Supporting Info

Inverted Ligand Field in a Pentanuclear Bow Tie Au/Fe Carbonyl Cluster

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Table S1. Selected bond lengths (Å) for of $[Au\{\eta^1\text{-}Fe_2(CO)_8\}\{\eta^2\text{-}Fe_2(CO)_6(\mu\text{-}CO)_2\}]^{3-}$. The labeling is the same of Figure 2.

Au(1)-C(10)	2.596(6)	Fe(5)-C(15)	1.780(9)
Au(1)-C(11)	2.604(7)	C(1)-O(1)	1.164(7)
Fe(2)-C(5)	1.757(8)	C(4)-O(4)	1.170(8)
Fe(2)-C(6)	1.983(7)	C(5)-O(5)	1.152(7)
Fe(2)-C(9)	1.792(8)	C(6)-O(6)	1.173(7)
Fe(2)-C(12)	1.979(7)	C(7)-O(7)	1.207(8)
Fe(2)-C(16)	1.797(8)	C(8)-O(8)	1.148(8)
Fe(3)-C(2)	1.751(7)	C(9)-O(9)	1.165(8)
Fe(3)-C(6)	1.977(7)	C(10)-O(10)	1.157(7)
Fe(3)-C(8)	1.805(8)	C(11)-O(11)	1.176(8)
Fe(3)-C(12)	1.959(7)	C(12)-O(12)	1.188(7)
Fe(3)-C(13)	1.796(8)	C(13)-O(13)	1.139(7)
Fe(4)-C(1)	1.755(7)	C(14)-O(14)	1.158(8)
Fe(4)-C(7)	1.712(8)	C(15)-O(15)	1.148(8)

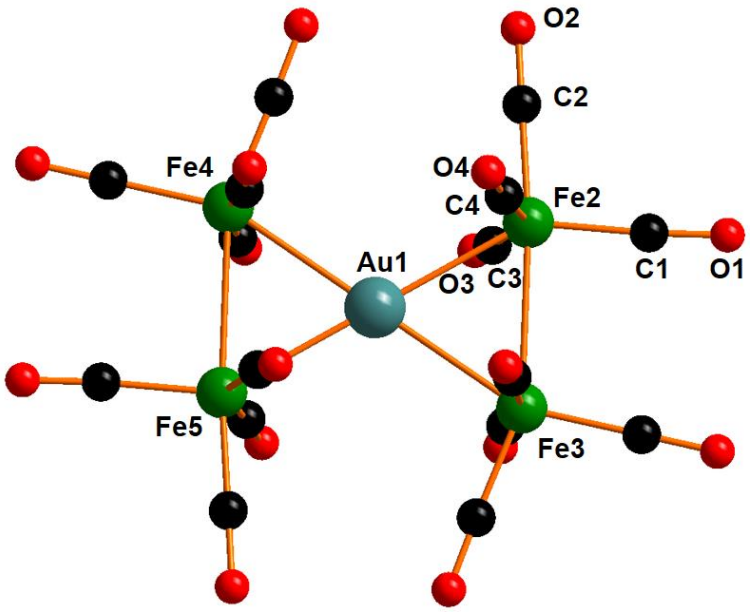

Table S2. Comparison between some selected distances of the X-ray structure of [Au{η²-Fe₂(CO)₈}₂]⁻ (ref. 31) with those in the calculated one.

Distance	X-ray Structure	Calculated structure
Au1-Fe2	2.584	2.671
Au1-Fe3	2.607	2.670
Au1-Fe4	2.606	2.673
Au1-Fe5	2.584	2.669
Fe2-C1	1.769	1.786
Fe2-C2	1.768	1.776
Fe2-C3	1.769	1.812
Fe2-C4	1.794	1.805
C1-O1	1.147	1.147
C2-O2	1.144	1.146
C3-O3	1.137	1.150
C4-O4	1.130	1.150
Fe2-Fe3	2.771	2.790
Fe4-Fe5	2.771	2.790

Table S3. Comparison between some selected distances of the X-ray structure of [Au{η^1-$Fe_2(CO)_8$}{η^2-$Fe_2(CO)_6(\mu\text{-}CO)_2$}]$^{3-}$ with those in the calculated one The labeling is the same of Figure 2 in the text.

