SUPPORTING INFORMATION

Disobedient Boron Clusters: Synthesis, Structure and Bonding of Hypoelectronic Open and *Closo* Osmaborane Clusters

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I.1 Supplementary Data

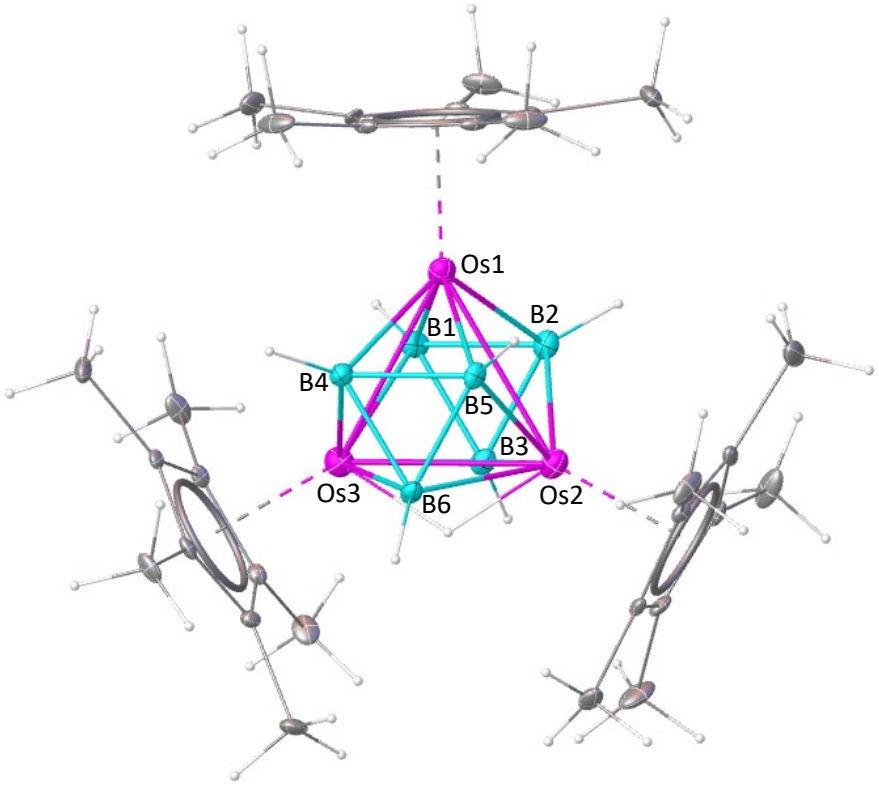

Figure S1. Molecular structure and labelling diagram of **3**. Selected bond lengths (Å): B1 B2 1.694(16), B1 B3 1.698(16), B1 Os1 2.173(11), B1 Os3 2.174(12), B2 B3 1.706(17), B2 Os1 2.186(11), B2 Os2 2.192(12), B3 Os3 2.188(10), B3 Os2 2.190(11), B4 B6 1.707(14),B4 B5 1.730(15), B4 Os3 2.174(11), B4 Os1 2.184(11), B5 B6 1.707(16), B5 Os2 2.188(10), B5 Os1 2.200(10), B6 Os2 2.174(10), B6 Os3 2.188(10), Os1 Os3 2.7782(5), Os1 Os2 2.7841(5), Os2 Os3 2.7786(5).

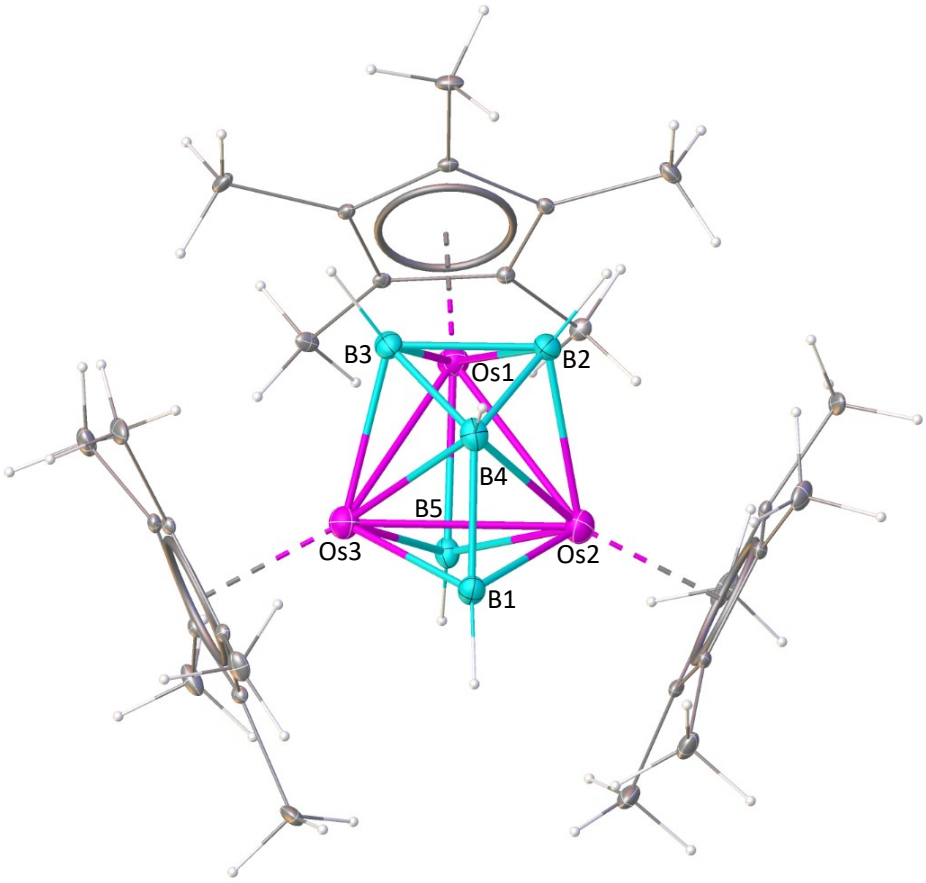

Figure S2. Molecular structure and labelling diagram of **4**. Selected bond lengths (Å): Os1 Os2 2.7893(11), Os1 Os3 2.8017(10), Os2 Os3 2.721, B1 B4 1.793(9), B1 Os2 2.041(6), B1 Os3 2.045(6), B2 B4 1.714(9), B2 B3 1.832(9), B2 Os2 2.146(6), B3 B4 1.711(9), B3 Os3 2.134(6), B4 Os3 2.232(6), B4 Os2 2.243(6), B5 Os3 2.119(5), B5 Os2 2.139(5).

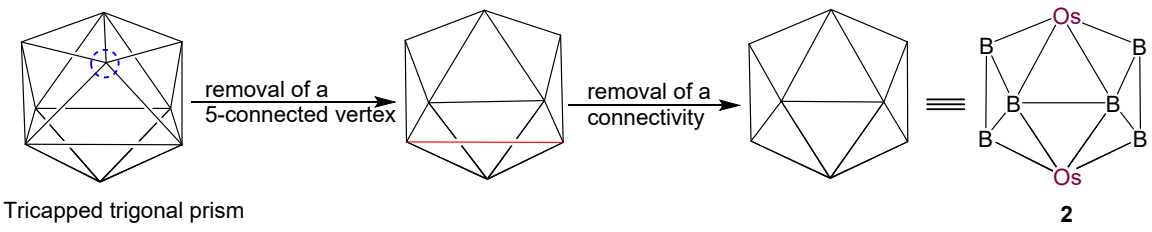

Figure S3. Schematic generation of the cluster framework of **2** from tricapped trigonal prism.

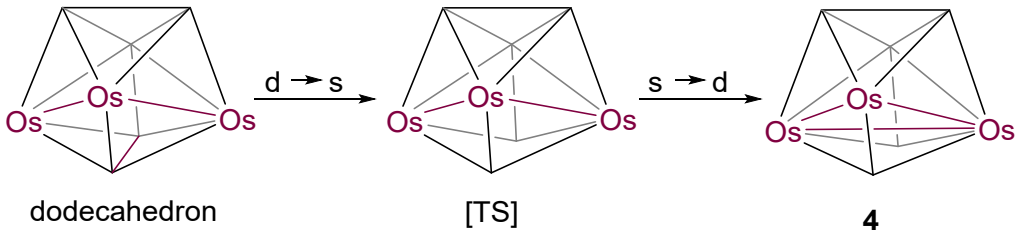

Figure S4. Diamond-Square-Diamond (DSD) rearrangement of the parent *closo*-cluster to form the corresponding hypoelectronic cluster **4**.

I.2 Spectroscopic details

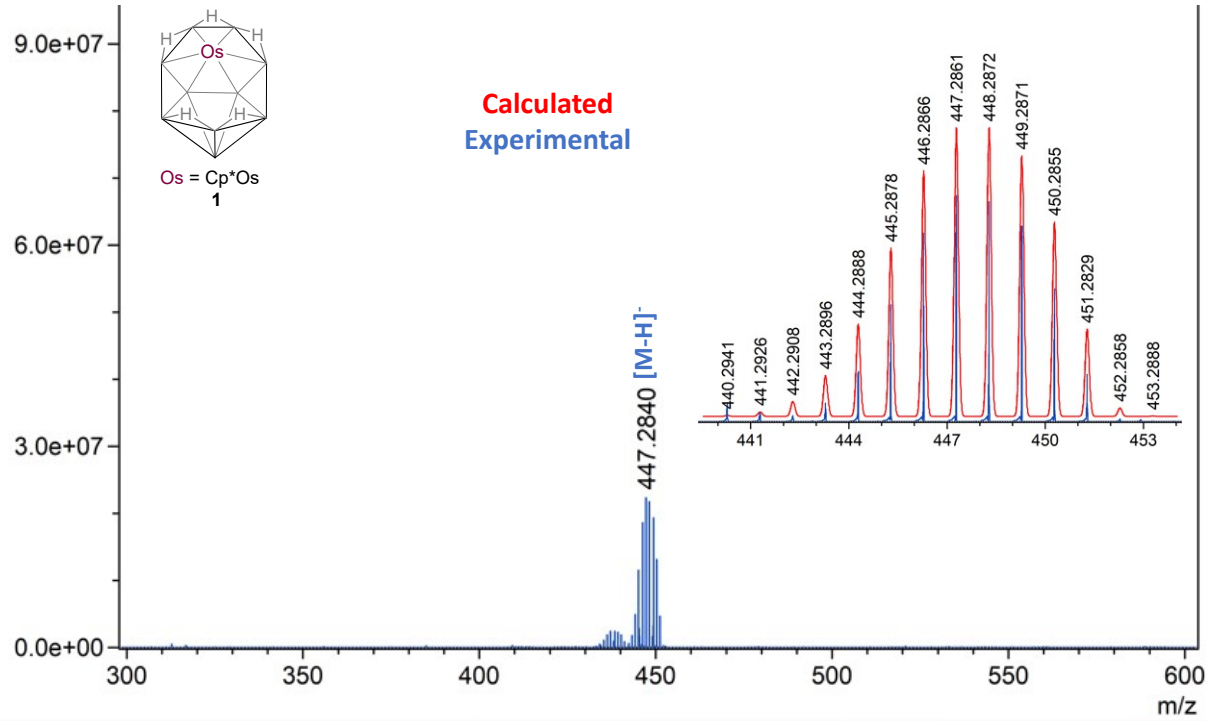

Figure S5. ESI-MS spectrum of **1** in CH_2Cl_2.

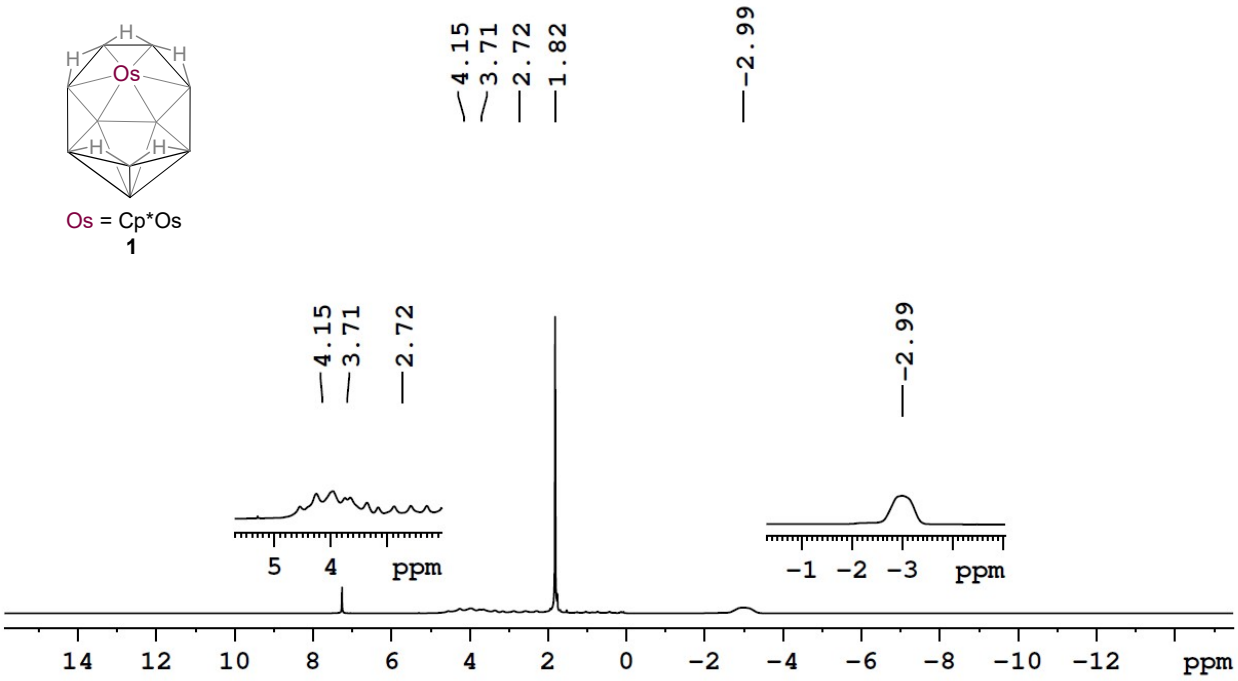

Figure S6. ^1H NMR spectrum of **1** in $CDCl_3$.

