Supporting Information Part II for:

Multi-Phosphine-Chelated Iron-Carbide Clusters via Redox–Promoted Ligand Exchange on an Inert Hexa-Iron-Carbide Carbonyl Cluster, $[Fe_6(\mu_6\text{-}C)(\mu_2\text{-}CO)_4(CO)_{12}]^{2-}$

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Contents – Selected Input Files for Computational Analysis **Page**

C-PCM model of Fe5

```
================================================================================
                        INPUT FILE
================================================================================
NAME = Fe5_BP86_TZ_D4_DCE.inp
|  1> !BP86 ma-def2-SVP def2/J RijCosX LargePrint
|  2>
|  3> #SCF
|  4> !verytightSCF DEFGRID2 KDIIS NOSOSCF TIGHTOPT D4 NumFreq
|  5>
|  6> %scf
|  7>       MaxIter 100000
|  8>       SOSCFStart 0.00033
|  9> end
| 10>
| 11> %cpcm
| 12>       smd true
| 13>       SMDsolvent "1,2-DICHLOROETHANE"
| 14> end
| 15>
| 16> #nprocs
| 17> %PAL NPROCS 48 end
| 18>
| 19> %method
| 20>       Z_solver Pople
| 21>       Z_MaxIter 3000
| 22> end
| 23>
```

```
| 24> # charge analyses
| 25> ! MULLIKEN
| 26> ! LOEWDIN
| 27>
| 28> %output
| 29>       Print[P_Basis] 5
| 30>       Print[P_MOs] 1
| 31>       Print[P_Mulliken] 1
| 32>       Print[P_Loewdin] 1
| 33> end
| 34>
| 35> * xyz 0 1
| 36>   C   11.07478929185126     -0.30313363407221      4.00075987851672
| 37>   C   12.71383755903513      2.62879634263514      4.55858983668477
| 38>   C   10.54248942316409      2.31220556211306      5.78282358065967
| 39>   C   12.34865403144072      0.68230060671600      6.49455843657446
| 40>   C   14.20823907203956      0.28523903285433      4.16887072504836
| 41>   C   13.32949337408001     -2.08391260209270      4.61956994242571
| 42>   C   13.85260902438712     -1.16391854222115      2.12019239683611
| 43>   C   10.12185858296032     -2.96848033903685      4.18557884116730
| 44>   C   11.63741068358602     -2.81703069945544      2.08116333666846
| 45>   C    9.21098155104056     -2.29644006765723      1.78527330471099
| 46>   C    7.89010256663446     -0.57284247887523      3.48620756708578
| 47>   C    8.26064557038337      1.69154810590612      4.39527766257863
| 48>   C    8.89294452829639     -0.41911791886422      5.90449160298954
| 49>   C   12.55851325529056      1.48492256840201      1.71891255974399
| 50>   C   10.56253052449420      0.08404252158514      0.82809655182070
| 51>   C   10.10512000076226      2.27268448442193      2.22280644941361
| 52>   Fe  11.66065713505835      1.22221057040351      4.94024405266889 newGTO "ma-def2-TZVP" end
| 53>   Fe  12.87318660353608     -0.72175098360757      3.56565994284733 newGTO "ma-def2-TZVP" end
| 54>   Fe  10.49218407195726     -1.75959460314377      2.93704960923732 newGTO "ma-def2-TZVP" end
| 55>   Fe   9.27269504006693      0.20933430003105      4.28077449934449 newGTO "ma-def2-TZVP" end
```

| 56> Fe 11.06598511218787 0.77906188069523 2.39103962370227 newGTO "ma-def2-TZVP" end

