

## *SUPPORTING INFORMATION*

# **Metal Rich Metallaboranes: Synthesis, Structure and Bonding of *pileo*-[(Cp\*Ru)<sub>2</sub>M(CO)<sub>3</sub>( $\mu$ -H)( $\mu$ -E)( $\mu_3$ -BH)B<sub>2</sub>H<sub>5</sub>] (M = Mo, W, E = CO, and M = Mn, E = H) Clusters**

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## I. Spectroscopic Details

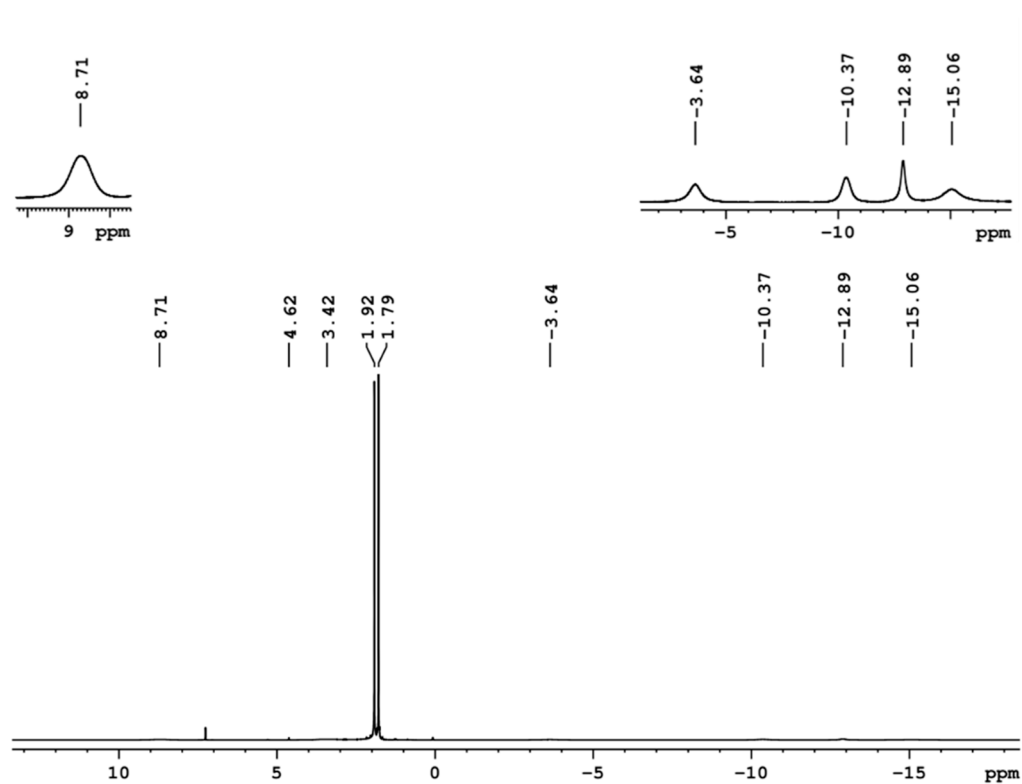


Figure S1.  $^1\text{H}$  NMR spectrum of **2** in  $\text{CDCl}_3$ .

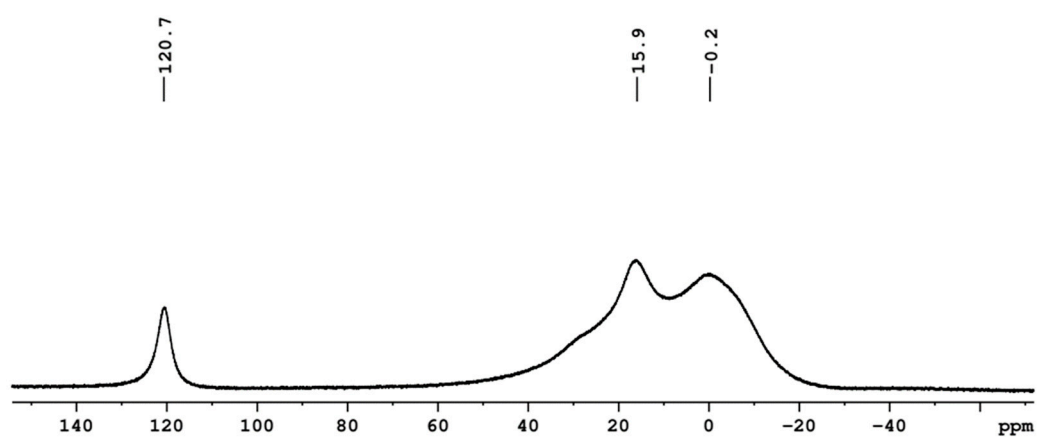
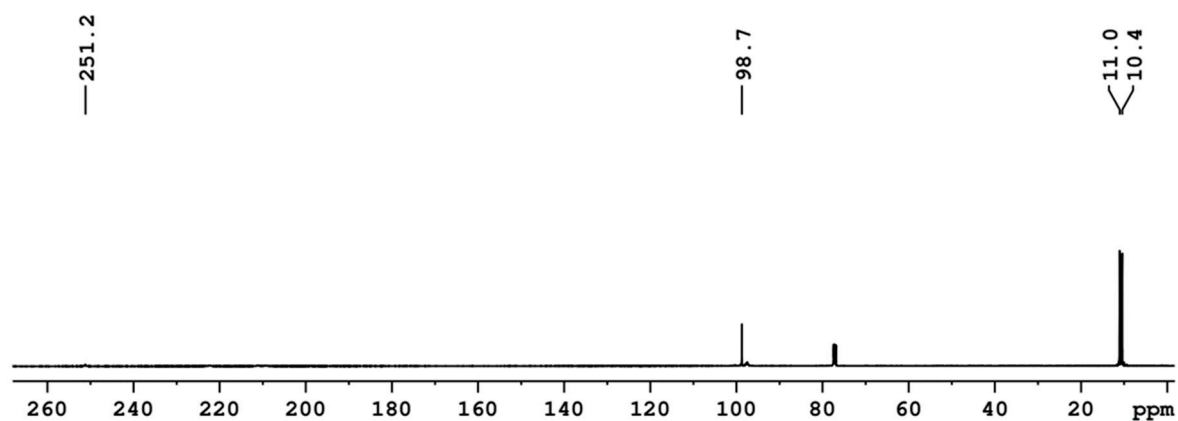
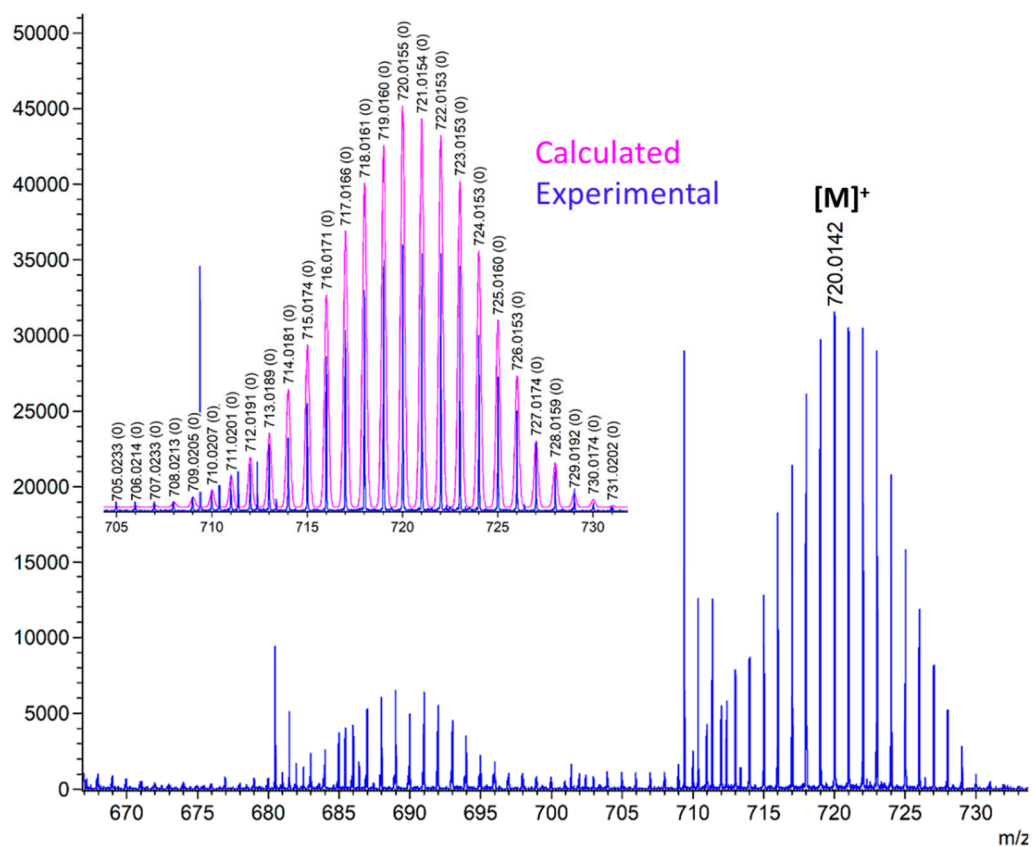


