Supporting information

An Electron-poor Di-Molybdenum Triple-decker with a puckered [B₄Ru₂] bridging ring is an *oblato-closo* Cluster†

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Experimental Details

I.   Supplementary Data

Fig. S1 Molecular structure of **2**. Selected bond lengths (Å) and angles (deg): Mo1-Mo_1 2.7510(5), Mo1-Ru1 2.6625(4), Mo_1-Ru1 2.9529(4), Mo1-B1 2.261(4), Mo1-B2 2.276(4), Mo1-B1 2.261(4), Mo1-B2 2.133(5), Mo_1-B2 2.133(5), Ru1-Ru_1 2.8822(5), B1-B2 1.622(5), B2-B_2 1.679(7), B1-Ru1 2.180(4), B1-H1 1.080(19), B2-H2 1.224(19), B1-B2-B_1 118.5(2), B2-B_1-Ru1 136.9(3), B1-Ru1-Ru_1 93.73(10), B2-B1-Mo1 75.5(2), Mo1-B1-Ru1 88.41(15), B2-B1-Mo1 64.2(2), Mo1-B1-Mo_1 79.08(13), Ru1-B1-Mo1 73.66(12), B1-B2-Mo1 60.9(2), Mo1-B2-Mo1 77.15(15), B1-Mo1-B2 85.32(16), B1-Mo1-B1 100.48(13), B1-Mo1-Ru1 103.59(11), B2-Mo1-Ru1 94.58(11), B1-Mo1-Mo_1 53.79(11), B2-Mo1-Mo_1 53.75(12).
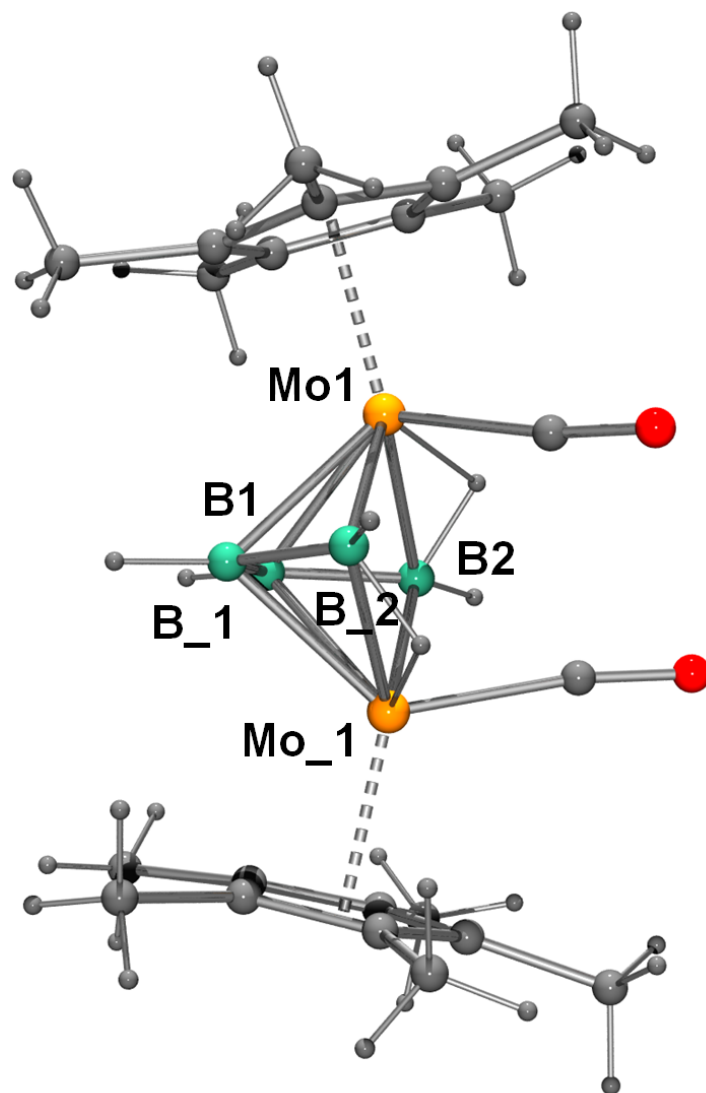
Fig. S2 Molecular structure of **3**. Selected bond lengths (Å) and angles (deg): B1-B2 1.63(3), B1-B_1 1.73(6), Mo1-Mo_1 2.9262(11), Mo1-B1 2.195(13), B_1-Mo1 2.211(14), Mo1-B2 2.222(14), B_2-Mo1 2.260(11), Mo1-B1 2.195(13), B1-H1 1.13(2), B2-H2 1.150(11), B2-H2A 1.156(11), B2-B1-B_1 120.6(10), B2-B1-Mo1 70.7(7), B1-B_1-Mo1 67.3(8), B2-B1-Mo1 68.8(7), B1-B_1-Mo1 66.4(11), Mo1-B1-Mo_1 83.2(5), B1-B2-Mo1 68.0(9), B1-B2-Mo1 66.4(7), Mo1-B2-Mo_1 81.5(4), B1-Mo1-B_1 46.3(15), B1 Mo1 B_2 82.8(10), B1-Mo1-B2 43.2(8), B1-Mo_1-B2 42.9(8), B1-Mo1-B2 81.6(9), B2-Mo_1-B2 98.5(4), B1-Mo1-Mo_1 48.6(4), B1-Mo_1-Mo1 48.1(3), B2-Mo1-Mo_1 49.8(3), B2-Mo_1-Mo1 48.7(3).
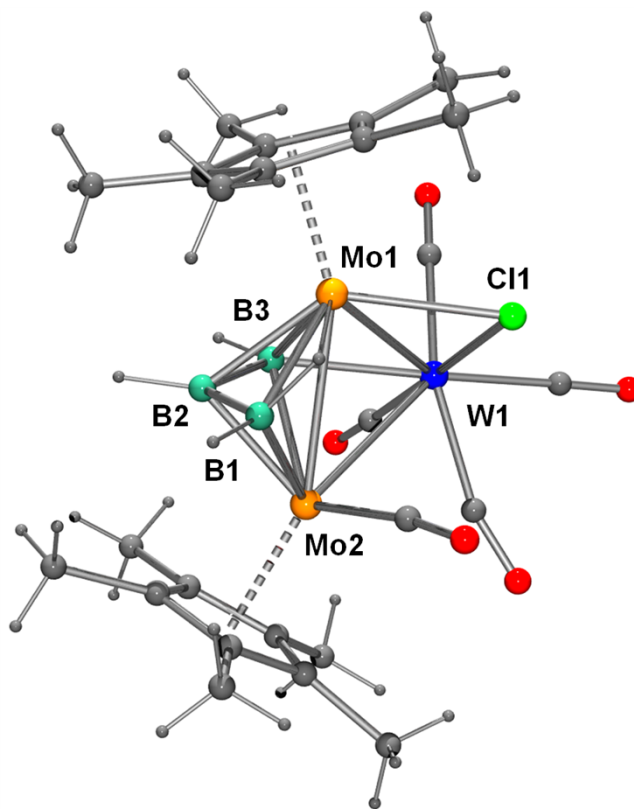
Fig. S3 Molecular structure of **4**. Selected bond lengths (Å) and angles (deg): Mo1-Mo2 2.9611(7), B1-B2 1.719(12), B2-B3 1.736(10), B3-W1 2.340(7), Mo1-B1 2.247(8), Mo1-B2 2.134(7), Mo1-B3 2.333(7), Mo2-B1 2.189(8), Mo2-B2 2.185(7), Mo2-B3 2.172(7), Mo1-W1 3.0004(6), Mo2-W1 2.9433(6), Mo2-Cl1 2.4246(15), W1-Cl1 2.5203(16), B3-H3 1.15(2), B1-H1D 1.13(2), B1-H1E 1.15(2), Mo2-H1E 1.77(7), B2-H2 1.15(2), B1-B2-B3 121.2(6), B2-B3-W1 131.8(5), Mo2-Cl1-W1 73.03(4), B2-B1-Mo2 66.7(4), B2-B1-Mo1 63.5(4), Mo2-B1-Mo1 83.7(3), B1-B2-Mo1 70.4(4), B3-B2-Mo1 73.4(4), B1-B2-Mo2 67.0(4), B3-B2-Mo2 66.1(3), Mo1-B2-Mo2 86.6(3), B2-B3-Mo2 66.9(3), B2-B3-Mo1 61.2(3), Mo2-B3-Mo1 82.1(2), Mo2-B3-W1 81.3(2), Mo1-B3-W1 79.9(2), Cl1-W1-Mo1 86.44(4), Mo2-W1-Mo1 59.752(14)
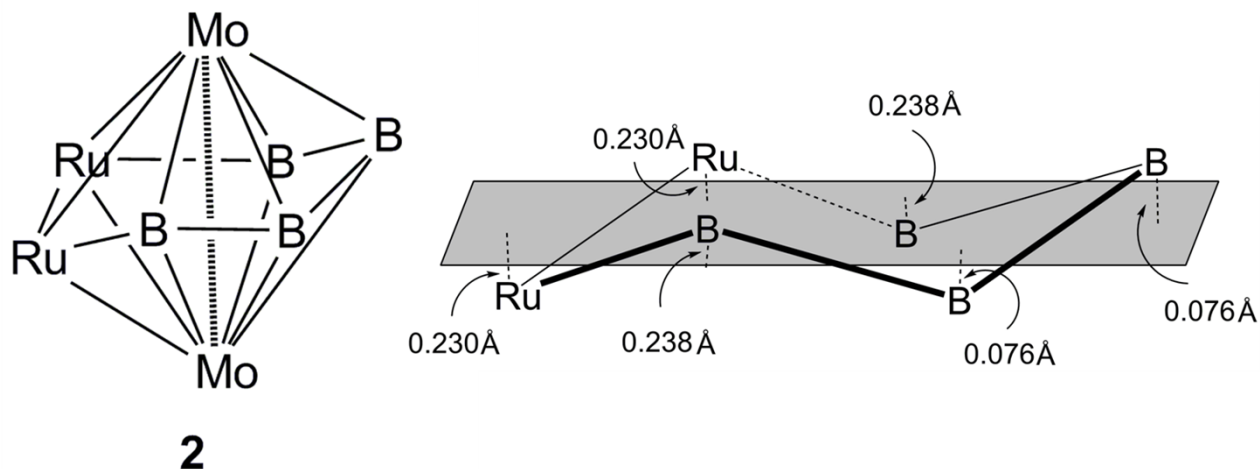
Fig. S4 Schematic representation of atomic deviations from the mean plane of $[Ru_2B_4]$ in **2**.