Distance	X-ray Structure	Calculated structure
Au1-Fe2	2.6502	2.750
Au1-Fe3	2.7290	2.831
Au1-Fe4	2.6173	2.713
Au1-Fe5	4.452	4.703
Fe2-Fe3	2.6094	2.667
Fe4-Fe5	2.8763	2.948
Fe2-C5	1.757	1.748
Fe2-C6	1.983	1.988
Fe2-C9	1.792	1.798
Fe2-C12	1.979	1.978
Fe2-C16	1.797	1.798
Fe3-C2	1.751	1.746
Fe3-C6	1.977	1.979
Fe3-C8	1.805	1.797
Fe3-C12	1.959	1.979
Fe3-C13	1.796	1.797
Fe4-C1	1.755	1.765
Fe4-C7	1.712	1.762
Fe4-C11	1.782	1.793
Fe5-C3	1.763	1.781
Fe5-C4	1.730	1.744
Fe5-C14	1.776	1.782
Fe5-C15	1.780	1.783

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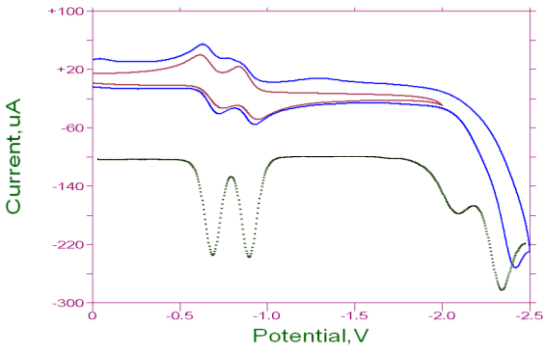

Figure S1. Cyclic voltammograms (blue and brown full lines) and square wave Oesteryoung voltammogram (green dotted line) of a solution 3.8 x 10^{-4} M of $[NEt_4][Au\{Fe_2(CO)_8\}_2]$ in THF/$[NBu_4]PF_6$ 0.2 M. Scan rate 0.2 V s^{-1}.

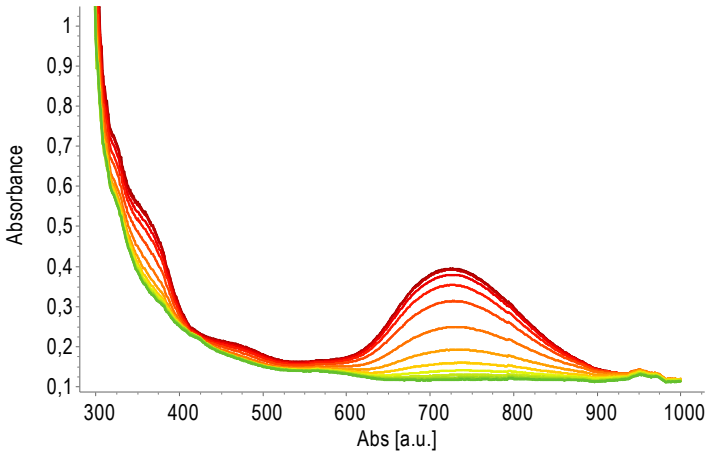

Figure S2. UV-vis spectra recorded in an OTTLE cell during the stepwise overall reduction of a 3.8 x 10^{-4} M of $[NEt_4][Au\{Fe_2(CO)_8\}_2]$ in THF/$[NBu_4]PF_6$ 0.2 M. E_w from –0.40 V to –2.0 V, *vs*. pseudo-Ag electrode. Initial spectrum: red line, final spectrum: green line.

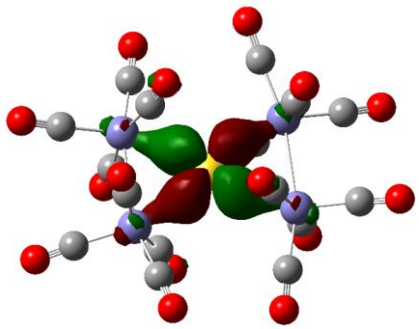

Figure S3. σ-bonding counterpart orbital of the LUMO, namely the HOMO-20, mainly centered on the gold rather than on the two $Fe_2(CO)_8$ units.