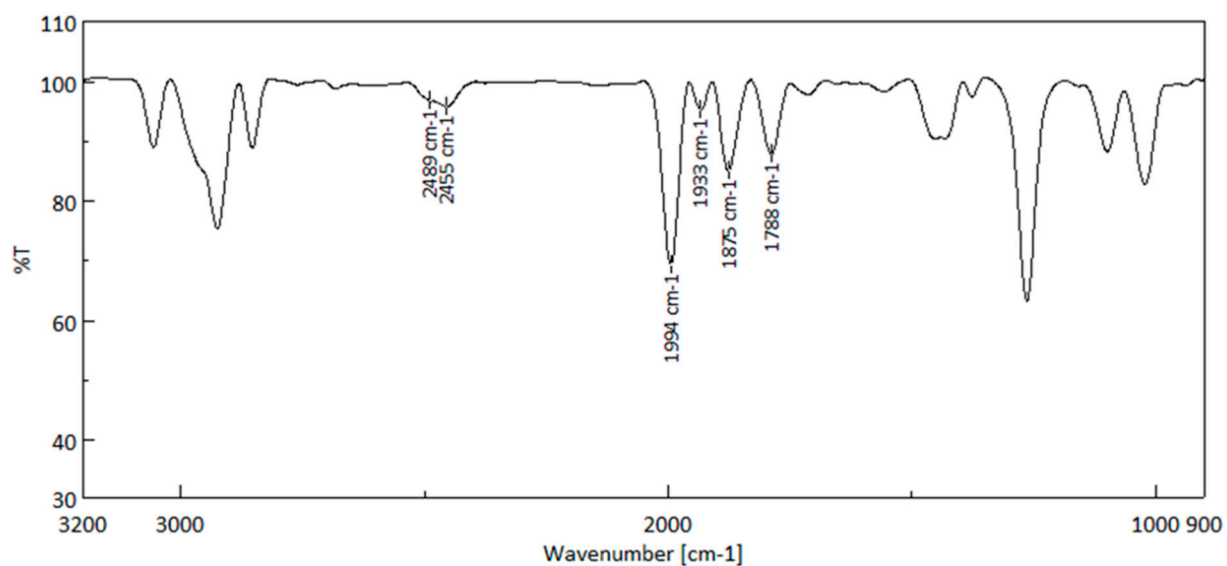
Figure S2.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of **2** in  $\text{CDCl}_3$ .



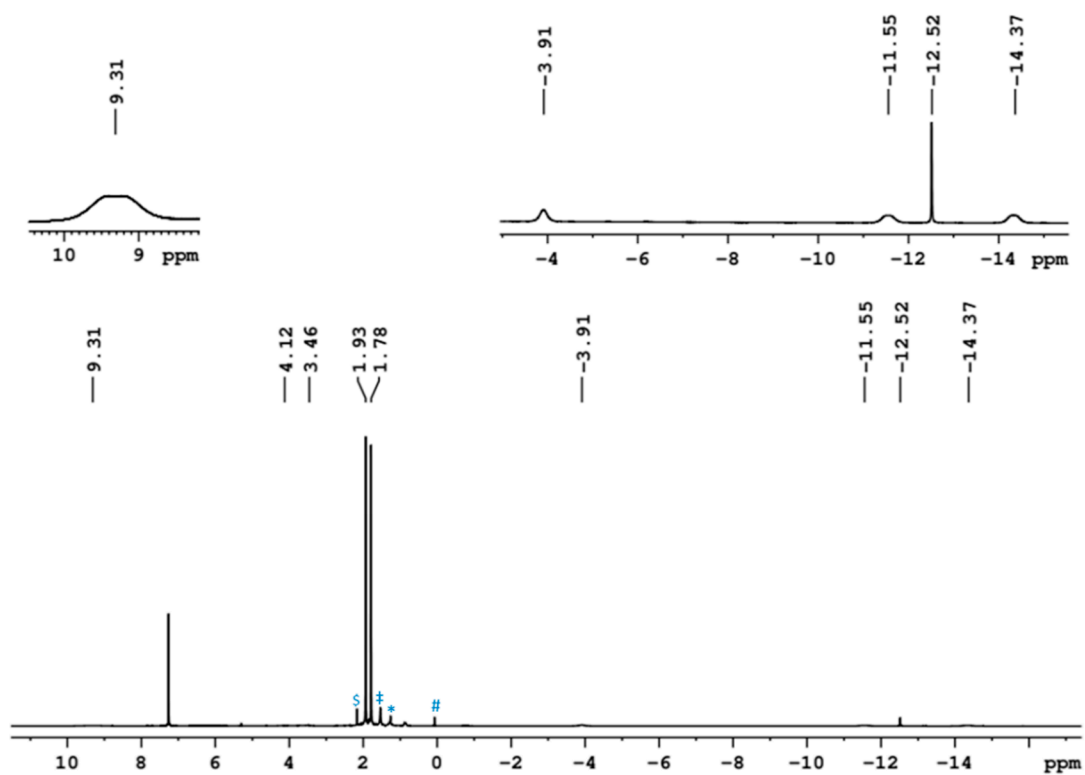
**Figure S3.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2** in  $\text{CDCl}_3$ .



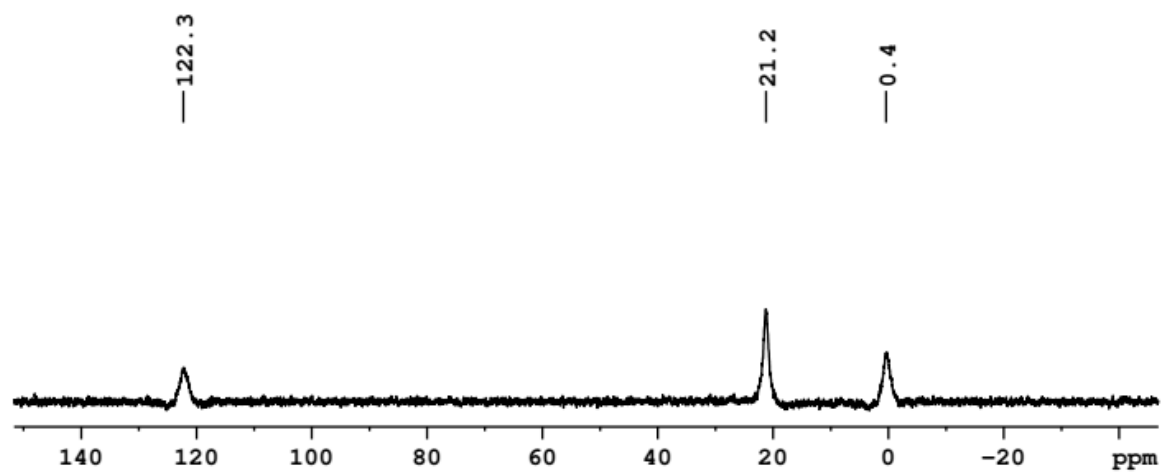
**Figure S4.** ESI-MS spectrum of **2**.



