

Supporting Information for:

Ring Contraction of Metallabenzooxirene to Metal Carbonyl Complexes – A Comparative Study with the Wolff Rearrangement of Oxirene and Benzooxirene

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Table S1: Atomic orbital occupancies by natural population analysis (M06/def2-TZVPP//BP86/def2-SVP level of theory) on the selected atoms.

		Atomic Orbital Occupancy			
		2s	2p _x	2p _y	2p _z
1A	C1	1.04	1.19	1.0	1.0
2A	C1	1.01	1.16	0.78	0.99
	O	1.81	1.47	1.24	1.98
3A	C1	1.01	0.97	1.04	0.75
	C2	1.32	0.63	0.77	1.34
	O	1.76	1.48	1.57	1.63
3A-TS	C1	1.43	0.92	0.20	1.34
	C2	0.98	0.93	1.09	0.80
	O	1.72	1.57	1.77	1.45
4A	C1	0.85	0.87	0.62	0.91
	C2	1.09	1.10	1.23	1.37
	O	1.70	1.57	1.45	1.69
1C	C1	0.97	1.09	0.93	0.96
2C	C1	0.95	0.82	0.82	1.09
	C2	0.95	0.82	0.82	1.09
	O	1.87	1.36	1.36	1.39
3C	C1	0.88	1.10	0.87	0.85
	C2	1.01	1.04	0.67	1.02
	O	1.77	1.54	1.39	1.76
4C	C1	0.84	0.86	0.61	0.86
	C2	0.94	1.08	1.11	1.23
	O	1.71	1.57	1.45	1.64

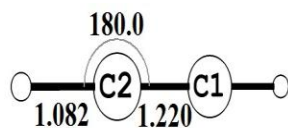
Table S2: Bond lengths and bond angles in the experimental products $C_5H(CH_3)(SiMe_3)_2Os(PPh_3)_2Cl_2$, $C_5HO(CH_3)Cl_2Os(PPh_3)_2Cl_2$ and optimized model geometries **10s** and **20s**.

	$C_5H(CH_3)(SiMe_3)_2Os(PPh_3)_2Cl_2$	$C_5HO(CH_3)Cl_2Os(PPh_3)_2Cl_2$	10s	20s
Bond Lengths (Å)				
Os-P1	2.410	2.427	2.382	2.377
Os-P2	2.412	2.421	2.382	2.376
Os-Cl1	2.4798	2.444	2.469	2.459
Os-Cl2	2.4811	2.381	2.498	2.432
Os-C1	1.815	1.956	1.793	2.003
Os-C5	1.939	2.041	1.386	2.067
Os-O	-	2.144	-	2.209
O-C1	1.376	1.234	-	1.255
C1-C2	1.420	1.370	1.411	1.403
C2-C3	1.416	1.380	1.422	1.394
C3-C4	1.378	1.411	1.399	1.421
C4-C5	1.515	1.347	2.052	1.390
Bond Angles (deg)				
C1-Os-C5	78.1	77.8	81.0	79.2
C1-Os-O1	-	34.6	-	34.2
C5-Os-O1	-	112.4	-	113.4
O-C1-Os	-	81.1	-	81.9
C2-C1-Os	148.7	142.1	149.3	142.3

Table S3: Wiberg bond indices (M06/def2-TZVPP level of theory) of **1M**, **2M**, **5M** and **6M** (M = Fe, Ru, Os) at the M06/def2-TZVPP//BP86 /def2-SVP level of theory.

Wiberg bond indices					
	C1-O	M-C1	M-C5	M-O	M-C2
1Fe		1.565	0.853		
1Ru		1.750	0.912		
1Os		1.781	0.904		
2Fe	1.598	0.644	0.798	0.548	
2Ru	1.539	0.760	0.875	0.559	
2Os	1.481	0.904	0.872	0.547	
3Fe	1.774	0.668	0.846	0.256	
3Ru	1.770	0.737	0.909	0.252	
3Os	1.744	0.750	0.907	0.238	
4Fe	1.935	0.664	0.988		0.506
4Ru	1.916	0.785	1.039		0.550
4Os	1.875	0.831	1.029		0.556

Table S4: Optimized Cartesian coordinates and total energies including zero point energy correction E1 (in a.u.) of all calculated molecules at BP86/def2-SVP level of theory and E2 energy at M06/TZVPP level of theory including zero point energy correction from BP86/def2-SVP level of theory using G09 program package.



