DT-ART-10-2025-002371

SUPPORTING INFORMATION

Inverted Ligand Fields: A Conceptual Dilemma for Molecular Orbital Theory

Contents

S1: $[CuL_4]^-$ optimised coordinates and aiLFT data for Figure 7 2
S2: B3LYP and TPSSh additional calculations 10
S3: $[Rh(AlMe)_4]^+$ structure and aiLFT results 10
S4: $[M(CF_3)_4]$ systems 11
S5: $[M(CF_3)_4]^m$ reactivities: Nucleophilic attack by F^- 14
S6: $[Cu(CF_3)_4]^m$ reactivities: Reductive elimination transition states.....17
S7: $[Ni(CF_3)_4]^m$ F^- dissociation 18
S8: $[Cu(NHC_2)(NCMe)]^m$, m = +2, +3 and $[Cu(NHC_4)]^{3+}$ structures and aiLFT results 18
S9: Optimised structures and aiLFT data for other Cu^{III} systems shown in Figure 16.....24

S1: $[CuL_4]^-$ optimised coordinates and aiLFT data for Figure 7

The general procedures are illustrated using $[CuF_4]^-$ as an example.

Geometry optimisations are straightforward. Frequency calculations confirm the nature of the point on the PE surface.

ORCA run file

```
!PAL8
!RKS BP RI def2-TZVP AutoAux TightSCF SlowConv TightOpt
!CPCM(ethanol)
!D3BJ
!Freq

* xyz -1 1
Cu      0.0  0.0  0.0
F       1.9  0.0  0.0
F      -1.9  0.0  0.0
F       0.0  1.9  0.0
F       0.0 -1.9  0.0
*
%Output
   Print[P_ReducedOrbPopMO_L] 1
end
```

Four lowest vibrational mode energies (modes 0-5 are rotations/translations)

```
   6:       108.81 cm**-1
   7:       247.29 cm**-1
   8:       277.21 cm**-1
   9:       277.21 cm**-1
```

Optimised coordinates

```
Cu       0.000000000      0.000000000      0.000000000
F        1.787363000      0.000000000      0.000000000
F       -1.787363000      0.000000000      0.000000000
F        0.000000000      1.787363000      0.000000000
F        0.000000000     -1.787363000      0.000000000
```

aiLFT calculations

The first step in aiLFT is to generate a suitable set of starting orbitals. In general, we are looking for five, mostly-d (or failing that, noticeably d) MOs. For a notional low-spin d^8 system, this may require orbital rotations to bring the top 4 occupied and the lowest unoccupied d MOs to the frontier. For unrestricted systems, a preliminary quasi-restricted open shell calculation is required (keyword UNO). This step is not particularly functional or basis-set dependent.

The next step is to run the CASSCF/NEVPT2 calculation. The aiLFT procedure is generally quite robust. However, near the d-level breach, convergence of the CASSCF step sometimes becomes an issue which, counterintuitively, can often be helped by **not** allowing the optimiser to switch to the Newton-Raphson method.

ORCA aiLFT input

```
!PAL8
!ROHF def2-SVP AutoAux TightSCF SlowConv
!CPCM(ethanol)

!MOREAD
%moinp "c:\users\rjdee\files\orca5\inverted_LF\cuIIIf4_ailft1.gbw"

%basis
   NewGTO Cu
      "def2-TZVP"
   end
end

%casscf
   nel 8
   norb 5
   mult 3, 1
   actorbs dorbs
   nroots 10, 15
   trafostep RI
```

```
   nevpt2 true
   switchstep nr
   switchconv 0.1
   switchiter 60
end

%scf
   rotate { 25, 30, 90 } end
end

* xyz -1 1
Cu       0.000000000      0.000000000      0.000000000
F        1.787363000      0.000000000      0.000000000
F       -1.787363000      0.000000000      0.000000000
F        0.000000000      1.787363000      0.000000000
F        0.000000000     -1.787363000      0.000000000
*
%Output
   Print[P_ReducedOrbPopMO_L] 1
end
```

ORCA aiLFT results

A successful aiLFT transformation is signalled as follows.

```
   E(CAS)= -2036.390536706 Eh DE=   -1.658736e-08
   --- Energy gap subspaces: Ext-Act = 0.730   Act-Int = -0.248
   --- current l-shift: Up(Ext-Act) = 0.27   Dn(Act-Int) = 1.25
   N(occ)=  1.60000 1.60000 1.60000 1.60000 1.60000
   ||g|| =     1.539502e-04 Max(G)=    1.387142e-04 Rot=33,1
                    ---- THE CAS-SCF ENERGY   HAS CONVERGED ----
                    ---- THE CAS-SCF GRADIENT HAS CONVERGED ----
                          --- FINALIZING ORBITALS ---
                   ---- DOING ONE FINAL ITERATION FOR PRINTING ----
   --- d-orbitals (depends on the molecular axis frame)
 L-Center:  0 Cu [0.000, 0.000, 0.000]
   --- The active space contains 5 d Orbitals : OK
 Setting 29 active MO to AO dz2     (15)
 Setting 30 active MO to AO dxz     (16)
 Setting 31 active MO to AO dyz     (17)
 Setting 32 active MO to AO dx2y2   (18)
 Setting 33 active MO to AO dxy     (19)


----------------------------
LOEWDIN REDUCED ACTIVE MOs
----------------------------
```

	24	25	26	27	28	29
	-0.57182	-0.53575	-0.53522	-0.53522	-0.51634	-0.76458
	2.00000	2.00000	2.00000	2.00000	2.00000	1.60000
0 Cu pz	7.1	0.0	0.0	0.0	0.0	0.0
0 Cu dz2	0.0	0.0	0.0	0.0	0.0	94.8
1 F pz	23.2	25.0	0.0	0.0	0.0	0.0
1 F px	0.0	0.0	14.7	0.0	0.0	0.8
1 F py	0.0	0.0	0.0	35.2	25.0	0.0
2 F pz	23.2	25.0	0.0	0.0	0.0	0.0
2 F px	0.0	0.0	14.7	0.0	0.0	0.8
2 F py	0.0	0.0	0.0	35.2	25.0	0.0
3 F pz	23.2	25.0	0.0	0.0	0.0	0.0
3 F px	0.0	0.0	35.2	0.0	25.0	0.0
3 F py	0.0	0.0	0.0	14.7	0.0	0.8
4 F pz	23.2	25.0	0.0	0.0	0.0	0.0
4 F px	0.0	0.0	35.2	0.0	25.0	0.0
4 F py	0.0	0.0	0.0	14.7	0.0	0.8

