Mo Fischer carbene complexes: A DFT study on the prediction of redox potentials

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Supporting Information

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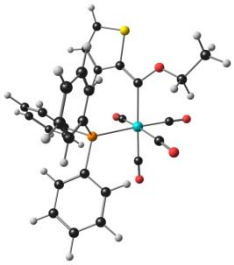
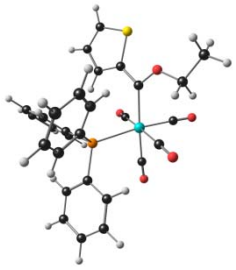
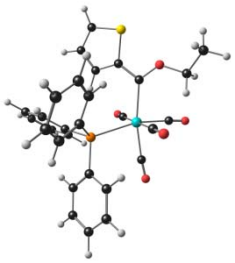
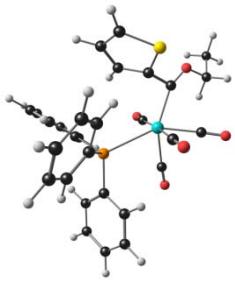
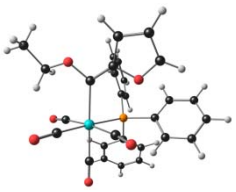
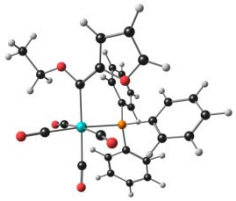
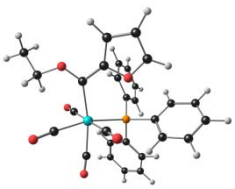
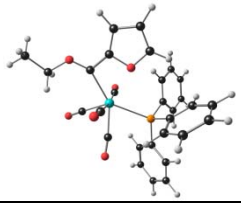
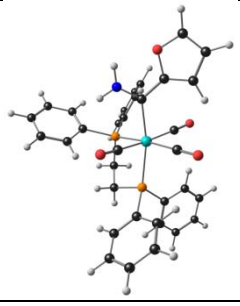
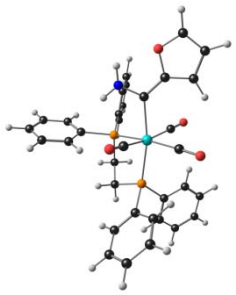
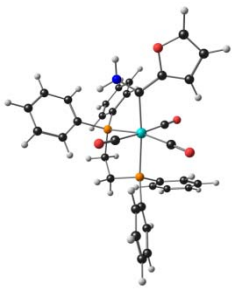
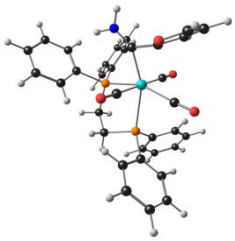
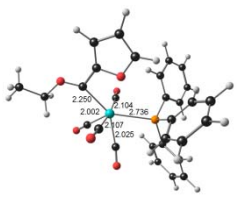
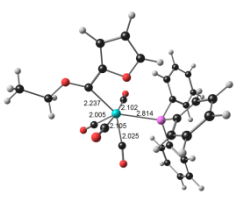
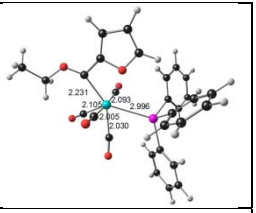
No	M^-	M	M^+	M^{2+}
1b				
4b				
5c				

Figure S1: Optimized geometry of the indicated molecules in their neutral (M), reduced (M^-), 1e$^-$ oxidized (M^+) and 2e$^-$ oxidized (M^{2+}) states.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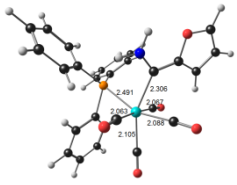	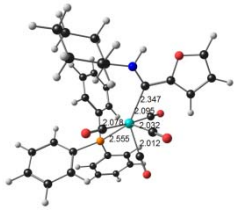	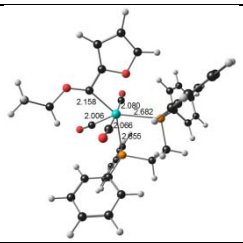	
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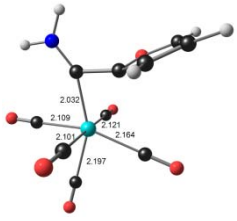	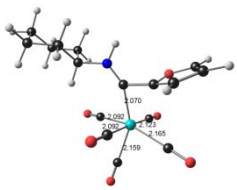	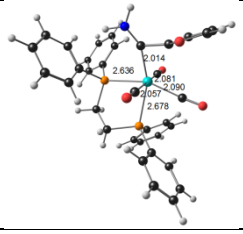	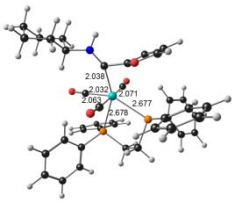
4e	**4f**	**5b**	**5c**

