Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information for:

Ring Contraction of Six-membered Metallabenzynes to Five-membered Metal-carbene Complexes: A Comparison with Organic Analogues

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Table S1: Optimized Cartesian coordinates (BP86/def2-SVP level) and total energies of all the calculated molecules using G09 program package. E1 is the total energy including zero point energy correction at the BP86/def2-SVP level of theory. E2 is the total energy at the M06/def2-TZVPP level of theory including zero point energy correction from BP86/def2-SVP level of theory.

Table S2: Natural atomic orbital occupancies on the selected atoms (C1 and M) in **1C**, **2C**, **3C**, **1M**, **2M** and **3M (**M = Fe, Ru and Os**)** at the BP86/def2-SVP level of theory.

Figure S1: Plots of the ten frontier MOs of **1Fe**. Eigen values are given in eV at the BP86/def2-SVP level of theory.

Figure S2: Plots of the ten frontier MOs of **1Ru.** Eigen values are given in eV at the BP86/def2-SVP level of theory.

Figure S3: Plots of the ten frontier MOs of **2Fe**. Eigen values are given in eV at the BP86/def2-SVP level of theory.

Figure S4: Plots of the ten frontier MOs of **2Ru.** Eigen values are given in eV at the BP86/def2-SVP level of theory.

Figure S5: Plots of the ten frontier MOs of **3Fe**. Eigen values are given in eV at the BP86/def2-SVP level of theory.

Figure S6: Plots of the ten frontier MOs of **3Ru**. Eigen values are given in eV at the BP86/def2-SVP level of theory.

Figure S7: Plots of the ten frontier MOs of **3Os**. Eigen values are given in eV at the BP86/def2-SVP level of theory.

Figure S8: Plots of the ten frontier MOs of **2Os'**. Eigen values are given in eV at the BP86/def2-SVP level of theory.

Table S1: Optimized Cartesian coordinates (BP86/def2-SVP level) and total energies of all the calculated molecules using G09 program package. E1 is the total energy including zero point energy correction at the BP86/def2-SVP level of theory. E2 is the total energy at the M06/def2-TZVPP level of theory including zero point energy correction from BP86/def2-SVP level of theory.

1C

E1 = -230.673568a.u

E2 =-230.7340687a.u

6	0.000000000	0.633552000	-1.246642000
6	0.000000000	-0.633552000	-1.246642000
6	0.000000000	-1.473906000	-0.135104000
6	0.000000000	-0.707165000	1.065241000
6	0.000000000	0.707165000	1.065241000
6	0.000000000	1.473906000	-0.135104000
1	0.000000000	-2.574644000	-0.131563000
1	0.000000000	-1.241260000	2.030596000
1	0.000000000	1.241260000	2.030596000
1	0.000000000	2.574644000	-0.131563000

2C

E1 = -230.618142a.u

E2 =-230.689684a.u

6	0.000000000	0.000000000	0.898751000
6	0.000000000	1.197939000	0.014027000
1	0.000000000	2.231389000	0.377653000
6	0.000000000	0.731331000	-1.276065000
1	0.000000000	1.365404000	-2.174621000
6	0.000000000	-1.197939000	0.014027000
1	0.000000000	-2.231389000	0.377653000
6	0.000000000	-0.731331000	-1.276065000
1	0.000000000	-1.365404000	-2.174621000
6	0.000000000	0.000000000	2.224314000

3C

E1 = -230.621547a.u

E2 =-230.6942356a.u

6	-1.891807000	-0.379657000	0.001076000
6	-0.651036000	-0.764451000	-0.000725000
1	-1.467741000	1.736057000	-0.001004000
6	0.683988000	-1.178482000	-0.000419000
1	1.009897000	2.180151000	-0.000148000
6	1.459277000	-0.015578000	0.000074000
1	2.559116000	0.002283000	0.000812000
6	0.628921000	1.148426000	0.000676000
1	1.008502000	-2.225611000	0.000965000
6	-0.747639000	0.907595000	-0.000785000