	30	31	32	33	34	35
	-0.75780	-0.75780	-0.62246	-0.73720	0.10792	0.26646
	1.60000	1.60000	1.60000	1.60000	0.00000	0.00000
0 Cu s	0.0	0.0	0.0	0.0	85.2	0.0
0 Cu pz	0.0	0.0	0.0	0.0	0.0	90.4
0 Cu dz2	0.0	0.0	0.0	0.0	10.0	0.0
0 Cu dxz	94.3	0.0	0.0	0.0	0.0	0.0
0 Cu dyz	0.0	94.3	0.0	0.0	0.0	0.0
0 Cu dx2y2	0.0	0.0	**81.0**	0.0	0.0	0.0
0 Cu dxy	0.0	0.0	0.0	93.9	0.0	0.0

```
------------------------------
AILFT MATRIX ELEMENTS (NEVPT2)
------------------------------

Ligand field one-electron matrix VLFT (a.u.) :
Orbital          dz2        dxz        dyz        dx2-y2     dxy
  dz2         -7.631072  -0.000000   0.000000   0.000000  -0.000000
  dxz         -0.000000  -7.622536  -0.000000   0.000000  -0.000000
  dyz          0.000000  -0.000000  -7.622536   0.000000  -0.000000
  dx2-y2       0.000000   0.000000   0.000000  -7.492920  -0.000000
  dxy         -0.000000  -0.000000  -0.000000  -0.000000  -7.605935

-------------------------------------------------
Slater-Condon Parameters (electronic repulsion) :
-------------------------------------------------
F2dd                    =  0.426984643 a.u. =    11.619 eV =   93712.3 cm**-1
F4dd                    =  0.208634927 a.u. =     5.677 eV =   45790.1 cm**-1
-------------------
Racah Parameters :
-------------------
B                       =  0.006348497 a.u. =     0.173 eV =    1393.3 cm**-1
C                       =  0.016558328 a.u. =     0.451 eV =    3634.1 cm**-1
C/B                     =  2.608
--------------------------------------------------------------------------------

-----------------------------------------
The ligand field one electron eigenfunctions:
-----------------------------------------
Orbital    Energy (eV)  Energy(cm-1)      dz2        dxz        dyz        dx2-y2     dxy
    1          0.000        0.0         1.000000   0.000000  -0.000000  -0.000000   0.000000
    2          0.232     1873.5         0.000000  -0.999842  -0.017794   0.000000  -0.000000
    3          0.232     1873.5        -0.000000   0.017794  -0.999842   0.000000  -0.000000
    4          0.684     5517.0        -0.000000  -0.000000  -0.000000   0.000000   1.000000
    5          3.759    30320.9        -0.000000  -0.000000  -0.000000  -1.000000   0.000000
Ligand field orbitals were stored in .\cuIIIf4_ailft2.nevpt2.lft.gbw

Calculating ligand field Hamiltonian matrices          ... done
Diagonalizing and fitting the ligand field Hamiltonian ... done
Calculating statistical parameters                     ... done

Reference energy AI-LFT =    -34.130650194 au
Reference energy AI     =    -34.145292684 au

-------------------------------------------------
COMPARISON OF AB INITIO AND LIGAND FIELD RESULTS
-------------------------------------------------

Block   1
---------
   AI-Root   0: E(AI)=    1.276 eV -> LF-Root   0:     0.688 eV    S= 1.000 Delta=    0.587 eV
   AI-Root   1: E(AI)=    1.280 eV -> LF-Root   1:     0.772 eV    S= 0.997 Delta=    0.508 eV
   AI-Root   2: E(AI)=    1.280 eV -> LF-Root   2:     0.772 eV    S= 0.997 Delta=    0.508 eV
   AI-Root   3: E(AI)=    1.936 eV -> LF-Root   3:     1.694 eV    S= 0.997 Delta=    0.242 eV
   AI-Root   4: E(AI)=    4.160 eV -> LF-Root   4:     3.671 eV    S= 1.000 Delta=    0.489 eV
   AI-Root   5: E(AI)=    4.160 eV -> LF-Root   5:     3.671 eV    S= 1.000 Delta=    0.489 eV
   AI-Root   6: E(AI)=    4.293 eV -> LF-Root   6:     3.763 eV    S= 1.000 Delta=    0.530 eV
   AI-Root   7: E(AI)=    5.037 eV -> LF-Root   7:     4.884 eV    S= 0.997 Delta=    0.153 eV
   AI-Root   8: E(AI)=    6.519 eV -> LF-Root   8:     6.350 eV    S= 0.999 Delta=    0.169 eV
   AI-Root   9: E(AI)=    6.519 eV -> LF-Root   9:     6.350 eV    S= 0.999 Delta=    0.169 eV
   RMS error for this block =     0.419 eV =    3381.4 cm**-1

Block   2
---------
   AI-Root   0: E(AI)=   -0.000 eV -> LF-Root   0:     0.000 eV    S= 0.999 Delta=   -0.000 eV
   AI-Root   1: E(AI)=    3.106 eV -> LF-Root   1:     2.799 eV    S= 0.998 Delta=    0.307 eV
   AI-Root   2: E(AI)=    3.106 eV -> LF-Root   2:     2.799 eV    S= 0.998 Delta=    0.307 eV
   AI-Root   3: E(AI)=    3.119 eV -> LF-Root   3:     2.978 eV    S= 1.000 Delta=    0.141 eV
   AI-Root   4: E(AI)=    3.312 eV -> LF-Root   4:     2.871 eV    S= 1.000 Delta=    0.441 eV
   AI-Root   5: E(AI)=    6.010 eV -> LF-Root   5:     5.611 eV    S= 0.998 Delta=    0.399 eV
   AI-Root   6: E(AI)=    6.246 eV -> LF-Root   6:     5.613 eV    S= 0.999 Delta=    0.633 eV
   AI-Root   7: E(AI)=    6.440 eV -> LF-Root   7:     6.013 eV    S= 0.998 Delta=    0.427 eV
   AI-Root   8: E(AI)=    6.440 eV -> LF-Root   8:     6.013 eV    S= 0.998 Delta=    0.427 eV
   AI-Root   9: E(AI)=    7.065 eV -> LF-Root   9:     6.539 eV    S= 1.000 Delta=    0.526 eV
   AI-Root  10: E(AI)=    7.385 eV -> LF-Root  10:     6.872 eV    S= 0.999 Delta=    0.512 eV
   AI-Root  11: E(AI)=    7.710 eV -> LF-Root  11:     7.103 eV    S= 0.982 Delta=    0.607 eV
```

```
   AI-Root  12: E(AI)=    7.710 eV -> LF-Root  12:     7.103 eV    S= 0.982 Delta=    0.607 eV
   AI-Root  13: E(AI)=    7.865 eV -> LF-Root  13:     7.211 eV    S= 0.998 Delta=    0.654 eV
   AI-Root  14: E(AI)=   10.415 eV -> LF-Root  14:    10.284 eV    S= 0.998 Delta=    0.131 eV
   RMS error for this block =     0.451 eV =    3635.9 cm**-1

Total RMS error g=     0.447 eV =    3609.2 cm**-1
Note: Dropped RMS error for the reference energy.

Confidence intervals (95) computed from the square root of the
diagonal elements of the covariance matrix:
H(dz2   ,dz2   )=  0.002765812 a.u. =     0.075 eV =     607.0 cm**-1
H(dxz   ,dz2   )=  0.002081886 a.u. =     0.057 eV =     456.9 cm**-1
H(dxz   ,dxz   )=  0.002765812 a.u. =     0.075 eV =     607.0 cm**-1
H(dyz   ,dz2   )=  0.002081886 a.u. =     0.057 eV =     456.9 cm**-1
H(dyz   ,dxz   )=  0.002081886 a.u. =     0.057 eV =     456.9 cm**-1
H(dyz   ,dyz   )=  0.002765812 a.u. =     0.075 eV =     607.0 cm**-1
H(dx2-y2,dz2   )=  0.002081886 a.u. =     0.057 eV =     456.9 cm**-1
H(dx2-y2,dxz   )=  0.002081886 a.u. =     0.057 eV =     456.9 cm**-1
H(dx2-y2,dyz   )=  0.002081886 a.u. =     0.057 eV =     456.9 cm**-1
H(dx2-y2,dx2-y2)=  0.002765812 a.u. =     0.075 eV =     607.0 cm**-1
H(dxy   ,dz2   )=  0.002081886 a.u. =     0.057 eV =     456.9 cm**-1
H(dxy   ,dxz   )=  0.002081886 a.u. =     0.057 eV =     456.9 cm**-1
H(dxy   ,dyz   )=  0.002081886 a.u. =     0.057 eV =     456.9 cm**-1
H(dxy   ,dx2-y2)=  0.002081886 a.u. =     0.057 eV =     456.9 cm**-1
H(dxy   ,dxy   )=  0.002765812 a.u. =     0.075 eV =     607.0 cm**-1
F2dd            =  0.012424247 a.u. =     0.338 eV =    2726.8 cm**-1
F4dd            =  0.016055558 a.u. =     0.437 eV =    3523.8 cm**-1
Pearson's correlation coefficient =    1.000 (should be close to 1)


---AILFT COMPLETED SUCCESFULLY!---
```

Summary for other $[CuL_4]^-$ complexes

$[Cu(OH)_4]^-$

```
Cu       0.000000000      0.000000000      0.000080000
O        1.842850000      0.113015000      0.000066000
O       -1.842851000     -0.113015000      0.000066000
O       -0.113018000      1.842850000      0.000032000
O        0.113018000     -1.842851000      0.000032000
H        0.829315000      2.097164000     -0.000081000
H        2.097160000     -0.829319000     -0.000057000
H       -0.829315000     -2.097165000     -0.000081000
H       -2.097160000      0.829319000     -0.000057000

   6:       109.24 cm**-1
   7:       114.72 cm**-1
   8:       247.13 cm**-1
   9:       247.13 cm**-1

----------------------------
LOEWDIN REDUCED ACTIVE MOs
----------------------------

                    24        25        26        27        28        29
                 -0.48357  -0.45810  -0.45043  -0.45043  -0.40468  -0.69903
                  2.00000   2.00000   2.00000   2.00000   2.00000   1.60000
                 --------  --------  --------  --------  --------  --------
 0 Cu pz             0.0       9.7       0.0       0.0       0.0       0.0
 0 Cu dz2            1.1       0.0       0.0       0.0       0.0      94.0
 1 O  pz             0.0      22.0       0.0       0.0      24.4       0.0
 1 O  px             4.5       0.0      36.7       0.3       0.0       0.8
 1 O  py            15.3       0.0       5.6       1.7       0.0       0.0
 2 O  pz             0.0      22.0       0.0       0.0      24.4       0.0
 2 O  px             4.5       0.0      36.7       0.3       0.0       0.8
 2 O  py            15.3       0.0       5.6       1.7       0.0       0.0
 3 O  pz             0.0      22.0       0.0       0.0      24.4       0.0
 3 O  px            15.3       0.0       1.7       5.6       0.0       0.0
 3 O  py             4.5       0.0       0.3      36.7       0.0       0.8
 4 O  pz             0.0      22.0       0.0       0.0      24.4       0.0
 4 O  px            15.3       0.0       1.7       5.6       0.0       0.0
 4 O  py             4.5       0.0       0.3      36.7       0.0       0.8

                    30        31        32        33        34        35
                 -0.67246  -0.67246  -0.51458  -0.68999   0.10716   0.26763
                  1.60000   1.60000   1.60000   1.60000   0.00000   0.00000
```

0	Cu	s	0.0	0.0	0.0	0.0	72.8	0.0
0	Cu	dz2	0.0	0.0	0.0	0.0	10.5	0.0
0	Cu	dxz	90.5	0.0	0.0	0.0	0.0	0.0
0	Cu	dyz	0.0	90.5	0.0	0.0	0.0	0.0
0	Cu	dx2y2	0.0	0.0	**74.5**	0.1	0.0	0.0
0	Cu	dxy	0.0	0.0	0.1	96.4	0.0	0.0
1	O	px	0.0	0.0	5.6	0.1	0.2	0.4
2	O	px	0.0	0.0	5.6	0.1	0.2	0.4
3	O	py	0.0	0.0	5.6	0.1	0.2	0.1
4	O	py	0.0	0.0	5.6	0.1	0.2	0.1
6	H	s	0.0	0.0	0.1	0.2	2.4	36.7
8	H	s	0.0	0.0	0.1	0.2	2.4	36.7

$[Cu(NH_2)_4]^-$

Cu	0.000035000	-0.000009000	0.000005000
N	0.439717000	-0.864057000	-1.658348000
N	-0.439545000	0.863979000	1.658418000
N	-1.155481000	-1.450126000	0.499311000
N	1.155347000	1.450231000	-0.499417000
H	-1.009169000	-1.560176000	1.511811000
H	0.456775000	-1.876994000	-1.482577000
H	0.760804000	2.311797000	-0.100667000
H	-0.456610000	1.876922000	1.482685000
H	1.008953000	1.560243000	-1.511909000
H	1.428342000	-0.627723000	-1.817088000
H	-0.761006000	-2.311728000	0.100570000
H	-1.428162000	0.627642000	1.817206000

6: 104.88 cm**-1
7: 154.59 cm**-1
8: 202.29 cm**-1
9: 221.51 cm**-1

LOEWDIN REDUCED ACTIVE MOs

			24	25	26	27	28	29
			-0.43860	-0.42786	-0.42554	-0.36708	-0.33059	-0.66776
			2.00000	2.00000	2.00000	2.00000	2.00000	1.60000
0	Cu	py	0.0	0.0	5.2	3.0	1.0	0.0
0	Cu	dz2	0.0	1.2	0.0	0.0	0.0	93.7
0	Cu	dxz	8.9	9.3	0.0	0.0	0.0	0.0
0	Cu	dyz	9.5	8.9	0.0	0.0	0.0	0.0
1	N	pz	15.6	13.2	7.0	6.3	13.4	0.0
1	N	py	1.1	3.5	10.0	14.0	8.9	0.8
2	N	pz	15.5	13.3	6.8	6.3	13.4	0.0
2	N	py	1.1	3.4	10.1	14.0	8.9	0.8
3	N	pz	14.0	14.5	6.7	6.4	13.3	0.0
3	N	px	0.9	3.5	9.3	14.8	8.5	0.8
4	N	pz	14.0	14.3	6.8	6.3	13.3	0.0
4	N	px	0.9	3.6	9.2	14.8	8.5	0.8