Figure S2: Optimized geometry of the indicated molecules, all containing a furyl group, in 2e$^-$ oxidized (M^{2+}) state.

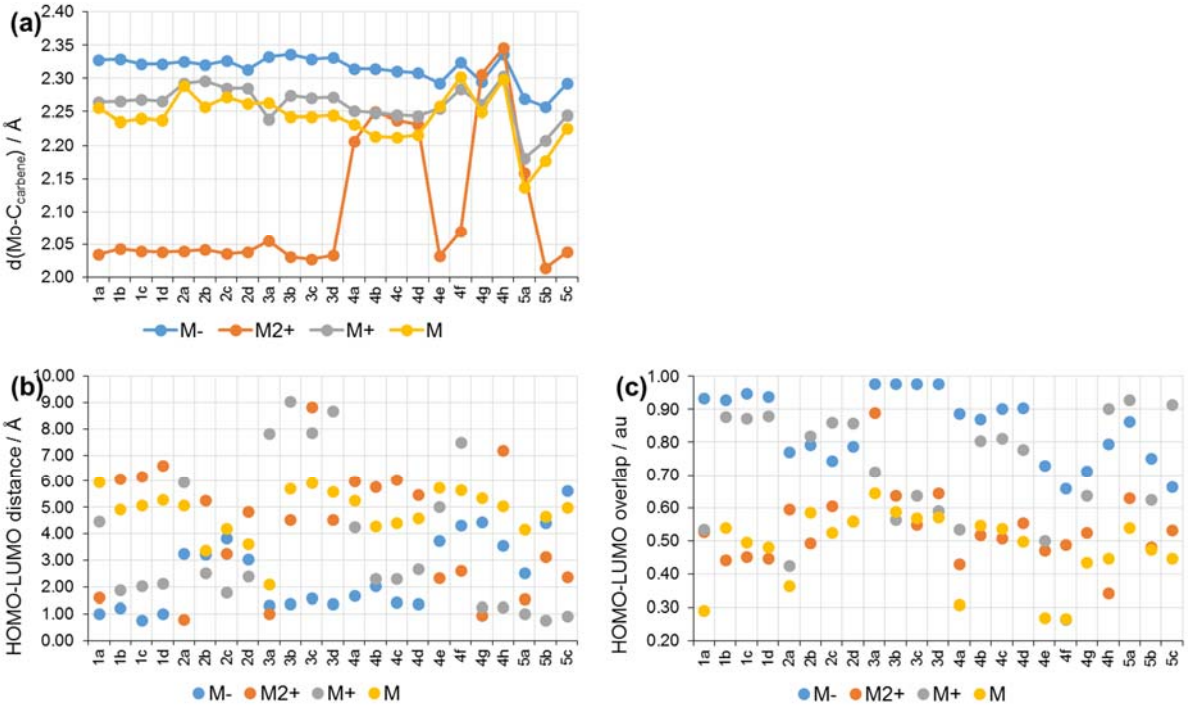

Figure S3: (a) The Mo-$C_{carbene}$ bond distance (Å), (b) The HOMO and LUMO distance (in Å), (c) the overlap between the HOMO and LUMO (in au) across the 23 derivatives