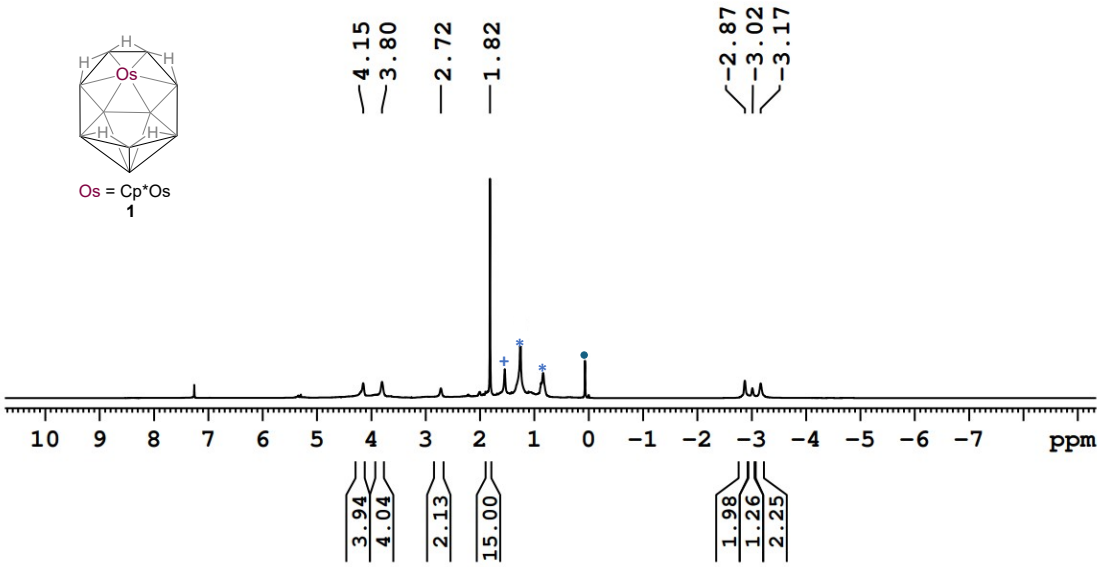

Figure S7. $^{1}H\{^{11}B\}$ NMR spectrum of **1** in $CDCl_3$ (*hexane, ●silicon-grease, +H_2O).

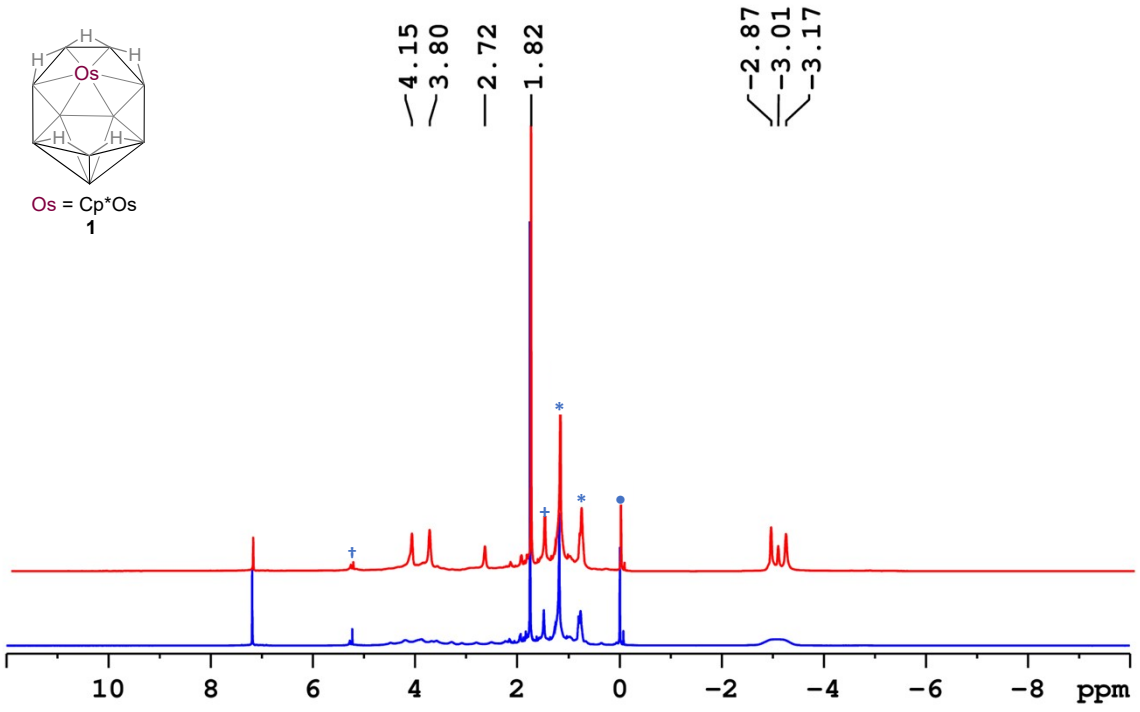

Figure S8. Stacked ^{1}H (bottom) and $^{1}H\{^{11}B\}$ NMR (top) spectra of **1** in $CDCl_3$ (†CH_2Cl_2, *hexane, ●silicon-grease, +H_2O).

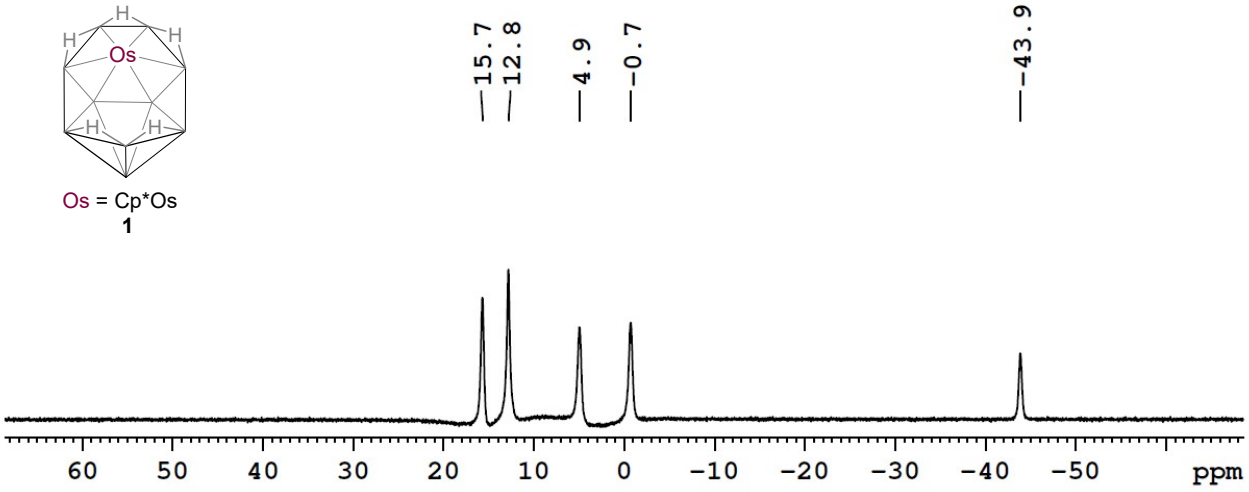

Figure S9. $^{11}B\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$.

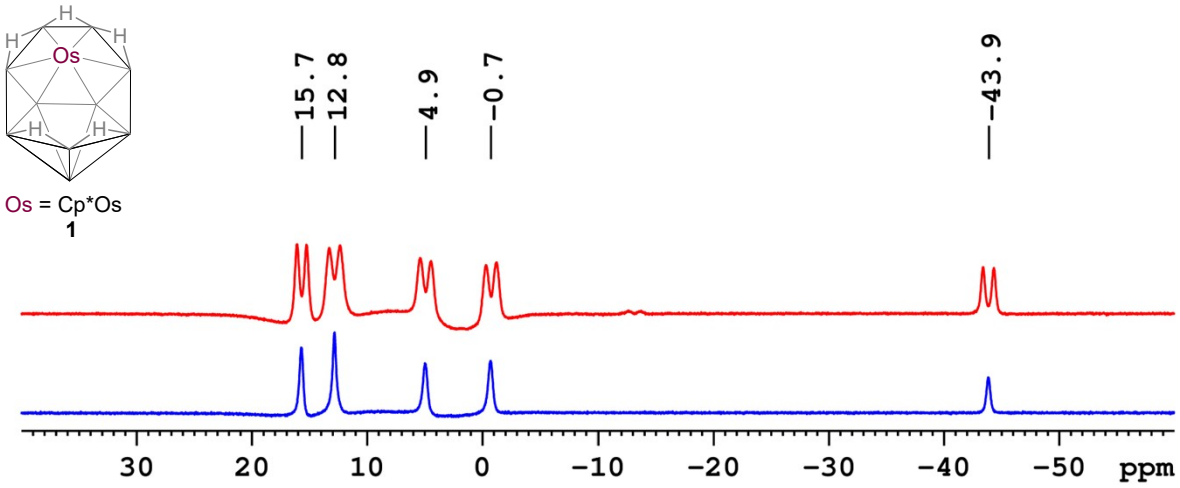

Figure S10. Stacked $^{11}B\{^{1}H\}$ (bottom) and ^{11}B NMR (top) spectra of **1** in $CDCl_3$.

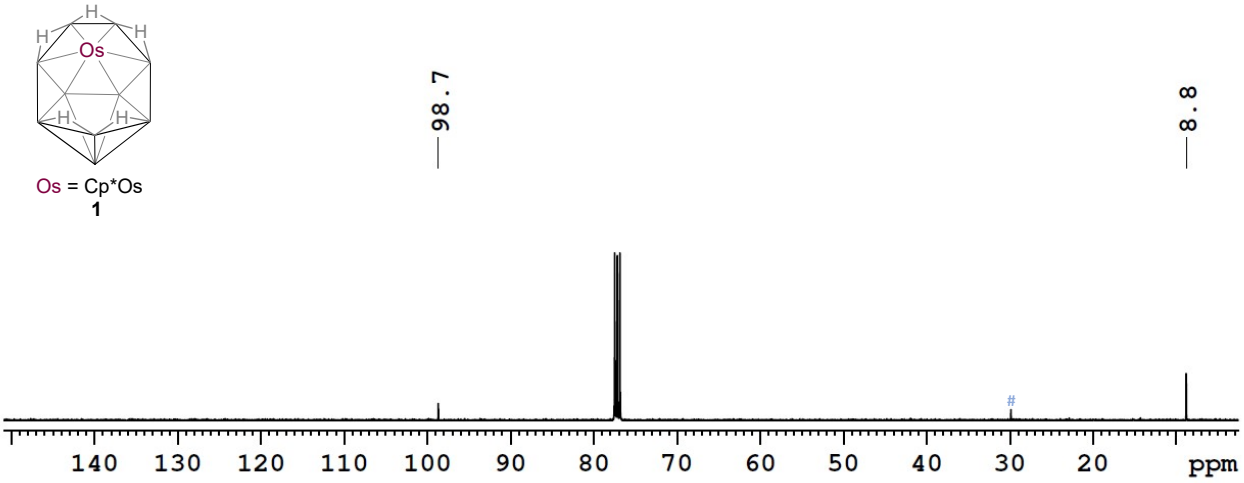

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$ (#H-grease).

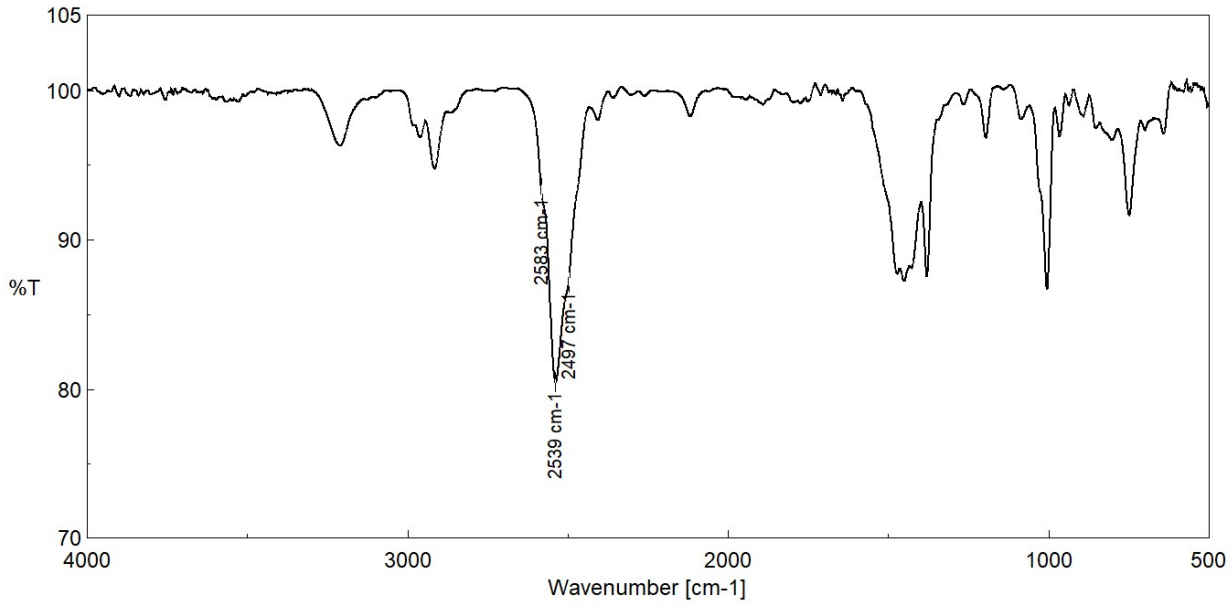

Figure S12. IR spectrum of **1** in CH_2Cl_2.

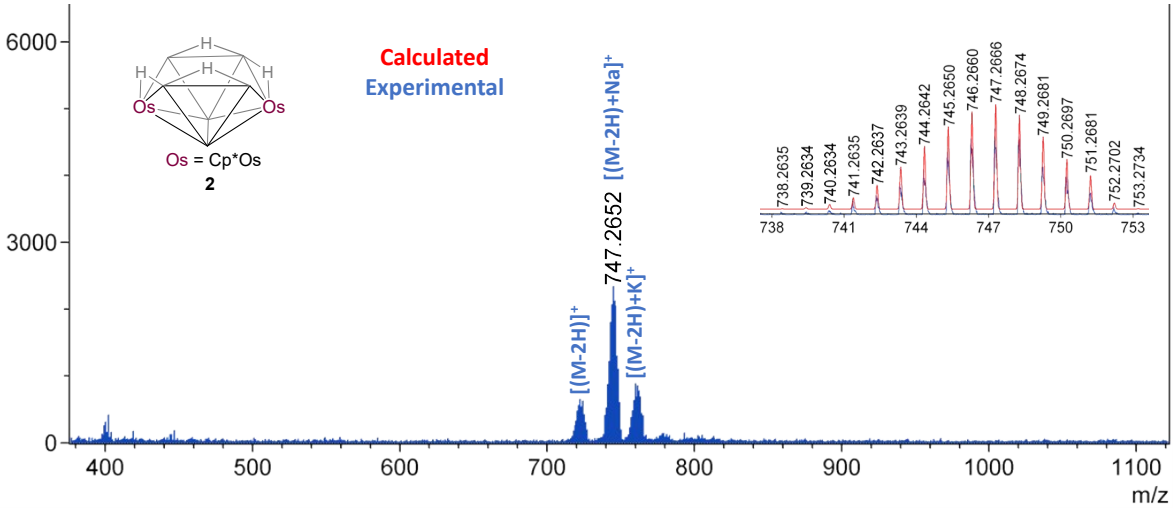

Figure S13. ESI-MS spectrum of **2** in CH_2Cl_2.