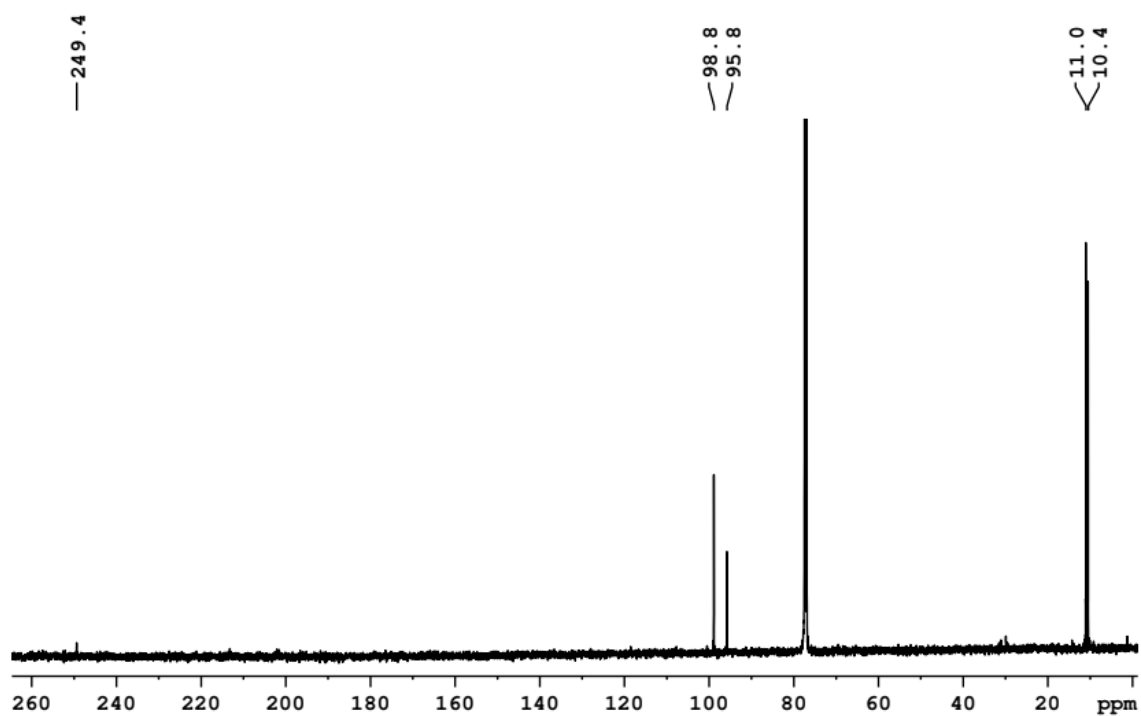
**Figure S5.** IR spectrum of **2** in  $\text{CH}_2\text{Cl}_2$ .



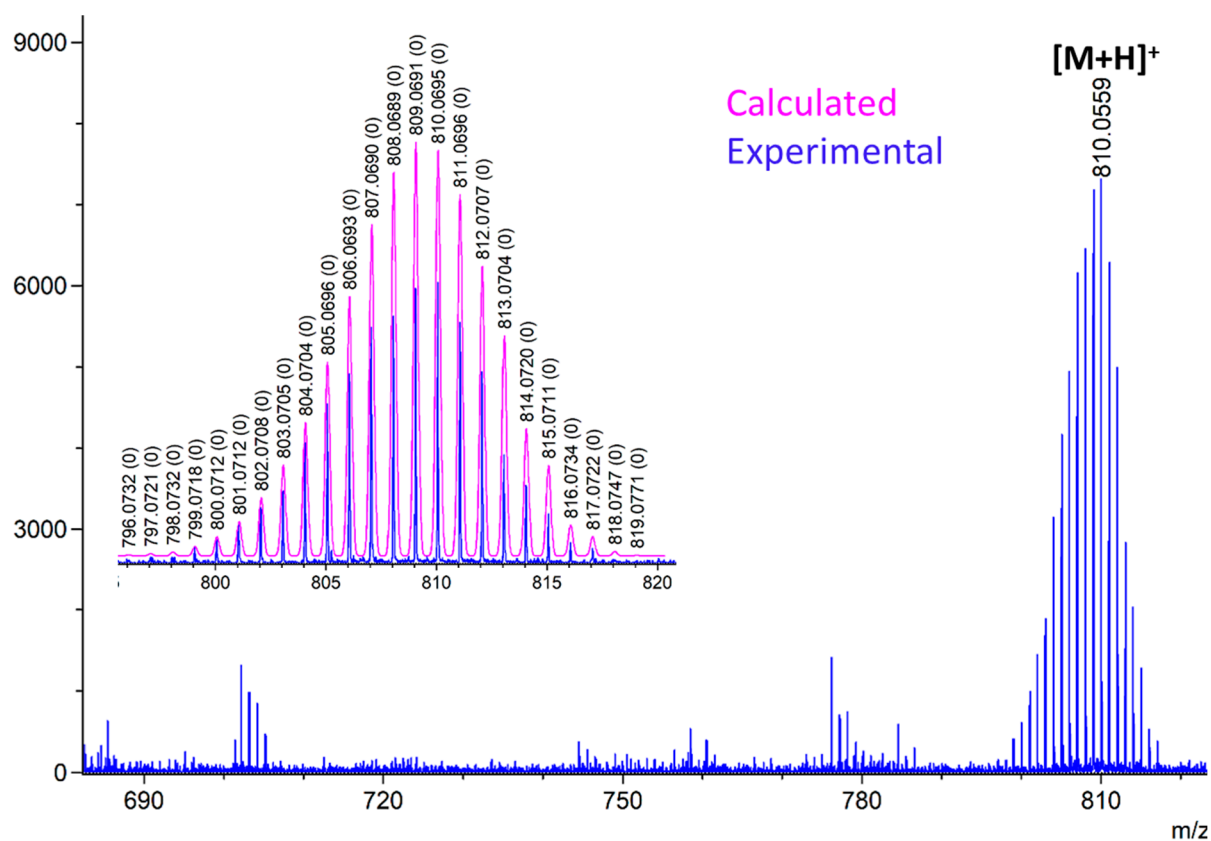
**Figure S6.** <sup>1</sup>H NMR spectrum of **3** in  $\text{CDCl}_3$ . (#Silicone grease, \* H-Grease, ‡Hexane,, § $\text{CH}_3\text{OH}$ )



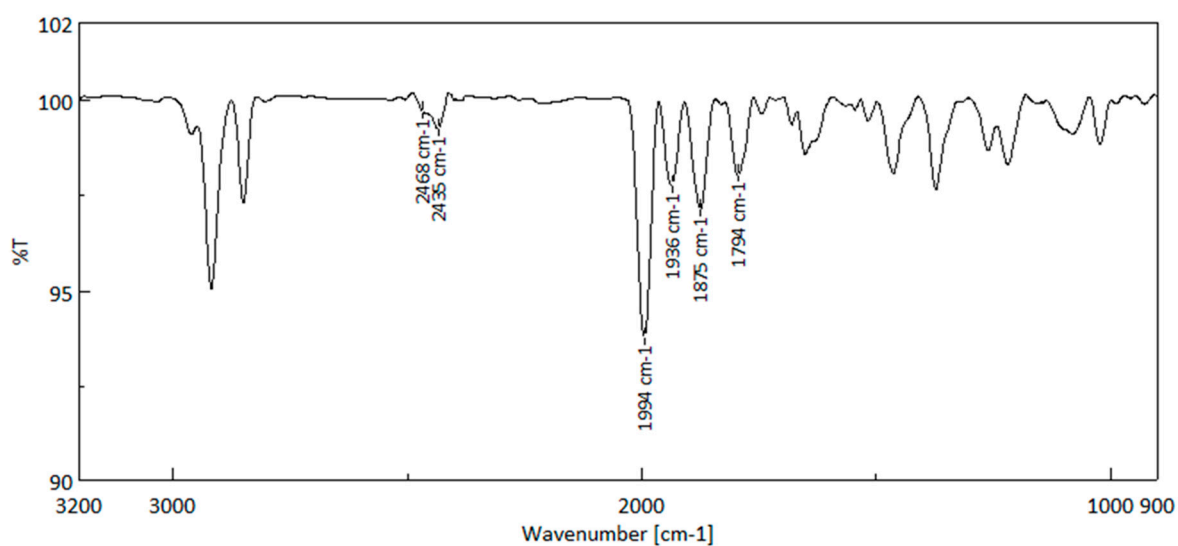
**Figure S7.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of **3** in  $\text{CDCl}_3$ .