I.1   Experimental Section

General Considerations:

All the manipulations were conducted under an Ar atmosphere using standard Schlenk techniques. Solvent were distilled prior to use under Argon atmosphere. $[Cp*MoCl_4]$, $[Mo(CO)_5].thf$ and $[W(CO)_5].thf$ were prepared according to literature methods,[1] while other chemicals such as, $[LiBH_4]$ 2.0 M in THF, Cp*H, n-BuLi, $[Mo(CO)_6]$, $[W(CO)_6]$ and $[Ru_3(CO)_{12}]$ were obtained commercially (Aldrich) and used as received. MeI was purchased from Aldrich and freshly distilled prior to use. The external reference for the ^{11}B NMR, $[Bu_4N(B_3H_8)]$ was synthesized with the literature method.[2] Preparative thin layer chromatography (TLC) was carried on 250 mm dia aluminum supported silica gel TLC plates (MERCK TLC Plates). NMR spectra were recorded on 400 and 500 MHz Bruker FT-NMR spectrometer. The residual solvent protons were used as reference (δ, ppm, $CDCl_3$, 7.26), while a sealed tube containing $[Bu_4N(B_3H_8)]$ in $[D_6]$benzene (δ_B, ppm, -30.07) was used as an external reference for the ^{11}B NMR. Infrared spectra were recorded on a Nicolet iS10 spectrometer. The photo-reactions described in this report were conducted in a Luzchem LZC-4 V photo reactor, with irradiation at 254−350 nm. MALDI-

TOF mass spectra were recorded on a Bruker Ultraflextreme by using 2,5-dihydroxybenzoic acid as a matrix and a groundsteel target plate and CH analyses were obtained on Perkin Elmer Instruments series II model 2400.

I.2 Synthetic Section

Preparation of [(Cp*Mo)$_2${μ-η^6:η^6-B$_4$H$_4$Ru$_2$(CO)$_6$}] (2):

In a flame-dried Schlenk tube [Cp*MoCl$_4$], (0.1 g, 0.27 mmol) in 10 mL of toluene was treated with 5-fold excess of [LiBH$_4$.thf] (0.7 mL, 1.4 mmol) at -40°C and allowed to stir at room temperature for one hour. After removal of toluene, the residue was extracted into hexane and filtered through a frit using Celite. The brownish-green hexane extract was dried and taken in 10 mL of toluene and heated at 90 °C for 72 hours wth [Ru$_3$(CO)$_{12}$] (0.18 g, 0.28 mmol). The volatile components were removed under vacuum and the remaining residue was extracted into hexane and passed through celite. After removal of solvent, the residue was subjected to chromatographic work up using silica gel TLC plates. Elution with a hexane/CH$_2$Cl$_2$ (90:10 v/v) mixture yielded brown **2** (0.01 g, 4%).