1A ($D_{\infty h}$)

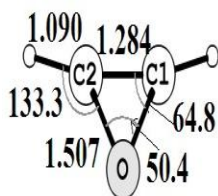
Charge = 0 Multiplicity = 1
 Nimg = 0
 E1 = 0.026231
 E2 = -77.2974307

6	0.000000000	0.000000000	0.610199000
1	0.000000000	0.000000000	1.692216000
6	0.000000000	0.000000000	-0.610199000
1	0.000000000	0.000000000	-1.692216000

3A (C_1)

Charge = 0 Multiplicity = 1
 Nimg = 1
 E1 = 0.029161
 E2 = -152.4459635

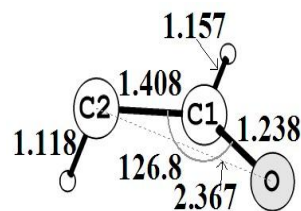
6	1.038080000	-0.147638000	-0.157344000
1	1.561041000	-0.702062000	0.642804000
6	-0.096743000	0.587315000	0.043395000
1	-0.417186000	1.650748000	0.084475000
8	-0.848985000	-0.448343000	-0.005448000



2A (C_{2v})

Charge = 0 Multiplicity = 1
 Nimg = 1
 E1 = 0.027862
 E2 = -152.4415929

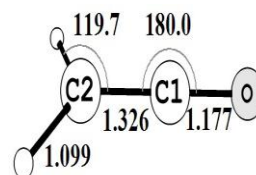
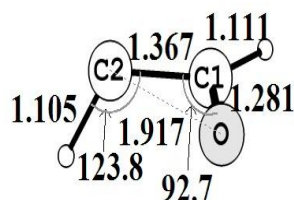
6	0.000000000	0.641766000	-0.465199000
1	0.000000000	1.678296000	-0.803947000
6	0.000000000	-0.641766000	-0.465199000
1	0.000000000	-1.678296000	-0.803947000
8	0.000000000	0.000000000	0.898785000



3A-TS (C_1)

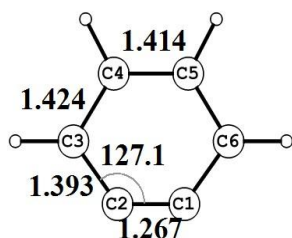
Charge = 0 Multiplicity = 1
 Nimg = 1
 E1 = 0.026313
 E2 = -152.440885

6	1.236687000	-0.187214000	-0.172881000
1	1.798774000	-0.481924000	0.747881000
6	-0.046436000	0.356709000	0.025811000
1	0.039965000	1.509514000	0.082359000
8	-1.122530000	-0.255570000	0.006523000



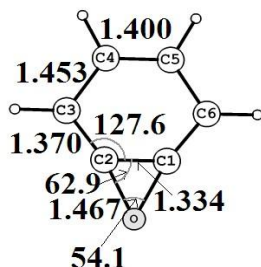
4A (C_{2v})
 Charge = 0 Multiplicity = 1
 Nlmg = 0
 E1 = 0.030470
 E2 = -152.5727171

6	0.000000000	0.000000000	0.103754000
6	0.000000000	0.000000000	-1.221818000
1	0.000000000	0.954334000	-1.767095000
1	0.000000000	-0.954334000	-1.767095000
8	0.000000000	0.000000000	1.280322000



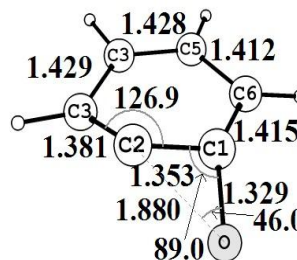
1C (C_{2v})
 Charge = 0 Multiplicity = 1
 Nlmg = 0
 E1 = 0.073062
 E2 = -230.8071307

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



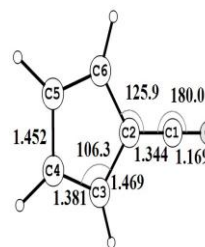
2C (C_{2v})
 Charge = 0 Multiplicity = 1
 Nlmg = 0
 E1 = 0.076605
 E2 = -306.0076533