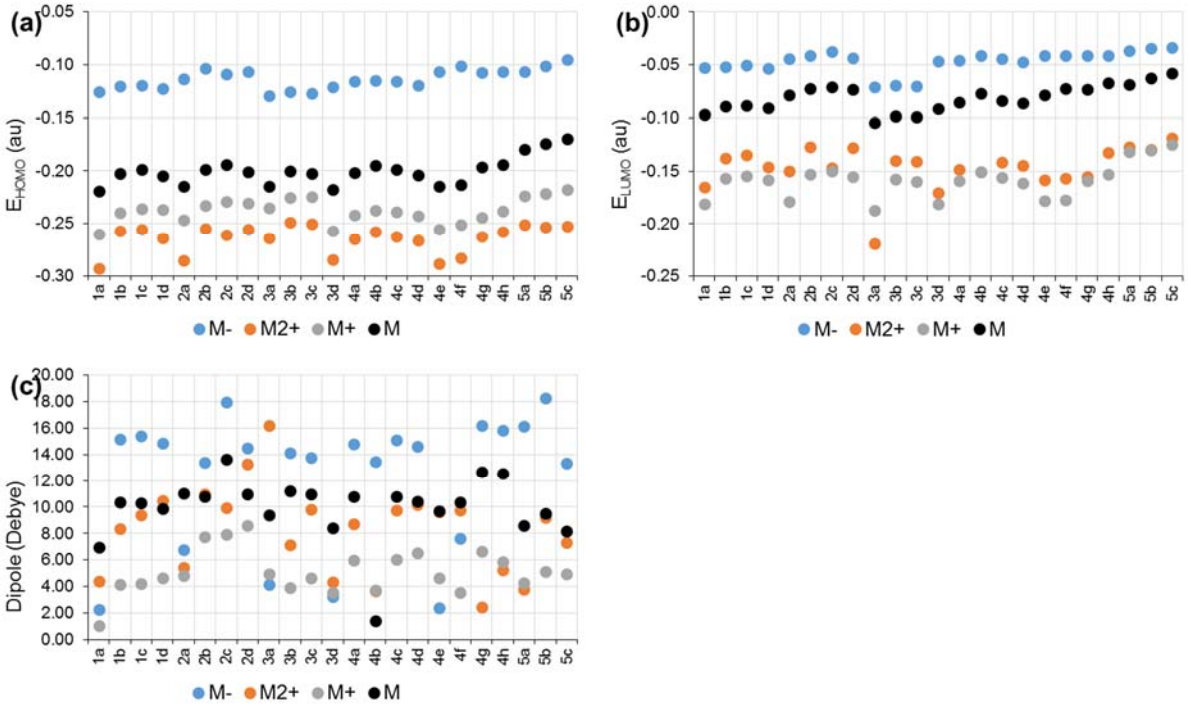

Figure S4: The plots of the (a) HOMO, (b) LUMO and (c) dipole moments of the molecules in their neutral (M), reduced (M^-), 1e- oxidized (M^+) and 2e- oxidized (M^{2+}) calculated in acetonitrile medium