			30	31	32	33	34	35
			-0.64851	-0.64862	-0.42442	-0.66548	0.10857	0.23840
			1.60000	1.60000	1.60000	1.60000	0.00000	0.00000
0	Cu	s	0.0	0.0	0.0	0.0	66.1	0.0
0	Cu	dz2	0.0	0.0	0.0	0.0	12.2	0.0
0	Cu	dxz	91.9	0.0	0.0	0.0	0.1	0.0
0	Cu	dyz	0.0	91.9	0.0	0.0	0.1	0.0
0	Cu	dx2y2	0.1	0.1	**67.3**	0.0	0.0	0.0
0	Cu	dxy	0.0	0.0	0.0	98.0	0.0	0.0
1	N	py	0.0	0.4	6.5	0.0	0.1	0.5
2	N	py	0.0	0.4	6.5	0.0	0.1	0.5
3	N	px	0.4	0.0	6.5	0.0	0.1	0.5
4	N	px	0.4	0.0	6.5	0.0	0.1	0.5
6	H	s	0.0	0.1	0.1	0.1	1.5	14.6
7	H	s	0.1	0.0	0.2	0.1	1.5	14.6
8	H	s	0.0	0.1	0.1	0.1	1.5	14.6
11	H	s	0.1	0.0	0.2	0.1	1.5	14.6

$[Cu(CH_3)_4]^-$

Cu	-0.001241000	-0.001083000	0.000584000

C	-1.422311000	1.398527000	0.015805000
C	1.398789000	1.419469000	-0.019448000
C	-1.401011000	-1.422096000	-0.000274000
C	1.419159000	-1.401406000	0.007055000
H	-2.239886000	-1.157666000	0.664076000
H	-1.474429000	1.787705000	1.048288000
H	1.787037000	1.469948000	-1.052332000
H	2.412745000	-1.015034000	-0.271263000
H	-1.795596000	-1.479110000	-1.030445000
H	1.474217000	-1.794662000	1.037806000
H	1.013308000	2.414170000	0.256123000
H	-2.416413000	1.011849000	-0.260299000
H	-1.013363000	-2.415006000	0.278712000
H	1.154922000	-2.241007000	-0.656498000
H	2.241645000	1.158696000	0.641355000
H	-1.161599000	2.240906000	-0.645581000

6:	68.44	cm**-1
7:	83.01	cm**-1
8:	120.26	cm**-1
9:	120.42	cm**-1

LOEWDIN REDUCED ACTIVE MOs

		24	25	26	27	28	29
		-0.49012	-0.47408	-0.44453	-0.32788	-0.32788	-0.65116
		2.00000	2.00000	2.00000	2.00000	2.00000	1.60000
0	Cu px	0.7	0.0	0.0	12.4	6.5	0.0
0	Cu py	0.6	0.0	0.0	6.5	12.4	0.0
0	Cu dz2	0.0	0.7	0.0	0.0	0.0	92.7
1	C pz	0.6	12.5	0.0	0.0	0.2	0.0
1	C px	0.9	0.3	6.1	1.5	14.6	0.5
1	C py	1.0	0.3	6.1	0.1	16.1	0.5
2	C pz	0.0	12.5	0.0	0.2	0.0	0.0
2	C px	11.9	0.3	6.1	16.1	0.1	0.5
2	C py	12.0	0.3	6.1	14.6	1.5	0.5
3	C pz	0.0	12.5	0.0	0.2	0.0	0.0
3	C px	11.9	0.3	6.1	16.1	0.1	0.5
3	C py	12.0	0.3	6.1	14.6	1.5	0.5
4	C pz	0.6	12.5	0.0	0.0	0.2	0.0
4	C px	0.9	0.3	6.1	1.5	14.6	0.5
4	C py	1.0	0.3	6.1	0.1	16.1	0.5
5	H s	10.2	1.3	6.0	0.6	1.2	0.0
6	H s	0.0	8.4	0.0	0.0	0.6	0.0
7	H s	0.0	8.4	0.0	0.6	0.0	0.0
8	H s	0.5	1.3	6.0	0.6	1.1	0.0
9	H s	0.0	8.4	0.0	0.6	0.0	0.0
10	H s	0.0	8.4	0.0	0.0	0.6	0.0
11	H s	10.2	1.3	6.0	1.1	0.6	0.0
12	H s	0.5	1.3	6.0	0.6	1.1	0.0
13	H s	10.2	1.3	6.0	1.1	0.6	0.0
14	H s	0.4	1.3	6.0	1.2	0.6	0.0
15	H s	10.2	1.3	6.0	0.6	1.2	0.0
16	H s	0.4	1.3	6.0	1.2	0.6	0.0

		30	31	32	33	34	35
		-0.66739	-0.66739	-0.64592	-0.30929	0.10700	0.23322
		1.60000	1.60000	1.60000	1.60000	0.00000	0.00000
0	Cu s	0.0	0.0	0.0	0.0	65.2	0.0
0	Cu dz2	0.0	0.0	0.0	0.0	13.5	0.0
0	Cu dxz	98.3	0.0	0.0	0.0	0.0	0.1
0	Cu dyz	0.0	98.3	0.0	0.0	0.0	0.0
0	Cu dx2y2	0.0	0.0	98.4	0.0	0.0	0.0
0	Cu dxy	0.0	0.0	0.0	**58.8**	0.0	0.0
2	C s	0.0	0.0	0.0	1.5	1.8	6.4
3	C s	0.0	0.0	0.0	1.5	1.8	6.4
5	H s	0.0	0.0	0.1	0.1	0.6	9.6
7	H s	0.2	0.2	0.0	0.1	1.5	13.3
9	H s	0.2	0.2	0.0	0.1	1.5	13.3
11	H s	0.0	0.0	0.1	0.1	0.6	6.2
13	H s	0.0	0.0	0.1	0.1	0.6	6.2
15	H s	0.0	0.0	0.1	0.1	0.6	9.6

$[Cu(BH_2)_4]^-$

Cu	-0.000009000	-0.000044000	-0.003937000
B	1.924207000	0.118284000	-0.004277000
B	-1.924226000	-0.118371000	-0.004280000
B	-0.118339000	1.924173000	-0.004071000
B	0.118321000	-1.924261000	-0.004062000
H	-0.157866000	2.577119000	-1.025565000
H	2.577038000	0.158055000	-1.025835000
H	0.157926000	-2.577206000	-1.025553000
H	-2.577072000	-0.157867000	-1.025838000
H	0.157931000	-2.577284000	1.017253000
H	2.577324000	0.158081000	1.016971000
H	-0.157875000	2.577204000	1.017241000
H	-2.577361000	-0.157883000	1.016967000

```
   6:        58.33 cm**-1
   7:        70.83 cm**-1
   8:        70.85 cm**-1
   9:        89.73 cm**-1

   E(CAS)= -1741.847552011 Eh DE=   -4.199001e-08
   --- Energy gap subspaces: Ext-Act = 0.382   Act-Int = 0.178
   --- current l-shift: Up(Ext-Act) = 0.62   Dn(Act-Int) = 0.82
   N(occ)=  1.60000 1.60000 1.60000 1.60000 1.60000
   ||g|| =     1.777255e-04 Max(G)=    1.118768e-04 Rot=27,12
                    ---- THE CAS-SCF GRADIENT HAS CONVERGED ----
                           --- FINALIZING ORBITALS ---
                   ---- DOING ONE FINAL ITERATION FOR PRINTING ----
   --- d-orbitals (depends on the molecular axis frame)

 L-Center:  0 Cu
[0.000, 0.000, 0.000]

   --- The active space contains 3 d Orbitals : not OK

   --- The active space contains 1 s Orbitals : not OK

   --- The active space contains 1 p Orbitals : not OK

Error (ORCA_CASSCF): Orbitals Entering AILFT D-Case have a problem!

AILFT D-Case expects 5 d Orbitals
```

$[Cu(BeH)_4]^-$: planar

Cu	-0.000009000	-0.000044000	-0.002741000
Be	2.078278000	0.130078000	-0.003889000
Be	-2.078296000	-0.130165000	-0.003892000
Be	-0.130132000	2.078243000	-0.004033000
Be	0.130114000	-2.078331000	-0.004022000
H	-0.211458000	3.459922000	-0.004737000
H	-3.459975000	-0.211487000	-0.004927000
H	3.459956000	0.211401000	-0.004922000
H	0.211440000	-3.460010000	-0.004721000

```
   6:       -64.87 cm**-1 ***imaginary mode***
   7:       -64.87 cm**-1 ***imaginary mode***
   8:       -61.23 cm**-1 ***imaginary mode***
   9:        60.92 cm**-1
```

$[Cu(BeH)_4]^-$: distorted

Cu	-0.000245000	-0.592408000	-0.007911000
Be	-1.432118000	-0.170628000	1.441589000
Be	1.433902000	-0.138458000	1.428390000
Be	-1.433251000	-0.129739000	-1.443999000
Be	1.437376000	-0.107656000	-1.432087000
H	-2.365592000	0.300152000	-2.372007000
H	2.360982000	0.283718000	2.365048000
H	-2.367037000	0.225601000	2.381385000
H	2.365984000	0.329418000	-2.360408000

```
   6:        51.25 cm**-1
   7:        55.93 cm**-1
   8:        58.22 cm**-1
   9:        67.89 cm**-1
```

```
----------------------------
LOEWDIN REDUCED ACTIVE MOs
----------------------------
```

	18	19	20	21	22	23
	-0.42928	-0.31628	-0.31596	-0.64227	-0.68808	-0.68801
	2.00000	2.00000	2.00000	1.60000	1.60000	1.60000
0 Cu s	0.0	0.0	0.0	7.0	0.0	0.0
0 Cu px	0.0	12.5	16.2	0.0	1.8	0.0
0 Cu py	0.0	16.2	12.5	0.0	0.0	1.8
0 Cu dz2	0.0	0.0	0.0	79.4	0.0	0.0
0 Cu dxz	0.0	2.8	3.6	0.0	93.6	0.0
0 Cu dyz	0.0	3.6	2.8	0.0	0.0	93.6
1 Be px	5.8	5.3	6.9	2.4	1.1	0.0
1 Be py	0.0	5.1	3.8	0.0	0.0	0.6
2 Be px	0.0	3.9	5.3	0.0	0.6	0.0
2 Be py	5.9	6.7	5.1	2.5	0.0	0.9
3 Be px	0.0	3.8	5.0	0.0	0.6	0.0
3 Be py	5.8	7.0	5.1	2.3	0.0	1.1
4 Be px	5.9	5.1	6.9	2.5	1.0	0.0
4 Be py	0.0	5.1	4.0	0.0	0.0	0.6
5 H s	14.1	1.7	1.3	0.1	0.0	0.1
6 H s	14.9	1.8	1.3	0.1	0.0	0.1
7 H s	14.2	1.3	1.7	0.1	0.1	0.0
8 H s	14.9	1.3	1.7	0.1	0.1	0.0