6	0.000000000	0.700071000	-1.487418000
6	0.000000000	1.502903000	-0.276284000
6	0.000000000	0.667206000	0.809378000
6	0.000000000	-0.667206000	0.809378000
6	0.000000000	-1.502903000	-0.276284000
6	0.000000000	-0.700071000	-1.487418000
1	0.000000000	1.227351000	-2.454810000
1	0.000000000	2.601611000	-0.283260000
1	0.000000000	-2.601611000	-0.283260000
1	0.000000000	-1.227351000	-2.454810000
8	0.000000000	0.000000000	2.116003000



3C (C_1)
 Charge = 0 Multiplicity = 1
 Nlmg = 1
 E1 = 0.075677
 E2 = -305.9899804

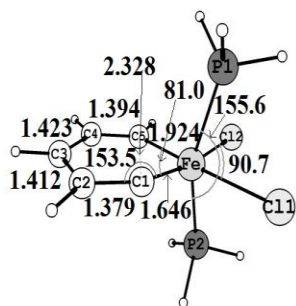
6	-1.650215000	-0.333984000	-0.045432000
6	-0.729225000	-1.424509000	-0.103204000
6	0.505757000	-0.948739000	0.292394000
6	0.978602000	0.309184000	0.136545000
6	0.123678000	1.429111000	0.008902000
6	-1.230610000	1.030141000	-0.004270000
1	-2.728156000	-0.559988000	0.020590000
1	-1.038643000	-2.471646000	-0.237630000
1	0.443793000	2.468305000	-0.155895000
1	-2.016631000	1.802839000	-0.035643000
8	2.168964000	-0.200842000	-0.162628000



4C (C_{2v})
 Charge = 0 Multiplicity = 1
 Nlmg = 0
 E1 = 0.077409
 E2 = -306.1124705

6	-1.844991000	-0.725848000	-0.000249000
6	-0.544162000	-1.189307000	0.000116000

6	0.317893000	-0.000044000	0.000344000
6	1.661939000	-0.000150000	-0.000285000
6	-0.544180000	1.189357000	0.000232000
6	-1.845011000	0.725902000	-0.000191000
1	-2.741281000	-1.361903000	0.000283000
1	-0.188198000	-2.226417000	0.000549000
1	-0.188154000	2.226501000	0.000540000
1	-2.741531000	1.361629000	-0.000497000
8	2.831280000	0.000091000	-0.000085000



1Fe (C₁)

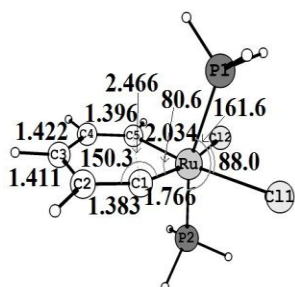
Charge = 0 Multiplicity = 1

Nlmg = 0

E1 = 0.125790

E2 = -3063.1730494

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



1Ru (C₁)

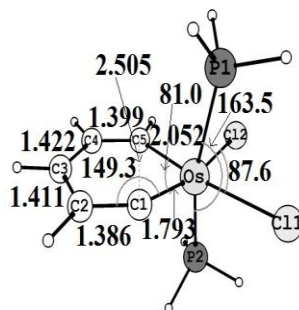
Charge = 0 Multiplicity = 1

Nlmg = 0

E1 = 0.125285

E2 = -1894.4823325

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



1Os (Cs)

Charge = 0 Multiplicity = 1

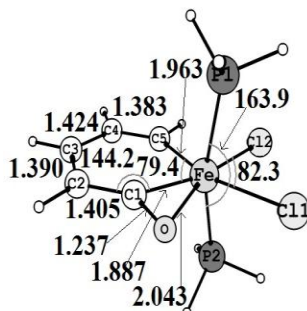
Nlmg = 0

E1 = 0.125188

E2 = -1890.2962721

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



2Fe (C₁)