1Fe

E1 = -3062.808009a.u

E2 =-3063.047259a.u

6	2.731133000	0.006727000	1.101584000
6	3.364571000	-0.003022000	-0.172357000
6	2.601107000	-0.011848000	-1.360246000
6	1.247868000	-0.010131000	-1.092876000
6	1.343759000	0.008525000	1.232791000
1	3.371360000	0.013154000	2.001013000
1	4.466419000	-0.003727000	-0.243627000
1	3.041018000	-0.019407000	-2.369088000
1	0.926035000	0.016671000	2.258820000
17	-1.876805000	-0.017613000	-1.598426000
17	-1.562700000	0.021996000	1.774037000
1	-0.116624000	2.984864000	-1.145767000
1	-1.900702000	2.477835000	0.034685000
1	0.003190000	2.971464000	1.029153000
1	-0.137443000	-2.999018000	-1.104656000
1	-1.904365000	-2.473723000	0.094814000
1	0.011581000	-2.959791000	1.068095000
26	-0.055668000	-0.000951000	-0.087513000
15	-0.516930000	2.169325000	-0.037538000
15	-0.521213000	-2.169299000	-0.001587000

2Fe

E1 = -3062.825532a.u

E2 =-3063.077726a.u

6	3.413850000	-0.688564000	-0.274176000
6	3.414271000	0.687058000	0.273730000
6	2.115837000	1.110104000	0.415424000
6	1.233271000	-0.000241000	0.000178000
6	2.115167000	-1.111035000	-0.415312000
1	4.317975000	-1.255956000	-0.541435000
1	4.318762000	1.254043000	0.540615000
1	1.781893000	2.055928000	0.860590000
1	1.780686000	-2.056773000	-0.860260000
17	-1.272539000	-0.605736000	-2.004713000
17	-1.271812000	0.606346000	2.004899000
1	-0.233472000	2.584613000	-1.889062000
1	-2.136771000	2.516768000	-0.861463000
1	-0.393273000	3.243407000	0.189788000
1	-0.394954000	-3.243213000	-0.189958000
1	-2.138415000	-2.515674000	0.860728000
1	-0.235554000	-2.584893000	1.889062000
26	-0.535879000	0.000124000	0.000045000
15	-0.773817000	2.139990000	-0.640857000
15	-0.775145000	-2.139708000	0.640724000

3Fe

E1 = -3062.791368a.u

E2 =-3063.044401a.u

6	-2.993954000	-0.002008000	1.039060000
6	-3.611265000	0.000157000	-0.268889000
6	-2.678577000	0.001832000	-1.301381000
6	-1.370241000	0.000970000	-0.781292000
6	-1.621821000	-0.002030000	1.015274000
1	-3.579204000	-0.003576000	1.971692000
1	-4.701981000	0.000429000	-0.427857000
1	-2.894318000	0.003511000	-2.378567000
1	-1.010563000	-0.003472000	1.937020000
17	1.785514000	0.002887000	-1.710195000
17	1.487033000	-0.002653000	1.899338000
1	0.396968000	-2.974016000	-1.140618000
1	2.105155000	-2.387055000	0.105273000
1	0.201431000	-2.968093000	1.038817000
1	0.397039000	2.976566000	-1.133523000
1	2.103866000	2.387542000	0.113375000
1	0.198750000	2.965750000	1.045648000
26	0.134130000	0.000075000	-0.082889000
15	0.711088000	-2.142579000	-0.016418000
15	0.710067000	2.142777000	-0.010797000

1Ru

E1 = -1894.102396a.u

E2 =-1894.357048a.u

6	2.798271000	-0.187382000	1.088012000
6	3.423540000	0.083377000	-0.160666000
6	2.692413000	0.319176000	-1.344163000
6	1.322643000	0.266117000	-1.158551000
6	1.413643000	-0.246108000	1.252318000
1	3.456610000	-0.357936000	1.958106000
1	4.526559000	0.110383000	-0.213190000
1	3.173537000	0.523643000	-2.313267000
1	1.038169000	-0.468974000	2.270354000
17	-2.114203000	0.363067000	-1.430903000
17	-1.524381000	-0.503655000	1.832384000
1	-0.599854000	3.183541000	-0.772147000
1	-1.729713000	2.521734000	1.003919000
1	0.386500000	3.064548000	1.174296000
1	0.271911000	-2.966295000	-1.513947000
1	-1.752179000	-2.621722000	-0.745906000
1	-0.113542000	-3.175107000	0.627168000
15	-0.492017000	2.296556000	0.339896000
15	-0.402173000	-2.283184000	-0.448668000
44	-0.074825000	0.021921000	-0.107516000