	24	25	26	27	28	29
	-0.68637	-0.17141	0.02220	0.10412	0.10437	0.12640
	1.60000	1.60000	0.00000	0.00000	0.00000	0.00000
0 Cu s	0.0	0.0	3.5	0.0	0.0	58.7
0 Cu pz	0.0	0.0	18.0	0.0	0.0	1.6
0 Cu dz2	0.0	0.0	0.4	0.0	0.0	16.0
0 Cu dxz	0.0	0.0	0.0	13.0	1.2	0.0
0 Cu dyz	0.0	0.0	0.0	1.2	13.0	0.0
0 Cu dx2y2	98.9	0.0	0.0	0.0	0.0	0.0
0 Cu dxy	0.0	35.3	0.0	0.0	0.0	0.0
1 Be pz	0.0	0.0	18.3	34.1	3.1	1.2
1 Be py	0.0	16.1	0.0	0.2	2.9	0.0
2 Be pz	0.0	0.0	18.1	3.0	33.2	1.2
2 Be px	0.0	16.1	0.0	2.9	0.2	0.0
3 Be pz	0.0	0.0	18.2	3.4	33.9	1.2
3 Be px	0.0	16.0	0.0	2.9	0.3	0.0
4 Be pz	0.0	0.0	18.2	33.0	3.4	1.2
4 Be py	0.0	16.1	0.0	0.3	2.7	0.0

[$CuLi_4$]$^-$: planar

Cu	0.000000000	0.000000000	0.000000000
Li	2.482109000	0.000000000	0.000000000
Li	-2.482109000	0.000000000	0.000000000
Li	0.000000000	2.482109000	0.000000000
Li	0.000000000	-2.482109000	0.000000000

```
   6:      -155.49 cm**-1 ***imaginary mode***
   7:      -118.85 cm**-1 ***imaginary mode***
   8:      -118.71 cm**-1 ***imaginary mode***
   9:       -68.75 cm**-1 ***imaginary mode***
```

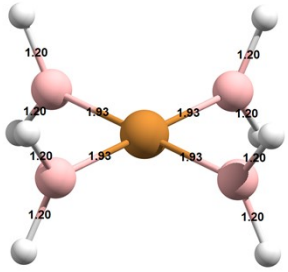
[$CuLi_4$]$^-$: distorted planar

Cu	0.134100000	-0.116043000	0.399482000
Li	2.520250000	0.566323000	0.397221000
Li	-2.393647000	0.186245000	0.398986000
Li	-0.187601000	2.410163000	0.393886000
Li	-0.535101000	-2.508325000	0.410550000

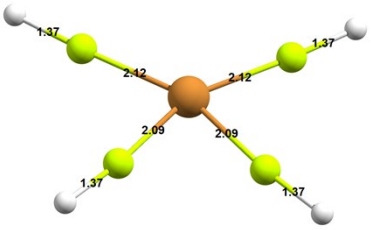
```
   6:        77.52 cm**-1
   7:        95.98 cm**-1
   8:       126.18 cm**-1
   9:       131.95 cm**-1
```

S2: B3LYP and TPSSh additional calculations

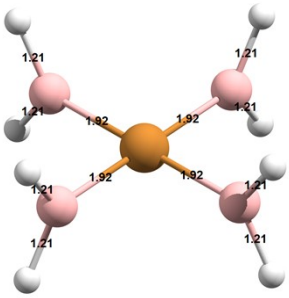
All structures confirmed as local minima.



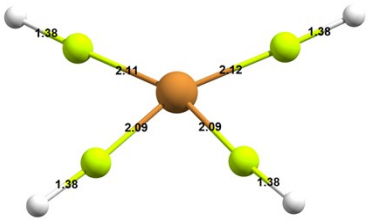
B3LYP



B3LYP



TPSSh

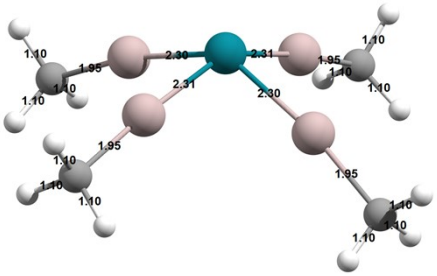


TPSSh

$[Cu(BH_2)_4]^-$ **$[Cu(BeH)_4]^-$**

Comparing the above structures to the BP86 geometries depicted in Figure 7 of the manuscript, the abrupt change in structure from planar to distorted occurs at $[Cu(BeH)_4]^-$ for all three functionals.

S3: $[Rh(AlMe)_4]^+$ structure and aiLFT results



Rh	0.000000000	0.000000000	0.001128000
Al	0.000000000	-2.225864000	0.616214000
Al	-2.144118000	0.000000000	0.822845000
Al	0.000000000	2.225864000	0.616215000
Al	2.144118000	0.000000000	0.822843000
C	0.000000000	4.048144000	1.315039000
H	-0.894220000	4.221872000	1.934100000
H	0.894220000	4.221872000	1.934102000
H	0.000001000	4.779820000	0.492045000
C	3.819115000	0.000000000	1.827119000
H	3.881064000	0.894168000	2.467270000
H	3.881059000	-0.894162000	2.467279000
H	4.683646000	-0.000006000	1.145217000
C	0.000000000	-4.048144000	1.315038000
H	0.894220000	-4.221873000	1.934099000
H	-0.894220000	-4.221872000	1.934100000
H	0.000000000	-4.779820000	0.492042000
C	-3.819115000	-0.000001000	1.827120000
H	-4.683646000	-0.000008000	1.145218000
H	-3.881059000	-0.894162000	2.467281000

```
H       -3.881066000      0.894167000      2.467271000

   6:        14.31 cm**-1
   7:        14.69 cm**-1
   8:        17.06 cm**-1
   9:        19.65 cm**-1

   E(CAS)= -1235.238464264 Eh DE=   -4.667959e-08
   --- Energy gap subspaces: Ext-Act = 0.263   Act-Int = 0.092
   --- current l-shift: Up(Ext-Act) = 0.74   Dn(Act-Int) = 0.91
   N(occ)=  1.60000 1.60000 1.60000 1.60000 1.60000
   ||g|| =     1.893546e-04 Max(G)=   -5.354631e-05 Rot=60,51
                    ---- THE CAS-SCF GRADIENT HAS CONVERGED ----
                         --- FINALIZING ORBITALS ---
                  ---- DOING ONE FINAL ITERATION FOR PRINTING ----
   --- d-orbitals (depends on the molecular axis frame)

 L-Center:  0 Rh
[0.000, 0.000, 0.000]

   --- The active space contains 4 d Orbitals : not OK

   --- The active space contains 1 p Orbitals : not OK

Error (ORCA_CASSCF): Orbitals Entering AILFT D-Case have a problem!

AILFT D-Case expects 5 d Orbitals
```

S4: [M(CF$_3$)$_4$] systems

[Cu(CF$_3$)$_4$] ground state

```
Cu       0.000000000      0.000000000     -0.199224000
C       -1.482915000     -1.352338000     -0.403617000
C       -1.444356000      1.330614000      0.488538000
C        1.444356000     -1.330614000      0.488538000
C        1.482915000      1.352338000     -0.403618000
F       -2.540426000     -0.897604000     -1.131922000
F       -1.978275000     -1.889935000      0.735346000
F       -0.934396000     -2.379492000     -1.129827000
F        0.796309000     -2.268238000      1.200649000
F        2.023528000     -1.901171000     -0.580325000
F        2.378921000     -0.780981000      1.270404000
F        2.540426000      0.897604000     -1.131922000
F        0.934396000      2.379492000     -1.129827000
F        1.978275000      1.889936000      0.735345000
F       -0.796309000      2.268239000      1.200649000
F       -2.023528000      1.901172000     -0.580325000
F       -2.378920000      0.780982000      1.270404000

   6:        27.87 cm**-1
   7:        43.62 cm**-1
   8:        47.95 cm**-1
   9:        54.65 cm**-1

Electronic energy                ...  -2991.90069970 Eh
Zero point energy                ...      0.05016217 Eh      31.48 kcal/mol
Final Gibbs free energy          ...  -2991.89679300 Eh
```

[Cu(CF$_3$)$_4$]: aiLFT for d^7

```
   E(CAS)= -1796.720205456 Eh DE=   -3.074524e-08
   --- Energy gap subspaces: Ext-Act = 0.215   Act-Int = 0.281
   --- current l-shift: Up(Ext-Act) = 0.79   Dn(Act-Int) = 0.72
   N(occ)=  1.40000 1.40000 1.40000 1.40000 1.40000
   ||g|| =     1.115885e-04 Max(G)=   -4.947764e-05 Rot=29,9
                    ---- THE CAS-SCF GRADIENT HAS CONVERGED ----
                           --- FINALIZING ORBITALS ---
                  ---- DOING ONE FINAL ITERATION FOR PRINTING ----
   --- d-orbitals (depends on the molecular axis frame)

 L-Center:  0 Cu
[0.000, 0.000, 0.000]

   --- The active space contains 3 d Orbitals : not OK
```

--- The active space contains 2 p Orbitals : not OK

Error (ORCA_CASSCF): Orbitals Entering AILFT D-Case have a problem!