2: MS(MALDI): m/z 908 [M+Na]$^+$. isotope envelope C$_{26}$H$_{34}$B$_4$O$_6$Mo$_2$Ru$_2$Na requires 908. ^{11}B NMR (22 °C, 128 MHz, [D$_6$]-benzene): δ = 91.3 (br, 2B). ^{1}H NMR (22 °C, 400 MHz, [D$_6$]-benzene): δ = 7.81 (B-H$_t$), 1.91 (s, 30H, 2Cp*),^{13}C NMR (22 °C, 100 MHz, [D$_6$]-benzene): δ = 188.3, 183 (*C*O), 97.0 (*C*$_5$Me$_5$), 14.1 (C$_5$*Me*$_5$). IR vbar/cm^{-1}: 2403 (B-H$_t$), 1799, 1743 (CO).

Preparation of [(Cp*MoCO)$_2$B$_4$H$_6$] (3):

In a flame-dried Schlenk tube [Cp*MoCl$_4$], (0.1 g, 0.27 mmol) in 10 mL of toluene was treated with 5-fold excess of [LiBH$_4$.thf] (0.7 mL, 1.4 mmol) at -40 °C and allowed to stir at room temperature for one hour. After removal of toluene, the residue was extracted into hexane and filtered through a frit using Celite. The brownish-green hexane extract was dried and taken in 10 mL of thf. The resulting solution was heated at 65 °C with previously made [Mo(CO)$_5$].thf for 24 hours. The solvent was evaporated in vacuo and residue was extracted into hexane and passed through Celite. After removal of solvent from the filtrate, the residue was subjected to chromatographic workup using silica gel TLC plates. Elution with a hexane/CH$_2$Cl$_2$ (80:20 v/v) mixture yielded **3** (0.06 g, 40%).

3: MS(MALDI): m/z 572 $[M]^+$. isotope envelope $C_{22}H_{36}B_4O_2Mo_2$ requires 572. ^{11}B NMR (22 °C, 128 MHz, $[D_6]$-benzene): δ = 15.8 (br, 2B), 63.7 (br, 2B). ^1H NMR (22 °C, 400 MHz, $[D_6]$-benzene): δ = 4.56 (br, 4H, BH_t), 1.94 (s, 30H, 2Cp*), -9.81 (br, 2H, Mo–H–B). ^{13}C NMR (22 °C, 100 MHz, $[D_6]$-benzene): δ = 185 (CO), 102.3 (C_5Me_5), 10.3 (C_5Me_5). IR (hexane) v/cm^{-1}: 2417w (BH_t), 1912 (CO). Elemental analysis (%) calcd for $^{12}C_{22}{}^1H_{36}{}^{11}B_4{}^{16}O_2{}^{96}Mo_2$: C, 46.54; H, 6.39. Found: C, 46.28; H, 6.12.

Preparation of [(Cp*MoCO)(Cp*MoCl)(µ-H)B₃H₃W(CO)₄] (4):

In a flame-dried Schlenk tube [Cp*MoCl₄], (0.1 g, 0.27 mmol) in 10 mL of toluene was treated with 5-fold excess of [LiBH₄.thf] (0.7 mL, 1.4 mmol) at -40°C and allowed to stir at room temperature for one hour. After removal of toluene, the residue was extracted into hexane and filtered through a frit using Celite. The brownish-green hexane extract was dried in vacuo, extracted with 10 mL of thf and heated at 65°C with [W(CO)₅] thf for 24 hours. The solvent was evaporated in vacuo and residue was extracted into hexane and passed through Celite. After removal of solvent from the filtrate, the residue was subjected to chromatographic workup using silica gel TLC plates. Elution with a hexane/CH₂Cl₂ (80:20 v/v) mixture yielded **4** (0.025 g, 10%) along with **3** (0.01 g, 6%)

4: MS(MALDI): m/z 806 $[M-2CO]^+$. isotope envelope $C_{23}H_{34}B_3O_3Cl_1Mo_2W_1$ requires 806. ^{11}B NMR (22 °C, 128 MHz, $[D_6]$-benzene): δ = 75.4 (br, 1B), 99.2 (br, 1B), 106.6 (br, 1B). ^1H NMR (22 °C, 400 MHz, $[D_6]$-benzene): δ = 6.1, (br, 3H, BH_t), 1.8 (s, 30H, 2Cp*), -8.04 (br, 1H, Mo–H–B). ^{13}C NMR (22 °C, 100 MHz, $[D_6]$-benzene): δ = 193, 183 (CO), 103.5 (C_5Me_5), 10.2 (C_5Me_5). IR (hexane) v/cm^{-1}: 2403w (BH_t), 2002, 1894, 1836 (CO). Elemental analysis (%) calcd for $^{12}C_{25}{}^1H_{34}{}^{11}B_3{}^{16}O_5{}^{35.5}Cl_1{}^{96}Mo_2{}^{184}W_1$: C, 34.98; H, 3.99. Found: C, 35.19; H, 3.79.

Preparation of [(Cp*Mo)₂(CO)₄(µ₄-B)Ru₂(CO)₆(µ-H)] (5):

In a flame-dried Schlenk tube, a green solution of **3** (0.1 g, 0.17 mmol) and Ru₃(CO)₁₂ (0.11 g, 0.17 mmol) in toluene (15 mL) was thermolysed for 72 hours at 90°C temperature. The volatile components were removed under vacuum and the remaining residue was extracted into hexane and passed through celite. After removal of solvent, the residue was subjected to chromatographic work up using silica gel TLC plates. Elution with a hexane/CH₂Cl₂ (80:20 v/v) mixture yielded orange solid **5** (0.013 g, 8%).

5: MS(MALDI): m/z 962 [M]$^+$. isotope envelope $C_{30}H_{31}B_1O_{10}Mo_2Ru_2$ requires 962. ^{11}B NMR (22 °C, 128 MHz, [D_6]-benzene): δ 128.4 (s, 1B). ^{1}H NMR (22 °C, 400 MHz, [D_6]-benzene): δ 2.04 (s, 30H, 2Cp*), -18.9 (s, 1H, Ru-H-Ru). ^{13}C NMR (22 °C, 100 MHz, [D_6]-benzene): δ 196.1, 191.3 (CO), 99.7 (*C*5Me5), 11.6 (C5*Me5*). IR vbar/cm^{-1}: 2046, 2017, 1976 (CO). Elemental analysis (%) calcd for $^{12}C_{30}{}^1H_{31}{}^{11}B_{116}O_{10}{}^{96}Mo_2{}^{101}Ru_2$: C, 37.67; H, 3.26. Found: C, 37.75; H, 3.20.