2Ru

E1 = -1894.11654 a.u

E2 = -1894.37252 a.u

6	-3.578495000	0.738648000	-0.020378000
6	-3.578444000	-0.738913000	0.019738000
6	-2.281621000	-1.181814000	0.029004000
6	-1.387489000	-0.000050000	-0.000312000
6	-2.281705000	1.181651000	-0.029395000
1	-4.482112000	1.365528000	-0.040605000
1	-4.482017000	-1.365856000	0.039948000
1	-1.963937000	-2.231539000	0.062979000
1	-1.964100000	2.231403000	-0.063307000
17	1.268983000	0.018048000	-2.201398000
17	1.268052000	-0.017953000	2.201747000
1	0.230921000	-3.125768000	-1.113474000
1	2.084946000	-2.772155000	-0.057263000
1	0.276141000	-3.146616000	1.067490000
1	0.275746000	3.146706000	-1.067275000
1	2.084625000	2.772387000	0.057382000
1	0.230572000	3.125658000	1.113689000
44	0.490040000	0.000016000	0.000011000
15	0.722279000	-2.335672000	-0.025180000
15	0.722014000	2.335726000	0.025317000

3Ru

E1 =-1894.056918a.u

E2 =-1894.322797a.u

6	3.207357000	-0.250192000	1.050121000
6	3.806260000	0.024030000	-0.249328000
6	2.850531000	0.251486000	-1.226076000
6	1.544642000	0.132541000	-0.675883000
6	1.840761000	-0.229289000	1.017485000
1	3.800581000	-0.445149000	1.956650000
1	4.893752000	0.044695000	-0.426617000
1	3.032432000	0.474071000	-2.286106000
1	1.208101000	-0.395241000	1.907166000
17	-1.911484000	0.362907000	-1.632903000
17	-1.747012000	-0.378616000	1.801053000
1	-0.488050000	3.206319000	-0.761270000
1	-1.956012000	2.506004000	0.726660000
1	0.086790000	3.007355000	1.337956000
1	-0.111458000	-3.015575000	-1.437645000
1	-2.057535000	-2.476245000	-0.591882000
1	-0.424148000	-3.165155000	0.721615000
15	-0.612833000	2.278627000	0.319048000
15	-0.672921000	-2.258541000	-0.354573000
44	-0.136387000	0.014846000	-0.067503000

1Os

E1 = -1889.937828 a.u

E2 = -1890.171084 a.u

6	2.803801000	-0.016290000	1.131641000
6	3.438186000	-0.017813000	-0.141524000
6	2.727178000	-0.012631000	-1.359935000
6	1.351478000	-0.005517000	-1.195581000
6	1.416496000	-0.009057000	1.308976000
1	3.460373000	-0.021352000	2.019814000
1	4.542043000	-0.023473000	-0.183279000
1	3.230916000	-0.014003000	-2.339415000
1	1.056541000	-0.009308000	2.356999000
76	-0.070830000	0.001126000	-0.103989000
17	-2.117751000	0.012501000	-1.484812000
17	-1.551570000	0.001381000	1.907782000
1	-1.672382000	2.789853000	-0.396969000
1	-0.257320000	2.980840000	1.289847000
1	0.448290000	3.237980000	-0.766311000
1	0.347391000	-3.236641000	-0.830285000
1	-1.739074000	-2.752307000	-0.336139000
1	-0.235055000	-2.997036000	1.264681000
15	-0.375700000	2.360936000	0.009317000
15	-0.413837000	-2.354821000	0.002167000

2Os

E1 = -1889.937929 a.u

E2 = -1890.170957 a.u

6	3.688982000	0.737398000	0.014783000
6	3.688980000	-0.737391000	-0.015082000
6	2.391236000	-1.179540000	-0.021808000
6	1.493430000	0.000005000	-0.000108000
6	2.391238000	1.179549000	0.021556000
1	4.591978000	1.365357000	0.030255000
1	4.591975000	-1.365352000	-0.030575000
1	2.073827000	-2.230221000	-0.047606000
1	2.073831000	2.230229000	0.047398000
17	-1.193824000	0.015466000	2.220639000
17	-1.194285000	-0.015477000	-2.220441000
1	-0.104502000	-3.138413000	1.102920000
1	-1.971696000	-2.823260000	0.060994000
1	-0.165358000	-3.149514000	-1.081124000
1	-0.166282000	3.149429000	1.081516000
1	-1.971682000	2.823247000	-0.062152000
1	-0.103642000	3.138507000	-1.102477000
76	-0.415960000	0.000001000	0.000027000
15	-0.618686000	-2.354437000	0.020422000
15	-0.618702000	2.354436000	-0.020465000