AILFT D-Case expects 5 d Orbitals

$[Ni(CF_3)_4]^-$ D_{2d} state

Ni	-0.000042000	0.000030000	-0.000139000
C	-1.402218000	-1.420514000	-0.179912000
C	-1.420504000	1.402150000	0.179990000
C	1.420478000	-1.402054000	0.180109000
C	1.402201000	1.420434000	-0.180204000
F	-1.883625000	-1.892857000	1.022102000
F	-2.520111000	-1.020479000	-0.892213000
F	-0.986119000	-2.543286000	-0.874612000
F	-2.543343000	0.986114000	0.874494000
F	-1.892794000	1.884110000	-1.021914000
F	-1.020117000	2.519664000	0.892573000
F	1.020178000	-2.519578000	0.892717000
F	1.892815000	-1.884016000	-1.021777000
F	2.543275000	-0.985903000	0.874609000
F	2.519875000	1.020247000	-0.892759000
F	0.986132000	2.543298000	-0.874761000
F	1.883916000	1.892641000	1.021735000

6: 12.10 cm**-1
7: 43.98 cm**-1
8: 56.99 cm**-1
9: 57.03 cm**-1

Electronic energy ... -2859.93437508 Eh
Zero point energy ... 0.04949613 Eh 31.06 kcal/mol
Final Gibbs free energy ... -2859.93109160 Eh

$[Ni(CF_3)_4]^-$ C_{2v} state

Ni	-0.156277000	-0.126829000	1.253099000
C	-1.058711000	-1.023820000	-0.278099000
C	-1.617238000	1.180334000	1.504106000
C	1.158929000	-1.583032000	1.487291000
C	1.247465000	1.284206000	1.133150000
F	-1.750701000	-0.175257000	-1.103744000
F	-1.979273000	-1.949763000	0.166224000
F	-0.212324000	-1.708633000	-1.112010000
F	0.504756000	-2.785369000	1.750589000
F	2.080298000	-1.892036000	0.521051000
F	1.912727000	-1.357789000	2.638689000
F	2.385379000	0.894973000	0.474508000
F	0.846612000	2.426832000	0.489740000
F	1.656323000	1.682695000	2.388109000
F	-1.385907000	1.930899000	2.656457000
F	-1.939104000	2.103757000	0.544078000
F	-2.813924000	0.519099000	1.775121000

6: 18.21 cm**-1
7: 30.49 cm**-1
8: 34.94 cm**-1
9: 53.81 cm**-1

Electronic energy ... -2859.94960028 Eh
Zero point energy ... 0.04889618 Eh 30.68 kcal/mol
Final Gibbs free energy ... -2859.94752858 Eh

$[Ni(CF_3)_4]^-$ d^7 aiLFT

LOEWDIN REDUCED ACTIVE MOs

	72	73	74	75	76	77
	-0.61260	-0.60249	-0.57099	-0.46231	-0.46231	-0.61719
	2.00000	2.00000	2.00000	2.00000	2.00000	1.40000
0 Ni s	0.0	0.0	14.7	0.0	0.0	3.2
0 Ni px	0.0	0.0	0.0	0.0	17.8	0.0
0 Ni py	0.0	0.0	0.0	17.8	0.0	0.0
0 Ni dz2	0.0	0.0	5.0	0.0	0.0	93.3
6 F py	3.8	7.7	2.2	0.6	1.6	0.0

7	F	pz	8.7	2.7	0.0	0.1	0.0	0.0
7	F	px	4.7	7.7	2.2	1.6	0.6	0.0
8	F	py	3.8	7.7	2.2	0.6	1.6	0.0
10	F	pz	8.7	2.7	0.0	0.1	0.0	0.0
10	F	px	4.7	7.7	2.2	1.6	0.6	0.0
11	F	pz	8.7	2.7	0.0	0.1	0.0	0.0
11	F	px	4.7	7.7	2.2	1.6	0.6	0.0
13	F	py	3.8	7.7	2.2	0.6	1.6	0.0
14	F	py	3.8	7.7	2.2	0.6	1.6	0.0
15	F	pz	8.7	2.7	0.0	0.1	0.0	0.0
15	F	px	4.7	7.7	2.2	1.6	0.6	0.0

			78	79	80	81	82	83
			-0.62964	-0.62964	-0.61506	-0.37646	0.12325	0.15813
			1.40000	1.40000	1.40000	1.40000	0.00000	0.00000
0	Ni	s	0.0	0.0	0.0	0.0	0.0	64.8
0	Ni	pz	0.0	0.0	0.0	1.2	65.5	0.0
0	Ni	dz2	0.0	0.0	0.0	0.0	0.0	24.1
0	Ni	dxz	98.1	0.0	0.0	0.0	0.0	0.0
0	Ni	dyz	0.0	98.1	0.0	0.0	0.0	0.0
0	Ni	dx2y2	0.0	0.0	99.2	0.0	0.0	0.0
0	Ni	dxy	0.0	0.0	0.0	65.9	1.6	0.0

$[Ni(CF_3)_4]^{2-}$ D_{2d} structure and vib. modes

Ni	0.000026000	-0.000007000	0.000001000
C	-1.381073000	-1.381061000	-0.224084000
C	1.381086000	-1.381093000	0.224110000
C	1.381078000	1.381090000	-0.224088000
F	-2.522819000	-0.989845000	-0.951449000
F	-0.989939000	-2.522810000	-0.951487000
F	-1.934660000	-1.934653000	0.943553000
F	0.989877000	-2.522838000	0.951481000
F	1.934698000	-1.934684000	-0.943516000
F	2.522819000	-0.989938000	0.951527000
F	2.522785000	0.989973000	-0.951568000
F	1.934733000	1.934621000	0.943545000
F	0.989840000	2.522872000	-0.951385000
C	-1.381066000	1.381058000	0.224063000
F	-0.989906000	2.522841000	0.951398000
F	-1.934689000	1.934595000	-0.943583000
F	-2.522790000	0.989879000	0.951482000

6:	21.98 cm**-1
7:	38.78 cm**-1
8:	44.91 cm**-1
9:	44.93 cm**-1

$[Ni(CF_3)_4]^{2-}$ d^8 aiLFT

```
----------------------------
LOEWDIN REDUCED ACTIVE MOs
----------------------------
```

			72	73	74	75	76	77
			-0.56284	-0.49751	-0.45736	-0.40683	-0.40683	-0.41788
			2.00000	2.00000	2.00000	2.00000	2.00000	1.60000
0	Ni	s	0.0	14.9	0.0	0.0	0.0	2.3
0	Ni	px	0.0	0.0	0.0	8.4	8.4	0.0
0	Ni	py	0.0	0.0	0.0	8.4	8.4	0.0
0	Ni	dz2	0.0	2.7	0.0	0.0	0.0	96.1
0	Ni	dxy	0.0	0.0	30.3	0.0	0.0	0.0
1	C	s	0.0	2.0	2.4	7.1	0.0	0.1
1	C	px	0.1	3.1	3.4	8.3	0.1	0.1
1	C	py	0.1	3.1	3.4	8.3	0.1	0.1
2	C	s	0.0	2.0	2.4	0.0	7.1	0.1
2	C	px	0.1	3.1	3.4	0.1	8.3	0.1
2	C	py	0.1	3.1	3.4	0.1	8.3	0.1
3	C	s	0.0	2.0	2.4	7.1	0.0	0.1
3	C	px	0.1	3.1	3.4	8.3	0.1	0.1
3	C	py	0.1	3.1	3.4	8.3	0.1	0.1
4	F	py	8.2	1.8	0.7	1.7	0.1	0.0
5	F	px	8.2	1.8	0.7	1.7	0.1	0.0
7	F	px	8.2	1.8	0.7	0.1	1.7	0.0

9	F	py	8.2	1.8	0.7	0.1	1.7	0.0
10	F	py	8.2	1.8	0.7	1.7	0.1	0.0
12	F	px	8.2	1.8	0.7	1.7	0.1	0.0
13	C	s	0.0	2.0	2.4	0.0	7.1	0.1
13	C	px	0.1	3.1	3.4	0.1	8.3	0.1
13	C	py	0.1	3.1	3.4	0.1	8.3	0.1
14	F	px	8.2	1.8	0.7	0.1	1.7	0.0
16	F	py	8.2	1.8	0.7	0.1	1.7	0.0

			78	79	80	81	82	83
			-0.42563	-0.42563	-0.41407	-0.28302	0.18036	0.19400
			1.60000	1.60000	1.60000	1.60000	0.00000	0.00000
			---	---	---	---	---	---
0	Ni	s	0.0	0.0	0.0	0.0	69.9	0.0
0	Ni	pz	0.0	0.0	0.0	1.6	0.0	54.9
0	Ni	dz2	0.0	0.0	0.0	0.0	19.0	0.0
0	Ni	dxz	98.6	0.0	0.0	0.0	0.0	0.0
0	Ni	dyz	0.0	98.6	0.0	0.0	0.0	0.0
0	Ni	dx2y2	0.0	0.0	98.5	0.0	0.0	0.0
0	Ni	dxy	0.0	0.0	0.0	83.4	0.0	3.2
1	C	pz	0.1	0.1	0.0	0.0	0.1	6.3
2	C	pz	0.1	0.1	0.0	0.0	0.1	6.3
3	C	pz	0.1	0.1	0.0	0.0	0.1	6.3
13	C	pz	0.1	0.1	0.0	0.0	0.1	6.3

S5: $[M(CF_3)_4]^m$ reactivities: Nucleophilic attack by F^-

All transitions states were confirmed as first-order saddle points with one and only one imaginary mode. However, given that the reactants and products comprise pairs of weakly interacting components, a few residual imaginary modes (lower than -20 cm^{-1}) remained.

$[Cu(CF_3)_4]^-$: Reactants

Cu	0.024846000	0.043173000	0.025626000
C	-1.391532000	-1.344349000	-0.241048000
C	-1.372574000	1.453473000	0.269661000
C	1.413236000	-1.381717000	0.231838000
C	1.444867000	1.441432000	-0.150911000
F	-2.485017000	-0.887410000	-0.946074000
F	-1.891095000	-1.863225000	0.927243000
F	-0.965884000	-2.427238000	-0.981354000
F	0.967356000	-2.496747000	0.911971000
F	1.923929000	-1.853413000	-0.953981000
F	2.508122000	-0.978432000	0.971723000
F	2.553184000	1.019301000	-0.858708000
F	1.032464000	2.559267000	-0.849740000
F	1.931645000	1.914350000	1.044895000
F	-0.939312000	2.537841000	1.007752000
F	-1.860368000	1.978796000	-0.903126000
F	-2.479713000	1.018516000	0.969763000
F	-4.294825000	-4.185842000	-0.378354000

$[Cu(CF_3)_4]^-$: TS (602i cm^{-1})

Cu	0.003733000	0.017710000	0.104691000
C	-1.778975000	-1.730295000	-0.356004000
C	-1.477892000	1.283887000	0.477433000
C	1.255166000	-1.483194000	0.434546000
C	1.434917000	1.445606000	-0.445924000
F	-2.478240000	-0.848090000	-1.055325000
F	-2.033347000	-1.956117000	0.922282000
F	-0.921935000	-2.486915000	-1.024043000
F	0.815514000	-2.597393000	1.172645000
F	1.858446000	-2.070004000	-0.683300000
F	2.355591000	-1.052306000	1.198561000
F	2.497005000	0.976049000	-1.249005000
F	0.963552000	2.537300000	-1.205939000
F	2.115502000	2.085875000	0.609060000
F	-1.025498000	2.345295000	1.283550000
F	-2.043536000	1.940237000	-0.621426000
F	-2.607803000	0.845496000	1.191325000
F	-3.155994000	-3.040333000	-0.772895000