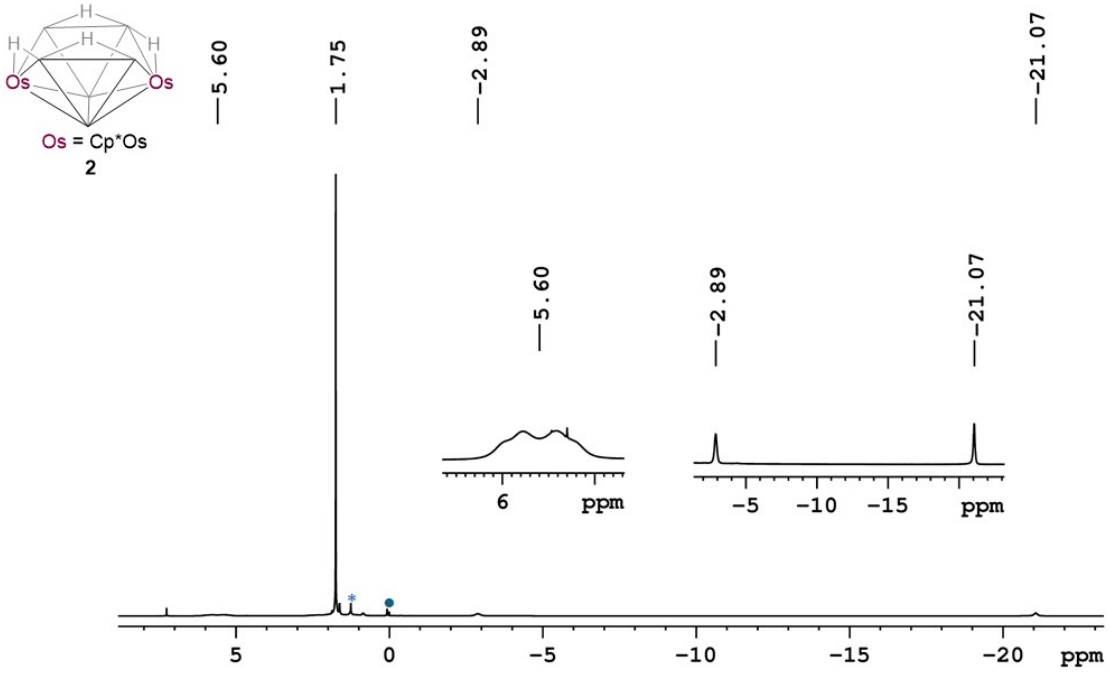

Figure S14. ^{1}H NMR spectrum of **2** in $CDCl_3$ (•silicone grease, *hexane).

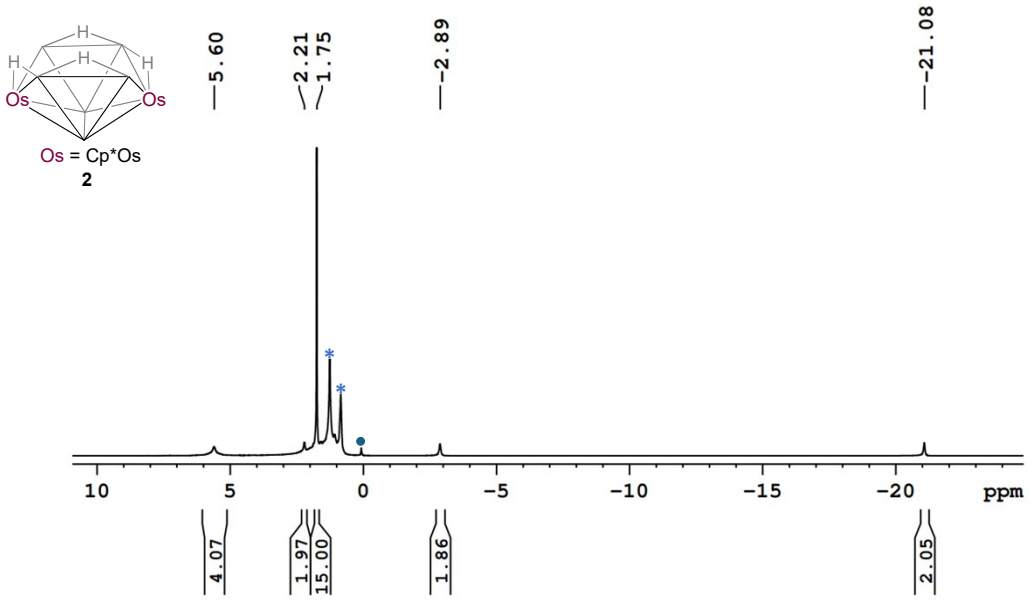

Figure S15. $^{1}H\{^{11}B\}$ NMR spectrum of **2** in $CDCl_3$ (•silicone grease, *hexane).

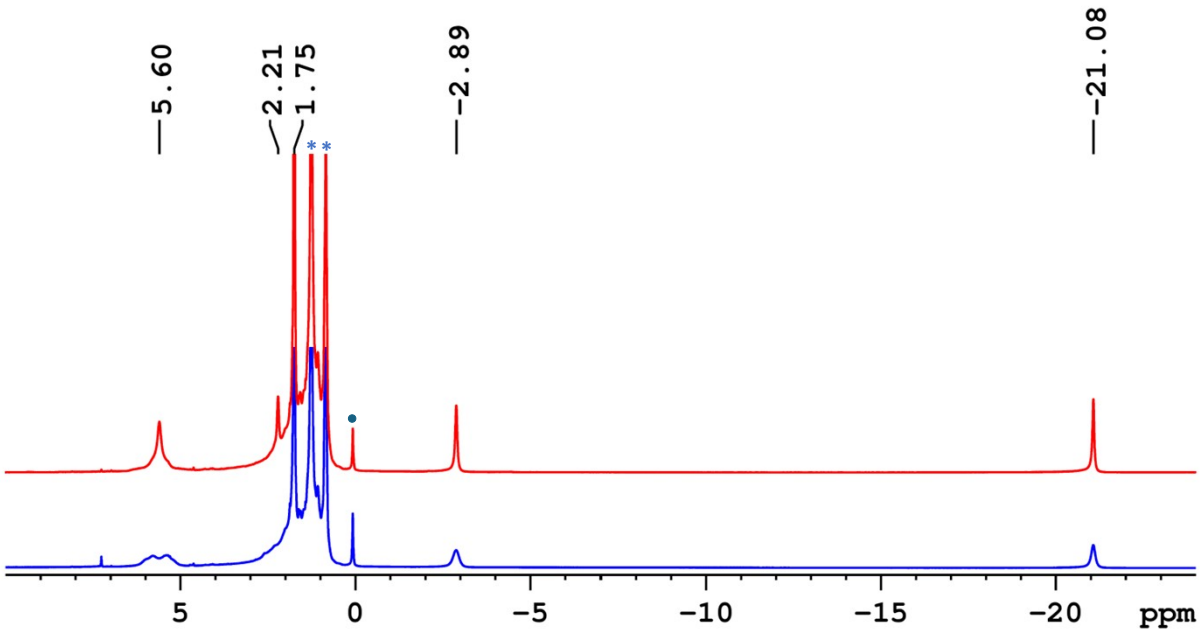

Figure S16. Stacked ^{1}H (bottom) and $^{1}H\{^{11}B\}$ NMR (top) spectra of **2** in $CDCl_3$ (•silicone grease, *hexane).

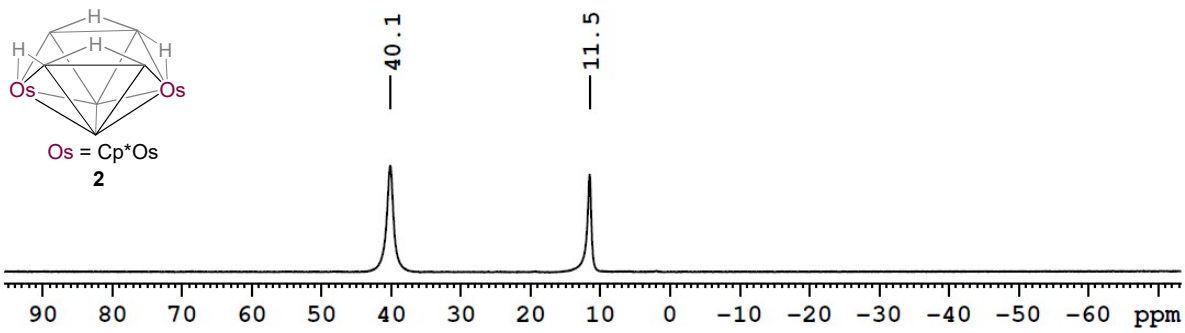

Figure S17. $^{11}B\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$.

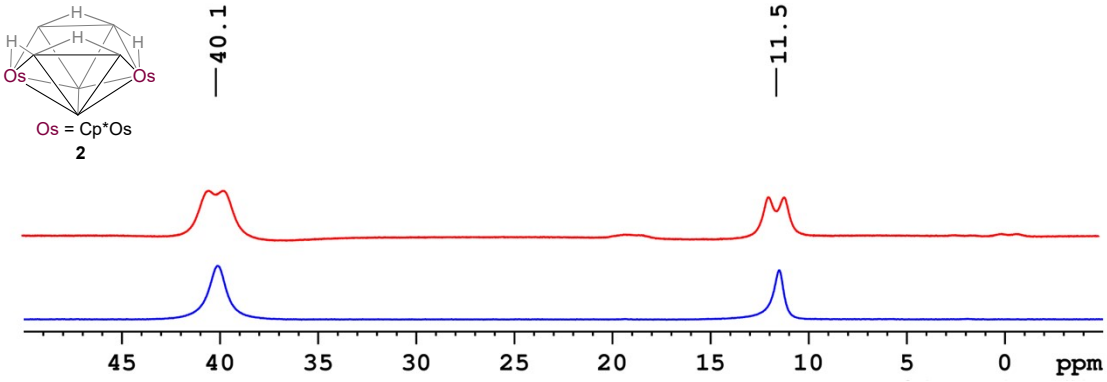

Figure S18. Stacked $^{11}B\{^{1}H\}$ (bottom) and ^{11}B NMR (top) spectra of **2** in $CDCl_3$.

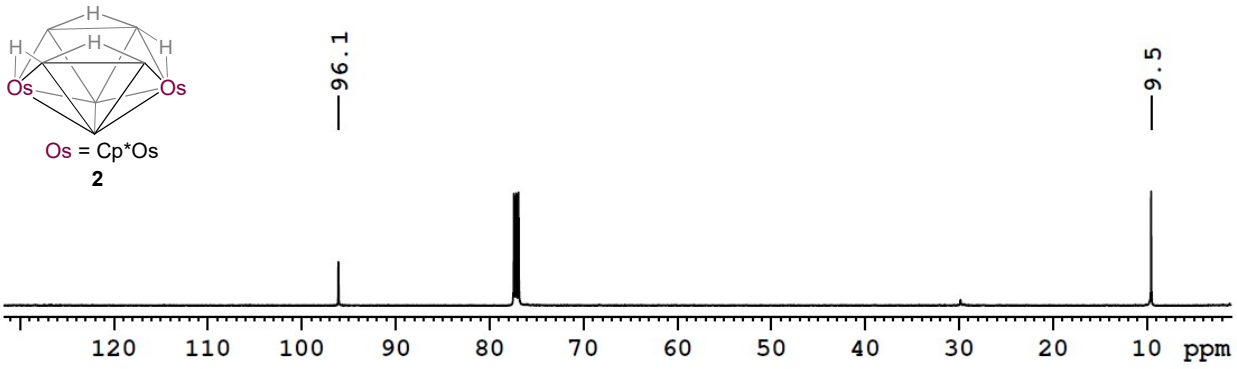

Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$.

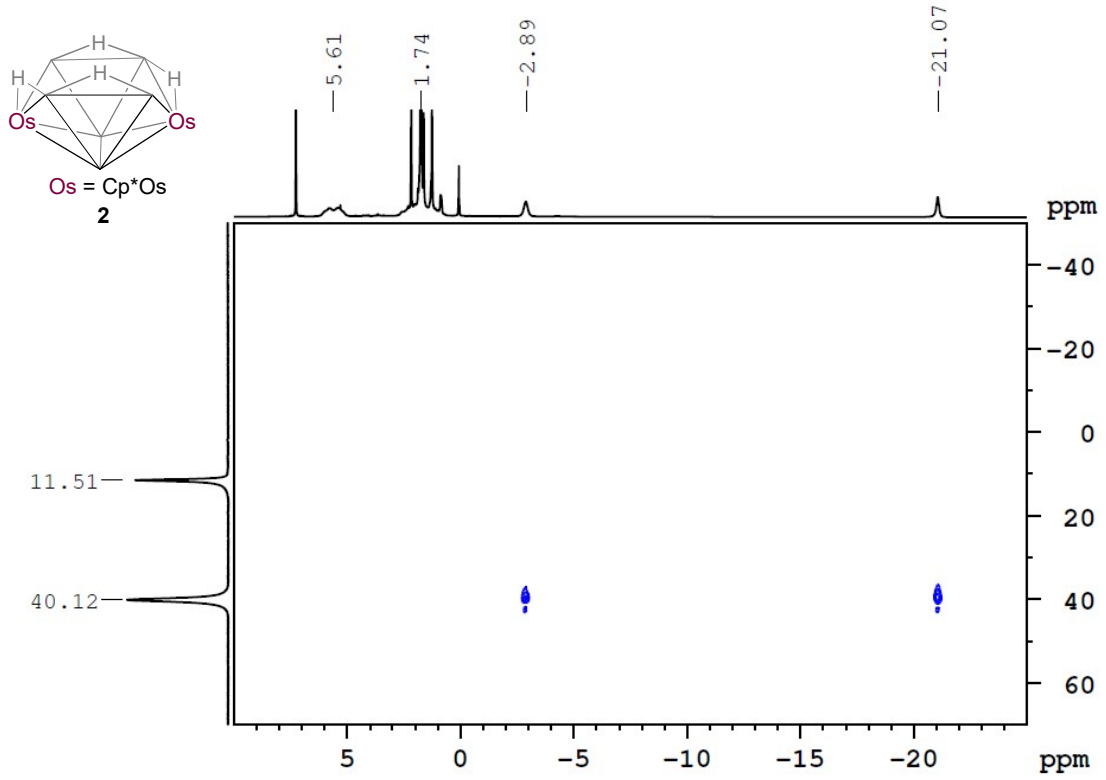

Figure S20. ^{1}H-^{11}B HSQC NMR spectrum of **2** in $CDCl_3$.