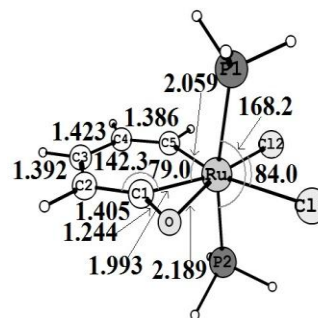
Charge = 0 Multiplicity = 1

Nlmg = 0

E1 = 0.130034

E2 = -3138.4291167

6	-2.601871000	0.342854000	1.334403000
6	-3.408127000	0.046550000	0.198658000
6	-2.826587000	-0.229291000	-1.033866000
6	-1.422994000	-0.211000000	-1.091279000
6	-1.219848000	0.364490000	1.292327000
1	-3.111736000	0.569493000	2.287596000
1	-4.507087000	0.044638000	0.291605000
1	-3.401211000	-0.444082000	-1.947651000
1	-0.714139000	0.617916000	2.241243000
17	2.199839000	-0.464869000	-1.132138000
17	1.565505000	0.475592000	1.753389000
1	0.269509000	-3.124664000	-0.582248000
1	1.633849000	-2.502373000	1.030463000
1	-0.500120000	-2.795831000	1.426676000
1	0.021842000	2.755848000	-1.694478000
1	1.917665000	2.503603000	-0.629690000
1	0.113276000	3.164571000	0.441582000
26	0.148086000	0.001474000	-0.068326000
15	0.370569000	-2.163535000	0.473885000
15	0.541821000	2.168148000	-0.489523000
8	-0.549029000	-0.370068000	-1.952099000



2Ru (C₁)

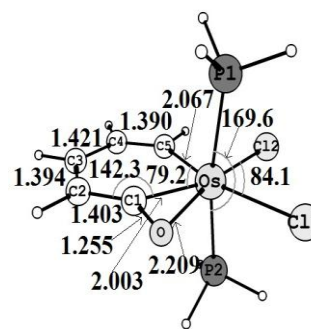
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Nlmg = 0

E1 = 0.129620

E2 = -1969.7369376

6	-2.669558000	0.210440000	1.381316000
6	-3.454967000	-0.002334000	0.213797000
6	-2.890589000	-0.205002000	-1.042108000
6	-1.489474000	-0.201093000	-1.140662000
6	-1.283850000	0.239142000	1.389857000
1	-3.208810000	0.364002000	2.333017000
1	-4.554643000	-0.005344000	0.304316000
1	-3.490727000	-0.365373000	-1.950957000
1	-0.822836000	0.421039000	2.377628000
17	2.310461000	-0.290630000	-1.178166000
17	1.532832000	0.419778000	1.891901000
1	0.359634000	-3.174363000	-0.796524000
1	1.685366000	-2.682386000	0.884536000
1	-0.449794000	-3.027041000	1.221999000
1	-0.227924000	2.909909000	-1.557701000
1	1.738283000	2.742558000	-0.612579000
1	-0.036050000	3.229936000	0.590312000
15	0.423710000	-2.309285000	0.340491000
15	0.395133000	2.309621000	-0.413864000
44	0.167068000	-0.001833000	-0.050765000
8	-0.653935000	-0.347470000	-2.050808000



2Os (C₁)

vshift) freq

Charge = 0 Multiplicity = 1

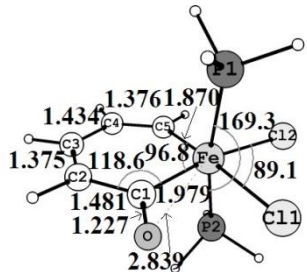
Nlmg = 0

E1 = 0.129694

E2 = -1965.5441479

6	-2.702435000	0.035688000	1.404718000
6	-3.481984000	-0.011952000	0.217179000
6	-2.918726000	-0.052344000	-1.057718000

6	-1.519162000	-0.046322000	-1.151453000
6	-1.312529000	0.047729000	1.432611000
1	-3.248896000	0.065952000	2.364277000
1	-4.581859000	-0.016438000	0.306091000
1	-3.523933000	-0.087499000	-1.976883000
1	-0.871244000	0.088125000	2.445475000
76	0.142820000	0.001429000	-0.034795000
17	2.304090000	-0.052063000	-1.206727000
17	1.518032000	0.083005000	1.969247000
1	1.713213000	-2.826115000	0.155664000
1	-0.272497000	-3.129529000	1.048759000
1	-0.045551000	-3.112384000	-1.120742000
1	-0.245148000	3.068601000	-1.224956000
1	1.686092000	2.839474000	-0.217418000
1	-0.148318000	3.167826000	0.952835000
15	0.371909000	-2.363838000	0.026656000
15	0.344615000	2.366773000	-0.123603000
8	-0.678891000	-0.071680000	-2.083671000