$[Cu(CF_3)_4]^-$: products

Cu	0.552125000	0.523583000	0.456733000
C	-2.311643000	-2.233339000	-1.439480000
C	-1.131571000	1.342769000	1.178134000
C	1.283715000	-1.229305000	1.084275000
C	1.578599000	1.598194000	-0.903074000
F	-2.579387000	-0.956651000	-1.736770000
F	-2.499443000	-2.438501000	-0.131793000
F	-1.043165000	-2.510777000	-1.760520000
F	0.442789000	-2.106954000	1.836907000
F	1.769304000	-2.125442000	0.087058000
F	2.412920000	-1.131475000	1.948141000
F	2.643804000	0.971289000	-1.622437000
F	0.850883000	2.187549000	-1.978748000
F	2.249316000	2.734002000	-0.362739000
F	-0.940412000	2.484381000	2.010689000
F	-2.061203000	1.845644000	0.220663000
F	-1.999447000	0.556007000	1.997769000
F	-3.131164000	-3.032972000	-2.137073000

$Cu(CF_3)_4$: Reactants

Cu	-0.011558000	0.005695000	0.150844000
C	-1.430642000	-1.381525000	-0.421371000
C	-1.407529000	1.420744000	0.375761000
C	1.383890000	-1.415038000	0.338221000
C	1.413085000	1.411299000	-0.240834000
F	-2.410436000	-0.811395000	-1.153992000
F	-1.973788000	-1.937841000	0.674171000
F	-0.885814000	-2.354489000	-1.182244000
F	0.887107000	-2.510852000	1.008572000
F	1.920403000	-1.893179000	-0.823140000
F	2.446008000	-0.994048000	1.105352000
F	2.436120000	0.905444000	-0.973016000
F	0.913157000	2.448904000	-0.956773000
F	1.929038000	1.908170000	0.909711000
F	-0.957885000	2.467923000	1.147162000
F	-1.895382000	1.977294000	-0.772028000
F	-2.500188000	0.933848000	1.058502000
F	-3.736258000	-3.633177000	-0.147723000

$Cu(CF_3)_4$: TS (595i cm^{-1})

Cu	0.013141000	0.027403000	0.235677000
C	-1.724734000	-1.665964000	-0.341059000
C	-1.396968000	1.413082000	0.430431000
C	1.374658000	-1.409941000	0.392232000
C	1.391019000	1.391593000	-0.345232000
F	-2.537415000	-0.892229000	-1.001508000
F	-2.025625000	-1.993566000	0.884184000
F	-0.974528000	-2.469007000	-1.040051000
F	0.871104000	-2.478883000	1.115369000
F	1.843673000	-1.946925000	-0.777902000
F	2.491099000	-1.015451000	1.096190000
F	2.379366000	0.842966000	-1.091635000
F	0.847857000	2.381496000	-1.093933000
F	1.959156000	1.957499000	0.747760000
F	-0.970406000	2.521350000	1.128081000
F	-1.953581000	1.894238000	-0.725500000
F	-2.456051000	0.922728000	1.177101000
F	-3.355560000	-3.267578000	-0.809974000

$Cu(CF_3)_4$: Products

Cu	0.318626000	0.323672000	0.453893000
C	-2.480226000	-2.409214000	-1.041014000
C	-1.254630000	1.509984000	0.643972000
C	1.484312000	-1.268482000	0.608558000
C	1.648142000	1.646269000	-0.339335000
F	-2.808411000	-1.190032000	-1.482857000
F	-2.462608000	-2.410928000	0.296703000
F	-1.270992000	-2.742887000	-1.505117000
F	0.891212000	-2.310450000	1.340054000
F	1.853724000	-1.880433000	-0.585278000
F	2.695979000	-1.063779000	1.267078000
F	2.626551000	1.086567000	-1.135806000
F	1.089892000	2.639568000	-1.118336000
F	2.333129000	2.312995000	0.660694000
F	-1.024584000	2.709671000	1.315802000
F	-1.875320000	1.903855000	-0.537459000
F	-2.296191000	0.922140000	1.380181000

F	-3.384100000	-3.297466000	-1.475599000

$[Ni(CF_3)_4]^-$: Reactants

Ni	0.016411000	0.034672000	0.025481000
C	-1.393183000	-1.346339000	-0.218560000
C	-1.373809000	1.450864000	0.231131000
C	1.410265000	-1.382909000	0.193067000
C	1.441467000	1.436888000	-0.107508000
F	-2.511662000	-0.914272000	-0.914406000
F	-1.881637000	-1.860212000	0.966228000
F	-0.992014000	-2.450160000	-0.955802000
F	0.987289000	-2.527740000	0.857500000
F	1.919310000	-1.840528000	-1.009307000
F	2.526609000	-1.010709000	0.932432000
F	2.580267000	1.042428000	-0.801584000
F	1.058952000	2.579902000	-0.801932000
F	1.917041000	1.906363000	1.104990000
F	-0.970199000	2.563269000	0.959281000
F	-1.857395000	1.965605000	-0.958503000
F	-2.504521000	1.039932000	0.927249000
F	-4.253863000	-4.139277000	-0.332580000

$[Ni(CF_3)_4]^-$: TS(597i cm^{-1})

Ni	-0.103451000	-0.090185000	0.716587000
C	-1.428258000	-1.387604000	-0.671239000
C	-1.515405000	1.195766000	1.146641000
C	1.166880000	-1.522050000	1.134367000
C	1.139336000	1.144489000	-0.238090000
F	-1.967129000	-0.310157000	-1.246640000
F	-2.003284000	-1.957871000	0.400370000
F	-0.360040000	-1.939564000	-1.251865000
F	0.603980000	-2.685057000	1.713463000
F	2.057923000	-2.056952000	0.202586000
F	2.033866000	-1.071829000	2.163852000
F	2.081085000	0.564956000	-1.100727000
F	0.564175000	2.131457000	-1.052266000
F	1.942654000	1.896755000	0.644329000
F	-1.041282000	2.069909000	2.159128000
F	-2.063688000	2.081821000	0.217818000
F	-2.670626000	0.644588000	1.753131000
F	-2.515711000	-2.456860000	-1.745878000

$[Ni(CF_3)_4]^-$: Products

Ni	0.396331000	0.407729000	0.448463000
C	-2.578510000	-2.516647000	-1.069577000
C	-1.190101000	1.509652000	0.633566000
C	1.482213000	-1.195326000	0.618647000
C	1.680190000	1.684496000	-0.293386000
F	-2.915077000	-1.308093000	-1.533255000
F	-2.546916000	-2.492366000	0.267066000
F	-1.374671000	-2.858493000	-1.541500000
F	0.877352000	-2.263452000	1.368892000
F	1.851683000	-1.882268000	-0.570199000
F	2.735639000	-1.086012000	1.280095000
F	2.663899000	1.199557000	-1.201084000
F	1.193264000	2.811439000	-1.011994000
F	2.492079000	2.313737000	0.694976000
F	-1.057131000	2.756498000	1.301763000
F	-1.872416000	1.897440000	-0.552619000
F	-2.267262000	0.919386000	1.382404000
F	-3.486061000	-3.416229000	-1.476125000

$[Ni(CF_3)_4]^{2-}$: Reactants

Ni	0.026835000	0.045382000	0.025626000
C	-1.367097000	-1.319580000	-0.230460000
C	-1.343331000	1.434549000	0.263668000
C	1.393081000	-1.353191000	0.227405000
C	1.423558000	1.418813000	-0.149094000
F	-2.513315000	-0.904168000	-0.933898000
F	-1.905652000	-1.897426000	0.929506000
F	-0.986317000	-2.440764000	-0.992626000
F	0.987837000	-2.521884000	0.899800000
F	1.970375000	-1.861339000	-0.950137000
F	2.520944000	-0.992708000	0.993787000
F	2.580762000	1.035352000	-0.856428000
F	1.055483000	2.575642000	-0.865835000
F	1.954267000	1.949815000	1.040456000

F	-0.947966000	2.565226000	1.007611000
F	-1.885089000	2.008093000	-0.900495000
F	-2.491715000	1.044479000	0.979723000
F	-4.353331000	-4.238513000	-0.391436000

$[Ni(CF_3)_4]^{2-}$: TS(625i cm^{-1})

Ni	0.057702000	0.077206000	0.150107000
C	-1.940950000	-1.877459000	-0.426635000
C	-1.391314000	1.275250000	0.556288000
C	1.229298000	-1.408308000	0.488184000
C	1.411686000	1.406737000	-0.529102000
F	-2.569028000	-0.856062000	-1.055802000
F	-2.155546000	-2.120034000	0.892645000
F	-0.942978000	-2.499663000	-1.097075000
F	0.805850000	-2.620607000	1.181810000
F	1.950586000	-2.019304000	-0.602978000
F	2.337949000	-1.055000000	1.358008000
F	2.575898000	0.950387000	-1.260216000
F	0.978300000	2.446971000	-1.444852000
F	2.066698000	2.222121000	0.471393000
F	-0.992123000	2.380390000	1.409242000
F	-2.044780000	2.006565000	-0.506390000
F	-2.575647000	0.859438000	1.301312000
F	-3.073010000	-2.986705000	-0.893293000

$[Ni(CF_3)_4]^{2-}$: Products

Ni	0.548425000	0.511606000	0.490400000
C	-2.324898000	-2.232770000	-1.537484000
C	-1.021667000	1.337864000	1.188753000
C	1.294004000	-1.131169000	1.111793000
C	1.474900000	1.514397000	-0.850045000
F	-2.590411000	-0.964387000	-1.867462000
F	-2.489337000	-2.398907000	-0.221152000
F	-1.066248000	-2.531325000	-1.875397000
F	0.490153000	-2.103292000	1.948113000
F	1.800281000	-2.127436000	0.150748000
F	2.455795000	-1.041658000	1.983657000
F	2.628766000	0.932409000	-1.632115000
F	0.758020000	2.074664000	-2.002781000
F	2.149946000	2.719482000	-0.384874000
F	-0.823573000	2.497688000	2.045560000
F	-2.037277000	1.884194000	0.277383000
F	-1.992435000	0.594639000	2.091135000
F	-3.164957000	-3.046870000	-2.195410000

Energetics (data in a.u.)