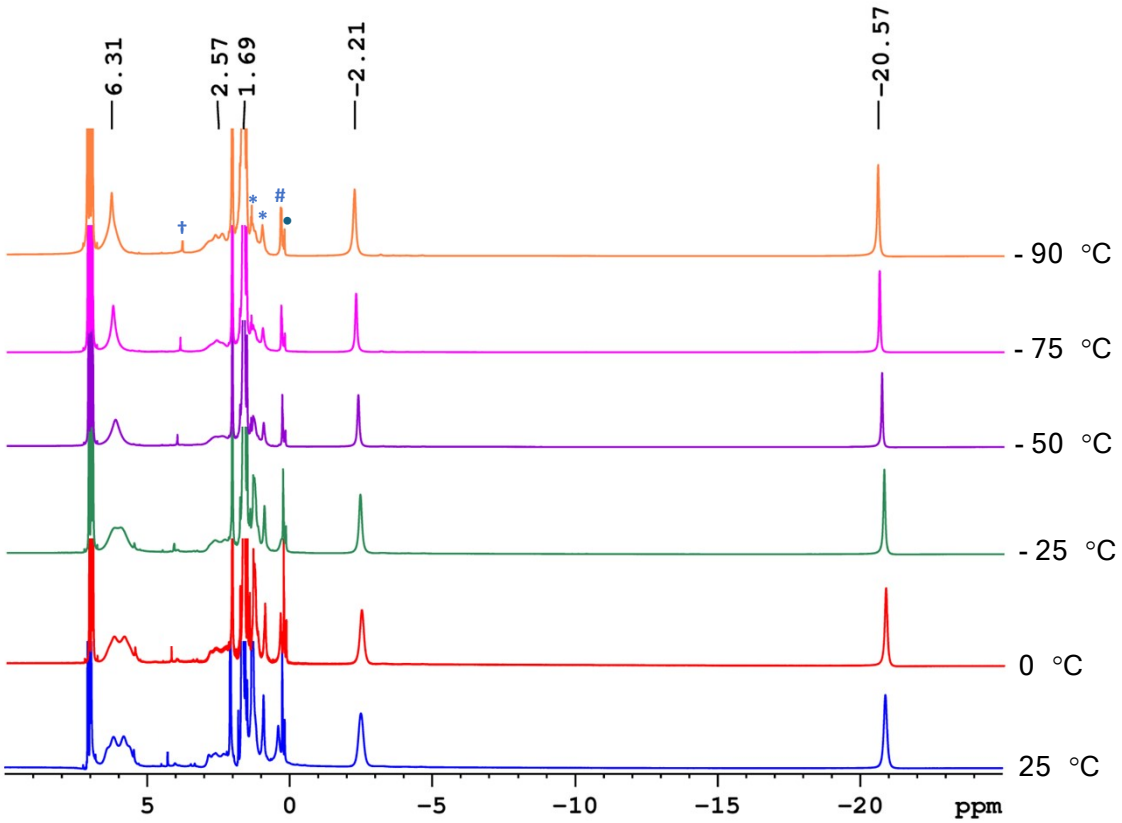

Figure S21. The variable temperature stacked ^{1}H NMR spectra of **2** in d_8-toluene (†CH_2Cl_2, •silicone grease, #H-grease, *hexane).

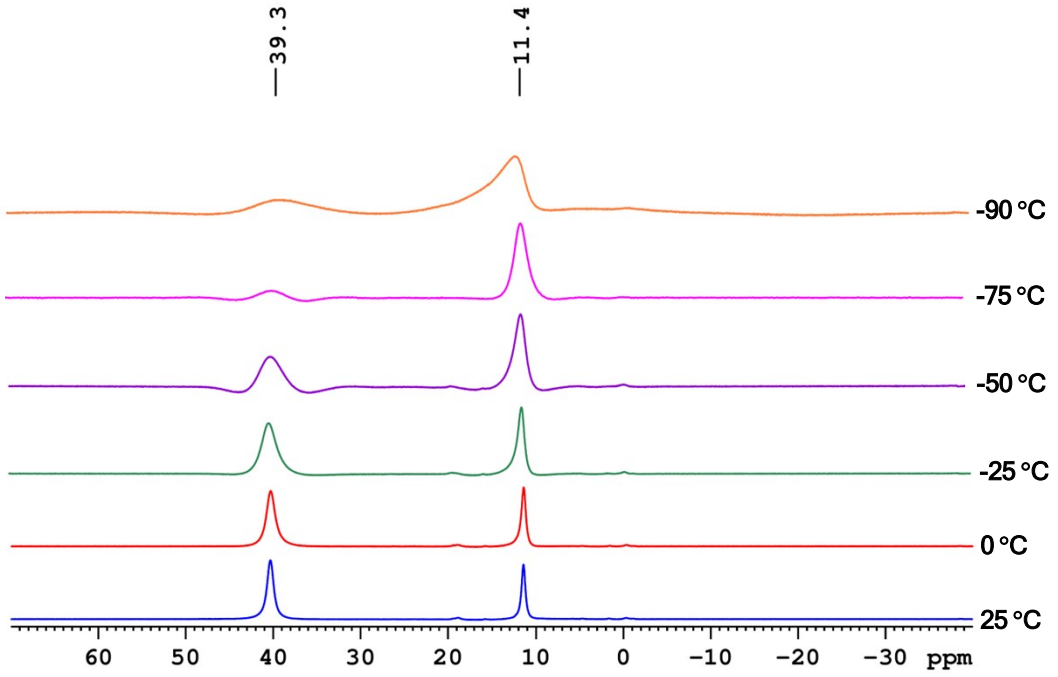

Figure S22. The variable temperature stacked $^{11}B\{^{1}H\}$ NMR spectra of **2** in d_8-toluene.

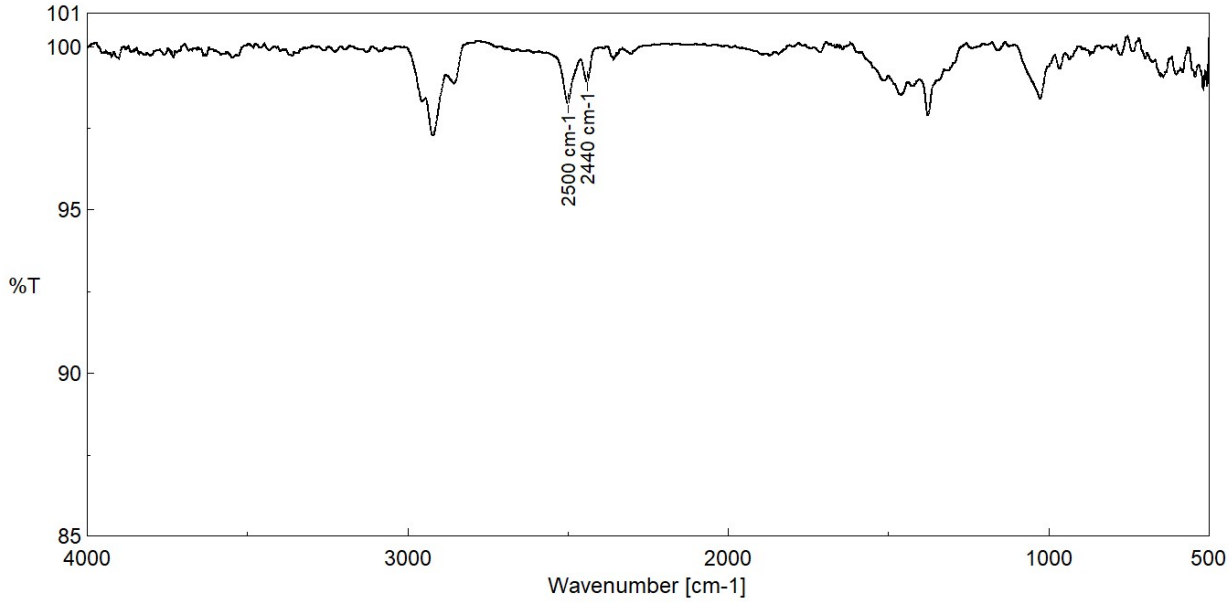

Figure S23. IR spectrum of **2** in CH_2Cl_2.

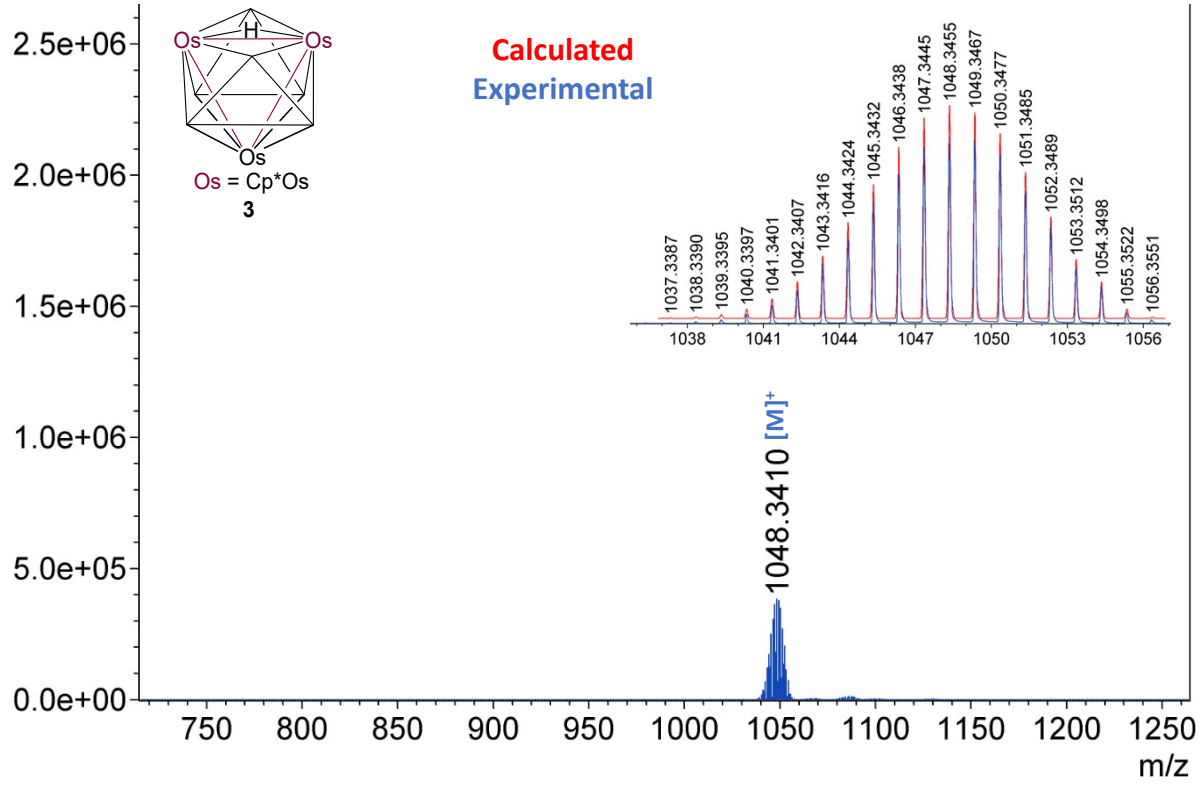

Figure S24. ESI-MS spectrum of **3** in CH_2Cl_2.

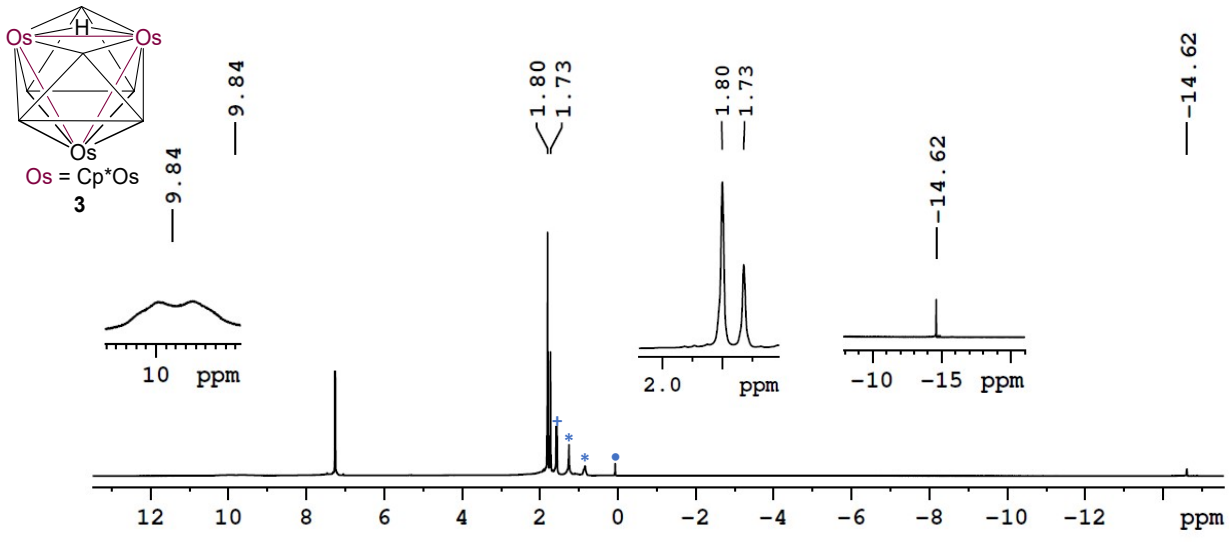

Figure S25. ^1H NMR spectrum of **3** in $CDCl_3$ (•silicone grease, *hexane, +H_2O).

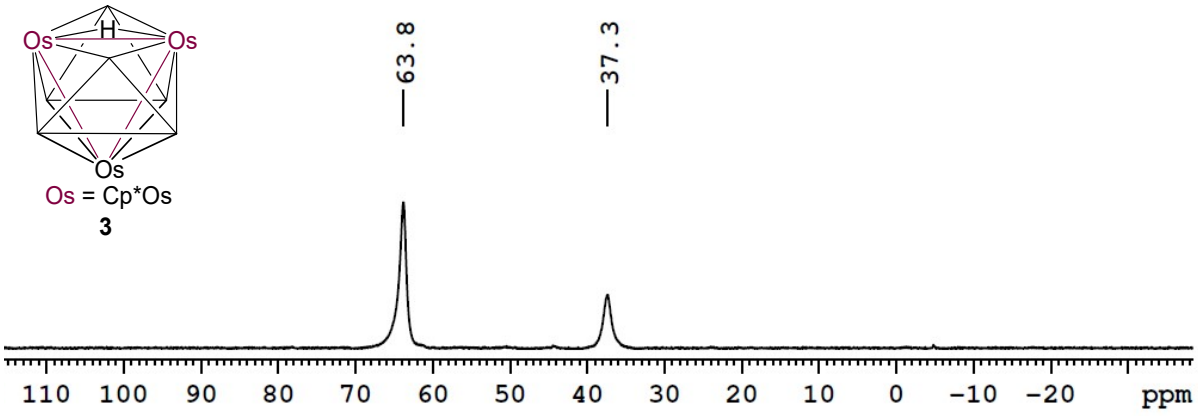

Figure S26. $^{11}B\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$.

