
8	-1.404829000	2.541162000	-1.638780000
8	-0.799939000	1.746112000	2.438590000
6	-0.961815000	1.104469000	1.483179000
6	-1.343520000	1.599958000	-0.962232000

$[Mn(CO)_5]^-$

25	1.817951000	-0.364577000	-0.346153000
6	1.786714000	-2.179027000	-0.507690000
6	1.844089000	1.450061000	-0.188418000
6	3.602994000	-0.368171000	-0.606361000
6	0.702336000	-0.224694000	-1.756808000
6	1.150049000	-0.500762000	1.324095000
8	1.760548000	-3.343268000	-0.614074000
8	4.765029000	-0.371461000	-0.775308000
8	1.860418000	2.614936000	-0.087288000
8	-0.022921000	-0.132589000	-2.675690000
8	0.715606000	-0.588983000	2.411442000

$[CpFeMn(CO)_5]^+$

6	-2.512549000	1.162711000	0.749544000
6	-2.237951000	0.038338000	1.583455000
6	-2.490753000	-1.139552000	0.819995000
6	-2.967254000	-0.738727000	-0.480071000
6	-2.980544000	0.675434000	-0.523814000
1	-2.391018000	2.207286000	1.023684000

1	-1.853955000	0.073067000	2.598959000
1	-2.349213000	-2.163195000	1.156424000
1	-3.235131000	-1.407172000	-1.293454000
1	-3.260360000	1.287946000	-1.376194000
26	-0.992970000	-0.001283000	-0.116591000
25	1.226053000	0.000449000	-0.297912000
6	2.518358000	-1.299840000	-0.203940000
6	0.907631000	0.005942000	1.473976000
6	-0.308476000	-1.423660000	-1.052589000
6	2.514706000	1.305059000	-0.213932000
8	0.868162000	0.008198000	2.630500000
8	3.286664000	-2.144758000	-0.096885000
8	-0.273326000	-2.408695000	-1.660038000
8	3.280589000	2.152945000	-0.113132000
8	-0.282050000	2.389715000	-1.688162000
6	-0.314294000	1.411676000	-1.069383000

$[CpFeMn(CO)_6]^+$ (no bridging CO ligands)

6	-2.669638000	-0.714753000	-1.682498000
6	-1.319524000	-1.161745000	-1.713409000
6	-0.461120000	-0.000115000	-1.689956000
6	-1.319457000	1.161559000	-1.713495000
6	-2.669599000	0.714646000	-1.682534000
1	-3.546080000	-1.355747000	-1.639931000
1	-0.992124000	-2.196950000	-1.728700000
1	0.635126000	-0.000151000	-1.971530000
1	-0.991999000	2.196743000	-1.728878000
1	-3.546009000	1.355688000	-1.640030000
26	-1.605930000	-0.000006000	0.034588000
25	1.140376000	0.000007000	-0.118309000

6	1.573330000	0.000052000	1.630868000
6	2.879442000	0.000094000	-0.622024000
6	1.194609000	1.860472000	-0.076220000
6	1.194729000	-1.860447000	-0.076215000
8	3.980148000	0.000074000	-0.952076000
8	1.813483000	0.000076000	2.754733000
8	1.303287000	3.000514000	-0.016511000
8	1.303525000	-3.000477000	-0.016488000
8	-1.378425000	2.218518000	1.960015000
8	-1.378016000	-2.218245000	1.960302000
6	-1.455975000	-1.346688000	1.216698000
6	-1.456251000	1.346845000	1.216534000

$[CpFeMn(CO)_6]^+$ (3 bridging CO ligands)

6	-2.692932000	1.052612000	0.686194000
6	-2.908939000	-0.285652000	1.140746000
6	-3.028844000	-1.139382000	-0.001129000
6	-2.888488000	-0.315004000	-1.164494000
6	-2.682715000	1.033185000	-0.740491000
1	-2.553229000	1.925494000	1.316797000
1	-2.969134000	-0.600504000	2.178994000
1	-3.198635000	-2.211429000	0.011555000
1	-2.932339000	-0.657574000	-2.194694000
1	-2.530855000	1.889791000	-1.390290000
26	-1.107126000	-0.228628000	0.002808000
25	1.298606000	0.289347000	0.001165000
6	-0.330789000	-1.077376000	1.369377000
6	1.979733000	0.742668000	-1.732277000
6	2.416787000	-1.244410000	0.067682000
6	-0.319534000	-1.190670000	-1.279847000

6	1.967567000	0.882652000	1.696559000
8	-0.034907000	-1.716896000	2.286572000
8	3.110938000	-2.152287000	0.107400000
8	2.393299000	1.042949000	-2.753208000
8	-0.011426000	-1.907920000	-2.132978000
8	2.373563000	1.268155000	2.691529000
8	-0.247219000	2.855673000	-0.101269000
6	0.181795000	1.780007000	-0.061479000