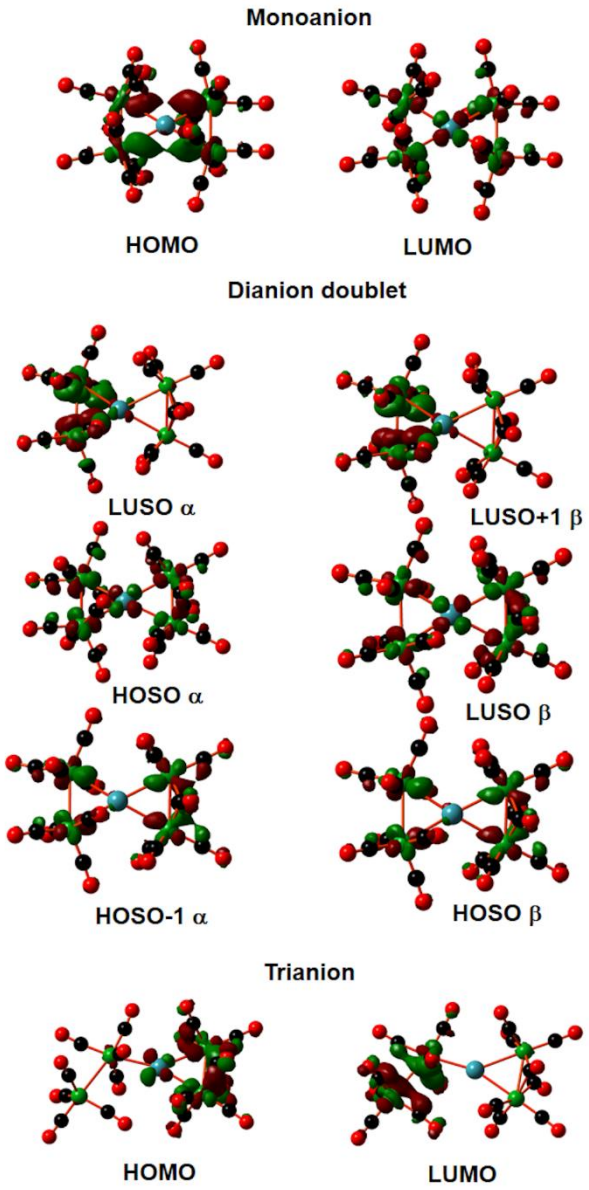

Figure S4: Frontier molecular orbitals/spinorbitals of the starting anion; the doublet dianion and the final direduced trianionic species. LUSO and HOSO are the Lowest Unoccupied SpinOrbital and the Highest Occupied SpinOrbital, respectively.

Cartesian coordinates, Energies and Thermal Parameters of all the structures optimized in the computational analysis (B3LYP level of theory)

Compound $[Au\{\eta^2\text{-}Fe_2(CO)_8\}_2]^-$

Cartesian Coordinates

Fe 10.340642 6.845959 1.687540
Fe 9.855471 6.819689 -1.064404
Au 11.805331 8.306171 -0.000215
C 8.986706 8.028674 1.522712
O 8.108403 8.769195 1.577729
C 11.962155 6.046139 1.563241
O 12.973096 5.500958 1.613263
C 10.715715 7.469573 3.307746
O 10.905657 7.841308 4.375719
C 9.366630 5.403618 2.090572
O 8.753059 4.483203 2.393653
C 9.335303 8.553247 -1.149907
O 8.931832 9.616771 -1.318795
C 8.237229 6.067774 -0.983833
O 7.195125 5.588466 -0.978900
C 10.838354 5.322625 -0.831412
O 11.413318 4.326558 -0.831112
C 10.172596 6.776814 -2.811259
O 10.335146 6.699751 -3.943821
Fe 13.373469 9.647554 -1.695903
Fe 13.669382 9.886116 1.074459
C 13.883099 7.909333 -1.754898
C 12.469011 11.170339 -1.344711
C 12.578436 9.518204 -3.278559
C 14.936339 10.386850 -2.146104
C 14.938082 8.668551 0.663800
C 14.695386 11.347746 1.038490
C 12.064554 10.687897 1.326708
C 13.770398 9.438817 2.790151
O 14.241682 6.830248 -1.924452
O 11.899652 12.167414 -1.279296
O 12.102881 9.482242 -4.321430
O 15.929331 10.853426 -2.480639
O 15.804587 7.921257 0.548505
O 15.354778 12.286010 1.061656
O 11.099460 11.249074 1.602556
O 13.890906 9.182228 3.901251