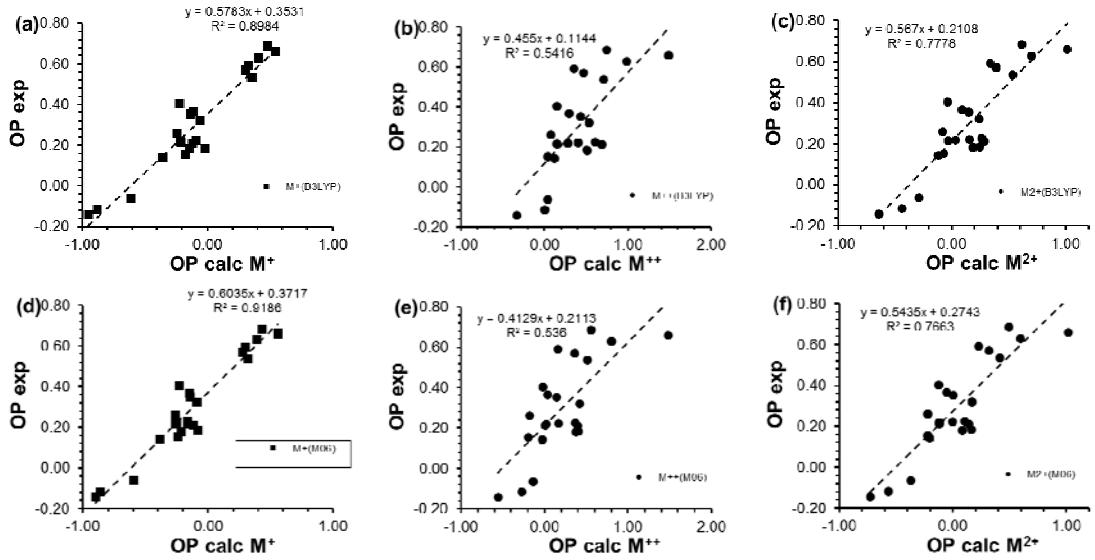

Figure S5: The correlation of the experimental and calculated reduction potential according to the M^{+}, M^{++} and M^{2+} calculated oxidation potential using (a) – (c) B3LYP and (d) - (f) M06 functional method.

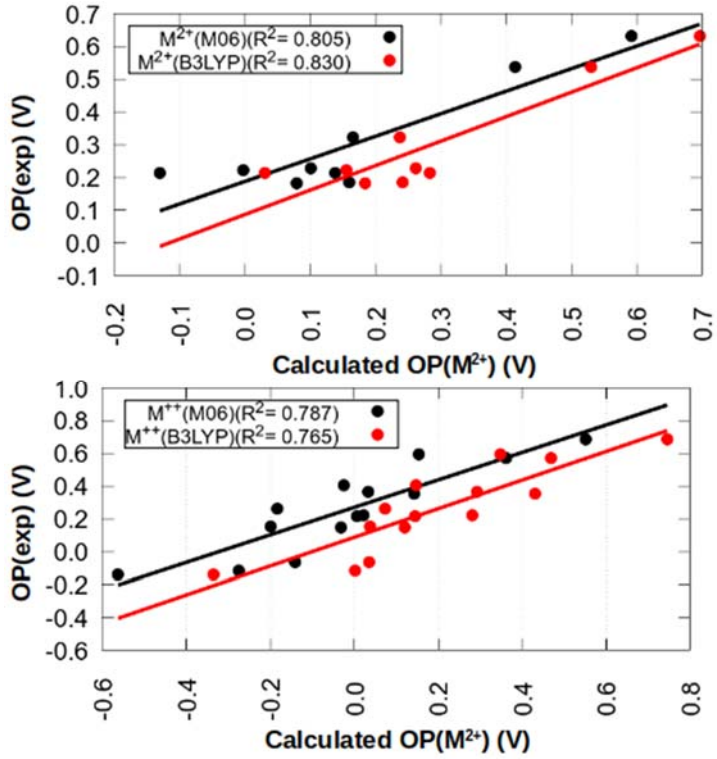

Figure S6: The correlation of the experimental oxidation potential (OP) with the calculated oxidation potential using the derivatives that best represent M^{2+} (**1d, 3d, 4a, 4b, 4c, 4d, 4e, 4g**) and M^{++} (**1a, 1b, 1c, 2a, 2b, 2c, 2d, 3b, 3c, 4f, 4h, 5a, 5b** and **5c**) oxidation potentials as indicated using the B3LYP and M06.