3Fe (C₁)

Charge = 0 Multiplicity = 1

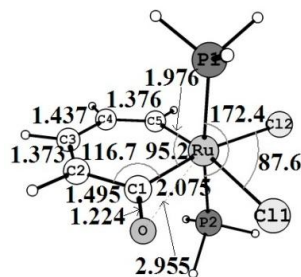
Nlmg = 0

E1 = 0.127914

E2 = -3138.3771273

6	3.121144000	-0.489032000	0.221450000
6	2.654072000	0.609225000	-0.460756000
6	1.238924000	0.979274000	-0.694848000
6	0.950491000	-1.451089000	0.823580000
6	2.324923000	-1.509634000	0.838485000
1	4.219234000	-0.590032000	0.287916000
1	3.364590000	1.352353000	-0.857146000
1	0.381858000	-2.298082000	1.258679000
1	2.845033000	-2.368062000	1.299324000
8	1.000881000	2.012306000	-1.312611000
26	-0.179413000	-0.144274000	0.106548000
15	-0.278226000	1.158277000	1.910234000
1	0.178755000	2.510199000	1.806955000
1	-1.596169000	1.378996000	2.409961000
1	0.377377000	0.799664000	3.134691000
15	-0.485235000	-1.359553000	-1.722867000
1	-1.729191000	-1.158923000	-2.389417000
1	0.402032000	-1.232530000	-2.844603000
1	-0.481455000	-2.784218000	-1.610223000
17	-1.490719000	1.568348000	-0.887005000

17	-2.132210000	-1.201879000	0.772684000
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3Ru (C₁)

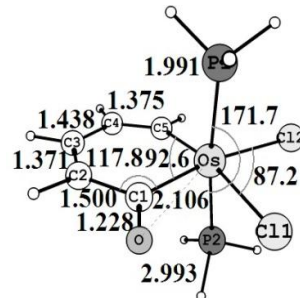
Charge = 0 Multiplicity = 1

Nlmg = 0

E1 = 0.127252

E2 = -1969.6782805

6	-3.183655000	0.108585000	-0.525194000
6	-2.685100000	-0.693995000	0.471123000
6	-1.262481000	-0.956044000	0.848539000
6	-1.073323000	0.994839000	-1.411152000
6	-2.445577000	0.905223000	-1.466893000
1	-4.285030000	0.128599000	-0.612481000
1	-3.387220000	-1.207850000	1.147777000
1	-0.561927000	1.558270000	-2.222205000
1	-3.011359000	1.416426000	-2.265110000
8	-1.048594000	-1.735624000	1.767297000
44	0.185243000	0.153606000	-0.141393000
15	-0.063491000	1.834014000	1.468746000
1	0.075486000	1.435259000	2.834675000
1	0.886327000	2.901416000	1.426089000
1	-1.272758000	2.595750000	1.565673000
15	0.693514000	-1.615691000	-1.603682000
1	2.083562000	-1.795522000	-1.871166000
1	0.341679000	-2.942332000	-1.204804000
1	0.188848000	-1.647787000	-2.945178000
17	1.505997000	-1.209175000	1.452627000
17	2.236999000	1.165505000	-0.819971000



3Os (C₁)