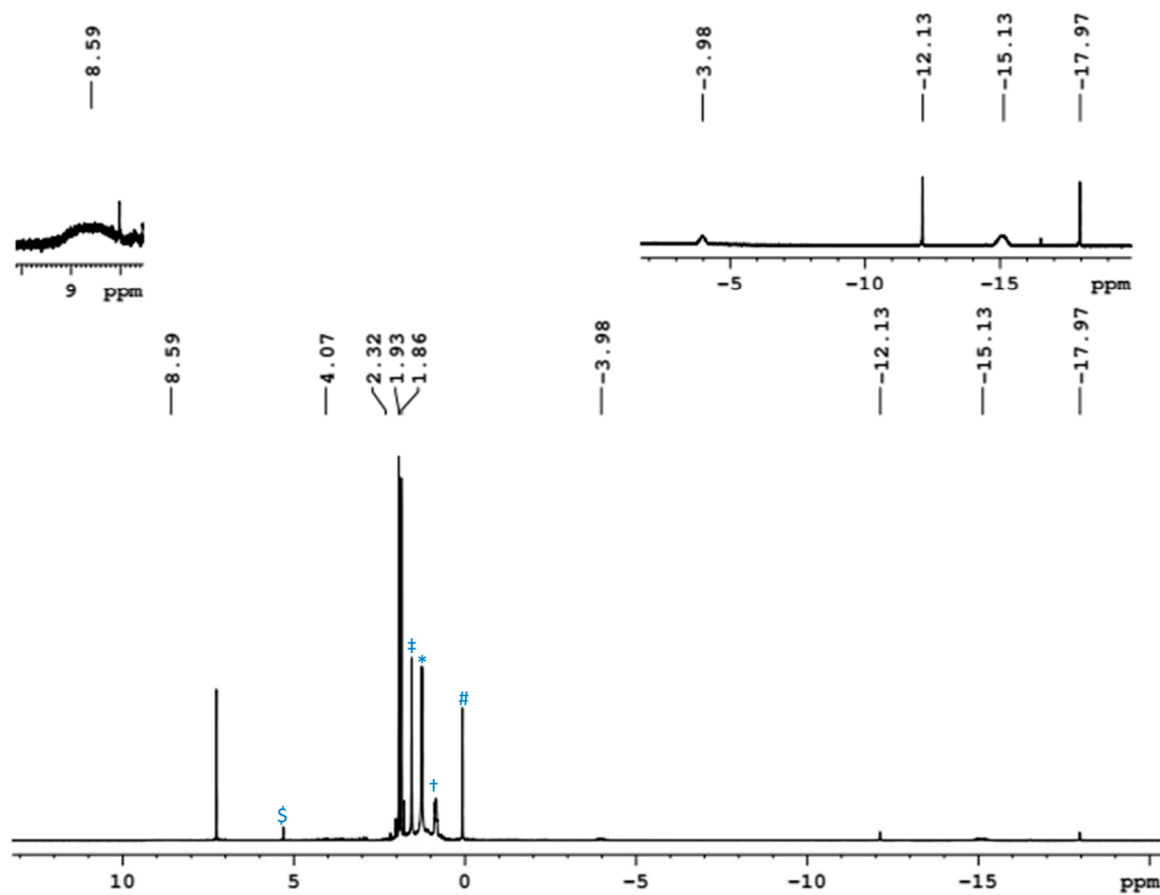
**Figure S8.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3** in  $\text{CDCl}_3$ .



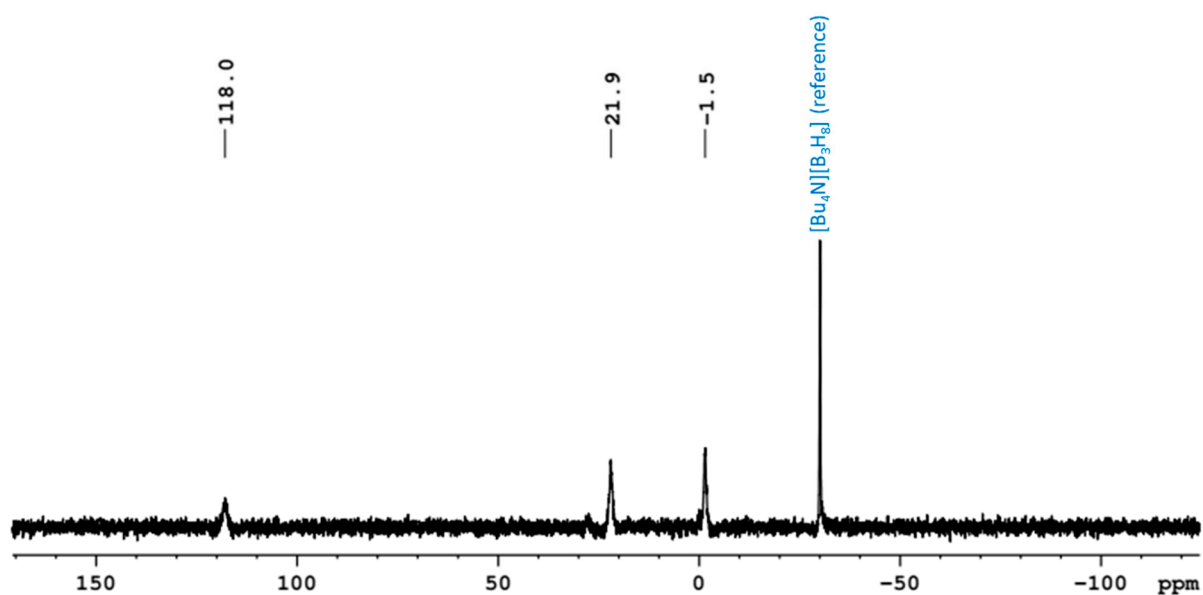
**Figure S9.** ESI-MS spectrum of **3**.



**Figure S10.** IR spectrum of **3** in  $CH_2Cl_2$ .

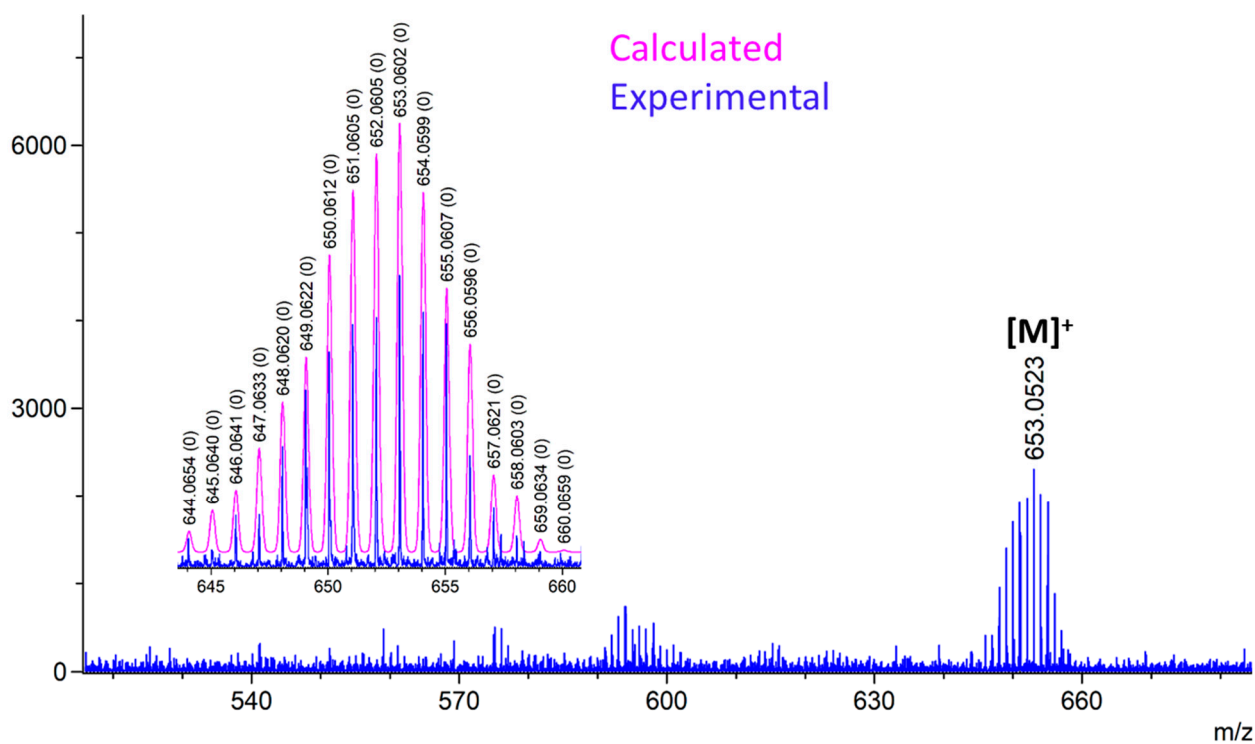


**Figure S11.**  $^1\text{H}$  NMR spectrum of **4** in  $\text{CDCl}_3$ . (#Silicone grease, †H-Grease, \*Hexane, ‡H<sub>2</sub>O, §CH<sub>2</sub>Cl<sub>2</sub>)