3Os

E1 = -1889.874715 a.u

E2 =-1890.116592 a.u

6	3.283610000	0.425863000	0.991844000
6	3.871605000	-0.073184000	-0.244279000
6	2.894081000	-0.516629000	-1.120815000
6	1.600164000	-0.247011000	-0.588764000
6	1.915018000	0.378473000	0.974653000
1	3.876161000	0.749861000	1.860975000
1	4.953704000	-0.086973000	-0.448924000
1	3.047062000	-0.909520000	-2.135067000
1	1.301583000	0.580995000	1.869273000
76	-0.138733000	-0.025095000	-0.060383000
17	-2.011164000	-0.396443000	-1.503270000
17	-1.780907000	0.491019000	1.759685000
1	-1.827158000	2.595561000	-0.911816000
1	-0.390961000	3.223876000	0.636633000
1	0.254025000	3.019981000	-1.446176000
1	0.443504000	-3.121438000	1.067797000
1	-0.844475000	-3.155106000	-0.704755000
1	-1.656469000	-2.522563000	1.245938000
15	-0.507304000	2.312827000	-0.457557000
15	-0.528358000	-2.304845000	0.398913000

2Fe'

E1 =-3062.748042a.u

E2 =-3063.005298a.u

6	0.000000000	0.706686000	-3.391271000
6	0.000000000	-0.706686000	-3.391271000
6	0.000000000	-1.191433000	-2.050405000
6	0.000000000	0.000000000	-1.258134000
6	0.000000000	1.191433000	-2.050405000
1	0.000000000	1.368236000	-4.271849000
1	0.000000000	-1.368236000	-4.271849000
1	0.000000000	-2.230755000	-1.700886000
1	0.000000000	2.230755000	-1.700886000
17	0.000000000	1.890727000	1.636284000
17	0.000000000	-1.890727000	1.636284000
1	2.772625000	1.096401000	-0.370877000
1	3.170611000	0.000000000	1.486572000
1	2.772625000	-1.096401000	-0.370877000
1	-2.772625000	1.096401000	-0.370877000
1	-3.170611000	0.000000000	1.486572000
1	-2.772625000	-1.096401000	-0.370877000
26	0.000000000	0.000000000	0.629961000
15	2.251904000	0.000000000	0.376404000
15	-2.251904000	0.000000000	0.376404000

2Ru'

E1 = -1894.031211 a.u

E2 = -1894.287784 a.u

6	0.000000000	0.704528000	-3.559657000
6	0.000000000	-0.704528000	-3.559657000
6	0.000000000	-1.188152000	-2.215357000
6	0.000000000	0.000000000	-1.414760000
6	0.000000000	1.188152000	-2.215357000
1	0.000000000	1.368174000	-4.438340000
1	0.000000000	-1.368174000	-4.438340000
1	0.000000000	-2.229401000	-1.869971000
1	0.000000000	2.229401000	-1.869971000
17	0.000000000	1.998316000	1.624045000
17	0.000000000	-1.998316000	1.624045000
1	2.860277000	1.093453000	-0.451926000
1	3.270946000	0.000000000	1.410557000
1	2.860277000	-1.093453000	-0.451926000
1	-2.860277000	1.093453000	-0.451926000
1	-3.270946000	0.000000000	1.410557000
1	-2.860277000	-1.093453000	-0.451926000
44	0.000000000	0.000000000	0.566515000
15	2.350443000	0.000000000	0.308259000
15	-2.350443000	0.000000000	0.308259000

2Os'

E1 = -1889.854634 a.u

E2 = -1890.089058 a.u

6	0.000000000	0.704133000	-3.673717000
6	0.000000000	-0.704133000	-3.673717000
6	0.000000000	-1.184012000	-2.329272000
6	0.000000000	0.000000000	-1.515667000
6	0.000000000	1.184012000	-2.329272000
1	0.000000000	1.367474000	-4.552550000
1	0.000000000	-1.367474000	-4.552550000
1	0.000000000	-2.225564000	-1.982917000
1	0.000000000	2.225564000	-1.982917000
17	0.000000000	2.056590000	1.477680000
17	0.000000000	-2.056590000	1.477680000
1	2.869219000	1.093567000	-0.544545000
1	3.295162000	0.000000000	1.314337000
1	2.869219000	-1.093567000	-0.544545000
1	-2.869219000	1.093567000	-0.544545000
1	-3.295162000	0.000000000	1.314337000
1	-2.869219000	-1.093567000	-0.544545000
76	0.000000000	0.000000000	0.485512000
15	2.365175000	0.000000000	0.220343000
15	-2.365175000	0.000000000	0.220343000