Energy and Thermal parameters

HF=-2445.8600776
Zero-point vibrational energy 359410.5 (Joules/Mol)
Zero-point correction= 0.136892 (Hartree/Particle)
Thermal correction to Energy= 0.181753
Thermal correction to Enthalpy= 0.182697
Thermal correction to Gibbs Free Energy= 0.049566
Sum of electronic and zero-point Energies= -2445.723185
Sum of electronic and thermal Energies= -2445.678324
Sum of electronic and thermal Enthalpies= -2445.677380
Sum of electronic and thermal Free Energies= -2445.810512

Compound $[Au\{\eta^2\text{-}Fe_2(CO)_8\}\{\eta^2\text{-}Fe_2(CO)_6(\mu\text{-}CO)_2\}]^-$

Cartesian Coordinates

Au 0.000070 -0.000027 0.019604
Fe -0.070748 -1.302687 -2.321995
Fe 0.070676 1.303263 -2.321756
Fe -0.183168 1.381087 2.309463
Fe 0.183148 -1.381620 2.309267
C 1.098576 -2.461499 -1.623823
O 1.847908 -3.246315 -1.253545
C -1.534362 -2.011495 -1.520827
O -2.458859 -2.519036 -1.072072
C -0.264617 -2.058101 -3.926030
O -0.381343 -2.580152 -4.939385
C 1.426190 -0.238297 -2.832553
O 2.524750 -0.228972 -3.236255
C -1.426140 0.238994 -2.832947
O -2.524583 0.229680 -3.236935
C 0.264826 2.059069 -3.925566
O 0.381814 2.581326 -4.938785
C -1.098842 2.461760 -1.623338
O -1.848248 3.246369 -1.252775
C 1.534149 2.011932 -1.520238
O 2.458581 2.519359 -1.071217
C -1.854036 1.260642 1.620320
O -2.935791 1.305900 1.234974
C -0.043525 3.080270 1.807500
O 0.054330 4.189785 1.535296
C 1.604023 1.285873 2.557356
O 2.731664 1.373984 2.760280
C -0.641837 1.545667 4.028695

O -0.943141 1.695973 5.124791
C 1.854025 -1.261358 1.620089
O 2.935835 -1.306918 1.234949
C 0.642199 -1.546528 4.028364
O 0.943809 -1.697142 5.124332
C 0.043048 -3.080616 1.806754
O -0.055060 -4.190027 1.534221
C -1.603962 -1.286329 2.557818
O -2.731557 -1.374210 2.761068

Energy and Thermal parameters

HF=-2445.8598914
Zero-point vibrational energy 358802.3 (Joules/Mol)
Zero-point correction= 0.136661 (Hartree/Particle)
Thermal correction to Energy= 0.181226
Thermal correction to Enthalpy= 0.182170
Thermal correction to Gibbs Free Energy= 0.051660
Sum of electronic and zero-point Energies= -2445.723231
Sum of electronic and thermal Energies= -2445.678665
Sum of electronic and thermal Enthalpies= -2445.677721
Sum of electronic and thermal Free Energies= -2445.808232

Compound doublet $[Au\{\eta^2\text{-}Fe_2(CO)_8\}_2]^{2-}$

Cartesian Coordinates

Fe 10.330436 6.981281 1.887651
Fe 9.803703 6.641990 -1.005717
Au 11.804566 8.313045 0.008340
C 9.682327 8.655189 1.865394
O 9.233662 9.714472 1.992335
C 11.895964 6.110631 1.774537
O 12.886665 5.516070 1.845479
C 10.467507 7.036897 3.629839
O 10.530224 7.048901 4.782995
C 8.987225 5.820003 1.793140
O 8.118906 5.062672 1.915274
C 8.773748 8.109838 -0.797851
O 8.060284 9.012333 -0.766565
C 8.441605 5.506617 -1.191431
O 7.570312 4.784367 -1.407578
C 11.071774 5.364925 -0.868725
O 11.836328 4.504903 -0.883674
C 10.235579 7.047855 -2.686444
O 10.434067 7.242455 -3.803940
Fe 13.230645 9.676451 -1.883848
Fe 13.866602 9.910754 1.005509
C 13.809432 7.978558 -1.938095
C 11.704540 10.600913 -1.688833
C 13.036768 9.685815 -3.621209
C 14.621526 10.781384 -1.796246
C 14.888099 8.459374 0.680284
C 15.231334 11.041254 1.183174
C 12.590669 11.186996 0.985743
C 13.503543 9.417474 2.677080
O 14.213883 6.908810 -2.117924
O 10.732648 11.229144 -1.701736
O 12.937513 9.715379 -4.771553
O 15.515542 11.507116 -1.924994
O 15.599440 7.561189 0.569766
O 16.108045 11.758289 1.396660
O 11.825643 12.042698 1.072739
O 13.352448 9.163764 3.790525