	Cu(III)	Cu(IV)	Ni(II)	Ni(III)
E(reac): BP86	-3092.150828	-3091.934798	-2960.125379	-2959.966081
E(TS): BP86	-3092.082796	-3091.916399	-2959.980037	-2959.905137
E(prod): BP86	-3092.164997	-3092.031676	-2960.032804	-2959.972134
G(reac): BP86	-3092.146892	-3091.933762	-2960.123356	-2959.966057
G(TS): BP86	-3092.083431	-3091.914927	-2959.986056	-2959.906785
G(prod): BP86	-3092.165705	-3092.030411	-2960.040063	-2959.973528
E(reac): B3LYP	-3091.226286	-3090.995573	-2959.208093	-2959.043889
E(TS): B3LYP	-3091.152822	-3090.98891	-2959.03352	-2958.978793
E(prod): B3LYP	-3091.249119	-3091.121758	-2959.089053	-2959.061463

S6: $[Cu(CF_3)_4]^m$ reactivities: Reductive elimination transition states

$[Cu(CF_3)_4]^-$: (261i cm^{-1})

Cu	-0.527658966	1.023272307	0.043875914
C	-1.316917366	-1.017127319	-0.317333683
F	-1.487970674	-2.172089480	0.371288777
F	-1.201680976	-1.324739684	-1.613272871
F	-2.486620699	-0.341483124	-0.110547049
C	0.571419515	-0.839348043	0.489321895
F	1.624119866	0.012336046	0.292640057
F	0.941069475	-1.958769267	-0.181952045
F	0.488049596	-1.144294005	1.788604886
C	-0.452619151	1.850041160	1.836645318
F	0.801747534	2.014983326	2.417839209

F	-1.190907414	1.209220426	2.835306662
F	-0.980149794	3.147013018	1.843569089
C	-0.727177576	1.751888298	-1.780904686
F	0.155312952	1.234956264	-2.734403310
F	-0.473339837	3.127930321	-1.836481369
F	-1.971435963	1.634425740	-2.394060006

$Cu(CF_3)_4$: (181i cm^{-1})

Cu	-0.610587000	1.297013000	0.049051000
C	-1.492641000	-0.823813000	-0.053210000
F	-1.511718000	-1.681561000	0.950930000
F	-1.441204000	-1.437941000	-1.221925000
F	-2.617479000	-0.078060000	0.002879000
C	0.807669000	-0.593485000	0.196034000
F	1.689090000	0.410163000	0.062544000
F	1.016034000	-1.484701000	-0.753893000
F	0.904332000	-1.122063000	1.398717000
C	-0.691663000	1.652071000	2.012120000
F	0.459353000	1.404033000	2.729322000
F	-1.699836000	1.025823000	2.706737000
F	-0.926375000	3.008503000	2.162460000
C	-0.557417000	1.558098000	-1.928046000
F	0.201239000	0.693075000	-2.676318000
F	-0.011784000	2.812316000	-2.150800000
F	-1.795812000	1.582519000	-2.529964000

S7: $[Ni(CF_3)_4]^m$ F^- dissociation

$[Ni(CF_3)_4]^-$: (506i cm^{-1})

Ni	-0.277605000	1.212036000	0.053267000
C	-1.604551000	-0.869916000	0.038478000
F	-1.903404000	-1.597745000	1.128822000
F	-1.824622000	-1.630609000	-1.048145000
F	-2.519162000	0.156669000	-0.010310000
C	0.384621000	-0.527361000	0.105691000
F	1.741103000	0.324677000	0.143016000
F	0.677153000	-1.288116000	-0.972089000
F	0.597291000	-1.255037000	1.223941000
C	-0.465379000	1.592960000	1.956790000
F	0.690270000	1.850296000	2.669238000
F	-1.196610000	0.757316000	2.775074000
F	-1.169350000	2.810754000	1.998678000
C	-0.316700000	1.526672000	-1.872454000
F	0.892182000	1.654329000	-2.528282000
F	-0.914041000	2.793239000	-2.011851000
F	-1.069992000	0.711824000	-2.693228000

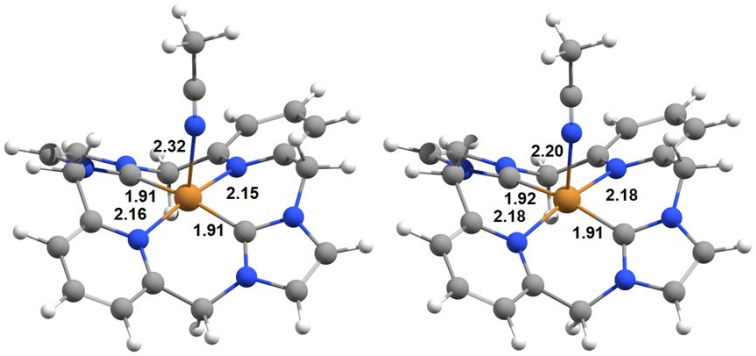
$[Ni(CF_3)_4]^{2-}$: (408i cm^{-1})

Ni	-0.258656935	1.277405536	0.075637615
C	-1.591057635	-1.023691548	-0.000683953
F	-1.918435547	-1.743022926	1.126061585
F	-1.776178765	-1.899545857	-1.047355209
F	-2.618528703	-0.111081427	-0.134561177
C	0.399084565	-0.429596209	0.077206815
F	1.962641842	0.245798792	0.151486112
F	0.708634277	-1.184548389	-1.032518844
F	0.619390366	-1.218361704	1.186141802
C	-0.457851431	1.628516900	1.960080473
F	0.662596398	1.749690179	2.789985176
F	-1.326494133	0.862522187	2.740248432
F	-1.041643623	2.928566555	2.047094761
C	-0.344240260	1.618470079	-1.818192090
F	0.823102220	1.762789146	-2.576803142
F	-0.952363968	2.902835387	-1.950635966
F	-1.142399330	0.825439746	-2.643750142

S8: $[Cu(NHC_2)(NCMe)]^m$, m = +2, +3 and $[Cu(NHC_4)]^{3+}$ structures and aiLFT results

DFT optimisations and aiLFT calculations used the same basis sets: def2-TZVP for Cu and def2-SVP for all other atoms.

$[Cu^{II}(NHC_2)(NCMe)]^{2+}$



Left: X-ray structure, right: DFT-optimised structure

Optimised coordinates

Cu	0.023275000	-0.018191000	-0.026036000
N	0.048573000	2.138716000	-0.325529000
N	2.758368000	0.982923000	0.138138000
N	2.712173000	-0.972072000	-0.776532000
N	-0.000976000	-2.197319000	-0.134525000
N	-2.711931000	-1.005542000	0.201054000
N	-2.659137000	0.858814000	-0.885963000
N	0.033828000	0.050185000	2.177322000
C	1.925963000	-0.012256000	-0.243221000
C	4.052611000	-0.588298000	-0.740244000
H	4.857074000	-1.217843000	-1.133740000
C	4.082400000	0.657075000	-0.154826000
H	4.919381000	1.322772000	0.078962000
C	2.269610000	2.168751000	0.837624000
H	3.101876000	2.890080000	0.912441000
H	1.992029000	1.877392000	1.873331000
C	1.075678000	2.857299000	0.190821000
C	1.046134000	4.263950000	0.206485000
H	1.899154000	4.819907000	0.621352000
C	-0.070960000	4.932782000	-0.303582000
H	-0.121801000	6.031464000	-0.287376000
C	-1.116353000	4.178962000	-0.851709000
H	-2.002211000	4.668188000	-1.281004000
C	-1.021358000	2.777364000	-0.867788000
C	-2.090378000	1.993725000	-1.614001000
H	-2.916002000	2.674758000	-1.883685000
H	-1.647732000	1.614382000	-2.560661000
C	-1.877366000	-0.045950000	-0.258435000
C	-3.998846000	0.474621000	-0.832504000
H	-4.799833000	1.062716000	-1.291738000
C	-4.032771000	-0.712881000	-0.137217000
H	-4.871015000	-1.358032000	0.144603000
C	-2.227187000	-2.119445000	1.012580000
H	-3.060144000	-2.829666000	1.155153000
H	-1.950467000	-1.728749000	2.015476000
C	-1.031712000	-2.866471000	0.437405000
C	-1.003807000	-4.266077000	0.579099000
H	-1.860041000	-4.782420000	1.036324000
C	0.116399000	-4.977742000	0.137913000
H	0.166129000	-6.070615000	0.252370000
C	1.166608000	-4.276023000	-0.467325000
H	2.055648000	-4.801047000	-0.844547000
C	1.072757000	-2.881370000	-0.608616000
C	2.148804000	-2.165220000	-1.409891000
H	2.975706000	-2.867368000	-1.613108000
H	1.714961000	-1.867945000	-2.389383000
C	0.137288000	0.088257000	3.340976000
C	0.266452000	0.137534000	4.784808000
H	0.246941000	1.191896000	5.125896000
H	1.224331000	-0.326624000	5.093302000
H	-0.572986000	-0.411626000	5.255890000

aiLFT results

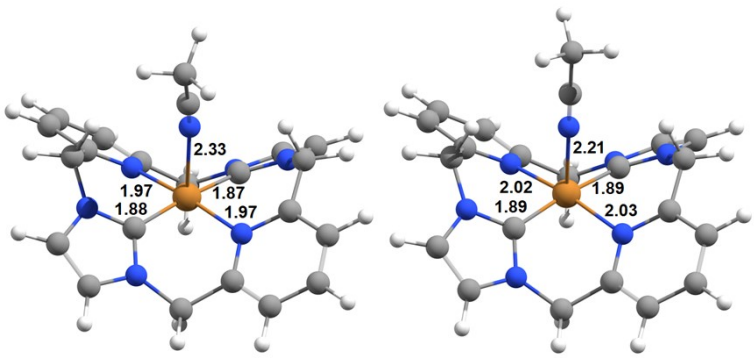
```
   E(CAS)= -2864.264641916 Eh DE=   -6.562914e-09
   --- Energy gap subspaces: Ext-Act = 0.602   Act-Int = -0.218
   --- current l-shift: Up(Ext-Act) = 0.40   Dn(Act-Int) = 1.22
   N(occ)=  1.80000 1.80000 1.80000 1.80000 1.80000
```

```
   ||g|| =     9.542181e-04 Max(G)=    3.636698e-04 Rot=112,51
                    ---- THE CAS-SCF ENERGY   HAS CONVERGED ----
                         --- FINALIZING ORBITALS ---
                    ---- DOING ONE FINAL ITERATION FOR PRINTING ----
   --- d-orbitals (depends on the molecular axis frame)
 L-Center:  0 Cu [0.044, -0.034, -0.049]
   --- The active space contains 5 d Orbitals : OK
 Setting 110 active MO to AO dz2     (15)
 Setting 111 active MO to AO dxz     (16)
 Setting 112 active MO to AO dyz     (17)
 Setting 113 active MO to AO dx2y2   (18)
 Setting 114 active MO to AO dxy     (19)

----------------------------
LOEWDIN REDUCED ACTIVE MOs
----------------------------
```