I.3 *Crystal structure determination*

Suitable X-ray quality crystals of **2-4** and **5** were grown by slow diffusion of a hexane:CH_2Cl_2 solution. The crystal data for **2-4** and **5** were collected and integrated using a Bruker Axs kappa apex2 CCD diffractometer, with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation at 173 K. The structures were solved by heavy atom methods using SHELXS-97 or SIR92[3a] and refined using SHELXL-97[3].

Crystal data for **2**: $C_{26}H_{34}B_4O_6Mo_2Ru_2$, M_r = 879.79, Monoclinic space group $C2/c$, a = 17.5892(4) Å, b = 15.9899(4) Å, c = 11.2183(3) Å, β = 102.02°, V = 3085.94 Å^3, Z = 4, ρ_{calcd}= 1.894 g•cm^{-3}, μ = 14.589 mm^{-1}, $F(000)$ = 1720, R$_1$= 0.0317, wR^2= 0.0872, 3019 independent reflections [2θ≤72.47°] and 192 parameters.

Crystal data for **3**: $C_{22}H_{36}B_4O_2Mo_2$, M$_r$ = 587.84, Tetragonal space group $P4_32_12$, a = 9.004(3) Å, b = 9.004(3) Å, c = 31.305(10) Å, β = 90°, V = 2538.06 Å^3, Z = 3, ρ_{calcd}= 2.826 g•cm^{-3}, μ = 5.103 mm^{-1}, $F(000)$ = 1978, R$_1$= 0.0371, wR^2= 0.0952, 2237 independent reflections [2θ≤50°] and 145 parameters.

Crystal data for **4**: $C_{25}H_{34}B_3O_5Cl_1Mo_2W_1$, M$_r$ = 858.13, Monoclinic space group $P2_1/n$, a = 9.005(8) Å, b = 18.588(14) Å, c = 17.767(14) Å, β = 99.38°, V = 2934.6 Å^3, Z = 4, ρ_{calcd}= 1.942 g•cm^{-3}, μ = 4.876 mm^{-1}, $F(000)$ = 1656, R$_1$= 0.0347, wR^2= 0.0686, 5173 independent reflections [2θ≤50°] and 350 parameters.

Crystal data for **5**: $C_{30}H_{31}B_1O_{10}Mo_2Ru_2$, M$_r$ = 955.37, Orthorhombic space group $Pccn$, a = 17.2668(7) Å, b = 30.7845(13) Å, c = 12.5659(6) Å, β = 90°, V = 6679.4 Å^3, Z = 8, ρ_{calcd}= 1.900 g•cm^{-3}, μ = 1.674 mm^{-1}, $F(000)$ = 3736, R$_1$= 0.0361, wR^2= 0.0816, 4726 independent reflections [2θ≤46.36°] and 416 parameters.
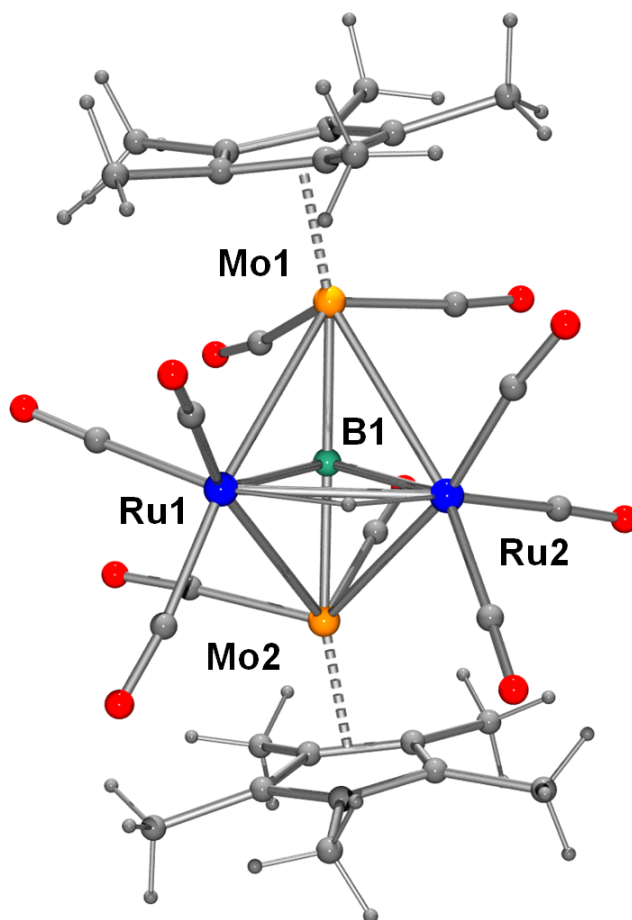
Fig. S5 Molecular structure of (**5**). Selected bond lengths (Å) and angles (deg): B1-Mo2 2.114(7), B1-Mo1 2.131(7), B1-Ru2 2.177(7), B1-Ru1 2.191(7), Mo1-Ru1 2.9782(8), Mo1-Ru2 3.0351(8), Mo2-Ru2 2.9858(7), Mo2-Ru1 3.0377(7), Ru1-Ru2 2.8293(7), Ru1-H1 1.81(6), Ru2-H1 1.62(6), Mo2-B1-Mo1 176.4(4), Mo2-B1-Ru2 88.2(3), Mo1-B1-Ru2 89.6(3), Mo2-B1-Ru1 89.7(3), Mo1-B1-Ru1 87.1(3), Ru2-B1-Ru1 80.7(2), B1-Mo1-Ru1 47.28(19), B1-Mo1-Ru2 45.83(19), Ru1-Mo1-Ru2 56.125(17), B1-Mo2-Ru2 46.79(19), B1-Mo2-Ru1 46.15(19), Ru2-Mo2-Ru1 56.022(16), B1-Ru1-Ru2 49.42(18), B1-Ru1-Mo1 45.61(19), Ru2-Ru1-Mo1 62.954(18), B1-Ru1-Mo2 44.10(19), Ru2-Ru1-Mo2 61.060(17), Mo1-Ru1-Mo2 89.691(19), B1-Ru2-Ru1 49.84(18), B1-Ru2-Mo2 45.04(19)