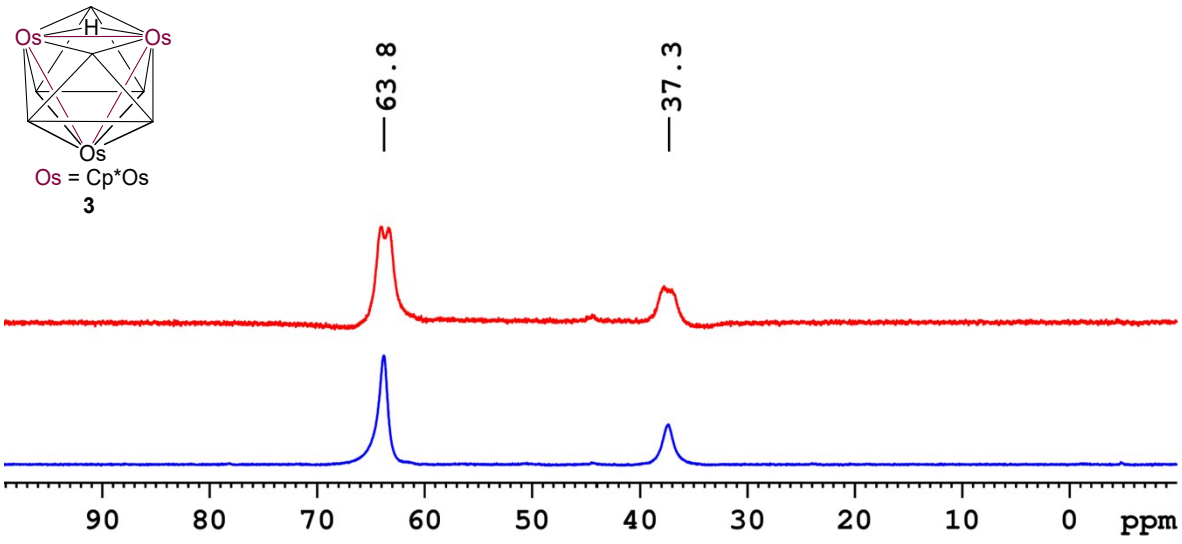

Figure S27. Stacked $^{11}B\{^{1}H\}$ (bottom) and ^{11}B NMR (top) spectra of **3** in $CDCl_3$.

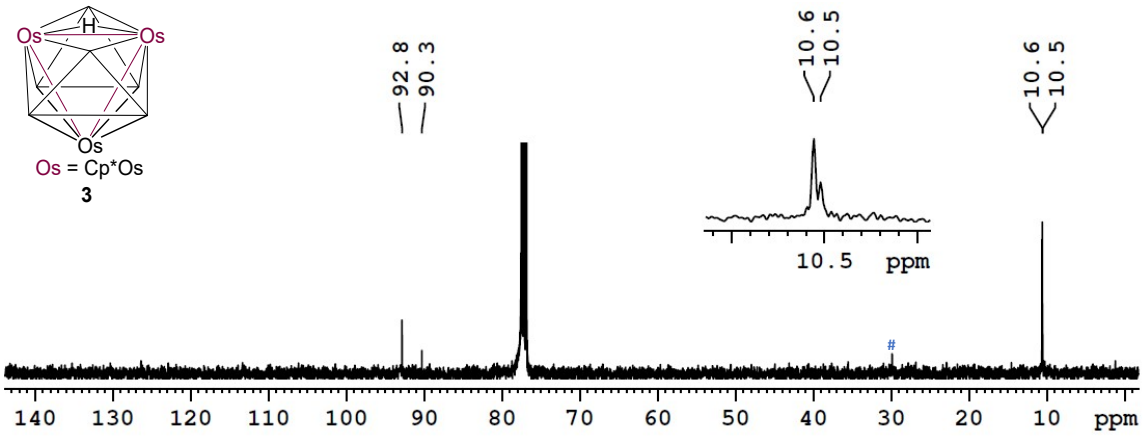

Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$ (#H-grease).

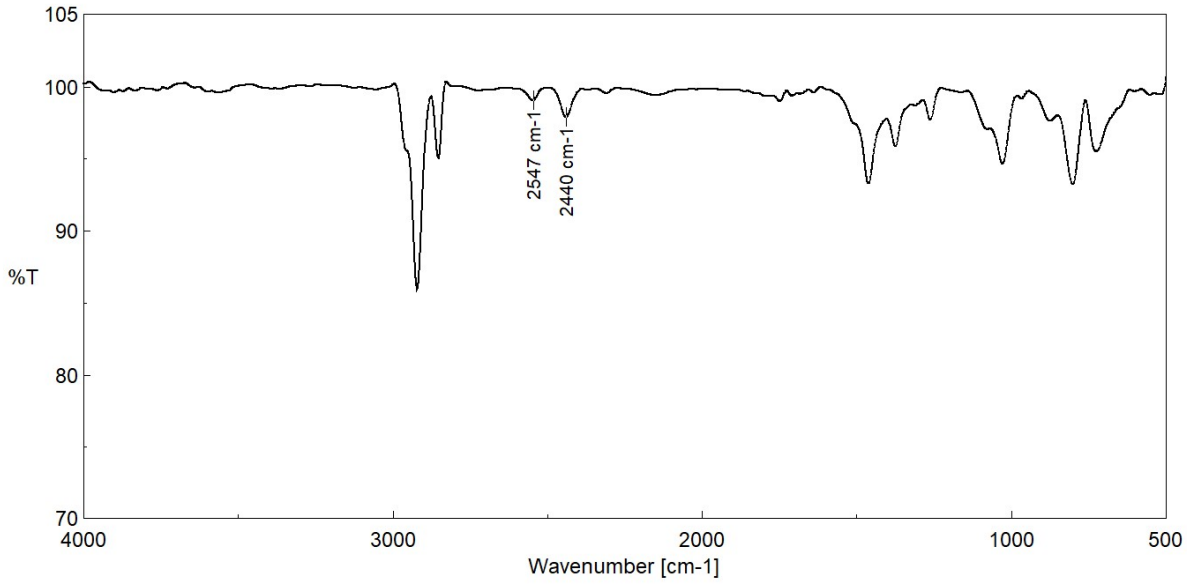

Figure S29. IR spectrum of **3** in CH_2Cl_2.

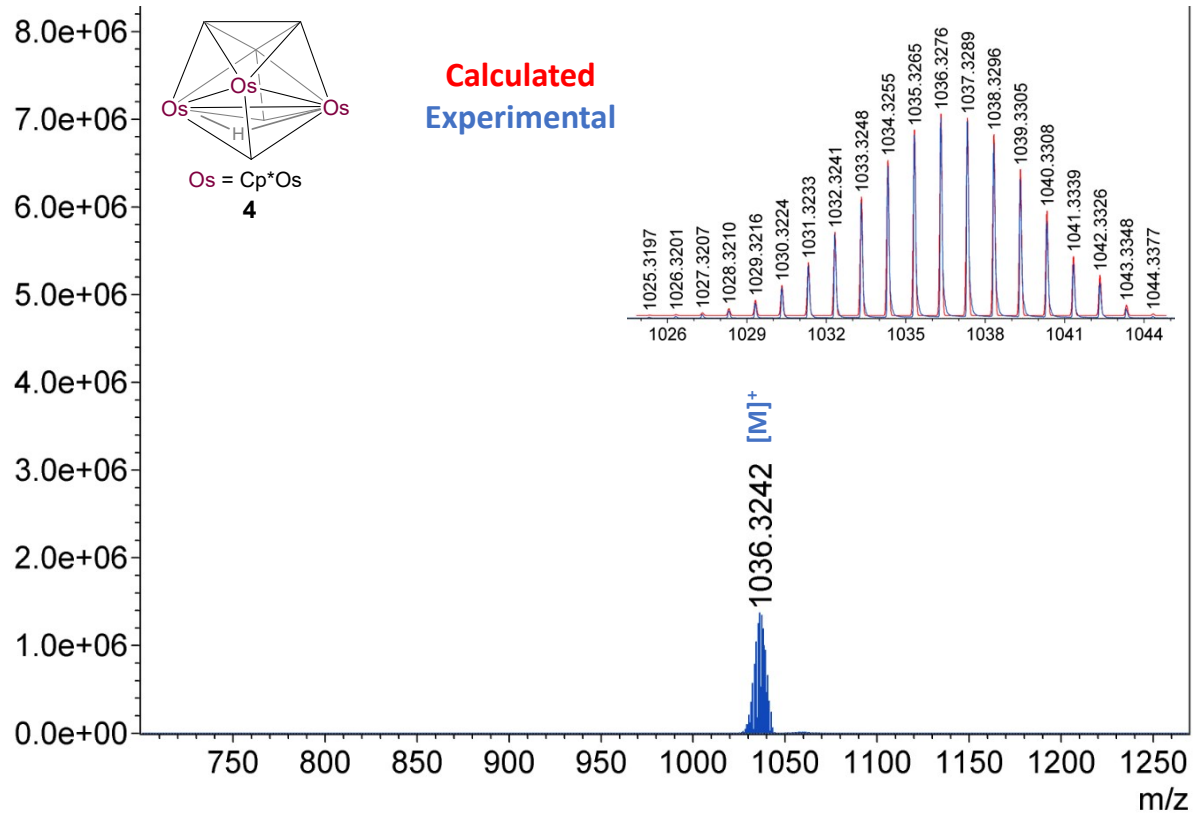

Figure S30. ESI-MS spectrum of **4** in CH_2Cl_2.

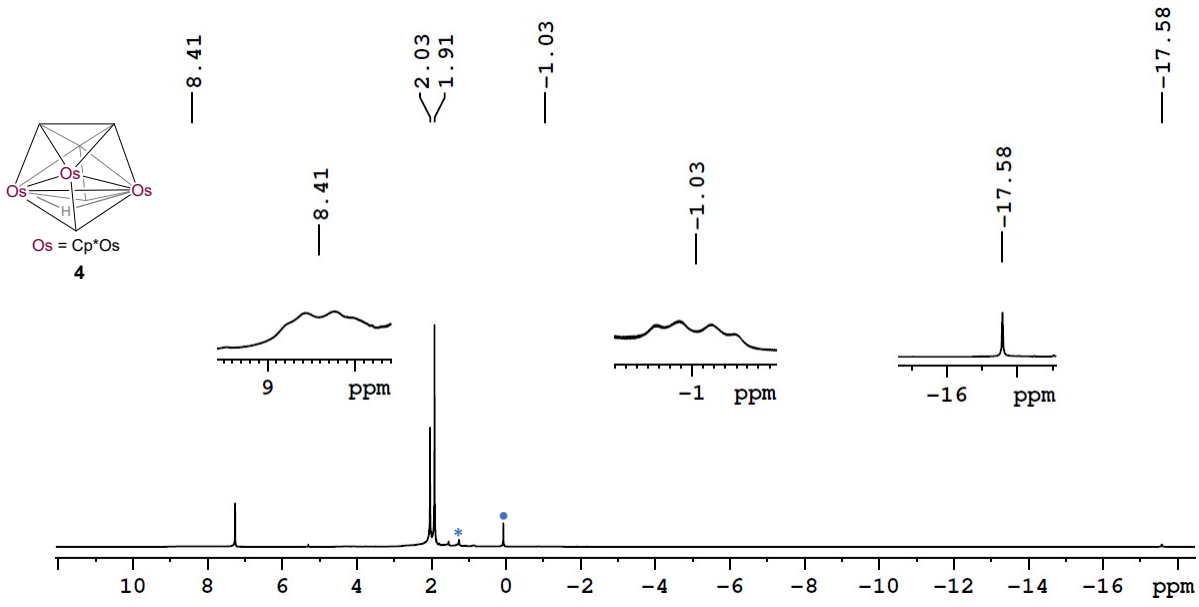

Figure S31. ^{1}H NMR spectrum of **4** in $CDCl_3$ (•silicone grease, *hexane).

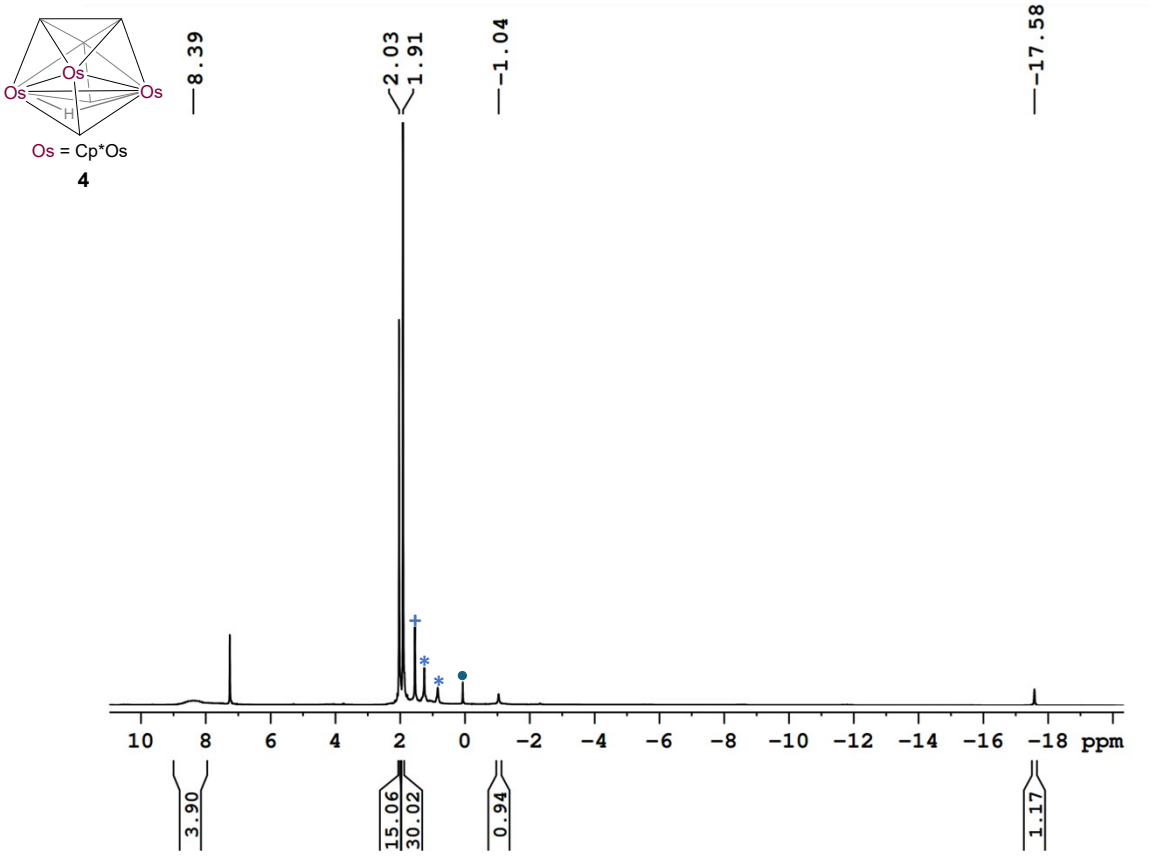

Figure S32. $^{1}H\{^{11}B\}$ NMR spectrum of **4** in $CDCl_3$ (•silicone grease, *hexane, +H_2O).