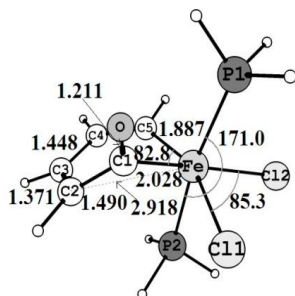
Charge = 0 Multiplicity = 1

Nlmg = 0

E1 = 0.127409

E2 = -1965.4882895

6	-3.260594000	-0.084951000	-0.513658000
6	-2.772498000	-0.302414000	0.749401000
6	-1.350276000	-0.375168000	1.219846000
6	-1.127916000	0.175389000	-1.682466000
6	-2.501539000	0.122457000	-1.717607000
1	-4.361118000	-0.081360000	-0.610947000
1	-3.480264000	-0.400520000	1.588522000
1	-0.598585000	0.233948000	-2.661863000
1	-3.047877000	0.196885000	-2.673138000
8	-1.182293000	-0.597423000	2.415511000
76	0.168356000	0.048039000	-0.176121000
15	0.011255000	2.331141000	0.417947000
1	0.039848000	2.621321000	1.817107000
1	1.071282000	3.176806000	-0.036627000
1	-1.115512000	3.123576000	0.026866000
15	0.587084000	-2.258296000	-0.548200000
1	1.934855000	-2.586355000	-0.891392000
1	0.382926000	-3.138104000	0.558323000
1	-0.105894000	-2.992363000	-1.565311000
17	1.422015000	-0.358783000	1.924197000
17	2.286543000	0.515846000	-1.210651000



3Fe-TS(C₁)

Charge = 0 Multiplicity = 1

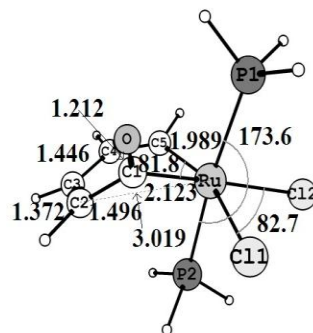
Nlmg = 1

E1 = 0.127536

E2 = -3138.3959114

6	-3.058876000	0.034398000	-0.340983000
6	-2.416357000	0.258541000	0.849691000
6	-1.093128000	0.942125000	0.871723000
6	-1.009865000	0.290211000	-1.634300000
6	-2.381299000	0.194830000	-1.610187000
1	-4.121991000	-0.260284000	-0.330006000
1	-2.895129000	0.075991000	1.826594000
1	-0.519548000	0.592736000	-2.586003000
1	-2.986397000	0.243668000	-2.532896000
8	-0.867725000	1.983546000	1.447297000
26	0.258601000	-0.041367000	-0.276599000
15	1.294426000	1.947536000	-0.498739000
1	2.251957000	2.231502000	0.520535000
1	2.113444000	2.154425000	-1.654064000
1	0.568235000	3.181264000	-0.496188000

15	-0.458738000	-2.159900000	0.024450000
1	0.605366000	-3.109768000	0.081745000
1	-1.177978000	-2.532225000	1.199225000
1	-1.288065000	-2.809979000	-0.954047000
17	0.940787000	-0.444851000	1.952187000
17	2.288043000	-0.831345000	-0.844130000



3Ru-TS(C₁)

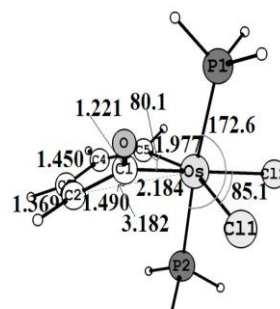
Charge = 0 Multiplicity = 1

Nlmg = 1

E1 = 0.126890

E2 = -1969.689393

6	3.181790000	-0.054872000	-0.293601000
6	2.531688000	-0.322555000	0.884038000
6	1.182218000	-0.965383000	0.933207000
6	1.161578000	-0.218391000	-1.655854000
6	2.533407000	-0.145169000	-1.583111000
1	4.250888000	0.215937000	-0.255821000
1	3.025391000	-0.185245000	1.861815000
1	0.706270000	-0.507689000	-2.629866000
1	3.161605000	-0.178652000	-2.490514000
8	0.940397000	-1.963478000	1.577545000
44	-0.232266000	0.068379000	-0.265806000
15	-1.253056000	-2.033109000	-0.603247000
1	-2.195564000	-2.395308000	0.405474000
1	-2.055935000	-2.251722000	-1.768215000
1	-0.467382000	-3.227913000	-0.633504000
15	0.563747000	2.230248000	0.194473000
1	-0.385440000	3.275373000	-0.037640000
1	0.943816000	2.551903000	1.532501000
1	1.684717000	2.777337000	-0.513762000
17	-1.122382000	0.248139000	2.016684000
17	-2.358577000	0.922817000	-0.838556000



3Os-TS (C₁)