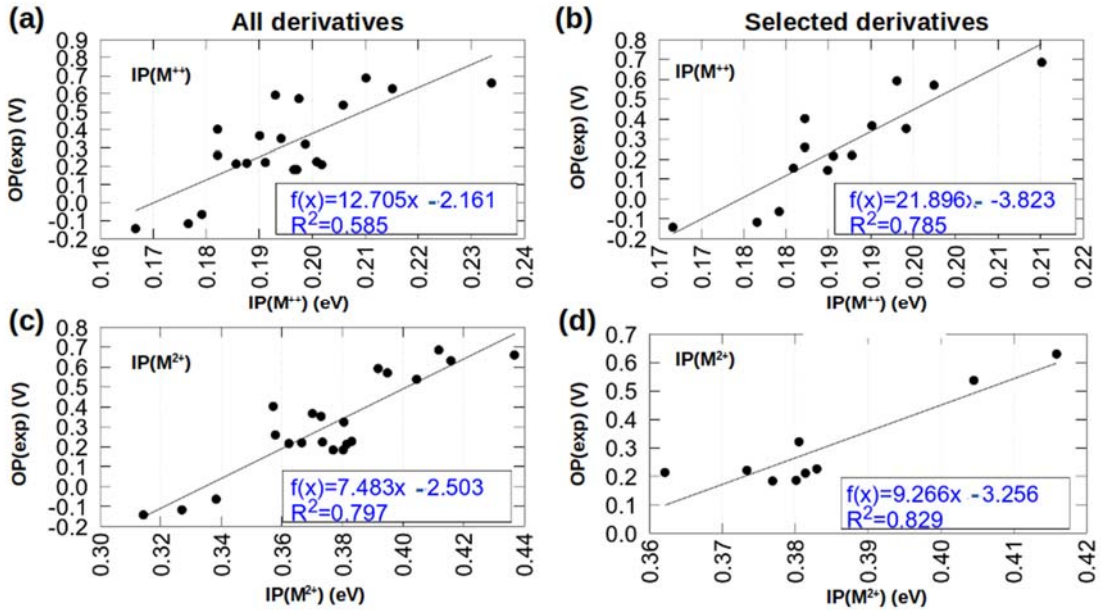

Figure S7: The correlation of the experimental oxidation potential (OP) with the calculated ionization potential of (a) M^{++} using all derivatives except *fac* isomers of model 5 (b) M^{++} using selected derivatives (**1a, 1b, 1c, 2a, 2b, 2c, 2d, 3b, 3c, 4f, 4h, 5a, 5b** and **5c**), (c) M^{2+} using all derivatives (b) M^{2+} using selected derivatives (**1d, 3d, 4a, 4b, 4c, 4d, 4e, 4g**).

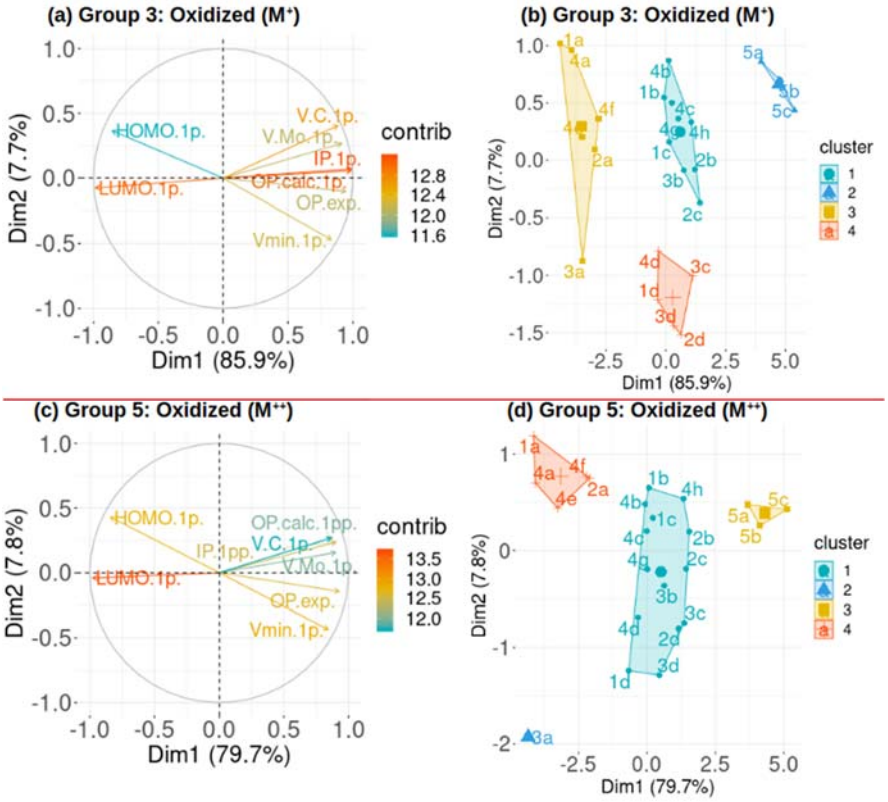

Figure S8: Relating the MESP minimum (V_{min}), Mo atomic potential (V(Mo)), carbene C atomic potential (V(C)), HOMO and LUMO energies and ionization potential (IP) calculated for $1e^-$ oxidized molecules (1p) and related to the experimental OP and (a) calculated OP at M^+ state and (b) the clustering of derivatives, (c) calculated OP at M^{++} state with the computed properties at M^+ state and (d) the clustering of derivatives