I.4   *Computational Method*

Geometry optimizations and electronic structure calculations were carried out on Gaussian09 (rev. C.01) program package[4] using BP86 functional[5] (composed of the Becke 1988 exchange functional and the Perdew 86 correlation functional) and def2-TZVP[6] basis set from EMSL Basis Set Exchange Library. The 28 core electrons of molybdenum, ruthenium and tungsten were replaced by the quasi-relativistic effective core potential def2-ECP[7]. To save computing time all the calculations were carried out with the Cp analogue model compounds, instead of Cp*. The model compounds were fully optimized in gaseous state (no solvent effect) without any symmetry constraints. Vibrational analysis was carried out for all structures, and the absence of any imaginary frequency confirmed that all structures represent minima on the potential energy hypersurface. The NMR chemical shifts were calculated on the BP86/def2-TZVP optimized geometries using the gradient corrected hybrid functional hybrid Becke−Lee−Yang−Parr (B3LYP) functional.[8] Computation of the NMR shielding tensors employed gauge-including atomic orbitals (GIAOs)[9]. The ^{11}B NMR chemical shifts were calculated relative to B_2H_6 (B3LYP B shielding constant 84.23 ppm) and converted to the usual $[BF_3.OEt_2]$ scale using the experimental $\delta(^{11}B)$ value of B_2H_6, 16.6 ppm[10] Population analysis was performed using natural bond orbital (NBO)[11, 12] as implemented in Gaussian09.

II. *Supplementary Data*

Table S1. Selected bond parameters for the compounds **2′-4′** optimized at the BP86/def2-TZVP Level.

	2′		3′		4′	
	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
d(Mo-Mo)	2.751	2.748	2.926	2.947	2.961	2.997
d(B1-B2)	1.622	1.625	1.626	1.658	1.719	1.739
d(B2-B_2)	1.679	1.681	1.736	1.718	-	-
d(B2-B3)	-	-	-	-	1.736	1.734
d(B3-W1)	-	-	-	-	2.339	2.356
d(Ru-Ru)	2.882	3.06	-	-	-	-
d(Ru-B)	2.180	2.24	-	-	-	-

Table S2. DFT calculated and experimental ^{11}B chemical shifts δ (ppm) and IR (cm^{-1}, uncorrected) stretching values for **2′-4′** at BP86/def2-TZVP.

Compound	2′		3′		4′	
^{11}B NMR	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
B1	91.3	93.3	15.8	15.1	75.4	72.5
B2	91.3	87.5	63.7	67.4	106.6	110.5
B3	-	-	-	-	99.2	93.2
IR-values						
CO$_t$	1799, 1743	1852 1780	1912.7, 1869.3	1916.3, 1874.7	1894, 2002	1894.1, 1899.8, 1937.5, 1993.1
CO$_{br}$	-	-	-	-	1836	1830.8

Table S3. DFT calculated energies of the HOMO and LUMO (eV), HOMO-LUMO gaps (ΔE = E_{LUMO} - E_{HOMO}, eV) for the compounds **2'-4'** and **[(Cp*Mo)$_2$B$_4$H$_8$]**.

Compound	2'	3'	4'	[(Cp*Mo)$_2$B$_4$H$_8$]
HOMO	-5.934	-4.515	-4.659	-3.409
LUMO	-5.039	-2.597	-3.342	-2.327
ΔE	0.859	1.918	1.317	1.082

Fig. S6 Comparison of the MO diagram of **2** with **[Cp$_3$Ni$_2$]$^+$**, **[(CpMo)$_2$P$_6$]**, **[(CpRe)$_2$B$_6$H$_6$]** and **[(CpTi)$_2$P$_6$]**.

Cartesian coordinates (xyz) for all the optimized geometries of 2′-4′ and [(Cp*Mo)₂B₄H₈] calculated at BP86(def2-TZVP level.)

Fig. S7 Optimized geometry of **2′** Complex.

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

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.710715	-1.966580	1.592412
2	6	0	-1.180834	-1.491497	2.220377
3	6	0	-0.375443	-3.502299	0.500395
4	6	0	2.544379	-0.781206	-2.929109
5	6	0	3.012665	-1.329480	-1.699438
6	6	0	3.439381	-0.290452	-0.883747
7	6	0	3.243861	0.926713	-1.588248
8	6	0	2.690127	0.621042	-2.862235
9	5	0	-0.647631	-1.713168	-1.321272

10	1	0	-0.745233	-2.729336	-1.914038
11	5	0	-0.968407	-0.467622	-2.620754
12	1	0	-1.216725	-0.929161	-3.685411
13	8	0	2.729521	-2.272287	2.009732
14	8	0	-1.959942	-1.458642	3.066990
15	8	0	-0.575810	-4.604643	0.390098
16	42	0	1.028512	-0.000153	-1.283324
17	44	0	0.004382	-1.622421	0.709009
18	6	0	-0.664634	1.550894	2.414846
19	6	0	2.122186	1.012440	2.071872
20	6	0	0.883800	3.302154	0.898252
21	6	0	-3.494202	1.752466	-0.953700
22	6	0	-3.546022	1.108073	0.381393
23	6	0	-3.784857	-0.314277	0.208383
24	6	0	-3.883442	-0.574075	-1.193190
25	6	0	-3.709070	0.671787	-1.902656
26	5	0	-0.385793	1.956520	-1.007105
27	1	0	-0.497872	3.116310	-1.249615
28	5	0	-0.270931	1.114160	-2.501827
29	1	0	-0.333104	1.772232	-3.495914
30	8	0	-1.384488	1.754209	3.286768
31	8	0	3.056576	0.808810	2.687709
32	8	0	1.097082	4.410941	0.889746
33	42	0	-1.630160	0.232056	-0.806959
34	44	0	0.566543	1.384748	0.940384
35	1	0	2.154858	-1.325910	-3.766012
36	1	0	3.047079	-2.381340	-1.448329
37	1	0	3.864045	-0.393511	0.092022
38	1	0	3.504624	1.922873	-1.229082
39	1	0	2.458182	1.317800	-3.640261
40	1	0	-3.744993	0.800955	-2.968504
41	1	0	-3.353184	2.810828	-1.171191
42	1	0	-4.062160	-1.552774	-1.650066
43	1	0	-3.878700	-1.046396	0.999658
44	1	0	-3.439659	1.604337	1.298182