| 57> O 13.34699046244165 3.57029276482883 4.35317266524697

| 58> O 9.96116254502790 3.07422655474898 6.43237169603252

| 59> O 12.79641921413875 0.33818909726267 7.50101743775056

| 60> O 15.18487711105813 0.79937745905674 4.51638806107244

| 61> O 13.63055355002915 -2.97047667334527 5.29323657374700

| 62> O 14.52976562975313 -1.40940671434982 1.22102260085249

| 63> O 9.87827538449850 -3.75716277568265 4.99049341846320

| 64> O 12.24235177332062 -3.62357858553975 1.51380987275206

| 65> O 8.44612679219386 -2.71478440442839 1.03330747015364

| 66> O 6.89040846113921 -0.98717394321579 3.07681125412861

| 67> O 7.53756576946578 2.58629594845880 4.45836760378555

| 68> O 8.64484673239548 -0.81907017892971 6.95712204998074

| 69> O 13.45304902406929 2.01571893351769 1.21112693048818

| 70> O 10.28218824640140 -0.19945140731598 -0.26045589430113

| 71> O 9.55979530181329 3.27290781819649 2.02168885912163

| 72>

| 73> *

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Modeling of 2, gas phase input file

```
                          INPUT FILE
================================================================================
NAME = BP86_TZ_TZVP_D4_freq.inp
|  1> #this one is restricted (for our first geo opt attempt), larger on irons
|  2> #in summary: Fe6CO16, multiplicity 1, charge 0, BP86, firstgeo opt attempt from coordinates of first
optimized geometry for Fe62-, normal SCF
|  3>
|  4> !BP86 ma-def2-TZVP def2/J RijCosX LargePrint D4  NumFreq
|  5>
|  6> %scf
|  7>       MaxIter 100000
|  8>       SOSCFStart 0.00033
|  9> end
| 10>
| 11> %PAL NPROCS 48 end
| 12>
| 13> %method
| 14>       Z_solver Pople
| 15>       Z_MaxIter 3000
| 16> end
| 17>
| 18> %maxcore 3500
| 19> %output
| 20>       Print[P_Basis] 5
| 21>       Print[P_MOs] 1
| 22> end
| 23>
| 24> #Coordinates from ORCA-job BP86_NOSOSCF_TZVP_D4
| 25>
| 26> * xyz 0 1
| 27>   Fe   8.78677708760399      2.92892872745673      6.09624980502840 newGTO "def2-TZVP" end
| 28>   Fe  10.11978006899749      1.59591444332205      4.39580719660307 newGTO "def2-TZVP" end
| 29>   C    7.84909375351062      1.99124269051433      7.29976601976119
| 30>   O    7.25001373258023      1.39216163968973      8.07990490717669
| 31>   C   10.28972217982573      1.42598087773525      6.23774871677079
| 32>   O   10.81073820275375      0.90496815567379      7.14649410866173
| 33>   C   11.81433216348871      1.56235628595832      3.89854774338802
| 34>   O   12.91574849115769      1.49590984152814      3.55769110870827
| 35>   C    8.78677351741413      2.92892442929753      4.21657482694071
| 36>   Fe   7.45376382470363      4.26193093474185      4.39580887895620 newGTO "def2-TZVP" end
| 37>   C    9.72446787116205      3.86661630295106      7.29975897933118
| 38>   O   10.32355150059978      4.46569856955564      8.07989414346033
| 39>   C    7.28383273007958      4.43187102264823      6.23775198886660
| 40>   O    6.76281944274094      4.95288805009757      7.14649661367328
| 41>   C    5.75920826058049      4.29549471200048      3.89855920871501
| 42>   O    4.65779000708044      4.36194528230121      3.55770985916993
| 43>   Fe   8.78677379322419      2.92892213817345      2.33689984686814 newGTO "def2-TZVP" end
```

```
| 44>  Fe   7.45376502612177     1.59591707714156     4.03733887945044 newGTO "def2-TZVP" end
| 45>  C    9.72446598290154     1.99123908715071     1.13338822511223
| 46>  O   10.32354991471624     1.39215884110867     0.35325173645902
| 47>  C    7.28383326605672     1.42598257817734     2.19539408888022
| 48>  O    6.76281786451110     0.90496613975516     1.28665020169881
| 49>  C    5.75921028661471     1.56235358220342     4.53459144326596
| 50>  O    4.65779257771016     1.49590308302743     4.87544258684980
| 51>  Fe  10.11978149501857     4.26193337742186     4.03734444693157 newGTO "def2-TZVP" end
| 52>  C    7.84909235262868     3.86661308885809     1.13338598148615
| 53>  O    7.25001299901323     4.46569636408407     0.35324829492756
| 54>  C   10.28972338619612     4.43187219284105     2.19540461649273
| 55>  O   10.81073769472181     4.95288511487402     1.28665849564616
| 56>  C   11.81433414790930     4.29549255255373     4.53460205881262
| 57>  O   12.91575078207085     4.36193942202371     4.87545758485767
| 58>  C    7.42020341346681    -0.09863673761497     4.53459407470668
| 59>  O    7.35375416852045    -1.20005394610094     4.87544716082474
| 60>  C   10.15334171611321     5.95648716554474     4.53459865686894
| 61>  O   10.21978937999622     7.05790447517807     4.87545178267026
| 62>  C   10.15334331305032    -0.09864064518047     3.89855633823820
| 63>  O   10.21979325796744    -1.20005862187641     3.55770593796136
| 64>  C    7.42020440053198     5.95648318463637     3.89854941042127
| 65>  O    7.35375694665849     7.05789952054713     3.55769304535768
| 66> *
| 67>
| 68>
| 69>
| 70>
| 71>
| 72>
| 73>                    ****END OF INPUT****
```