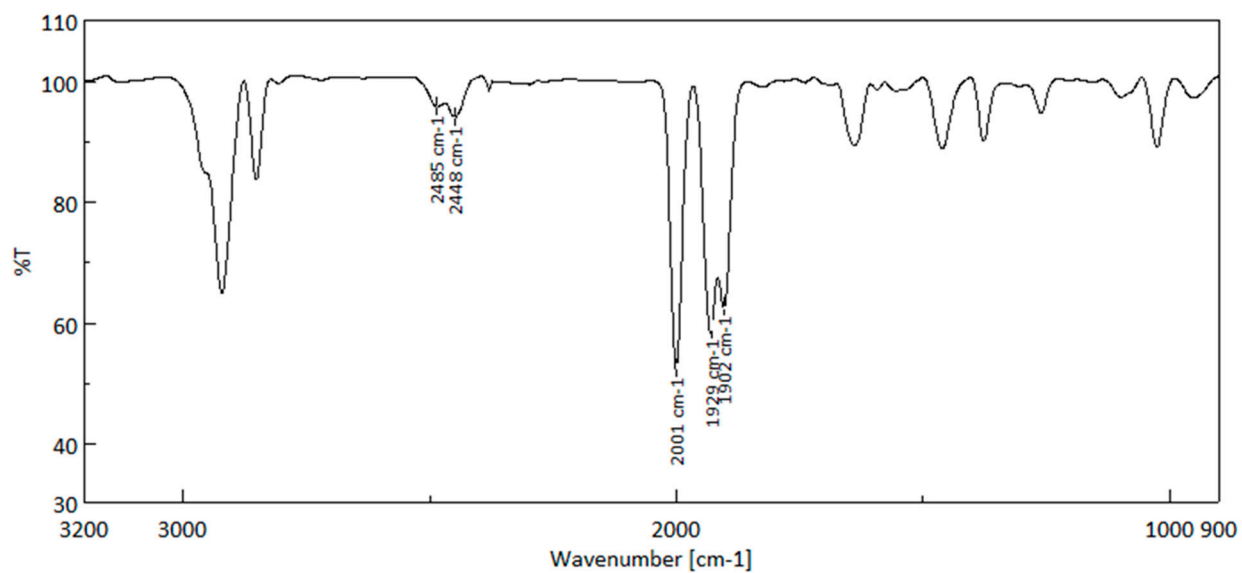


**Figure S12.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of **4** in  $\text{CDCl}_3$ .





**Figure S13.** ESI-MS spectrum of **4**.



**Figure S14.** IR spectrum of **4** in  $\text{CH}_2\text{Cl}_2$ .

## II. Computational data

**Table.S1.** Selected geometrical parameters and Wiberg bond indices (WBI) of **2**, **3** and **4**.

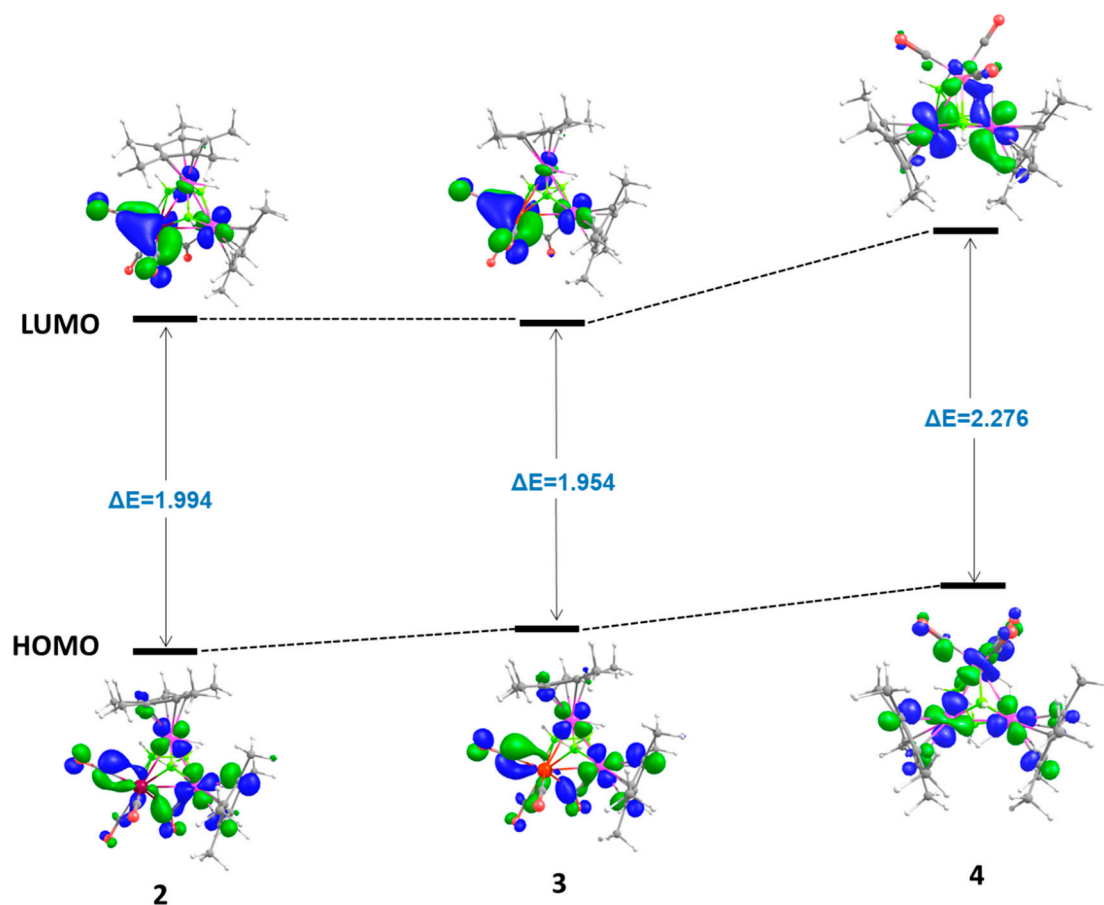
<b>2</b>				<b>3</b>			
	Expt.	Cal.	WBI		Expt.	Cal.	WBI
Ru1-Ru2	2.774	2.792	0.341	Ru1-Ru2	2.774	2.793	0.336
Ru1-Mo1	2.859	2.885	0.299	Ru1-W1	2.859	2.899	0.298
Ru2-Mo1	2.840	2.878	0.343	Ru2-W1	2.840	2.881	0.330
Ru2-B1	2.159	2.144	0.529	Ru2-B1	2.159	2.147	0.524
Ru2-B2	2.172	2.183	0.497	Ru2-B2	2.172	2.178	0.506
Ru2-B3	2.043	2.048	0.630	Ru2-B3	2.043	2.054	0.634
Ru1-B1	2.410	2.427	0.285	Ru1-B1	2.410	2.428	0.284
Ru1-B3	2.218	2.212	0.406	Ru1-B3	2.218	2.225	0.400
Mo1-B3	2.265	2.264	0.488	W1-B3	2.265	2.270	0.530
Mo1-B2	2.500	2.502	0.347	W1-B2	2.500	2.502	0.338
<b>4</b>							
	Expt.	Cal.	WBI				
Ru1-Ru2	2.754	2.772	0.329				
Ru1-Mn1	2.828	2.849	0.274				
Ru2-Mn1	2.710	2.731	0.350				
Ru2-B3	2.152	2.163	0.511				
Ru2-B1	2.007	2.038	0.625				
Ru2-B2	2.134	2.138	0.532				
Ru1-B1	2.177	2.178	0.459				
Ru1-B3	2.391	2.388	0.316				
Mn1-B1	2.154	2.150	0.415				
Mn1-B2	2.319	2.326	0.385				