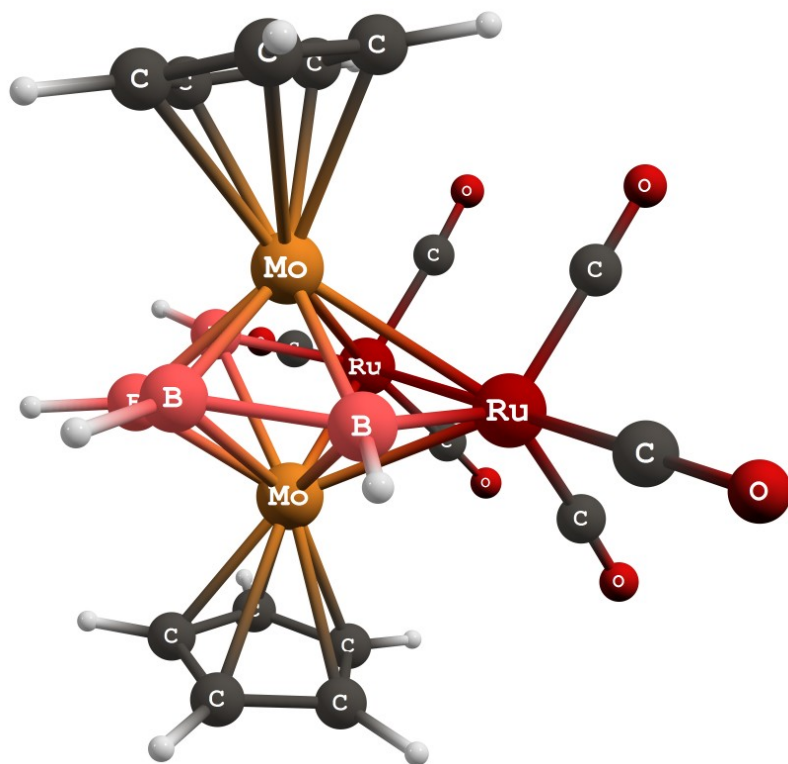---
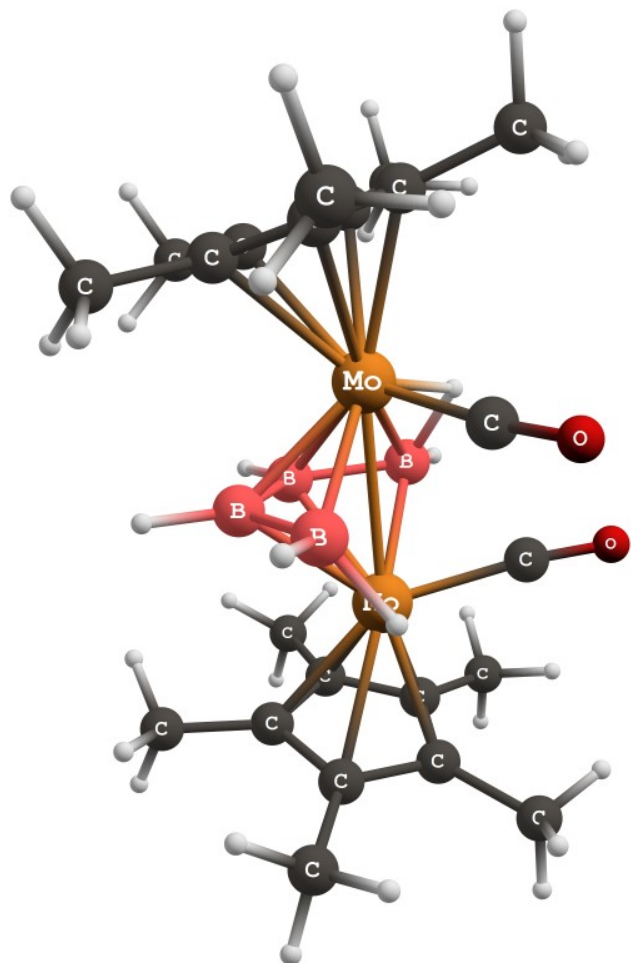
Fig. S8 Optimized geometry of **3′**.

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

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	5	0	-0.072512	1.377660	-0.826047
2	1	0	-0.143566	2.370040	-1.506440
3	5	0	0.125222	-0.066156	1.756240
4	6	0	-3.195245	1.219823	-0.846938
5	6	0	-3.163207	1.482471	0.570597
6	6	0	-3.484045	0.260917	1.255522
7	6	0	-3.717668	-0.760300	0.269340
8	6	0	-3.540321	-0.159823	-1.037186
9	6	0	-3.834252	-0.813752	-2.355966
10	1	0	-3.192910	-0.413492	-3.152368
11	1	0	-4.884100	-0.638031	-2.646892

12	1	0	-3.676838	-1.899744	-2.318180
13	6	0	-3.094243	2.252976	-1.927616
14	1	0	-4.089017	2.687893	-2.128433
15	1	0	-2.720312	1.822574	-2.865504
16	1	0	-2.418540	3.069738	-1.644361
17	6	0	-2.990986	2.831043	1.202590
18	1	0	-2.243612	3.434228	0.670418
19	1	0	-2.667090	2.749643	2.248180
20	1	0	-3.947150	3.382934	1.188470
21	6	0	-3.663661	0.111185	2.738910
22	1	0	-2.958363	0.739480	3.299168
23	1	0	-3.516133	-0.927521	3.062555
24	1	0	-4.684415	0.409634	3.032739
25	6	0	-4.239832	-2.142134	0.540755
26	1	0	-3.877422	-2.532128	1.501390
27	1	0	-3.938732	-2.853703	-0.239109
28	1	0	-5.342725	-2.134874	0.578507
29	6	0	-1.161481	-1.902070	-0.771934
30	1	0	-0.960498	-0.851203	1.671717
31	42	0	-1.471157	-0.132968	0.082744
32	8	0	-1.129511	-2.942560	-1.308271
33	5	0	0.072508	1.377649	0.826063
34	1	0	0.143556	2.370021	1.506468
35	5	0	-0.125222	-0.066136	-1.756240
36	6	0	3.195247	1.219809	0.846955
37	6	0	3.163207	1.482482	-0.570574
38	6	0	3.484042	0.260940	-1.255522
39	6	0	3.717666	-0.760295	-0.269360
40	6	0	3.540323	-0.159841	1.037178
41	6	0	3.834251	-0.813798	2.355945
42	1	0	3.192923	-0.413538	3.152358
43	1	0	4.884104	-0.638103	2.646866
44	1	0	3.676814	-1.899786	2.318142
45	6	0	3.094247	2.252942	1.927653
46	1	0	4.089019	2.687861	2.128471
47	1	0	2.720324	1.822521	2.865535
48	1	0	2.418537	3.069705	1.644416
49	6	0	2.990986	2.831064	-1.202545
50	1	0	2.243637	3.434254	-0.670342
51	1	0	2.667057	2.749682	-2.248126
52	1	0	3.947158	3.382942	-1.188447
53	6	0	3.663654	0.111235	-2.738914
54	1	0	2.958359	0.739543	-3.299159
55	1	0	3.516122	-0.927465	-3.062578
56	1	0	4.684409	0.409685	-3.032739
57	6	0	4.239827	-2.142126	-0.540799
58	1	0	3.877422	-2.532098	-1.501444
59	1	0	3.938718	-2.853710	0.239048