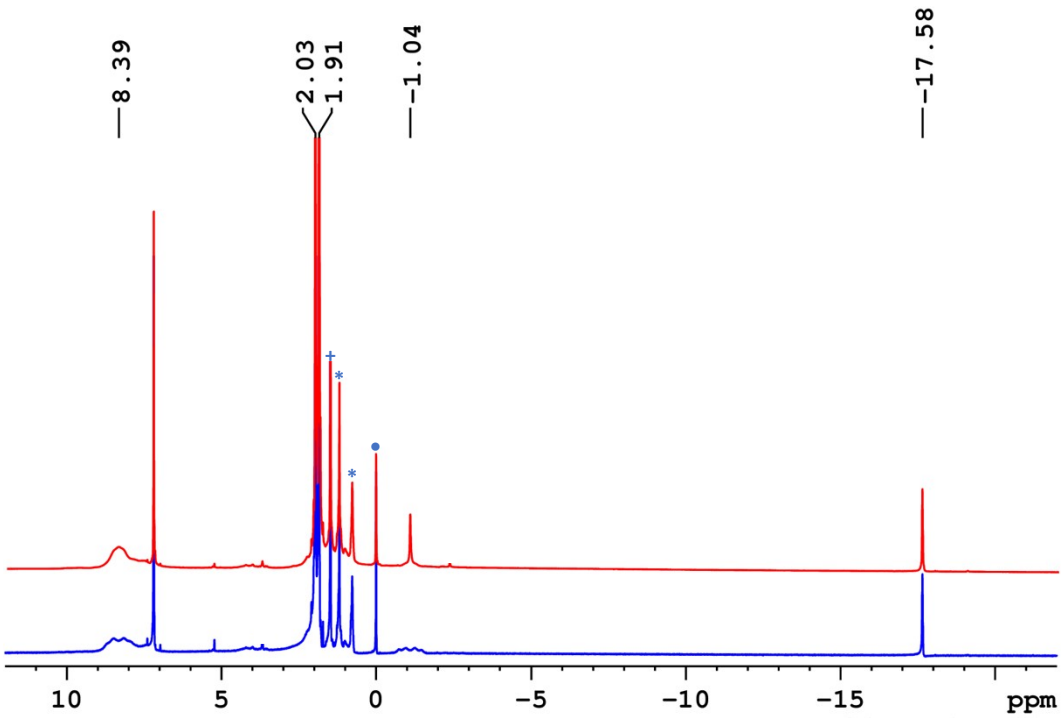

Figure S33. Stacked ^{1}H (bottom) and $^{1}H\{^{11}B\}$ NMR (top) spectra of **4** in $CDCl_3$ (•silicone grease, *hexane, +H_2O).

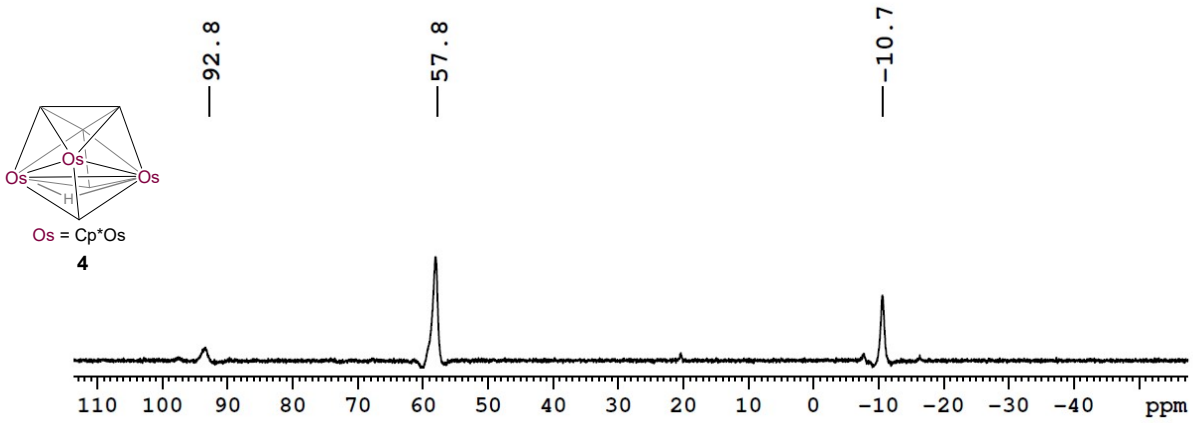

Figure S34. $^{11}B\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$.

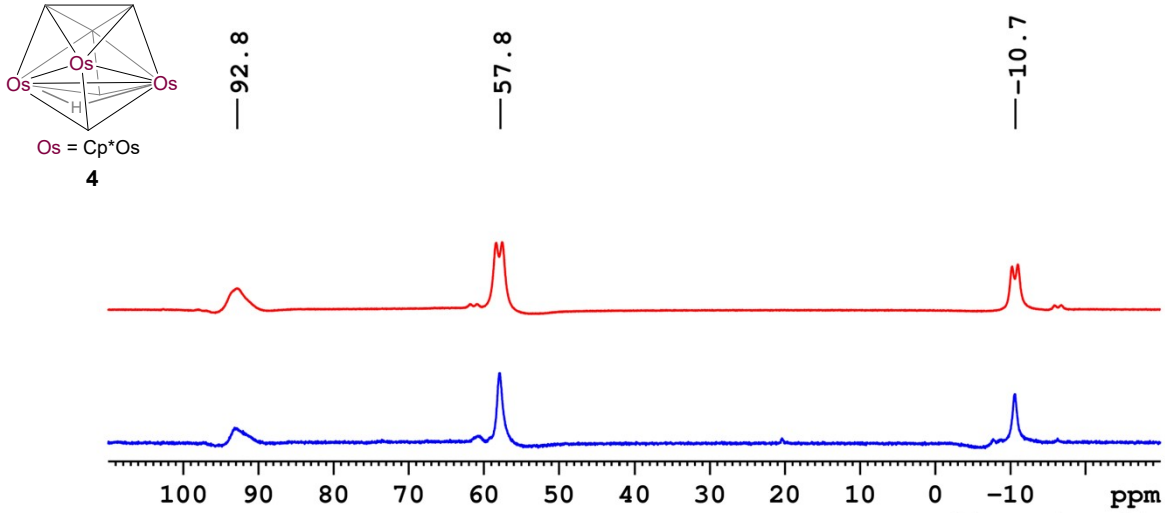

Figure S35. Stacked $^{11}B\{^{1}H\}$ (bottom) and ^{11}B NMR (top) spectra of **4** in $CDCl_3$.

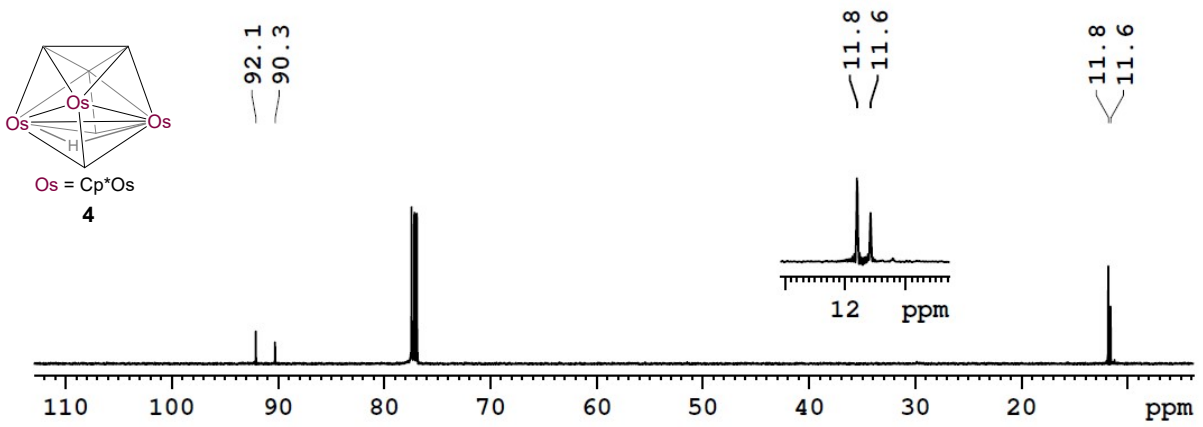

Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$.

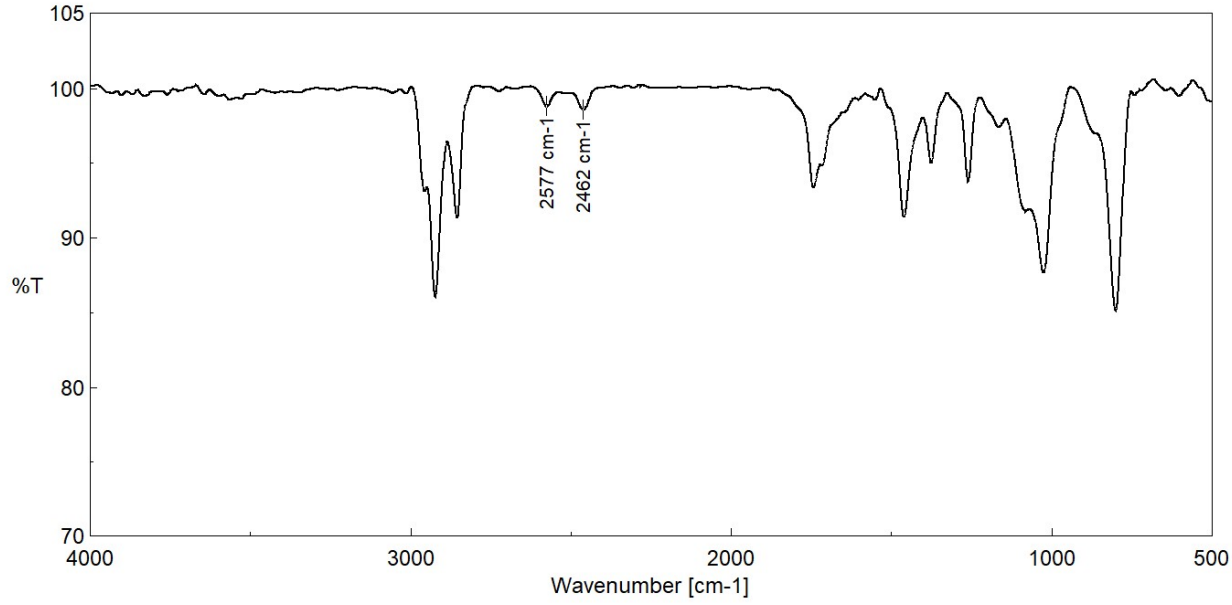

Figure S37. IR spectrum of **4** in CH_2Cl_2.

II Computational Data

Table S1. Selected geometrical parameters and Wiberg indices (WBIs) of **1′-4′**.

1/1′				**2/2′**			
	Expt.	Cal.	WBI		Expt.	Cal.	WBI
Os1-B1	2.130	2.148	0.511	Os1-B2	2.304	2.246	0.430
Os1-B24	2.114	2.148	0.511	Os2-B2	2.308	2.252	0.428
Os1-B3	2.210	2.239	0.446	Os1-B3	2.302	2.318	0.357
Os1-B4	2.218	2.250	0.404	Os1-B3	2.292	2.267	0.417
Os1-B5	2.209	2.250	0.404	Os1-B1	2.213	2.221	0.419
Os1-B6	2.198	2.239	0.446	Os1-B4	2.191	2.205	0.599
B1-B2	1.770	1.813	0.543	Os2-B5	2.209	2.136	0.843
B2-B3	1.799	1.810	0.553	Os2-B6	2.201	2.069	0.514
B3-B4	1.743	1.763	0.598	B2-B3	1.790	1.810	0.575
B4-B5	1.754	1.788	0.527	B2-B1	1.761	1.829	0.577
B5-B6	1.735	1.763	0.598	B2-B6	1.762	1.824	0.518
B6-B1	1.797	1.810	0.553	B1-B6	1.721	1.812	0.560
B3-B7	1.961	1.957	0.475	B3-B4	1.758	1.765	0.631
B6-B9	1.948	1.957	0.476	B3-B5	1.763	1.773	0.577
B4-B8	1.758	1.800	0.507	B4-B5	1.722	1.758	0.610
B5-B8	1.795	1.800	0.507				
B4-B7	1.751	1.773	0.558				
B7-B10	1.774	1.802	0.542				
B7-B8	1.729	1.788	0.536				
B9-B8	1.754	1.788	0.542				
B8-B10	1.690	1.729	0.596				
B9-B10	1.777	1.788	0.542				
3/3′				**4/4′**			
	Expt.	Cal.	WBI		Expt.	Cal.	WBI
Os1-Os2	2.778	2.798	0.379	Os1-Os2	2.785	2.758	0.386
Os2-Os3	2.779	2.779	0.363	Os2-Os3	2.716	2.720	0.357
Os3-Os1	2.784	2.795	0.383	Os3-Os1	2.796	2.759	0.383
Os1-B4	2.185	2.184	0.520	Os3-B5	2.115	2.188	0.551
Os1-B5	2.175	2.185	0.515	Os3-B1	2.055	2.216	0.538
Os1-B1	2.201	2.181	0.520	Os2-B1	2.033	2.212	0.552

Os1-B2	2.184	2.183	0.515	Os2-B5	2.148	2.218	0.531
Os2-B2	2.174	2.203	0.489	Os1-B2	2.146	2.150	0.563
Os2-B3	2.188	2.191	0.453	Os1-B3	2.168	2.148	0.566
Os2-B5	2.175	2.201	0.489	Os3-B3	2.132	2.214	0.485
Os2-B6	2.189	2.174	0.453	Os1-B5	2.202	2.083	0.737
Os3-B1	2.187	2.203	0.484	Os2-B4	2.239	2.213	0.405
Os3-B3	2.175	2.188	0.454	Os2-B2	2.117	2.200	0.497
Os3-B4	2.191	2.203	0.484	Os3-B4	2.262	2.224	0.485
Os3-B6	2.191	2.187	0.454	B4-B2	1.684	1.742	0.631
B1-B2	1.731	1.742	0.601	B4-B3	1.687	1.739	0.638
B2-B3	1.706	1.743	0.640	B4-B1	1.818	1.726	0.653
B3-B1	1.706	1.741	0.642				
B4-B5	1.695	1.741	0.601				
B5-B6	1.698	1.743	0.640				
B6-B4	1.706	1.744	0.642				

Table S2. Calculated ^{11}B chemical shifts for **1′-4′** (The experimental values are provided in parentheses).