Tables

Table S1: The electron affinity (EA in eV), ionization potential (IP in eV) and change in solvation energy from the neutral to reduced or oxidation state ($\Delta\Delta G_{sol}$) in eV) calculated using B3LYP

Molecules	M^-	M^+	M^{++}	M^{2+}	M^-	M^+	M^{++}	M^{2+}
	$EA(M^-)$	$IP(M^+)$	$IP(M^{++})$	$IP(M^{2+})$	$\Delta\Delta G_{sol}(M^-)$	$\Delta\Delta G_{sol}(M^+)$	$\Delta\Delta G_{sol}(M^{++})$	$\Delta\Delta G_{sol}(M^{2+})$
1a	-1.849	7.340	10.792	18.132	-1.290	1.878	5.042	6.920
1b	-1.620	6.423	9.624	16.047	-1.329	1.509	4.437	5.946
1c	-1.631	6.506	9.554	16.061	-1.321	1.631	4.431	6.062
1d	-1.738	6.598	9.510	16.107	-1.244	1.628	4.032	5.659
2a	-1.369	7.159	10.473	17.632	-1.286	1.750	5.215	6.965
2b	-1.189	6.250	9.368	15.618	-1.296	1.453	4.400	5.853
2c	-1.213	6.222	9.656	15.878	-1.228	1.538	4.619	6.157
2d	-1.301	6.416	9.264	15.681	-1.193	1.546	4.333	5.880
3a	-2.116	7.121	10.768	17.888	-1.176	1.602	4.453	6.055
3b	-1.896	6.278	9.263	15.541	-1.223	1.400	3.965	5.365
3c	-1.917	6.282	9.456	15.739	-1.176	1.464	4.400	5.864
3d	-1.996	6.450	9.142	15.592	-1.153	1.481	3.925	5.406
4a	-1.711	7.275	11.415	18.690	-1.304	1.812	5.559	7.371
4b	-1.499	6.371	9.692	16.063	-1.347	1.405	4.267	5.672
~~**4c**~~	~~-1.266~~	~~6.164~~	~~9.464~~	~~15.627~~	~~-1.419~~	~~1.434~~	~~4.061~~	~~5.495~~
4c	-1.531	6.413	9.713	16.127	-1.308	1.508	4.333	5.841
4d	-1.622	6.484	9.654	16.139	-1.256	1.474	4.289	5.763
4e	-1.414	7.319	11.036	18.355	-1.238	1.908	5.428	7.336
4f	-1.263	7.131	10.494	17.625	-1.242	1.760	5.114	6.874
4g	-1.220	6.311	9.666	15.977	-1.296	1.407	4.151	5.558
4h	-1.140	6.176	9.384	15.560	-1.242	1.395	4.401	5.796
5a	-1.074	5.633	8.869	14.501	-1.397	1.268	3.970	5.238
5b	-0.890	5.480	8.890	14.369	-1.396	1.354	4.068	5.421
5c	-0.834	5.353	8.468	13.821	-1.331	1.304	3.911	5.216

Table S2: The minimum MESP (V_{min}) and the maximum MESP (V_{max}) in the complexes (in kcal/mol).