$[CpFeMn(CO)_6]^+$ (1 bridging CO ligand)

6	3.205128000	-0.317139000	-0.721493000
6	2.357129000	-1.456896000	-0.627200000
6	1.860460000	-1.534039000	0.720757000
6	2.413362000	-0.450060000	1.458854000
6	3.229728000	0.312536000	0.574814000
1	3.737594000	0.018474000	-1.606212000
1	2.125476000	-2.149918000	-1.430997000
1	1.214224000	-2.310156000	1.117224000
1	2.208008000	-0.216533000	2.500269000
1	3.785977000	1.208997000	0.835026000
26	1.261073000	0.308402000	-0.203671000
25	-1.441768000	-0.173404000	-0.009508000
6	-1.284118000	-2.033128000	-0.039322000
6	-1.645435000	1.684479000	0.072880000
6	-3.251702000	-0.343844000	0.249933000
6	-1.021261000	-0.182850000	1.720946000
8	-1.212121000	-3.176957000	-0.006637000
8	-4.377238000	-0.449024000	0.440121000
8	-1.801374000	2.814635000	0.173783000
8	-0.758232000	-0.198192000	2.845802000

8	1.553600000	3.122691000	-0.997409000
8	-0.630803000	-0.106014000	-2.417035000
6	0.091789000	0.044001000	-1.500416000
6	1.414283000	2.033466000	-0.663468000

$[CpFeMn(CO)_7]^+$

6	-3.049388000	-0.659563000	0.938810000
6	-2.089413000	-1.708197000	0.730187000
6	-1.933912000	-1.888639000	-0.673840000
6	-2.764360000	-0.942502000	-1.342139000
6	-3.466850000	-0.188103000	-0.335693000
1	-3.389789000	-0.287329000	1.900736000
1	-1.594409000	-2.278075000	1.510192000
1	-1.276807000	-2.607765000	-1.154570000
1	-2.866596000	-0.822440000	-2.416680000
1	-4.185815000	0.605525000	-0.518706000
26	-1.393030000	0.126869000	-0.139272000
25	1.402023000	-0.086724000	0.137050000
6	1.120427000	-1.880140000	0.525276000
6	1.604154000	1.750724000	-0.169241000
6	3.060930000	-0.435486000	-0.533677000
6	0.665265000	-0.316334000	-1.564150000
6	2.075725000	0.141790000	1.876116000
8	0.986357000	-2.995931000	0.759477000
8	4.098046000	-0.660720000	-0.968358000
8	1.749227000	2.869255000	-0.361386000
8	0.399438000	-0.492661000	-2.673584000
8	2.509623000	0.271795000	2.925662000
8	-1.674307000	2.714402000	-1.487450000
8	-0.713934000	1.466619000	2.370346000

6	-0.834667000	0.912011000	1.362692000
6	-1.529719000	1.697840000	-0.971088000

Table S1: Comparison of relative intensities of positive fragments produced by dissociative ionization of $CpFe(CO)_2Mn(CO)_5$ between 30 and 60 eV. Relative DI intensities were calculated by integrating over the isotope distribution of each fragment and normalizing it to the single CO loss fragment at 60 eV. As can be seen here, the relative cross-section for each fragment increases with increasing incident electron energy. This is as expected for dissociative ionization. The average CO loss per dissociation incident was also calculated at each incident electron energy, as described in Table 2 within the text.

Mass	**Fragment**	**30 eV**	**40 eV**	**50 eV**	**60 eV**
372	$CpFe(CO)_2Mn(CO)_5$	25	59	117	160
344	$CpFe(CO)_2Mn(CO)_4$	14	37	66	100
288	$CpFe(CO)_2Mn(CO)_2$	6	14	22	29
260	$CpFe(CO)_2Mn(CO)$	10	22	42	60
232	$CpFe(CO)_2Mn$	60	153	288	430
204	CpFe(CO)Mn	54	156	298	416
195	$Mn(CO)_5$	1	4	5	6
177	$CpFe(CO)_2$	76	210	362	512
167	$Mn(CO)_4$	1	4	6	9
149	CpFe(CO)	8	31	57	79
139	$Mn(CO)_3$	2	9	26	29
121	CpFe	90	290	503	641
111	$FeMn/Mn(CO)_2$	9	59	127	177
83	Mn(CO)	4	20	43	75
66	Cp	2	5	12	19
56	Fe	6	37	88	151
55	Mn	11	91	182	303
44	CO_2	1	3	8	7
28	CO	14	43	112	146
16	O	0	0	2	2
Average CO loss (lower bound)		3	3	3	3
Average CO loss (upper bound)		5	6	6	6

Figure S1: Optimized structures of positive ions formed by dissociative ionisation of $CpFe(CO)_2Mn(CO)_5$: (a) ground state of $[CpFeMn(CO)_7]^+$, (b) ground state of $[CpFeMn(CO)_6]^+$ with one bridging carbonyl, (c) excited state of $[CpFeMn(CO)_6]^+$ with three bridging carbonyls, (d) ground state of $[CpFeMn(CO)_5]^+$ with three bridging carbonyls. These cations were geometrically optimized using the DFT method BP86 and the def2-TZVP basis set.