Cluster	Calculated ^{11}B chemical shifts (ppm)
1	20.1 (15.7), 11.51 (12.8), 6.68 (4.9), 1.79 (-0.7), -43.2 (-43.9)
2[a]	33.4, 6.2, -24.1
3	65.48 (63.8), 42.40 (37.3)
4	67.34 (92.8), 44.63 (57.8), -20.4 (-10.7)

[a]Note that, in case of cluster **2**, as the structure was optimized with two B-H-B and two Os-H-B (shown in Figure S36), the DFT study shows three ^{11}B peaks as expected.

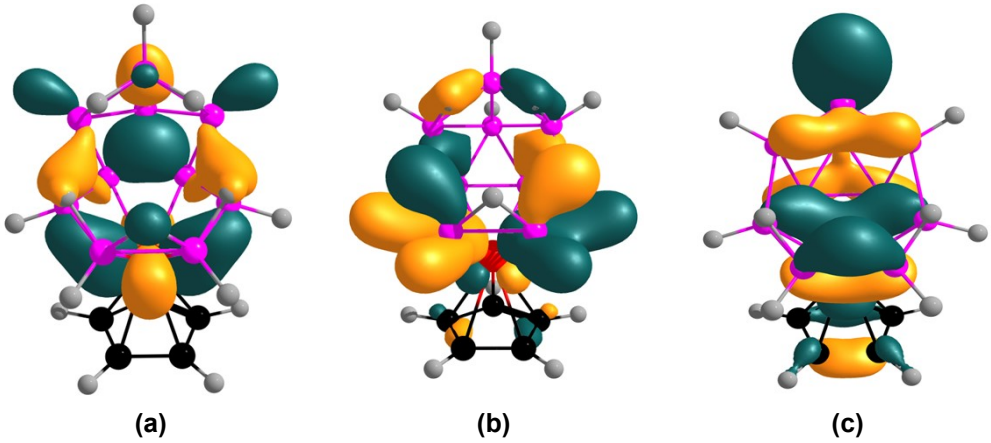

Figure S38. Selected molecular orbitals of **1**. (a) HOMO-2, (b) HOMO-12, (c) HOMO-13 of **1.** Isosurfaces are plotted at an isovalue of ±0.04 $(e/bohr^3)^{1/2}$.

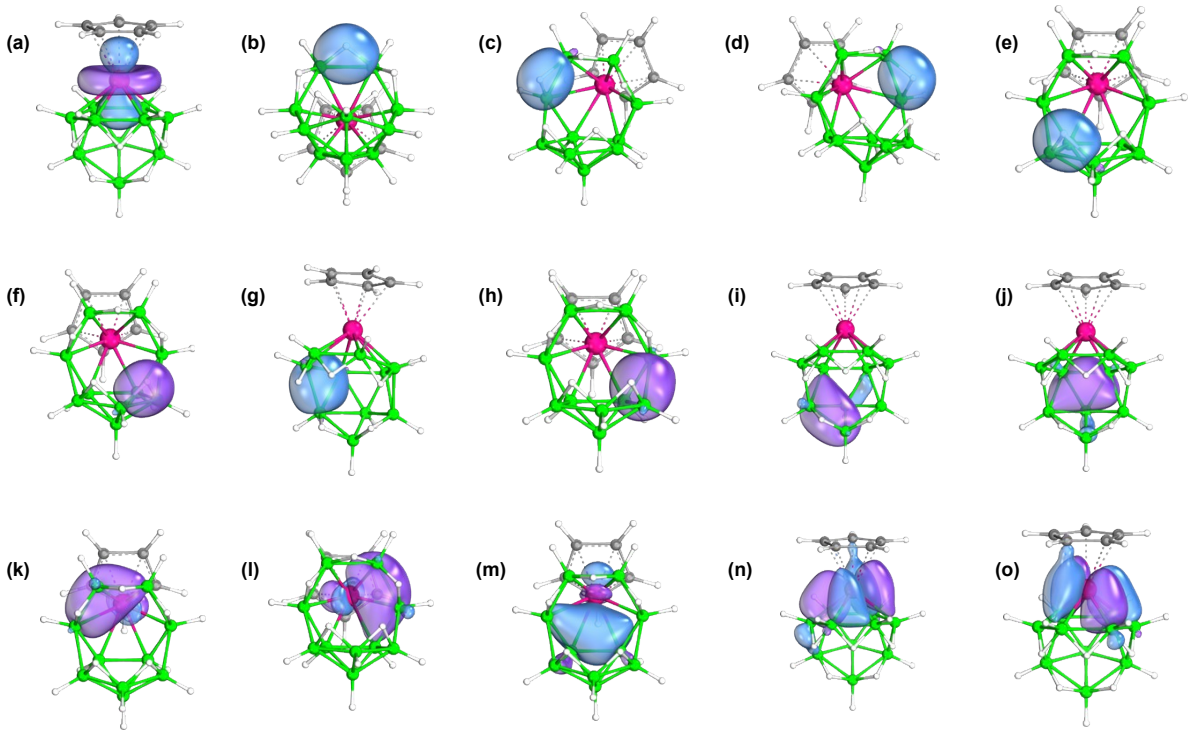

Figure S39. Selected localized orbitals of **1** computed using IBOview: (a) a 1c-2e lone pair on osmium; (b-h) five 3c-2e B-H-B bond orbitals and two 3C-2e B-B-B bond orbitals; and (i-o) multicenter osmium-boron and boron-boron bonding orbitals.

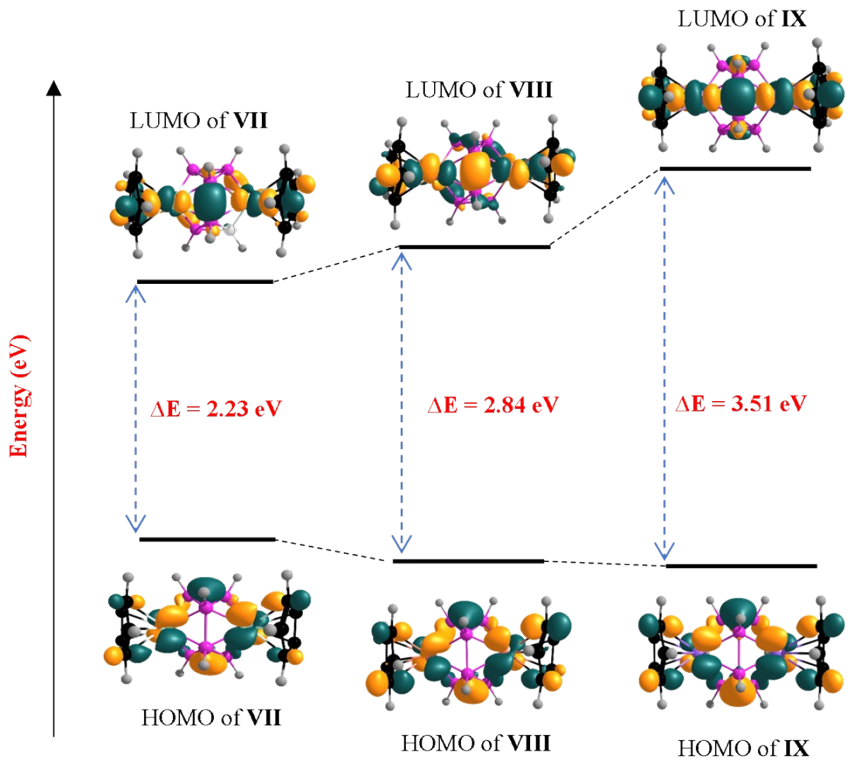

Figure S40. Frontier molecular orbitals and their respective energy levels for **VII**-**IX**. Isosurfaces are plotted at an isovalue of ±0.04 $(e/bohr^3)^{1/2}$ (ΔE = HOMO-LUMO energy gap).

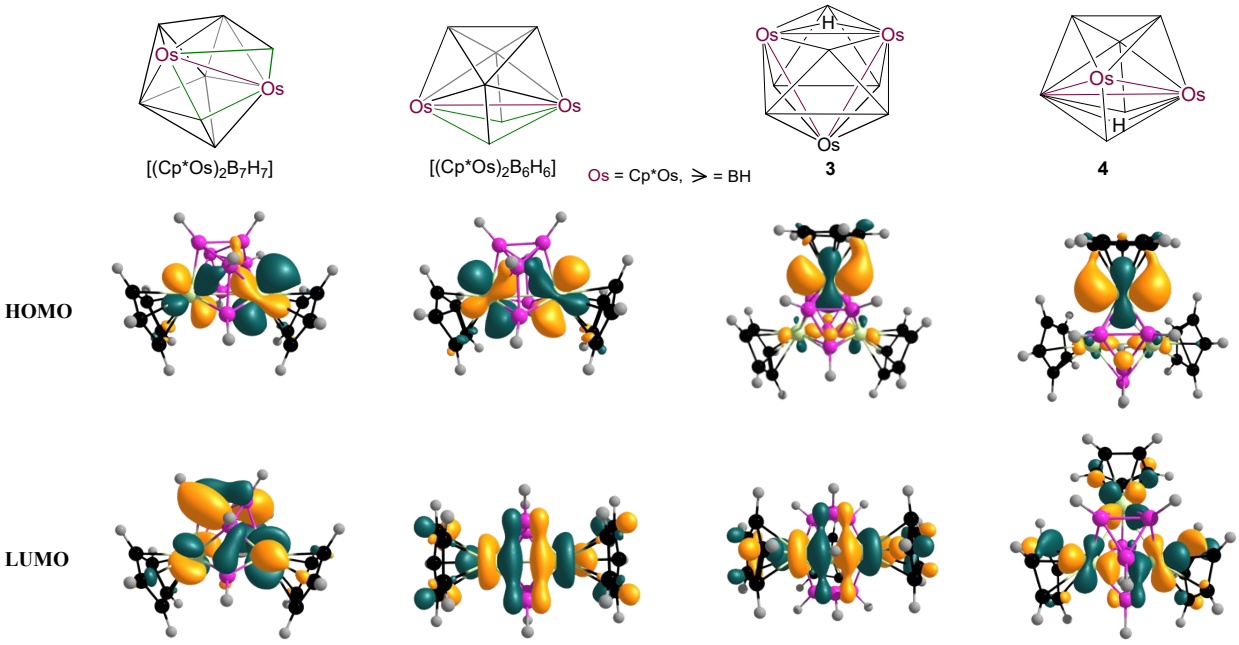

Figure S41. Frontier molecular orbitals of $[(Cp^*Os)_2B_7H_7]$, $[(Cp^*Os)_2B_6H_6]$, **3**, and **4**.

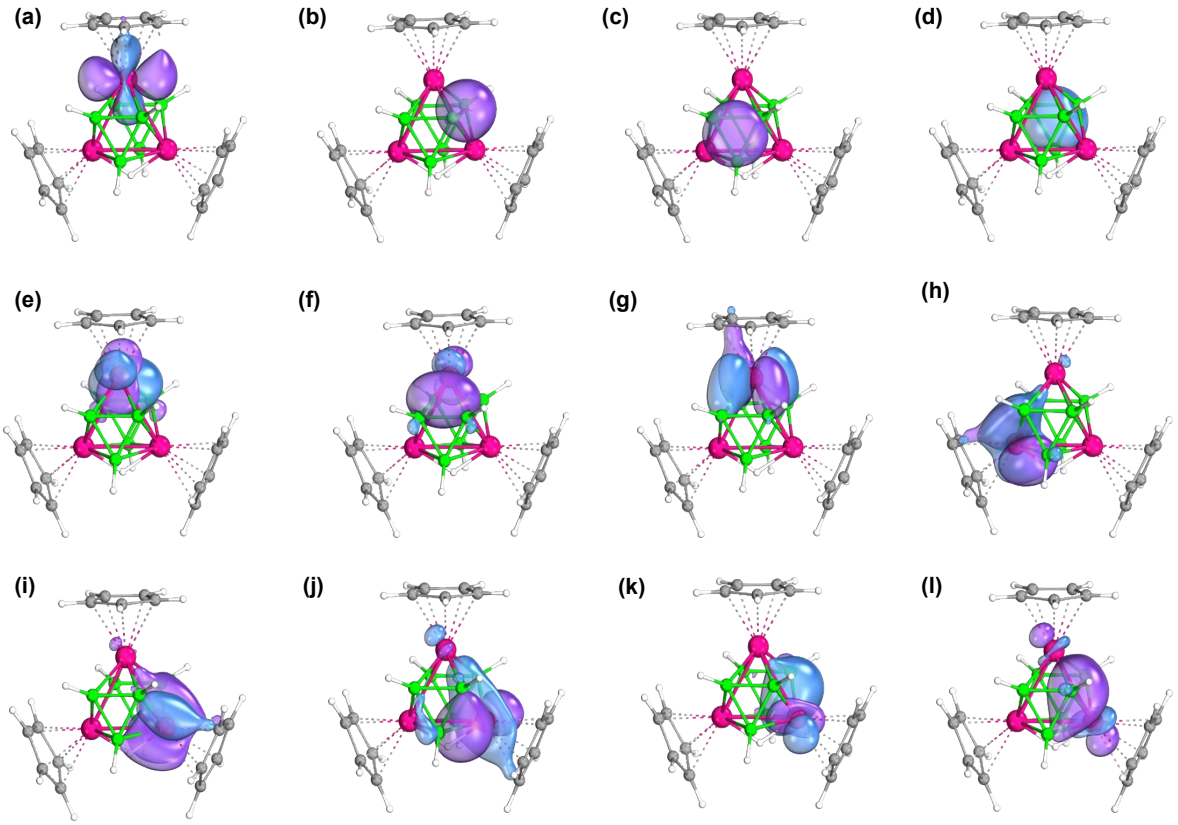

Figure S42. Selected localized orbitals of **3**: (a) a 1c-2e lone pair on osmium; (b) a 2c-2e B-H bond; (c-d) two 3c-2e B-B-B bond orbitals; and (e-l) multicenter osmium-boron and boron-boron bonding orbitals.