Table S2: Natural atomic orbital occupancies on C1 in **1C**, **2C**, **3C**, **1M**, **2M** and **3M** (M = Fe, Ru and Os) at the BP86/def2-SVP level of theory.

	s	**p_x**	**p_y**	**p_z**
1C	0.95	1.11	0.95	0.96
2C	1.59	1.24	0.13	0.70
3C	1.47	1.18	0.63	0.68
1Fe	1.11	1.00	0.67	0.83
2Fe	1.02	0.98	0.89	1.02
3Fe	1.08	1.05	0.77	0.87
1Ru	1.10	1.04	0.69	0.75
2Ru	0.97	0.99	0.86	1.04
3Ru	1.06	1.09	0.81	0.79
1Os	1.10	1.08	0.76	0.77
2Os	0.97	1.03	0.90	1.05
3Os	1.06	1.14	0.87	0.82

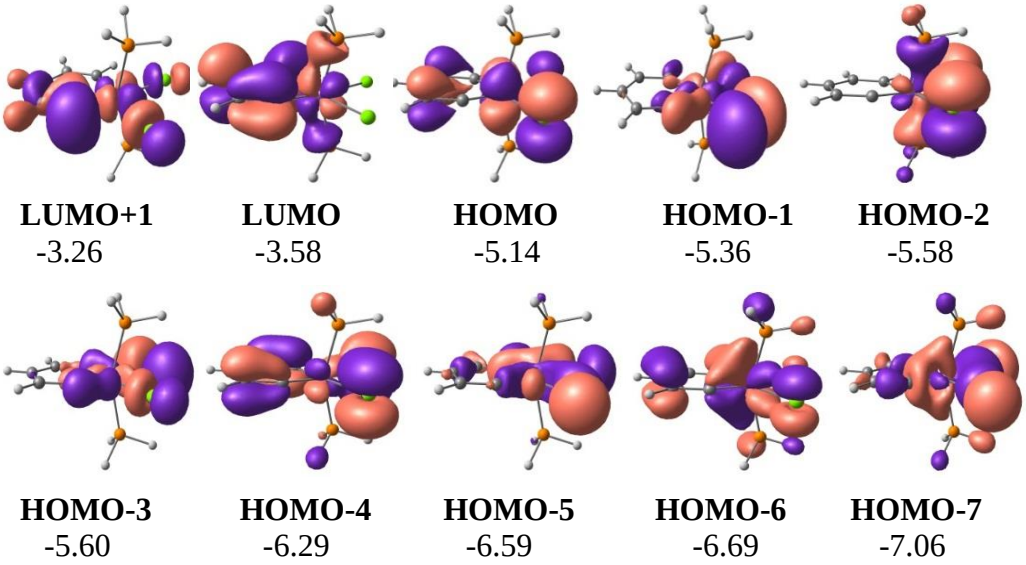

Figure S1: Plots of the ten frontier MOs of **1Fe**. Eigen values are given in eV at the BP86/def2-SVP level of theory.