60	1	0	5.342720	-2.134870	-0.578542
61	6	0	1.161474	-1.902074	0.771910
62	1	0	0.960500	-0.851182	-1.671727
63	42	0	1.471156	-0.132964	-0.082747
64	8	0	1.129537	-2.942554	1.308270
65	1	0	-0.402968	-0.129992	-2.924720
66	1	0	0.402968	-0.130023	2.924719
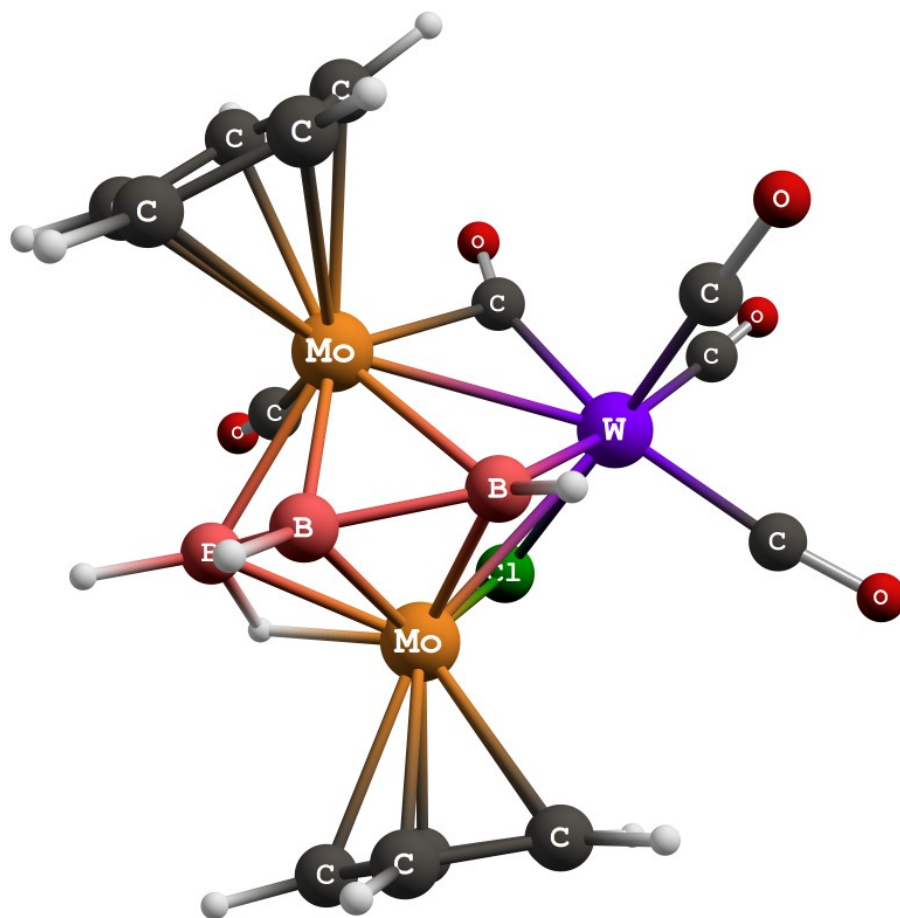
Fig. S9. Optimized geometry of **4′**.

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

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z

1	6	0	-4.225459	1.425546	0.743037
2	1	0	-4.238896	1.967737	-0.210222
3	1	0	-3.632200	2.007267	1.460197

4	1	0	-5.261739	1.394509	1.121558
5	6	0	-3.710766	0.025432	0.584516
6	6	0	-3.170946	-0.785967	1.635150
7	6	0	-2.986904	-2.118127	1.113521
8	6	0	-3.392825	-2.121458	-0.264598
9	6	0	-3.842507	-0.790739	-0.594668
10	6	0	-3.005149	-0.382941	3.069251
11	1	0	-2.157914	-0.899470	3.539938
12	1	0	-3.913471	-0.635292	3.644138
13	1	0	-2.835421	0.695984	3.172177
14	6	0	-2.713382	-3.343712	1.931061
15	1	0	-2.155940	-3.110443	2.846305
16	1	0	-2.141556	-4.095546	1.371275
17	1	0	-3.671220	-3.805064	2.228800
18	6	0	-3.538500	-3.339789	-1.128236
19	1	0	-3.477143	-3.093091	-2.196232
20	1	0	-4.517271	-3.818941	-0.953413
21	1	0	-2.759700	-4.083246	-0.912304
22	6	0	-4.550418	-0.408127	-1.862133
23	1	0	-4.186499	-0.984794	-2.723057
24	1	0	-4.425387	0.654686	-2.098590
25	1	0	-5.630905	-0.608245	-1.761417
26	6	0	2.584725	-2.859639	2.474851
27	1	0	1.989621	-2.291937	3.201820
28	1	0	3.520165	-3.169684	2.972935
29	1	0	2.024336	-3.767104	2.217653
30	6	0	2.913606	-2.041259	1.265465
31	6	0	3.139816	-2.548061	-0.060299
32	6	0	3.671275	-1.480045	-0.858731
33	6	0	3.808418	-0.321841	-0.011607
34	6	0	3.327708	-0.662195	1.295641
35	6	0	2.980652	-3.977511	-0.483518
36	1	0	2.891752	-4.072462	-1.573661
37	1	0	2.091136	-4.438830	-0.033407
38	1	0	3.860461	-4.563265	-0.168146
39	6	0	4.156928	-1.577123	-2.274885
40	1	0	4.035216	-0.625146	-2.808950
41	1	0	3.621207	-2.351344	-2.840376
42	1	0	5.230052	-1.833984	-2.294426
43	6	0	4.490381	0.947911	-0.419465
44	1	0	4.058810	1.369196	-1.339216
45	1	0	5.556525	0.746275	-0.616501
46	1	0	4.434278	1.713776	0.362060
47	6	0	3.444230	0.155889	2.544929
48	1	0	3.585450	1.220614	2.328816
49	1	0	4.311231	-0.186083	3.136055
50	1	0	2.550143	0.057128	3.175142
51	6	0	1.802762	2.759844	0.780525