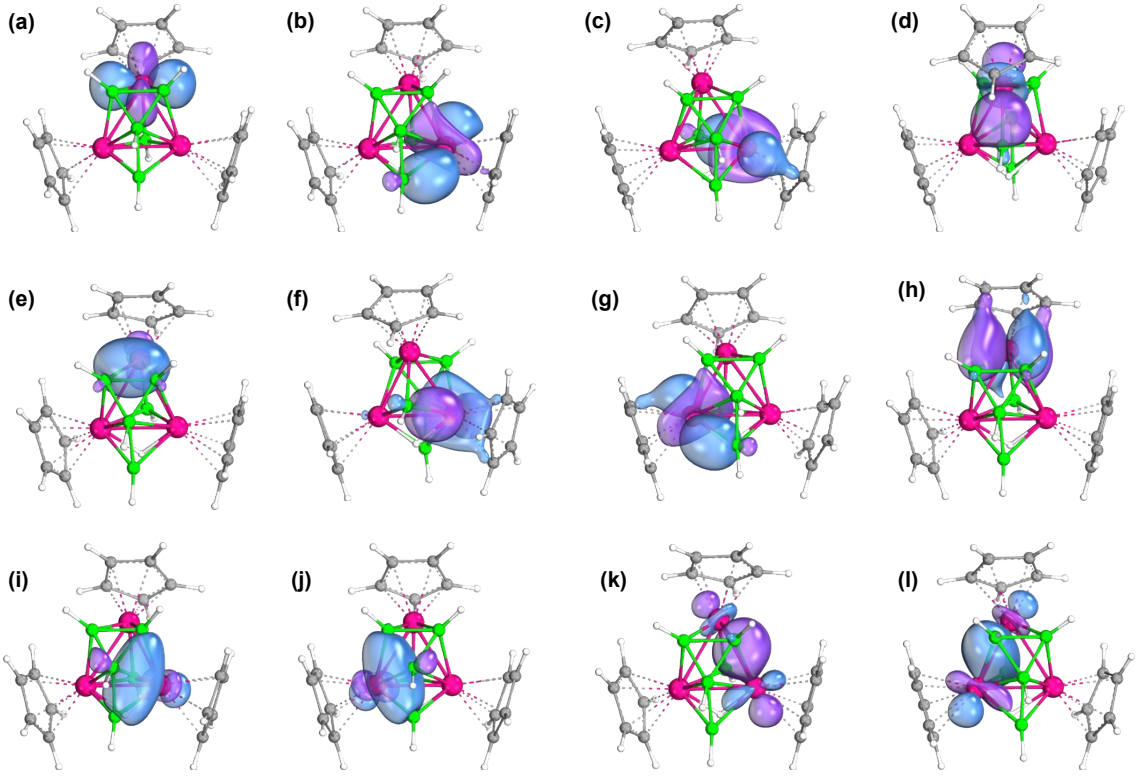

Figure S43. Selected localized orbitals of **4**: (a) a 1c-2e lone pair on osmium; (b-d) three 2c-2e Os-B bonding orbitals; (e) a 3c-2e Os-B-B bond orbital; and (f-l) multicenter osmium-boron and boron-boron bonding orbitals.

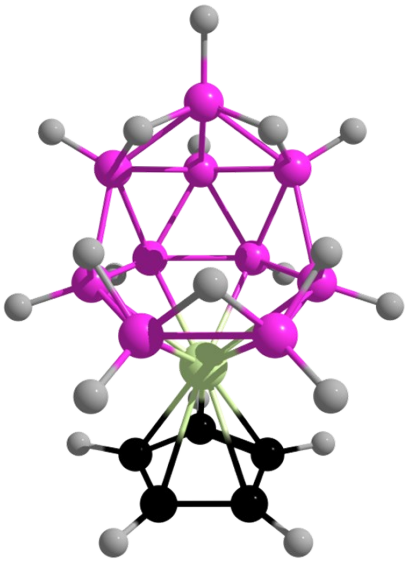

Figure S44. Optimized geometry of **1´**

T. E. = - 541.6766731 a. u.

Cartesian coordinates for the calculated structure of **1´** (in Å).

B	0.304848000	-0.904406000	1.897274000	H	4.916759000	0.000194000	0.352401000
B	0.304789000	0.909435000	1.894738000	H	3.365462000	2.469988000	-0.458578000
B	0.934753000	1.748268000	0.419018000	H	-0.347792000	-1.494671000	2.733118000
B	1.273724000	0.892638000	-1.084944000	H	3.374490000	-0.003158000	-2.381544000
B	1.273589000	-0.895371000	-1.082810000	H	0.947440000	1.590312000	-2.026256000
B	0.934596000	-1.746860000	0.423534000	H	1.419609000	-1.628408000	1.682141000
B	2.744170000	1.450545000	-0.265715000	H	0.947192000	-1.595427000	-2.022316000
B	2.820257000	-0.001751000	-1.307309000	H	3.182290000	0.979488000	0.923444000
B	2.743954000	-1.451493000	-0.262113000	H	-0.347780000	1.501918000	2.729073000
B	3.723113000	0.000016000	0.168033000	H	0.554336000	2.900433000	0.369032000
C	-2.594161000	-0.717949000	0.435992000	H	1.042366000	0.003424000	2.599661000
C	-2.593722000	0.721463000	0.432251000	H	1.419882000	1.632610000	1.677802000
C	-2.185786000	1.162723000	-0.874922000	H	0.554114000	-2.899155000	0.376641000
C	-1.937630000	-0.003940000	-1.677487000	H	-2.085306000	-2.210190000	-1.191288000
C	-2.186510000	-1.166254000	-0.868869000	H	-1.602129000	-0.006770000	-2.722340000
Os	-0.425891000	0.000187000	0.090176000	H	-2.084011000	2.204905000	-1.202790000
H	3.365135000	-2.471416000	-0.452806000	H	-2.868970000	1.369201000	1.273981000
H	3.182268000	-0.977718000	0.925820000	H	-2.869735000	-1.361127000	1.281105000

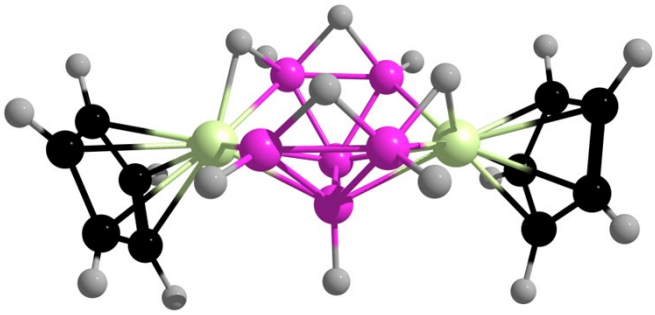

Figure S45. Optimized geometry of **2´**

T. E. = -723.5174469 a. u.

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

Os	1.974065000	0.150996000	-0.072950000	H	-0.046583000	2.222059000	-1.499209000
Os	-1.949359000	0.018757000	-0.169329000	H	-1.589903000	2.891178000	-0.449776000
C	3.399914000	-0.095698000	1.567113000	H	1.345806000	3.048573000	-0.399952000
C	4.004732000	0.846788000	0.622037000	H	0.165964000	-1.603575000	-1.927724000
C	4.253801000	0.149145000	-0.597980000	H	1.496531000	-2.733222000	-0.874669000
C	3.801063000	-1.201904000	-0.436320000	H	0.026270000	-1.532403000	1.547360000
C	3.311530000	-1.371246000	0.917090000	H	-1.272981000	-2.730608000	-1.078557000
C	-3.317133000	-0.202844000	1.657605000	H	-1.499040000	-0.558377000	-1.733202000
C	-3.650698000	-1.323564000	0.823743000	H	1.684230000	1.297225000	-1.394130000
C	-4.143910000	-0.811189000	-0.417637000	H	2.928459000	-2.298873000	1.357815000
C	-4.199909000	0.627919000	-0.340047000	H	3.837961000	-1.981398000	-1.205636000
C	-3.687661000	1.005853000	0.944127000	H	4.672385000	0.579936000	-1.516281000
B	-0.029322000	0.868913000	0.646562000	H	4.205098000	1.909595000	0.812240000
B	-1.010917000	1.821476000	-0.561252000	H	3.118098000	0.121038000	2.606009000
B	0.795352000	1.969415000	-0.560720000	H	-2.921806000	-0.250921000	2.680280000
B	0.948554000	-1.652296000	-0.823129000	H	-3.494637000	-2.381262000	1.070228000
B	0.001764000	-0.934058000	0.482555000	H	-4.451061000	-1.413585000	-1.282763000
B	-0.805890000	-1.612049000	-0.942841000	H	-4.578128000	1.304571000	-1.115807000
H	-0.032608000	1.131882000	1.844908000	H	-3.599816000	2.030349000	1.327768000

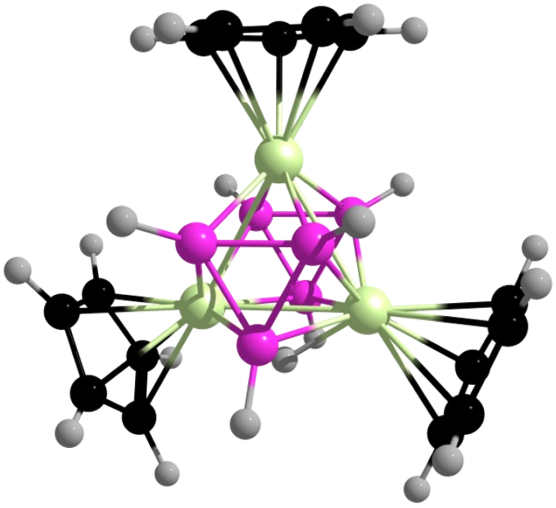

Figure S46. Optimized geometry of **3´**

T. E. = -1006.1239080 a. u.

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

Os	1.974065000	0.150996000	-0.072950000	H	-0.046583000	2.222059000	-1.499209000
Os	-1.949359000	0.018757000	-0.169329000	H	-1.589903000	2.891178000	-0.449776000
C	3.399914000	-0.095698000	1.567113000	H	1.345806000	3.048573000	-0.399952000
C	4.004732000	0.846788000	0.622037000	H	0.165964000	-1.603575000	-1.927724000
C	4.253801000	0.149145000	-0.597980000	H	1.496531000	-2.733222000	-0.874669000
C	3.801063000	-1.201904000	-0.436320000	H	0.026270000	-1.532403000	1.547360000
C	3.311530000	-1.371246000	0.917090000	H	-1.272981000	-2.730608000	-1.078557000
C	-3.317133000	-0.202844000	1.657605000	H	-1.499040000	-0.558377000	-1.733202000
C	-3.650698000	-1.323564000	0.823743000	H	1.684230000	1.297225000	-1.394130000
C	-4.143910000	-0.811189000	-0.417637000	H	2.928459000	-2.298873000	1.357815000
C	-4.199909000	0.627919000	-0.340047000	H	3.837961000	-1.981398000	-1.205636000
C	-3.687661000	1.005853000	0.944127000	H	4.672385000	0.579936000	-1.516281000
B	-0.029322000	0.868913000	0.646562000	H	4.205098000	1.909595000	0.812240000
B	-1.010917000	1.821476000	-0.561252000	H	3.118098000	0.121038000	2.606009000
B	0.795352000	1.969415000	-0.560720000	H	-2.921806000	-0.250921000	2.680280000
B	0.948554000	-1.652296000	-0.823129000	H	-3.494637000	-2.381262000	1.070228000
B	0.001764000	-0.934058000	0.482555000	H	-4.451061000	-1.413585000	-1.282763000
B	-0.805890000	-1.612049000	-0.942841000	H	-4.578128000	1.304571000	-1.115807000
H	-0.032608000	1.131882000	1.844908000	H	-3.599816000	2.030349000	1.327768000

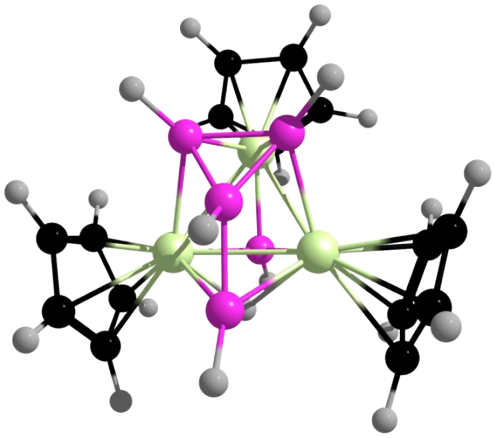

Figure S47. Optimized geometry of **4´**

T. E. = -980.6683821 a. u.

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

C	-1.170513000	3.362450000	0.669493000	C	-3.351754000	-0.133125000	0.838505000
C	-0.687230000	3.637148000	-0.658370000	C	2.950551000	-0.966449000	1.650067000
C	0.756367000	3.627243000	-0.622091000	C	2.801294000	-2.286256000	1.103156000
C	-0.024630000	3.187218000	1.525895000	C	3.184550000	-2.240833000	-0.285647000
Os	0.001870000	1.546009000	-0.106643000	C	3.577469000	-0.892889000	-0.599528000
B	-0.008590000	-2.419301000	-0.839700000	C	3.421188000	-0.105023000	0.597098000
B	-0.905087000	0.497282000	-1.750357000	H	2.750555000	-0.667206000	2.685449000
B	0.899677000	0.492950000	-1.749755000	H	3.621923000	0.968705000	0.684424000
B	-0.003890000	-0.992732000	-1.811506000	H	3.933733000	-0.527829000	-1.569896000
H	0.010789000	-2.009864000	-2.540969000	H	3.196853000	-3.091120000	-0.978465000
B	0.013610000	0.094275000	1.387638000	H	2.468726000	-3.177812000	1.649437000
Os	-1.365324000	-0.849416000	-0.071997000	H	-3.984415000	-0.146475000	-1.339965000
Os	1.354943000	-0.858521000	-0.054936000	H	-3.496673000	0.914537000	1.125255000
H	-0.004990000	-3.625783000	-0.892693000	H	-2.614702000	-1.077659000	2.757798000
H	-1.686451000	0.882284000	-2.602928000	H	-2.501620000	-3.377415000	1.289703000
H	1.702662000	0.865195000	-2.587737000	H	-3.334500000	-2.798211000	-1.245850000
H	0.003032000	0.006958000	2.601376000	H	2.199043000	3.309736000	1.094538000
C	1.165415000	3.346688000	0.728803000	H	1.424626000	3.812991000	-1.471894000
C	-2.876864000	-1.184068000	1.698543000	H	-1.309109000	3.828352000	-1.541576000
C	-2.812214000	-2.390629000	0.924438000	H	-2.222351000	3.344256000	0.980230000
C	-3.251725000	-2.085395000	-0.416106000	H	-0.053117000	2.983676000	2.603237000
C	-3.595127000	-0.687603000	-0.469854000	H	0.043590000	-1.603981000	0.764275000