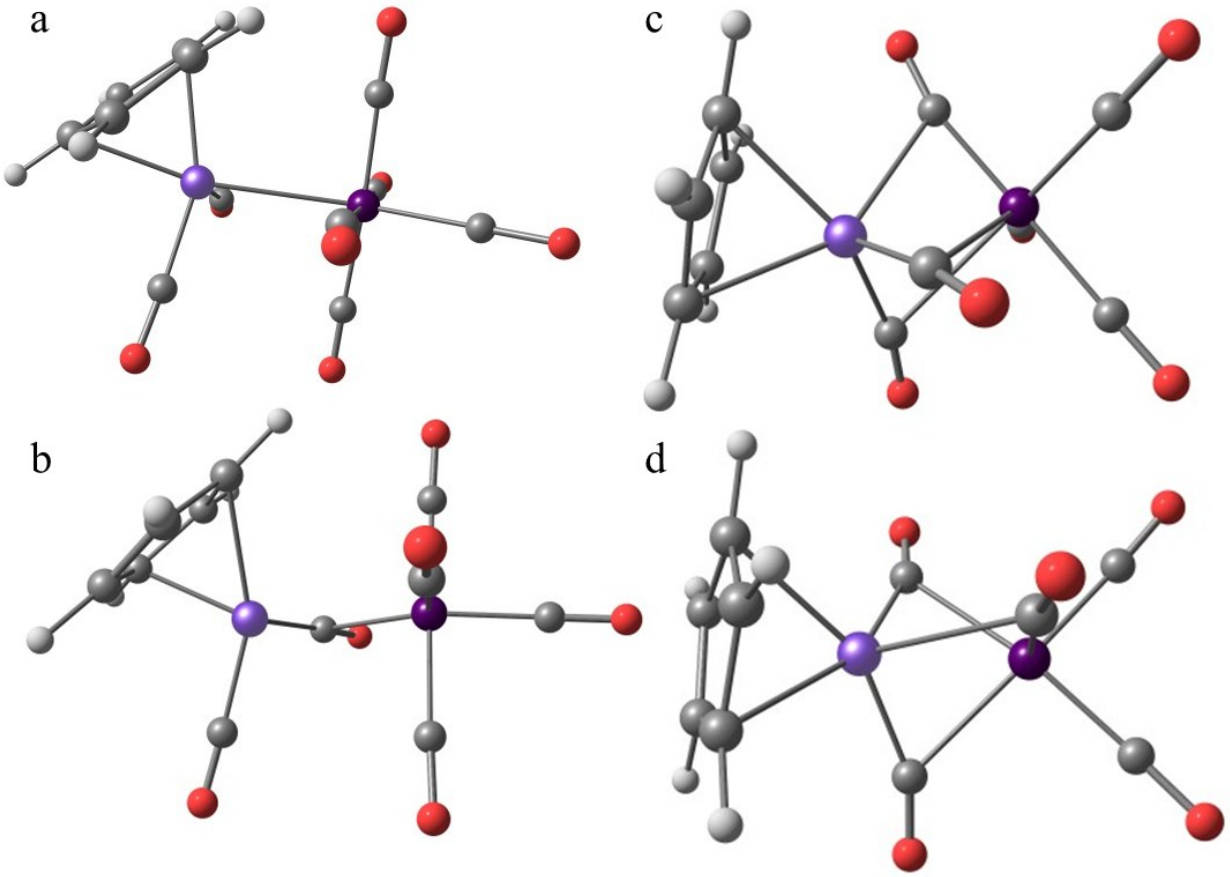

Table S2: Calculated thresholds (in eV) for the formation of $[CpFeMn(CO)_7]^+$, $[CpFeMn(CO)_6]^+$ and $[CpFeMn(CO)_5]^+$, with optimized geometries of each fragment shown in fig. S1. The thresholds are labeled (a) – (d), corresponding with the respective optimized geometries shown in fig. S1(a) – (d). Thresholds for the formation of the $[CpFeMn(CO)_6]^+$ fragment were calculated in the ground state, with a single carbonyl bridging the two metal centres, and in an excited state, with three carbonyls bridging the metal centres.

Cationic fragment		**Neutral fragment A**	**Threshold (BP86, eV)**	**Threshold (TZ, eV)**
M^+	(a)	–	6.8	6.4
$CpFeMn(CO)_6$	(b)	CO	8.6	7.4
$CpFeMn(CO)_6$	(c)	CO	8.5	7.7
$CpFeMn(CO)_5$	(d)	2CO	9.7	9.3