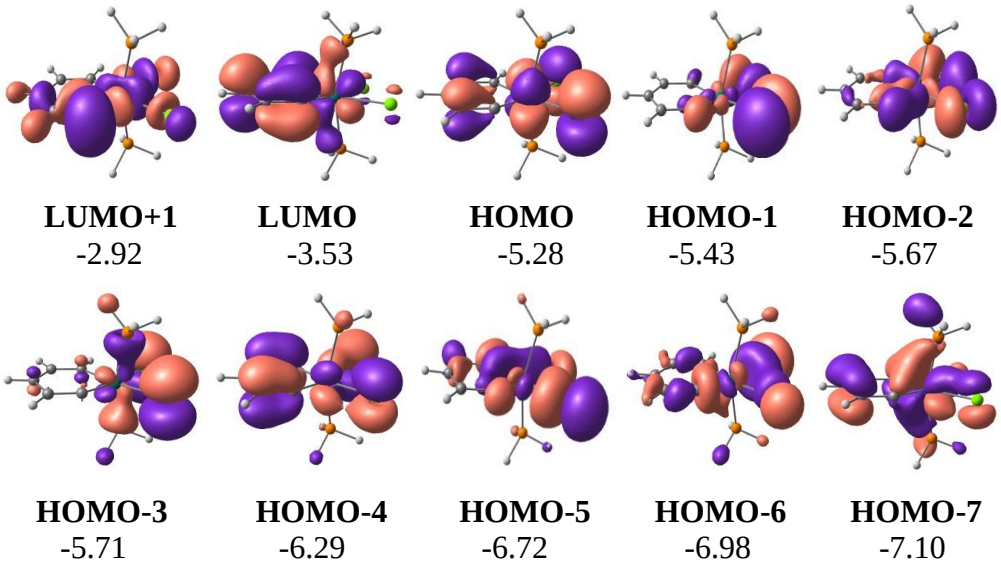

Figure S2: Plots of the ten frontier MOs of **1Ru.** Eigen values are given in eV at the BP86/def2-SVP level of theory.

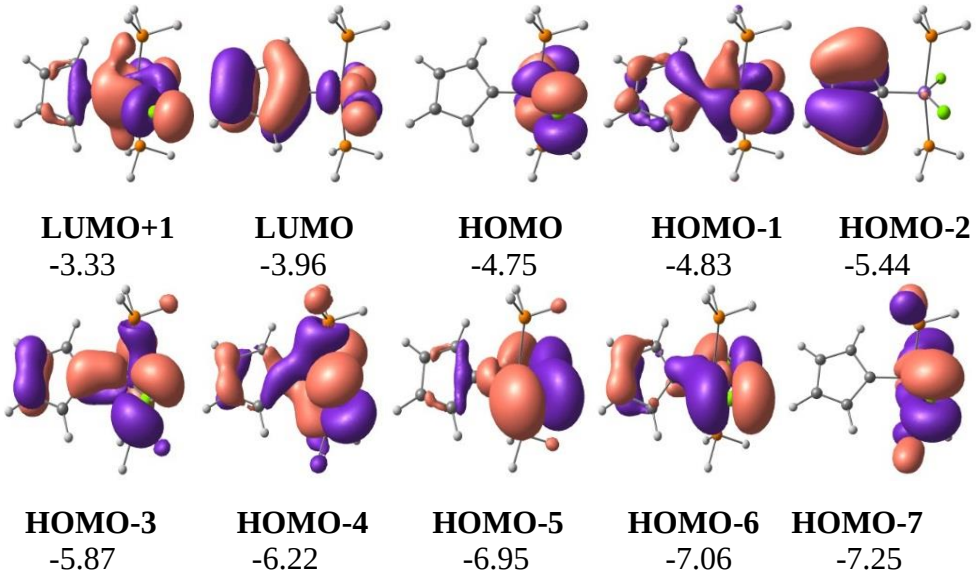

Figure S3: Plots of the ten frontier MOs of **2Fe**. Eigen values are given in eV at the BP86/def2-SVP level of theory.

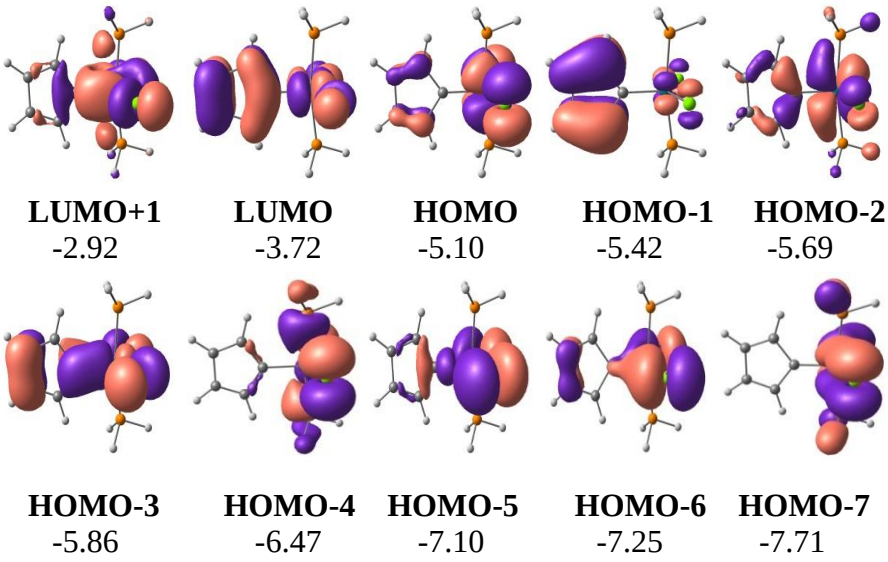

Figure S4: Plots of the ten frontier MOs of **2Ru.** Eigen values are given in eV at the BP86/def2-SVP level of theory.