Input file for freq. calculation of optimized geometry and optimized geometry coordinates for 3:

```
!BP86 def2-SVP D4 NumFreq

%freq
        CentralDiff true # use central-differences (this is the default)
        Increment 0.005 # increment in bohr for the
                        # differentiation (default 0.005)
end
* xyz 0 1
Fe   -1.604759000000    0.576040000000    2.574704000000
Fe    0.042676000000    1.986483000000    4.190714000000
Fe   -2.088918000000    3.286019000000    5.165049000000
O    -1.841447000000    5.926771000000    3.872337000000
O     0.429950000000   -1.468140000000    3.071074000000
O    -0.686181000000    1.506618000000   -0.058410000000
O     1.409400000000    4.504702000000    4.806434000000
O     2.239016000000    1.361467000000    2.333270000000
O    -4.485342000000    4.495975000000    6.339354000000
O    -3.056957000000   -1.631605000000    1.284886000000
O     1.371934000000    0.803281000000    6.524793000000
O    -0.582412000000    4.391659000000    7.431399000000
C    -1.841452000000    4.749301000000    3.872330000000
C    -1.841452000000    1.934261000000    3.872325000000
C     0.768665000000    1.186695000000    5.610548000000
C     0.811468000000    3.536219000000    4.585570000000
C    -3.556076000000    4.002558000000    5.848591000000
C    -2.527396000000   -0.733919000000    1.790515000000
C    -1.078078000000    1.335992000000    1.025771000000
C    -1.148885000000    3.965479000000    6.513051000000
C     1.356161000000    1.577432000000    3.050624000000
C    -0.339565000000   -0.612054000000    2.906566000000
Fe   -2.078136000000    0.576038000000    5.169948000000
Fe   -3.725579000000    1.986469000000    3.553937000000
Fe   -1.593997000000    3.286027000000    2.579611000000
O    -4.112846000000   -1.468144000000    4.673589000000
O    -2.996711000000    1.506617000000    7.803061000000
O    -5.092297000000    4.504692000000    2.938230000000
O    -5.921912000000    1.361477000000    5.411396000000
O     0.802434000000    4.495963000000    1.405300000000
O    -0.625947000000   -1.631608000000    6.459777000000
O    -5.054862000000    0.803267000000    1.219872000000
O    -3.100473000000    4.391688000000    0.313252000000
C    -4.451585000000    1.186683000000    2.134110000000
C    -4.494362000000    3.536209000000    3.159086000000
C    -0.126835000000    4.002553000000    1.896068000000
C    -1.155507000000   -0.733923000000    5.954144000000
C    -2.604817000000    1.336000000000    6.718877000000
C    -2.534015000000    3.965497000000    1.231603000000
C    -5.039059000000    1.577430000000    4.694036000000
C    -3.343333000000   -0.612055000000    4.838092000000
*
```