**Table S2.** Calculated natural charges (q), natural valence population (Pop) of **2**, **3** and **4**.

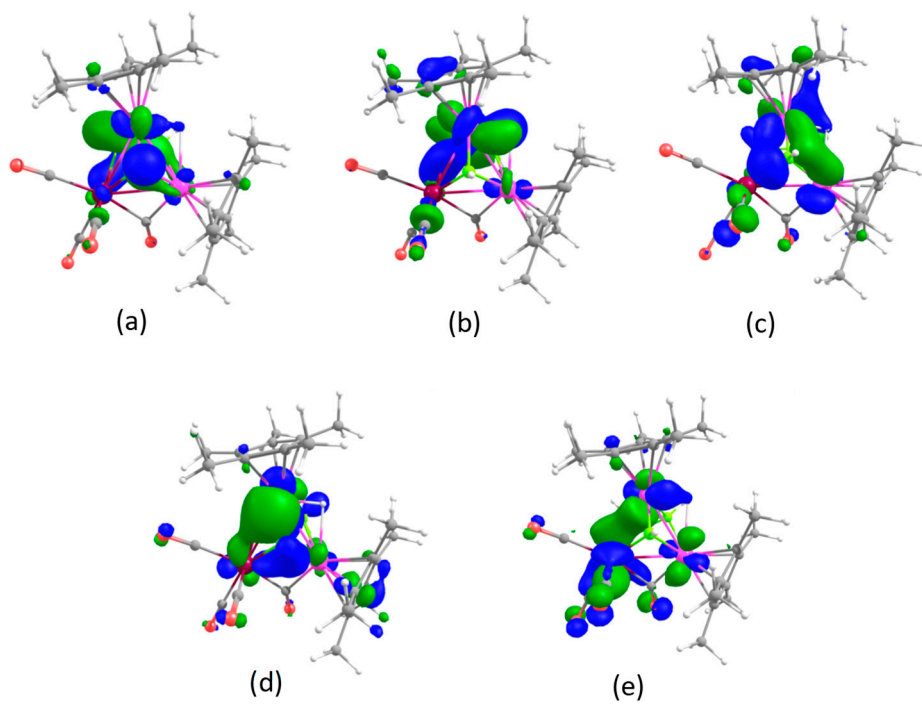
<b>2</b>			<b>3</b>		
	<b>q</b>	<b>Pop(val)</b>		<b>q</b>	<b>Pop(val)</b>
Ru1	-0.807	8.812	Ru1	-0.834	8.836
Ru2	-1.042	9.048	Ru2	-1.072	9.076
Mo1	-1.740	7.768	W1	-1.341	7.355
B1	-0.107	3.081	B1	-0.103	3.075
B2	-0.096	3.067	B2	-0.126	3.100
B3	0.737	2.205	B3	0.682	2.264
<b>4</b>					
	<b>q</b>	<b>Pop(val)</b>			
Ru1	-0.938	8.927			
Ru2	-0.937	8.940			
Mn1	-2.228	9.201			
B1	0.715	2.231			
B2	-0.058	3.028			
B3	-0.100	3.073			

**Table S3.** Calculated HOMO–LUMO energy gap of **2**, **3** and **4**.

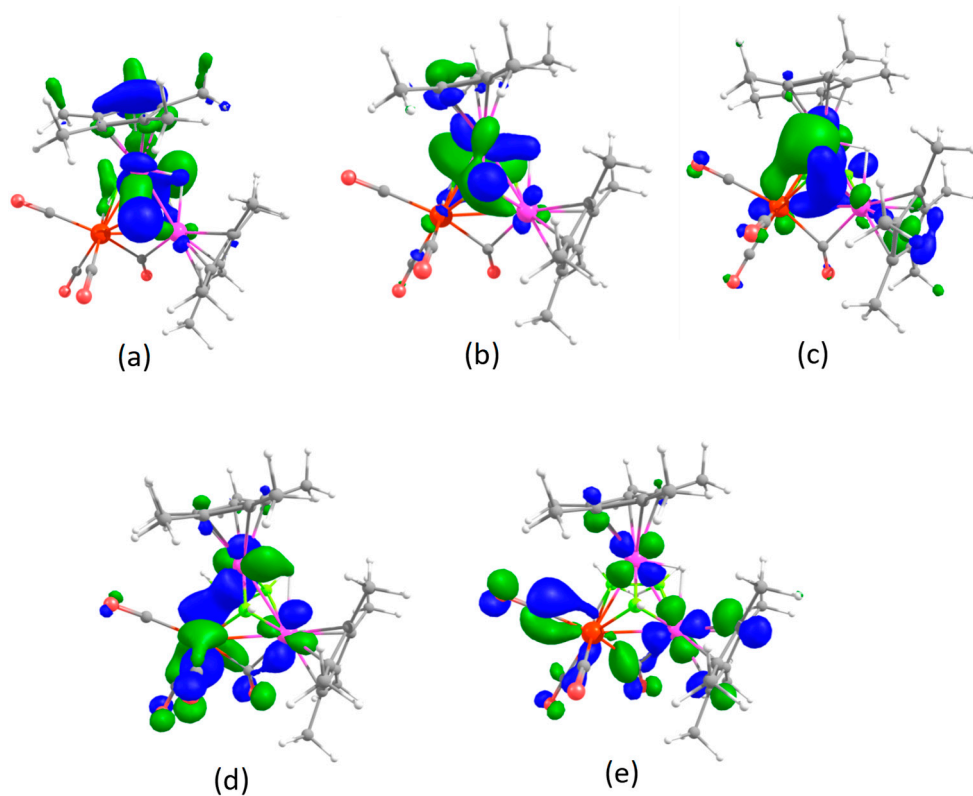
	<b>2</b>	<b>3</b>	<b>4</b>
$\Delta E_{H-L}$ (eV)	1.994	1.954	2.276



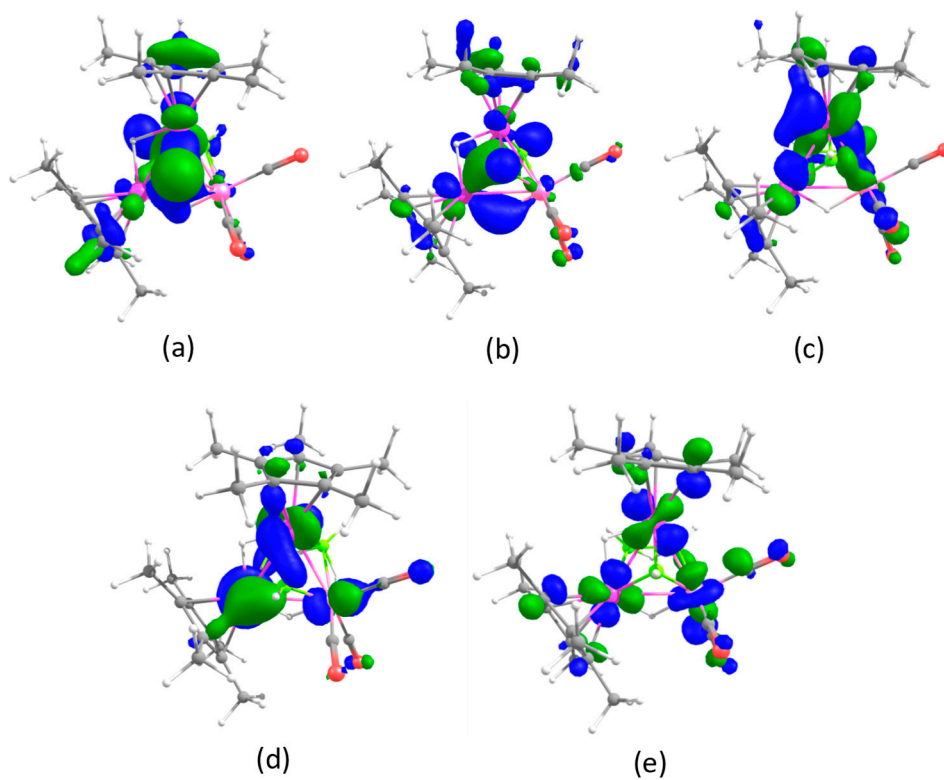
**Figure S15.** Comparison of Frontier molecular orbitals of 2, 3 and 4.