Energy and Thermal parameters

HF=-2445.9774314
Zero-point vibrational energy 351018.4 (Joules/Mol)
Zero-point correction= 0.133696 (Hartree/Particle)
Thermal correction to Energy= 0.178501
Thermal correction to Enthalpy= 0.179445
Thermal correction to Gibbs Free Energy= 0.044333
Sum of electronic and zero-point Energies= -2445.843736
Sum of electronic and thermal Energies= -2445.798930
Sum of electronic and thermal Enthalpies= -2445.797986
Sum of electronic and thermal Free Energies= -2445.933099

Compound doublet $[Au\{\eta^2\text{-}Fe_2(CO)_8\}\{\eta^2\text{-}Fe_2(CO)_6(\mu\text{-}CO)_2\}]^{2-}$

Cartesian Coordinates

Au -0.000153 0.000341 0.017093
Fe -0.823368 1.030929 -2.426011

Fe 0.823340 -1.030905 -2.425370
Fe 1.241662 -0.614774 2.416751
Fe -1.241499 0.614775 2.417350
C -2.446099 0.922458 -1.672035
O -3.533155 0.891886 -1.290818
C -0.285795 2.514879 -1.557281
O 0.036426 3.517019 -1.088193
C -1.262287 1.697046 -3.994707
O -1.583664 2.171921 -4.997387
C -1.085935 -0.826834 -3.013259
O -1.932264 -1.518279 -3.464009
C 1.085907 0.826537 -3.013743
O 1.932327 1.517544 -3.464988
C 1.262461 -1.697850 -3.993736
O 1.584000 -2.173291 -4.996055
C 2.445999 -0.921851 -1.671267
O 3.532784 -0.890899 -1.289342
C 0.285789 -2.514629 -1.556145
O -0.036638 -3.516494 -1.086662
C 2.258949 0.635470 1.583060
O 2.969716 1.412713 1.119579
C 2.045835 -2.022287 1.685017
O 2.593932 -2.958996 1.301288
C -0.137892 -1.636865 2.995379
O -0.774361 -2.509193 3.422964
C 2.024358 -0.485401 4.013494
O 2.580373 -0.451643 5.021673
C -2.259147 -0.634611 1.582683
O -2.970164 -1.411499 1.119044
C -2.024381 0.484591 4.014271
O -2.580829 0.450261 5.022143
C -2.045179 2.022851 1.685787
O -2.592856 2.959667 1.301799
C 0.137892 1.636676 2.996426
O 0.773922 2.508734 3.425207

Energy and Thermal parameters

HF=-2445.9846935
Zero-point vibrational energy 351211.3 (Joules/Mol)
Zero-point correction= 0.133769 (Hartree/Particle)
Thermal correction to Energy= 0.177901
Thermal correction to Enthalpy= 0.178845
Thermal correction to Gibbs Free Energy= 0.048738
Sum of electronic and zero-point Energies= -2445.850924
Sum of electronic and thermal Energies= -2445.806793
Sum of electronic and thermal Enthalpies= -2445.805849
Sum of electronic and thermal Free Energies= -2445.935956