	V_{min}				V_{max}			
	M	M^-	M^+	M^{2+}	M	M^-	M^+	M^{2+}
1a	-26.14	-92.84	50.10	108.16	34.66	-16.23	126.19	216.42
1b	-39.71	-104.47	36.07	89.09	31.39	-16.64	100.63	193.95
1c	-34.56	-101.08	37.14	85.38	34.97	-15.53	110.45	196.44
1d	-23.76	-93.73	28.72	75.19	32.58	-15.03	113.57	223.65
2a	-35.16	-100.33	41.01	108.93	47.47	-8.55	117.46	214.34
2b	-41.30	-106.27	27.96	86.74	31.21	-15.52	92.41	190.44
2c	-40.87	-104.54	29.58	80.17	41.02	-12.91	97.74	194.70
2d	-31.66	-112.67	24.45	71.53	43.25	2.21	113.99	219.90
3a	-27.18	-90.51	39.57	101.08	32.65	-3.18	106.97	194.23
3b	-37.69	-101.41	32.06	81.72	28.28	-8.07	96.37	182.27
3c	-35.97	-96.05	25.53	78.35	50.37	-10.23	104.39	191.78
3d	-24.53	-91.69	27.13	70.66	32.31	-2.57	110.13	214.58
4a	-27.34	-96.92	48.35	113.54	32.98	-16.36	121.85	235.36
4b	-41.41	-103.90	35.23	83.02	29.65	-17.43	96.30	208.63
4c	-36.64	-102.48	36.67	80.46	42.26	-17.63	104.60	210.28
4d	-25.51	-97.30	28.12	71.47	29.62	-17.76	115.42	210.43
4e	-34.57	-103.96	42.81	111.83	69.76	-3.67	154.04	216.54
4f	-39.07	-107.72	39.80	85.96	69.07	-4.01	124.93	215.87
4g	-41.17	-108.52	29.35	90.88	51.99	-15.69	118.37	214.43
4h	-38.36	-104.95	26.10	84.99	53.81	-12.34	113.85	160.52
5a	-36.16	-117.33	29.12	81.13	35.74	-15.37	98.34	162.81
5b	-39.67	-118.24	25.77	78.32	35.35	-16.09	102.38	178.29
5c	-41.30	-111.70	24.10	76.02	33.20	-17.26	100.11	176.67

Table S3: The atomic potential (V) of Mo and carbene carbon atom in the complexes in au.

	Mo				C(carbene)			
	V(Mo,M)	V(Mo,M^-)	V(Mo,M^+)	V(Mo,M^{2+})	V(C,M)	V(C,M^-)	V(C,M^+)	V(C,M^{2+})
1a	-46.618	-46.828	-46.468	-46.344	-14.586	-14.787	-14.457	-14.322
1b	-46.680	-46.858	-46.523	-46.367	-14.651	-14.820	-14.490	-14.349
1c	-46.675	-46.837	-46.500	-46.346	-14.627	-14.816	-14.489	-14.346
1d	-46.679	-46.835	-46.490	-46.352	-14.619	-14.787	-14.459	-14.324
2a	-46.640	-46.835	-46.489	-46.348	-14.586	-14.787	-14.462	-14.324
2b	-46.698	-46.876	-46.543	-46.389	-14.655	-14.817	-14.493	-14.355
2c	-46.693	-46.862	-46.522	-46.356	-14.637	-14.814	-14.490	-14.350
2d	-46.692	-46.822	-46.510	-46.364	-14.618	-14.748	-14.462	-14.323
3a	-46.620	-46.823	-46.476	-46.350	-14.588	-14.784	-14.452	-14.326
3b	-46.680	-46.848	-46.531	-46.397	-14.654	-14.815	-14.498	-14.374
3c	-46.667	-46.825	-46.504	-46.360	-14.644	-14.810	-14.497	-14.360
3d	-46.682	-46.833	-46.502	-46.375	-14.622	-14.786	-14.472	-14.343
4a	-46.626	-46.841	-46.480	-46.282	-14.593	-14.790	-14.461	-14.331
4b	-46.691	-46.871	-46.541	-46.399	-14.661	-14.829	-14.498	-14.356
4c	-46.679	-46.856	-46.519	-46.383	-14.651	-14.820	-14.493	-14.353
4d	-46.690	-46.847	-46.508	-46.385	-14.626	-14.792	-14.465	-14.315
4e	-46.623	-46.843	-46.468	-46.350	-14.586	-14.786	-14.456	-14.321
4f	-46.642	-46.858	-46.487	-46.360	-14.590	-14.792	-14.472	-14.334
4g	-46.702	-46.858	-46.535	-46.403	-14.651	-14.834	-14.497	-14.349
4h	-46.723	-46.879	-46.543	-46.459	-14.656	-14.831	-14.506	-14.432
5a	-46.733	-46.891	-46.569	-46.447	-14.693	-14.857	-14.534	-14.403
5b	-46.724	-46.883	-46.559	-46.453	-14.686	-14.858	-14.545	-14.416
5c	-46.743	-46.896	-46.581	-46.461	-14.688	-14.855	-14.532	-14.409