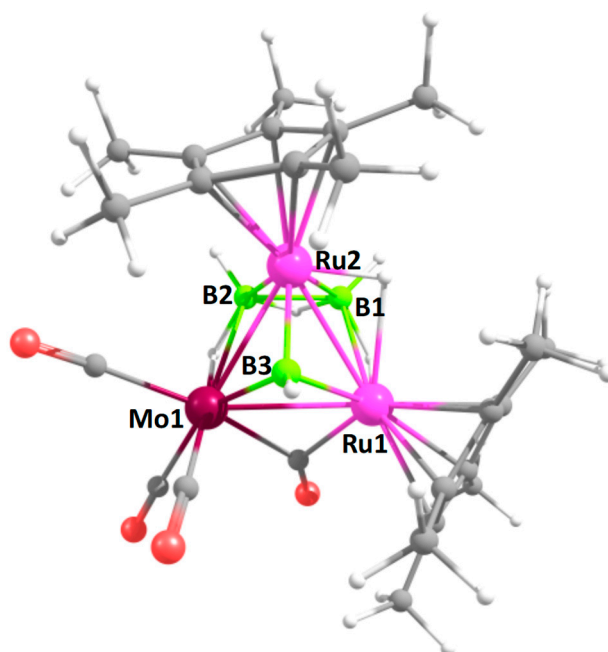
**Figure S16.** Selected molecular orbitals of 2. (a) HOMO-14, (b) HOMO-13, (c) HOMO-9 (d) HOMO-7 (e) HOMO-3



**Figure S17.** Selected molecular orbitals of **3**. (a) HOMO-16, (b) HOMO-13, (c) HOMO-7 (d) HOMO-3 (e) LUMO



**Figure S18.** Selected molecular orbitals of **4**. (a) HOMO-16, (b) HOMO-15, (c) HOMO-12 (d) HOMO-3 (e) LUMO

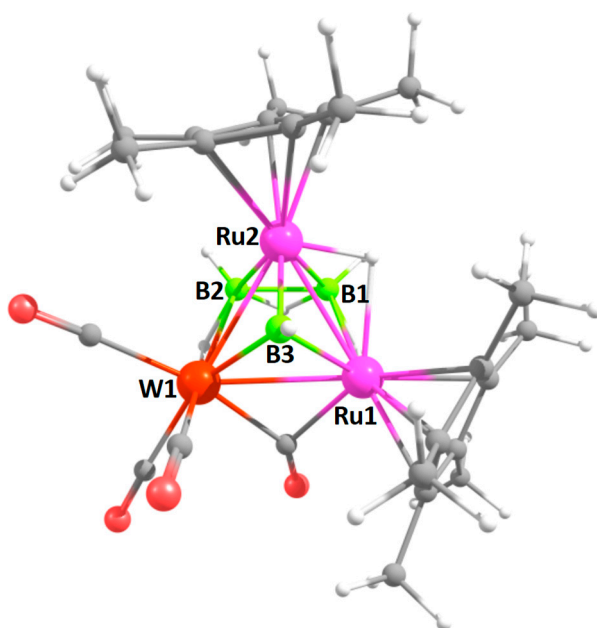


**Figure S19.** Optimized geometry of **2**.

Total energy = -1571.46431100 a.u.

Cartesian coordinates for the calculated structure **2** (in Å)

Ru	-1.408901000	-0.540745000	-0.309126000	C	3.650073000	-0.046140000	-0.259583000
H	0.427261000	-1.780492000	-0.369816000	C	3.213039000	-0.197352000	1.107164000
Ru	1.382877000	-0.498843000	-0.294879000	C	2.367451000	-2.167233000	2.585274000
Mo	-0.043621000	1.997946000	-0.181405000	H	3.281715000	-2.428571000	3.146025000
O	2.466951000	3.840915000	0.405361000	H	1.792062000	-3.092744000	2.451838000
O	-1.562863000	4.713915000	-0.783087000	H	1.778275000	-1.487117000	3.216161000
O	-1.016860000	2.634435000	2.741311000	C	2.632223000	-3.683329000	-0.241480000
O	-2.836097000	1.689775000	-1.733747000	H	3.563617000	-4.251457000	-0.075729000
C	-3.506044000	-0.561219000	0.537341000	H	2.307500000	-3.875165000	-1.272918000
C	-3.437452000	-1.386673000	-0.643490000	H	1.872107000	-4.094895000	0.435981000
C	-2.514123000	-2.474126000	-0.369803000	C	3.873841000	-1.620929000	-2.335690000
C	-2.031127000	-2.313189000	0.974182000	H	3.760969000	-0.751635000	-2.997239000
C	-2.622853000	-1.116121000	1.530895000	H	3.290170000	-2.446106000	-2.765007000
C	-4.449542000	0.578697000	0.764967000	H	4.936826000	-1.917923000	-2.353259000
H	-4.717959000	1.080291000	-0.172288000	C	4.410681000	1.113063000	-0.826174000
H	-4.023991000	1.329426000	1.444076000	H	5.493333000	0.900403000	-0.792855000
H	-5.378132000	0.200815000	1.226085000	H	4.234821000	2.036896000	-0.262898000
C	-4.292900000	-1.239844000	-1.866390000	H	4.141764000	1.302001000	-1.874096000
H	-5.295189000	-1.663757000	-1.684401000	C	3.416983000	0.784288000	2.221469000
H	-3.860881000	-1.768541000	-2.726503000	H	2.594759000	0.750563000	2.948670000
H	-4.416308000	-0.185931000	-2.146361000	H	3.498597000	1.813955000	1.854141000
C	-2.242679000	-3.641441000	-1.270630000	H	4.350082000	0.548577000	2.762589000
H	-1.247026000	-4.069019000	-1.092657000	C	1.568669000	3.132731000	0.184778000
H	-2.298439000	-3.358416000	-2.329737000	C	-0.985251000	3.730271000	-0.580011000
H	-2.985176000	-4.439438000	-1.098616000	C	-0.656024000	2.365075000	1.660414000
C	-1.184164000	-3.285511000	1.731938000	C	-1.923273000	1.317593000	-1.073157000
H	-1.825352000	-3.971864000	2.311725000	B	0.232037000	-0.766812000	-2.083408000
H	-0.520165000	-2.773978000	2.440098000	H	0.437250000	-1.729283000	-2.782892000
H	-0.566649000	-3.897572000	1.061435000	H	0.303348000	0.235668000	-2.952803000
C	-2.562262000	-0.690148000	2.965354000	H	-1.088219000	-0.707646000	-2.022102000
H	-2.615024000	0.400612000	3.074081000	B	1.119252000	0.789020000	-2.037805000
H	-1.638980000	-1.026544000	3.452639000	H	2.109596000	0.988814000	-2.696034000
H	-3.412986000	-1.126124000	3.517908000	H	0.473400000	1.900924000	-2.018903000
C	2.720617000	-1.537151000	1.272081000	B	0.094306000	0.171194000	1.149709000
C	2.864093000	-2.221119000	0.003759000	H	0.075590000	-0.031265000	2.334633000
C	3.441280000	-1.304310000	-0.936033000				

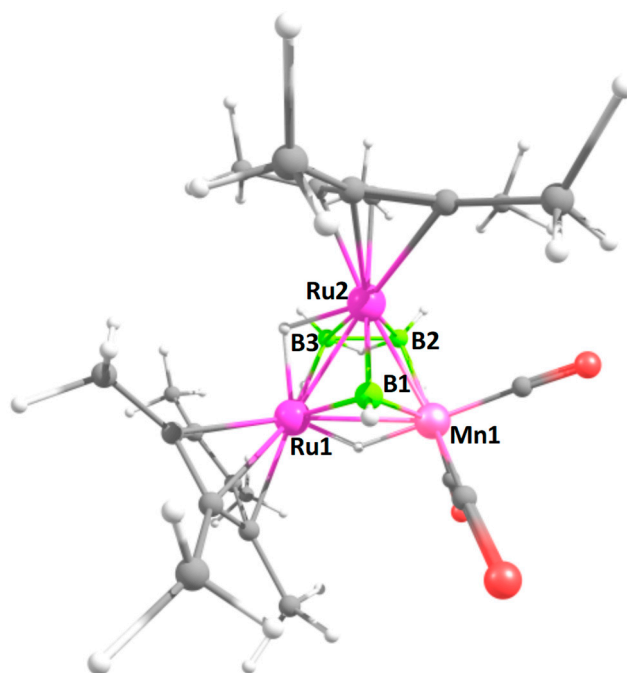


**Figure S20.** Optimized geometry of **3**.

Total energy = -1570.36584184 a.u.