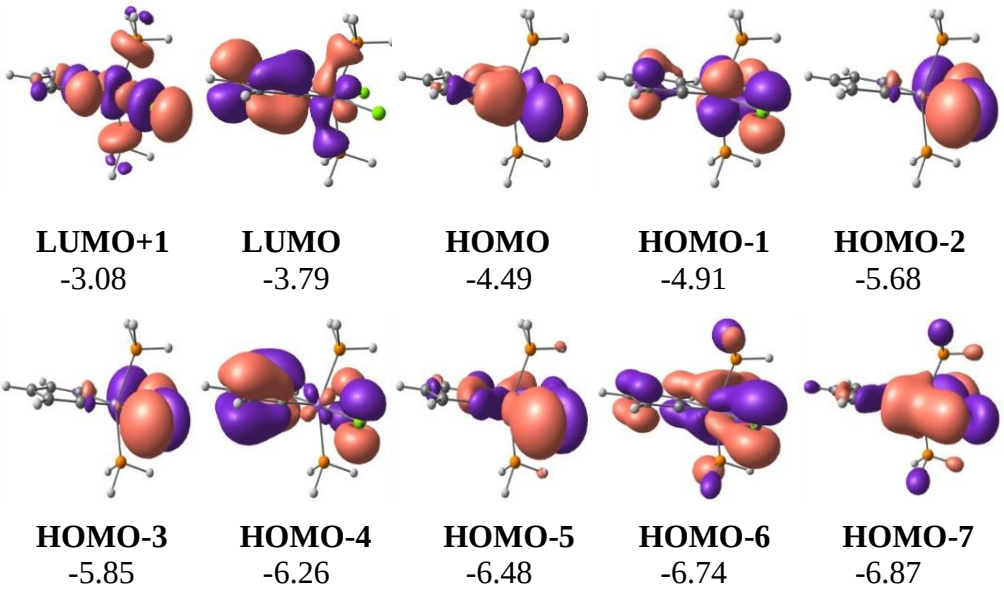

Figure S5: Plots of the ten frontier MOs of **3Fe**. Eigen values are given in eV at the BP86/def2-SVP level of theory.

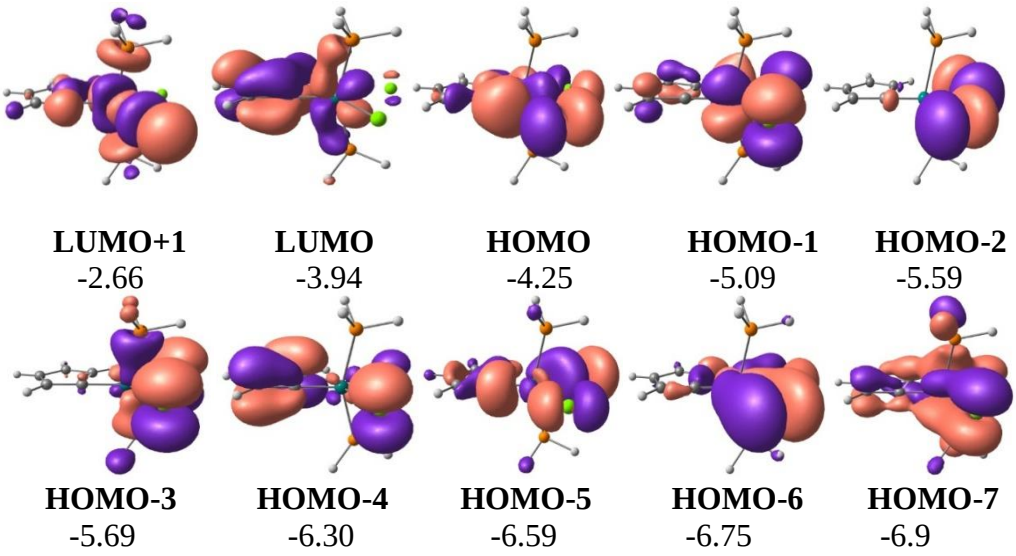

Figure S6: Plots of the ten frontier MOs of **3Ru**. Eigen values are given in eV at the BP86/def2-SVP level of theory.