52	6	0	-0.151904	3.663682	-0.751502
53	6	0	-0.796222	2.421021	1.620122
54	6	0	-1.523257	1.530361	-1.166176
55	6	0	-1.206372	-1.078975	-2.060163
56	5	0	-0.070708	-2.431240	-0.562694
57	5	0	-0.075619	-1.807190	1.061046
58	5	0	0.198036	-0.122061	1.364548
59	8	0	2.652505	3.404761	1.248285
60	8	0	-0.388316	4.714939	-1.177551
61	8	0	-1.353472	2.798442	2.576239
62	8	0	-2.336307	1.881197	-1.941296
63	8	0	-1.176246	-1.353094	-3.197944
64	17	0	1.445081	0.812478	-2.000108
65	42	0	-1.520762	-0.719797	-0.142343
66	42	0	1.471809	-0.875024	-0.230521
67	74	0	0.182014	1.807500	0.012912
68	1	0	-0.283945	-3.594835	-0.786502
69	1	0	-0.125563	-2.590621	1.966807
70	1	0	0.295835	0.036084	2.557997
71	1	0	0.899947	-2.149060	-1.389486

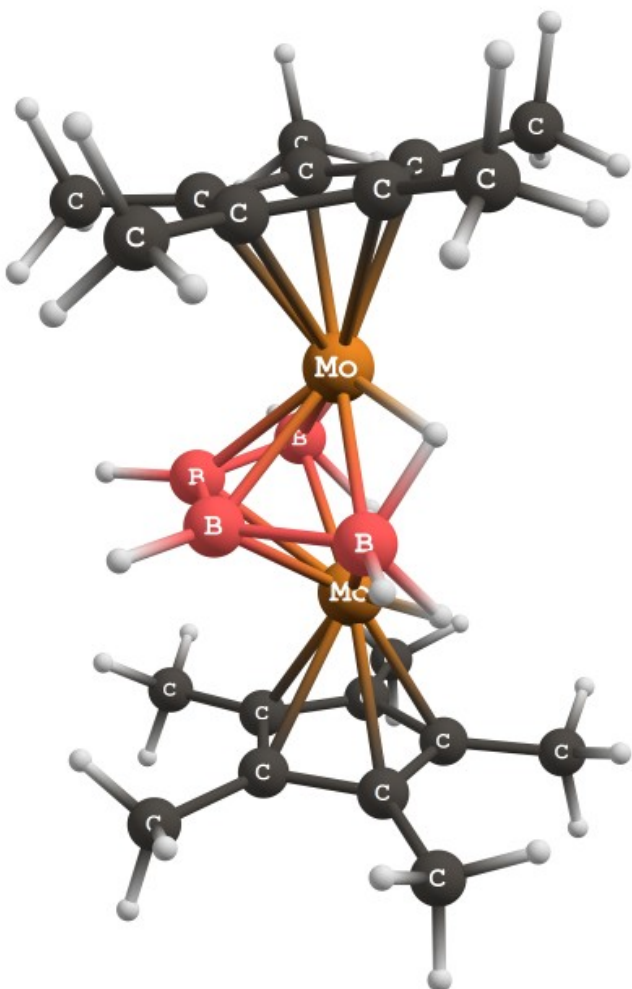---

Fig. S10. Optimized geometry of **[(Cp*Mo)₂B₄H₈]**.

Cartesian coordinates for the calculated structure of **[(Cp*Mo)₂B₄H₈]**. (in Å).

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---------------------------------------------------------------------
Center   Atomic   Atomic        Coordinates (Angstroms)
Number   Number   Type      X        Y        Z
---------------------------------------------------------------------
   1       5        0     -0.003385   0.826520   1.410044
   2       1        0     -0.004919   1.429390   2.454737
   3       5        0      0.006282  -1.848277  -0.015916
   4       6        0     -3.281565   0.855315   0.872114
   5       6        0     -3.253558  -0.569455   1.080857
   6       6        0     -3.376781  -1.207800  -0.201842
   7       6        0     -3.465380  -0.177915  -1.216909
   8       6        0     -3.424826   1.092646  -0.540112
   9       6        0     -3.631301   2.430138  -1.191718
```

10	1	0	-3.142024	3.237883	-0.631489
11	1	0	-4.707942	2.665296	-1.245519
12	1	0	-3.237844	2.447736	-2.217413
13	6	0	-3.308325	1.892124	1.955090
14	1	0	-4.327997	1.999067	2.364537
15	1	0	-2.993295	2.875215	1.581275
16	1	0	-2.637314	1.625423	2.782742
17	6	0	-3.261770	-1.248588	2.417570
18	1	0	-2.629598	-0.715349	3.140031
19	1	0	-2.888405	-2.278571	2.350972
20	1	0	-4.287813	-1.286618	2.823728
21	6	0	-3.541545	-2.682281	-0.432531
22	1	0	-2.965889	-3.272675	0.293022
23	1	0	-3.210129	-2.976523	-1.437707
24	1	0	-4.602110	-2.970766	-0.334755
25	6	0	-3.752793	-0.398103	-2.674641
26	1	0	-3.291862	-1.324465	-3.043460
27	1	0	-3.371082	0.426661	-3.291709
28	1	0	-4.840321	-0.474418	-2.857375
29	42	0	-1.369874	-0.004822	-0.203699
30	5	0	0.003256	-0.826748	1.409875
31	1	0	0.004639	-1.429826	2.454450
32	5	0	-0.006276	1.848335	-0.015548
33	6	0	3.281544	-0.855906	0.871787
34	6	0	3.253503	0.568729	1.081432
35	6	0	3.376799	1.207889	-0.200858
36	6	0	3.465474	0.178641	-1.216573
37	6	0	3.424892	-1.092334	-0.540588
38	6	0	3.631368	-2.429408	-1.193059
39	1	0	3.141995	-3.237510	-0.633429
40	1	0	4.708003	-2.664581	-1.246901
41	1	0	3.238022	-2.446287	-2.218809
42	6	0	3.308187	-1.893426	1.954085
43	1	0	4.327814	-2.000657	2.363569
44	1	0	2.993181	-2.876260	1.579577
45	1	0	2.637086	-1.627258	2.781840
46	6	0	3.261630	1.247041	2.418564
47	1	0	2.629536	0.713276	3.140706
48	1	0	2.888117	2.277010	2.352588
49	1	0	4.287670	1.284967	2.824740
50	6	0	3.541543	2.682520	-0.430599
51	1	0	2.965579	3.272440	0.295096
52	1	0	3.210464	2.977333	-1.435718
53	1	0	4.602050	2.971034	-0.332278
54	6	0	3.752920	0.399738	-2.674159
55	1	0	3.291928	1.326284	-3.042436
56	1	0	3.371295	-0.424693	-3.291726
57	1	0	4.840448	0.476247	-2.856809

58	1	0	1.014926	1.668787	-0.824765
59	42	0	1.369899	0.004921	-0.203567
60	1	0	-1.014816	-1.668538	-0.825235
61	1	0	-0.013035	3.050273	0.098339
62	1	0	0.013010	-3.050240	0.097709
63	1	0	1.014822	-1.652970	-0.838461
64	1	0	-1.014732	1.653192	-0.838240

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