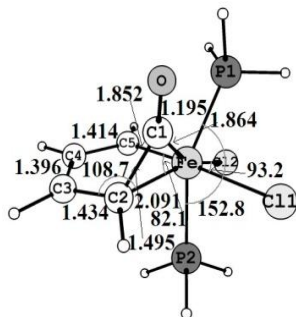
Charge = 0 Multiplicity = 1

Nlmg = 1

E1 = 0.126632

E2 = -1965.4966385

6	-3.320714000	-0.083085000	-0.380744000
6	-2.766870000	0.456090000	0.748730000
6	-1.378041000	0.991549000	0.826326000
6	-1.212052000	-0.215657000	-1.562676000
6	-2.570102000	-0.338931000	-1.595227000
1	-4.403820000	-0.294266000	-0.388242000
1	-3.390783000	0.675532000	1.631797000
1	-0.602258000	-0.253836000	-2.503835000
1	-3.109908000	-0.601653000	-2.520132000
8	-1.146549000	2.003579000	1.468869000
76	0.220241000	-0.079709000	-0.207087000
15	1.037328000	2.088494000	-0.783247000
1	1.880223000	2.660151000	0.216859000
1	1.876729000	2.257116000	-1.930739000
1	0.127872000	3.172167000	-0.985072000
15	-0.397191000	-2.212268000	0.602281000
1	0.627900000	-3.209961000	0.557265000
1	-0.775584000	-2.310375000	1.975224000
1	-1.469596000	-2.935196000	-0.013470000
17	1.078476000	0.174092000	2.054021000
17	2.424933000	-0.887833000	-0.733783000



4Fe (C₁)

Charge = 0 Multiplicity = 1

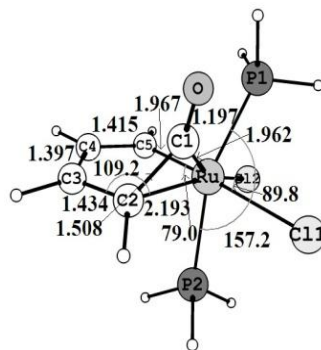
Nlmg = 0

E1 = 0.130301

E2 = -3138.4340041

6	-2.840625000	-0.129962000	-0.351673000
6	-1.892451000	0.058289000	0.708093000
6	-1.034421000	1.282464000	0.718360000

6	-0.909260000	-0.080945000	-1.689429000
6	-2.321966000	-0.120569000	-1.647857000
1	-3.906644000	-0.301348000	-0.121054000
1	-2.140193000	-0.242337000	1.743868000
1	-0.398025000	-0.141863000	-2.672702000
1	-2.964580000	-0.165283000	-2.544106000
8	-1.113740000	2.403860000	1.124363000
26	0.035476000	-0.006273000	-0.098833000
15	1.312471000	1.724779000	-0.734690000
1	2.625378000	1.705767000	-0.188874000
1	1.582412000	1.909697000	-2.124217000
1	0.906608000	3.054563000	-0.378066000
15	-0.255694000	-2.100515000	0.615337000
1	0.935570000	-2.871990000	0.715533000
1	-0.849984000	-2.350346000	1.888142000
1	-1.064471000	-2.973567000	-0.194095000
17	1.175851000	-0.028553000	1.999007000
17	1.847804000	-0.977958000	-1.245145000



4Ru (C₁)

Charge = 0 Multiplicity = 1

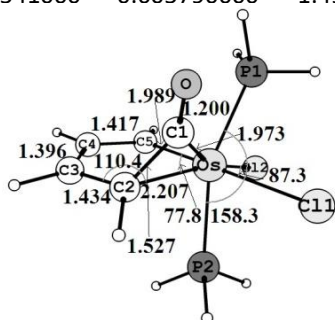
Nlmg = 0

E1 = 0.129235

E2 = -1969.7348802

6	2.943657000	0.115875000	-0.303450000
6	1.982534000	0.125592000	0.760463000
6	1.114798000	-1.066239000	1.078260000
6	1.065610000	-0.152433000	-1.713318000
6	2.475362000	-0.117485000	-1.598937000
1	4.002187000	0.341037000	-0.082888000
1	2.221499000	0.667641000	1.696151000
1	0.611285000	-0.233296000	-2.723259000
1	3.159417000	-0.221146000	-2.458673000
8	1.206489000	-2.062658000	1.735388000
44	-0.035024000	0.011031000	-0.091163000
15	-1.141590000	-2.041562000	-0.493546000
1	-2.459588000	-2.080305000	0.040664000
1	-1.367409000	-2.432885000	-1.845947000
1	-0.605014000	-3.254671000	0.048156000
15	0.174144000	2.324255000	0.305647000