Cartesian coordinates for the calculated structure **3** (in Å)

Ru	-1.387009000	-0.731446000	-0.299398000	C	3.668199000	-0.194305000	-0.249974000
H	0.389150000	-1.882294000	-0.337667000	C	3.236952000	-0.365918000	1.116047000
Ru	1.403666000	-0.629834000	-0.278624000	C	2.385485000	-2.355422000	2.564569000
W	-0.066482000	1.844363000	-0.139460000	H	3.300402000	-2.630908000	3.117413000
O	2.460162000	3.687697000	0.477970000	H	1.804754000	-3.275617000	2.417990000
O	-1.592831000	4.577829000	-0.738093000	H	1.801982000	-1.682964000	3.208758000
O	-1.106813000	2.432020000	2.792701000	C	2.624870000	-3.824944000	-0.290064000
O	-2.834879000	1.497393000	-1.734517000	H	3.552305000	-4.404687000	-0.142989000
C	-3.486892000	-0.761078000	0.536868000	H	2.289573000	-3.994649000	-1.322114000
C	-3.412321000	-1.571757000	-0.653927000	H	1.866764000	-4.242585000	0.386019000
C	-2.488218000	-2.661327000	-0.390903000	C	3.871286000	-1.735543000	-2.353500000
C	-2.010058000	-2.515797000	0.957176000	H	3.761393000	-0.854296000	-2.999625000
C	-2.606771000	-1.327382000	1.526697000	H	3.278981000	-2.548827000	-2.793561000
C	-4.431400000	0.375640000	0.775196000	H	4.931900000	-2.039996000	-2.382123000
H	-4.702418000	0.883857000	-0.157767000	C	4.428287000	0.973257000	-0.800043000
H	-4.004866000	1.121594000	1.459084000	H	5.511977000	0.767713000	-0.756291000
H	-5.358714000	-0.006314000	1.235656000	H	4.240336000	1.892175000	-0.232188000
C	-4.264971000	-1.414079000	-1.877211000	H	4.169664000	1.168237000	-1.849424000
H	-5.265281000	-1.845816000	-1.702493000	C	3.448892000	0.598793000	2.243624000
H	-3.828048000	-1.930294000	-2.742464000	H	2.636392000	0.547381000	2.980636000
H	-4.392857000	-0.357658000	-2.144698000	H	3.518362000	1.635053000	1.892035000
C	-2.213476000	-3.817778000	-1.304602000	H	4.390793000	0.361848000	2.768785000
H	-1.220146000	-4.250177000	-1.125063000	C	1.554706000	2.989677000	0.249767000
H	-2.260968000	-3.521060000	-2.360421000	C	-1.009866000	3.597060000	-0.532062000
H	-2.959127000	-4.616235000	-1.148470000	C	-0.723119000	2.191758000	1.711902000
C	-1.165122000	-3.496746000	1.706076000	C	-1.912965000	1.169609000	-1.061029000
H	-1.807773000	-4.193286000	2.271942000	B	0.259618000	-0.896017000	-2.076240000
H	-0.507012000	-2.994020000	2.425987000	H	0.492848000	-1.844623000	-2.785056000
H	-0.541896000	-4.097628000	1.030628000	H	0.319705000	0.122273000	-2.928452000
C	-2.553152000	-0.920883000	2.967080000	H	-1.059480000	-0.858451000	-2.020619000
H	-2.610511000	0.167981000	3.091380000	B	1.125856000	0.673582000	-2.001372000
H	-1.630882000	-1.261081000	3.453712000	H	2.112539000	0.906423000	-2.653272000
H	-3.404710000	-1.367829000	3.509647000	H	0.459533000	1.781819000	-1.984623000
C	2.737510000	-1.705781000	1.260574000	B	0.103619000	0.005138000	1.179621000
C	2.870343000	-2.369595000	-0.019721000	H	0.079247000	-0.218608000	2.359917000
C	3.448843000	-1.440135000	-0.946159000				



**Figure S21.** Optimized geometry of **4**.

Total energy = -2541.53511304 a.u.

Cartesian coordinates for the calculated structure **4** (in Å)

B	-0.004146000	0.421948000	1.085154000	H	-1.188642000	-2.864227000	2.480156000
B	-1.137968000	0.904994000	-1.988031000	H	-2.769271000	-2.536150000	3.214479000
B	-0.164516000	-0.584649000	-2.083812000	C	-3.395964000	0.716068000	2.257519000
C	3.457894000	0.098260000	0.511453000	H	-4.309728000	0.425892000	2.804978000
C	2.768952000	-0.768362000	1.437258000	H	-3.553603000	1.727957000	1.864018000
C	2.485109000	-2.012933000	0.757553000	H	-2.574419000	0.761620000	2.985310000
C	2.978525000	-1.910023000	-0.589358000	C	-4.497461000	0.858139000	-0.758876000
C	3.592987000	-0.599208000	-0.745387000	H	-4.306753000	1.022851000	-1.828092000
C	4.376836000	-0.126926000	-1.934645000	H	-4.372643000	1.820253000	-0.247030000
H	5.438034000	-0.415927000	-1.839411000	H	-5.553289000	0.554650000	-0.650791000
H	4.337802000	0.965701000	-2.035780000	C	-3.650791000	-1.824982000	-2.242895000
H	3.998435000	-0.561494000	-2.869542000	H	-4.643937000	-2.306869000	-2.231391000
C	4.054943000	1.432047000	0.844742000	H	-2.940891000	-2.534701000	-2.688200000
H	5.073600000	1.301109000	1.248761000	H	-3.712299000	-0.952972000	-2.907473000
H	3.464301000	1.966000000	1.600194000	C	-2.096102000	-3.669588000	-0.155137000
H	4.129063000	2.076548000	-0.040744000	H	-1.267103000	-3.957641000	0.505299000
C	2.598876000	-0.515627000	2.903660000	H	-1.770807000	-3.826032000	-1.192598000
H	3.499121000	-0.850593000	3.448079000	H	-2.930806000	-4.365023000	0.040152000
H	1.738781000	-1.059775000	3.315070000	C	0.501143000	2.535179000	1.345489000
H	2.452053000	0.549969000	3.121842000	C	0.884735000	3.463366000	-0.932833000
C	1.910274000	-3.240133000	1.395711000	C	-1.586707000	2.994839000	0.005083000
H	1.415801000	-3.887553000	0.659165000	Mn	-0.070162000	2.076832000	-0.285798000
H	1.177936000	-2.985335000	2.173509000	O	0.884331000	2.964968000	2.363907000
H	2.707740000	-3.833515000	1.876048000	O	1.510513000	4.358592000	-1.328162000
C	2.994162000	-3.011327000	-1.607820000	O	-2.542695000	3.627506000	0.207994000
H	3.907963000	-3.621722000	-1.504679000	Ru	1.454679000	-0.329272000	-0.346826000
H	2.973613000	-2.616237000	-2.632069000	Ru	-1.316467000	-0.352585000	-0.268196000
H	2.131211000	-3.681003000	-1.493516000	H	1.389340000	1.300627000	-0.871569000
C	-3.112472000	-0.270736000	1.164885000	H	0.034500000	0.325282000	2.283439000
C	-3.596633000	-0.198009000	-0.194535000	H	-0.348378000	-1.553766000	-2.778302000
C	-3.243339000	-1.431097000	-0.854872000	H	-2.121758000	1.165034000	-2.636381000
C	-2.524467000	-2.251177000	0.079923000	H	-0.320316000	0.421582000	-2.941815000
C	-2.450104000	-1.533927000	1.335786000	H	-0.464592000	2.026086000	-1.922601000
C	-1.945213000	-2.082969000	2.636399000	H	-0.018997000	-1.438982000	-0.272667000
H	-1.495522000	-1.298047000	3.259736000	H	1.152043000	-0.407906000	-2.060776000