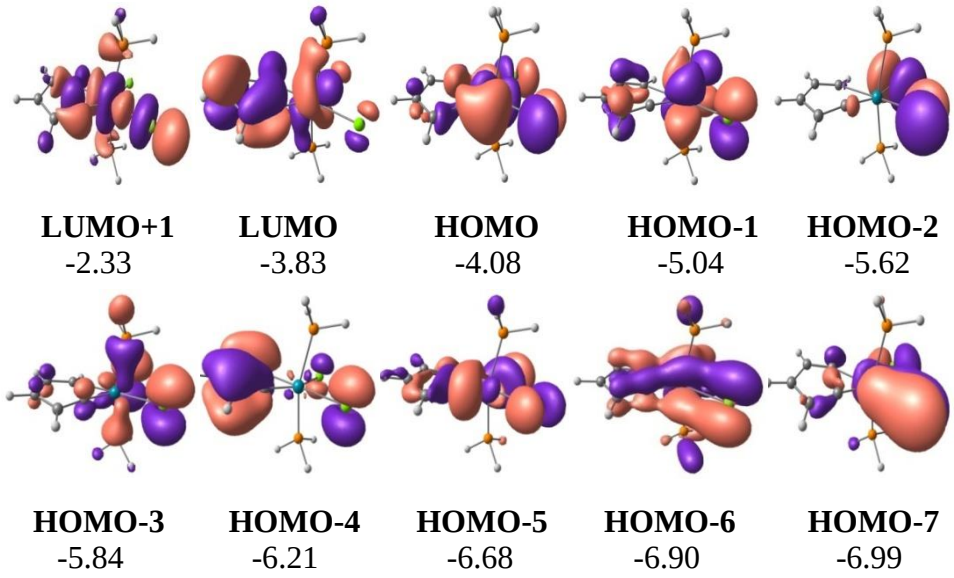

Figure S7: Plots of the ten frontier MOs of **3Os**. Eigen values are given in eV at the BP86/def2-SVP level of theory.

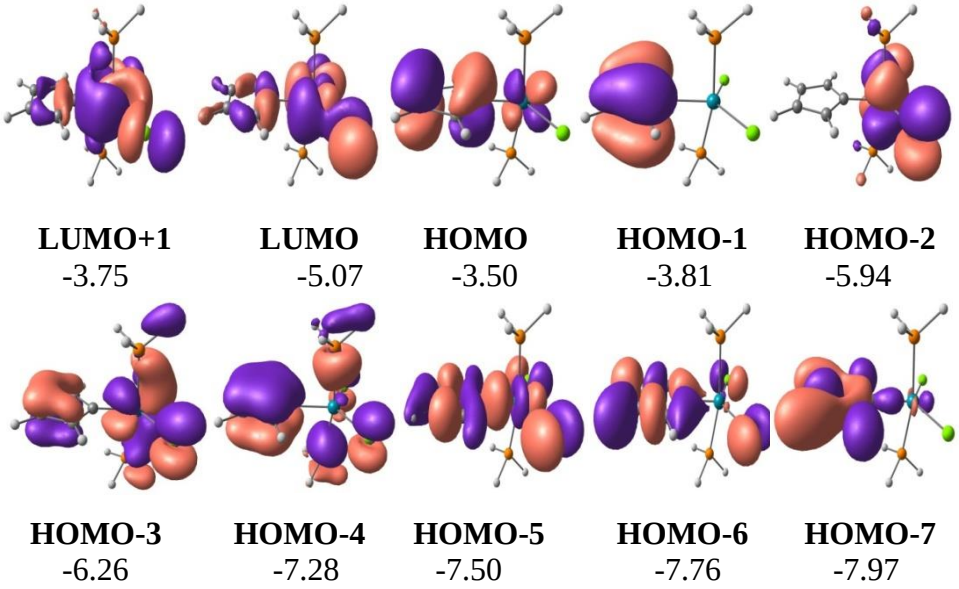

Figure S8: Plots of the ten frontier MOs of **2Os'**. Eigen values are given in eV at the BP86/def2-SVP level of theory.