1	-1.041258000	3.047672000	0.151595000
1	0.605885000	2.754264000	1.593813000
1	1.052134000	3.110567000	-0.517190000
17	-1.445287000	0.373313000	1.946286000
17	-1.923541000	0.605790000	-1.492991000



4OS

Charge = 0 Multiplicity = 1

Nlmg = 0

E1 = 0.129175

E2 = -1965.5391434

6	2.985084000	0.218908000	-0.272564000
6	1.989913000	0.362461000	0.749227000
6	1.152436000	-0.798236000	1.281555000
6	1.148717000	-0.321043000	-1.657849000
6	2.555388000	-0.214236000	-1.528203000
1	4.031280000	0.503100000	-0.062777000
1	2.189026000	1.061651000	1.585447000
1	0.729488000	-0.577909000	-2.653806000
1	3.259489000	-0.413227000	-2.353872000
8	1.303197000	-1.657528000	2.105944000
76	-0.022855000	0.006632000	-0.083758000
15	-0.937285000	-2.201997000	-0.251861000
1	-2.258138000	-2.293291000	0.270051000

1	-1.096945000	-2.770368000	-1.549682000
1	-0.299853000	-3.279072000	0.442815000
15	0.006216000	2.381733000	0.104730000
1	-1.249057000	2.993026000	-0.171983000
1	0.328052000	2.932092000	1.378600000
1	0.873457000	3.163739000	-0.732108000
17	-1.615915000	0.500156000	1.830437000
17	-1.926353000	0.279449000	-1.586947000
6	1.250521000	-0.129703000	1.161879000
1	3.280248000	-0.316403000	1.891748000
1	4.327821000	-0.238158000	-0.371861000
1	2.904274000	0.039615000	-2.432395000
1	0.850463000	-0.167345000	2.196484000
17	-1.742252000	0.022582000	-1.802938000
17	-1.806957000	0.079043000	1.756863000
1	-0.007646000	3.018673000	-1.078017000
1	-1.882433000	2.653444000	-0.000663000
1	-0.025910000	3.006099000	1.101568000
1	-0.051320000	-3.021688000	-0.884170000
1	-2.011426000	-2.512199000	-0.051818000
1	-0.302541000	-2.882416000	1.276503000
26	-0.236458000	0.026748000	0.006404000
15	-0.522500000	2.234438000	0.002522000
15	-0.641645000	-2.155164000	0.09213700

Table S5: Natural atomic orbital occupancies on the selected atoms (C1, O, M = Fe, Ru, Os) in **2M** and **3M** (M = Fe, Ru, Os) at the M06/def2-TZVPP//BP86 /def2-SVP level of theory.

		Valance Occupancy								
		s	p _x	p _y	p _z	d _{xy}	d _{xz}	d _{yz}	d _{x²-y²}	d _{z²}
2Fe	C1	0.86	0.92	0.80	0.73					
	Fe	0.38	0.36	0.30	0.38	1.30	1.82	1.80	1.28	1.34
	O	1.66	1.52	1.52	1.62					
2Ru	C1	0.86	0.94	0.80	0.74					
	Ru	0.40	0.35	0.29	0.40	1.31	1.79	1.84	1.29	1.38
	O	1.67	1.52	1.51	1.64					
2Os	C1	0.89	0.98	0.85	0.76					
	Os	0.46	0.23	0.19	0.21	1.20	1.75	1.87	1.13	1.28
	O	1.68	1.53	1.53	1.66					
3Fe	C1	0.93	0.93	0.79	0.74					
	Fe	0.42	0.32	0.34	0.36	1.54	1.77	1.37	1.18	1.59
	O	1.71	1.60	1.56	1.53					
3Ru	C1	0.93	0.93	0.76	0.77					
	Ru	0.43	0.30	0.34	0.33	1.59	1.57	1.36	1.30	1.75
	O	1.71	1.63	1.54	1.54					
3Os	C1	0.96	0.99	0.85	0.73					
	Os	0.51	0.21	0.21	0.20	1.31	1.77	1.73	1.21	1.19
	O	1.70	1.71	1.58	1.47					