Compound $[Au\{\eta^2\text{-}Fe_2(CO)_8\}_2]^{3-}$

Cartesian Coordinates

Fe 9.793923 6.972442 1.096368
Fe 8.365688 6.054134 -1.271138
Au 11.806841 8.303302 0.000568
C 9.084775 8.458119 0.382613
O 8.588499 9.458493 0.055670
C 11.092215 5.760649 0.875110
O 11.905130 4.931732 0.857577
C 10.331186 7.680045 2.611412
O 10.644711 8.116800 3.635628
C 8.496239 5.984925 1.776881
O 7.708270 5.347096 2.340310
C 6.903978 6.724429 -0.478662
O 5.937592 7.150031 -0.008102
C 7.745067 4.414535 -1.357781
O 7.287981 3.359833 -1.541324
C 10.033538 5.576807 -1.740931
O 11.044892 5.219024 -2.172218
C 8.150282 7.022829 -2.716231
O 7.944211 7.562482 -3.725946
Fe 13.820337 9.632694 -1.096216
Fe 15.256089 10.541228 1.270967
C 14.526691 8.143135 -0.387706
C 12.523856 10.845418 -0.869765
C 13.280470 8.930890 -2.612983
C 15.119316 10.619739 -1.775008
C 16.714258 9.868374 0.474107
C 15.883290 12.177990 1.362681
C 13.590796 11.024572 1.743618
C 15.468896 9.566709 2.712589
O 15.021057 7.140680 -0.064284
O 11.711883 11.675218 -0.848946
O 12.965142 8.497777 -3.638186
O 15.907865 11.257595 -2.337638
O 17.678382 9.441042 0.000493
O 16.344631 13.230290 1.549411
O 12.581565 11.385955 2.176902
O 15.673659 9.022791 3.720266

Energy and Thermal parameters

HF=-2446.0837573
Zero-point vibrational energy 352431.3 (Joules/Mol)
Zero-point correction= 0.134234 (Hartree/Particle)
Thermal correction to Energy= 0.179553
Thermal correction to Enthalpy= 0.180497
Thermal correction to Gibbs Free Energy= 0.041813
Sum of electronic and zero-point Energies= -2445.949523
Sum of electronic and thermal Energies= -2445.904204
Sum of electronic and thermal Enthalpies= -2445.903260
Sum of electronic and thermal Free Energies= -2446.041944

Compound $[Au\{\eta^2\text{-}Fe_2(CO)_8\}\{\eta^2\text{-}Fe_2(CO)_6(\mu\text{-}CO)_2\}]^{3-}$

Cartesian Coordinates

Au 3.241429 13.509373 2.292352
Fe 5.234066 11.322026 5.944959
Fe 2.794697 12.436052 4.738326
Fe 1.931424 14.837280 0.160710
Fe 4.533241 14.311964 -0.003883
C 6.006729 11.872256 4.434965
C 6.707447 10.672672 6.616248
C 4.978675 12.491525 7.264735
C 4.372242 9.762887 5.961710
C 3.617433 14.003108 5.027736
C 2.255030 11.809940 6.297613
C 1.187319 12.998631 4.288197
C 2.979386 11.048694 3.617014
C 1.379512 15.805332 1.570907
C 0.825926 13.446255 0.431190
C 1.162486 15.659361 -1.173749
C 2.971364 13.677088 -1.057768
C 3.516174 16.018025 0.064236
C 5.371522 14.809948 -1.454015
C 5.051660 12.595699 0.131159
C 5.608426 14.982234 1.271972
O 2.765798 12.926421 -1.955649
O 6.364385 15.472377 1.994184
O 0.605317 16.203886 -2.033815
O 0.970069 16.498366 2.399514
O 0.053529 12.590888 0.509509
O 0.099158 13.333946 4.080945
O 3.861639 8.719858 6.002726
O 7.686263 10.239942 7.064123
O 6.606883 12.187940 3.494275
O 3.754990 17.181891 0.083393
O 5.971000 15.120832 -2.396841
O 5.440461 11.508808 0.099793
O 3.017735 10.108822 2.936368
O 1.782063 11.439955 7.290099
O 4.863895 13.227587 8.156544
O 4.081527 15.034734 5.289420

Energy and Thermal parameters

HF=-2446.0899107
Zero-point vibrational energy 352197.9 (Joules/Mol)
Zero-point correction= 0.134145 (Hartree/Particle)
Thermal correction to Energy= 0.178928
Thermal correction to Enthalpy= 0.179872
Thermal correction to Gibbs Free Energy= 0.045917
Sum of electronic and zero-point Energies= -2445.955766
Sum of electronic and thermal Energies= -2445.910983
Sum of electronic and thermal Enthalpies= -2445.910039
Sum of electronic and thermal Free Energies= -2446.043994