	108	109	110	111	112	113
	-0.35715	-0.35480	-0.60259	-0.61359	-0.62158	-0.53897
	2.00000	2.00000	1.80000	1.80000	1.80000	1.80000
0 Cu dz2	0.0	0.2	95.9	0.0	0.0	0.0
0 Cu dxz	1.9	0.0	0.0	98.2	0.0	0.0
0 Cu dyz	0.0	0.0	0.0	0.0	99.3	0.0
0 Cu dx2y2	0.0	0.0	0.1	0.0	0.0	89.5
8 C pz	7.5	7.6	0.0	0.0	0.0	0.0
9 C pz	13.7	12.5	0.0	0.0	0.0	0.0
11 C pz	13.7	12.6	0.0	0.1	0.0	0.0
27 C pz	6.4	7.3	0.0	0.0	0.0	0.0
28 C pz	11.7	12.0	0.0	0.0	0.0	0.0
30 C pz	11.7	12.1	0.0	0.0	0.0	0.0

	114	115	116	117	118	119
	-0.61501	0.06054	0.06806	0.09154	0.09776	0.11639
	1.80000	0.00000	0.00000	0.00000	0.00000	0.00000
0 Cu s	0.0	1.1	0.0	8.3	0.0	14.3
0 Cu dz2	0.0	2.7	0.0	0.0	0.0	9.1
0 Cu dxy	99.0	0.7	0.0	0.4	0.0	0.6
1 N pz	0.0	6.3	7.0	0.0	0.0	2.0
4 N pz	0.0	5.8	7.6	0.0	0.1	2.0
8 C pz	0.0	1.6	0.0	0.0	0.0	8.9
16 C pz	0.0	4.1	4.0	7.9	8.5	0.1
17 C pz	0.0	1.6	2.1	7.3	7.7	1.5
19 C pz	0.0	10.9	12.2	0.0	0.0	2.6
21 C pz	0.0	0.9	1.1	8.0	8.6	0.1
23 C pz	0.0	4.7	4.6	5.8	6.7	0.8
27 C pz	0.0	1.4	0.0	0.0	0.0	7.3
35 C pz	0.0	3.7	4.3	7.1	9.4	0.1
36 C pz	0.0	1.5	2.2	6.5	8.5	1.5
38 C pz	0.0	9.8	13.0	0.0	0.1	2.6
40 C pz	0.0	0.8	1.2	7.1	9.4	0.1
42 C pz	0.0	4.3	4.9	5.2	7.2	0.8

$[Cu^{III}(NHC_2)(NCMe)]^{3+}$



Left: X-ray structure, right: DFT-optimised structure

Optimised coordinates

Cu	0.062829000	0.037344000	0.025922000

```
N        0.108185000     -1.974771000     -0.195434000
N        2.759977000     -0.899245000      0.431227000
N        2.701204000      0.915985000     -0.750530000
N        0.021960000      2.062269000     -0.097300000
N       -2.648331000      0.958456000      0.385598000
N       -2.545793000     -0.794396000     -0.883449000
N        0.057177000      0.016686000      2.232791000
C        1.945157000      0.031918000     -0.085082000
C        4.079594000     -0.605950000      0.092949000
H        4.918040000     -1.231024000      0.416483000
C        4.042333000      0.551418000     -0.654900000
H        4.839899000      1.130807000     -1.131095000
C        2.087551000      1.996722000     -1.517727000
H        1.624572000      1.566762000     -2.432144000
H        2.877625000      2.699480000     -1.830166000
C        1.038773000      2.734183000     -0.713361000
C        1.112959000      4.133002000     -0.651486000
H        1.949857000      4.641218000     -1.149734000
C        0.132587000      4.853416000      0.036810000
H        0.181145000      5.950239000      0.099317000
C       -0.919920000      4.151819000      0.627327000
H       -1.731183000      4.676887000      1.150845000
C       -0.965440000      2.750689000      0.545420000
C       -2.142080000      2.052633000      1.202358000
H       -1.846165000      1.659692000      2.196890000
H       -2.955388000      2.781231000      1.357850000
C       -1.815460000      0.049222000     -0.140687000
C       -3.953077000      0.691400000     -0.024257000
H       -4.802302000      1.304097000      0.294789000
C       -3.888152000     -0.426670000     -0.827726000
H       -4.666538000     -0.976651000     -1.366454000
C       -1.905192000     -1.834367000     -1.683993000
H       -1.410949000     -1.358005000     -2.558351000
H       -2.683460000     -2.518963000     -2.060288000
C       -0.883451000     -2.613251000     -0.884162000
C       -0.952499000     -4.013467000     -0.905317000
H       -1.768846000     -4.495019000     -1.460975000
C        0.007039000     -4.769329000     -0.225949000
H       -0.037720000     -5.868103000     -0.229179000
C        1.034486000     -4.099652000      0.440848000
H        1.829811000     -4.651055000      0.961517000
C        1.075885000     -2.696073000      0.441060000
C        2.225562000     -2.031965000      1.175274000
H        1.890300000     -1.687249000      2.175151000
H        3.033904000     -2.766934000      1.326742000
C        0.101858000      0.067717000      3.399197000
C        0.158857000      0.127613000      4.844113000
H        1.216609000      0.111412000      5.174900000
H       -0.374906000     -0.742715000      5.275350000
H       -0.320665000      1.062953000      5.196003000
```

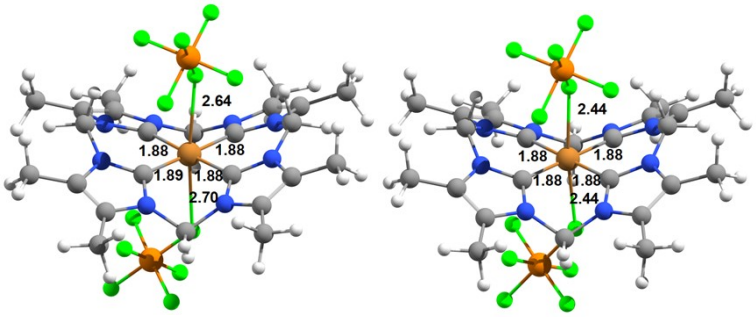
aiLFT results

```
   E(CAS)= -2863.856439411 Eh DE=    9.566065e-09
   --- Energy gap subspaces: Ext-Act = 0.606   Act-Int = -0.431
   --- current l-shift: Up(Ext-Act) = 0.39   Dn(Act-Int) = 1.43
   N(occ)=  1.60000 1.60000 1.60000 1.60000 1.60000
   ||g|| =     9.398322e-04 Max(G)=    3.596219e-04 Rot=110,108
                    ---- THE CAS-SCF ENERGY   HAS CONVERGED ----
                           --- FINALIZING ORBITALS ---
                  ---- DOING ONE FINAL ITERATION FOR PRINTING ----
   --- d-orbitals (depends on the molecular axis frame)
 L-Center:  0 Cu [0.119, 0.071, 0.049]
   --- The active space contains 5 d Orbitals : OK
 Setting 110 active MO to AO dz2     (15)
 Setting 111 active MO to AO dxz     (16)
 Setting 112 active MO to AO dyz     (17)
 Setting 113 active MO to AO dx2y2   (18)
 Setting 114 active MO to AO dxy     (19)

----------------------------
LOEWDIN REDUCED ACTIVE MOs
----------------------------

                   108       109       110       111       112       113
                -0.38623  -0.38499  -0.77785  -0.79567  -0.82004  -0.58078
                 2.00000   2.00000   1.60000   1.60000   1.60000   1.60000
                --------  --------  --------  --------  --------  --------
```

0	Cu	dz2	0.0	0.1	88.2	0.0	0.0	0.0
0	Cu	dxz	0.1	0.0	0.0	92.2	0.0	0.0
0	Cu	dyz	0.0	0.0	0.0	0.0	96.2	0.0
0	Cu	dx2y2	0.0	0.0	0.3	0.0	0.0	68.1
8	C	pz	0.0	5.2	0.0	0.4	0.0	0.0
9	C	pz	0.2	8.6	0.0	0.5	0.0	0.0
11	C	pz	0.1	8.1	0.0	0.5	0.0	0.0
16	C	pz	6.7	3.3	0.0	0.0	0.1	0.0
17	C	pz	7.4	1.2	0.0	0.0	0.0	0.0
21	C	pz	7.7	4.8	0.0	0.0	0.0	0.0
23	C	pz	7.1	1.8	0.0	0.0	0.1	0.0
28	C	pz	0.7	7.2	0.0	0.5	0.0	0.0
30	C	pz	0.6	6.8	0.0	0.4	0.0	0.0
35	C	pz	7.6	1.8	0.0	0.0	0.1	0.0
36	C	pz	7.7	0.4	0.0	0.0	0.0	0.0
40	C	pz	9.0	2.9	0.0	0.0	0.0	0.0
42	C	pz	7.7	0.8	0.0	0.0	0.1	0.0

			114	115	116	117	118	119
			-0.80797	0.02598	0.04039	0.07529	0.08024	0.09051
			1.60000	0.00000	0.00000	0.00000	0.00000	0.00000
			---	---	---	---	---	---
0	Cu	s	0.0	0.7	0.0	4.9	0.0	6.2
0	Cu	pz	0.0	6.1	0.0	0.0	0.0	7.4
0	Cu	dz2	0.0	2.6	0.0	0.3	0.0	5.8
0	Cu	dxy	96.2	1.4	0.0	0.3	0.0	0.9
1	N	pz	0.1	4.0	5.7	0.0	0.0	2.6
4	N	pz	0.1	4.1	6.0	0.0	0.0	2.9
8	C	pz	0.1	1.9	0.0	0.1	0.0	8.8
16	C	pz	0.1	4.4	4.9	5.8	6.1	0.3
17	C	pz	0.0	0.6	0.8	6.6	8.0	0.6
19	C	pz	0.0	8.2	11.2	0.0	0.0	3.5
21	C	pz	0.0	0.6	1.3	7.5	7.7	0.5
23	C	pz	0.0	4.6	4.9	6.2	7.8	0.8
27	C	pz	0.1	1.8	0.0	0.1	0.0	7.2
35	C	pz	0.1	4.3	4.7	5.6	5.9	0.3
36	C	pz	0.0	0.6	0.8	6.4	7.6	0.6
38	C	pz	0.0	7.9	10.7	0.0	0.0	3.3
38	C	px	0.0	3.9	5.1	0.0	0.0	1.3
40	C	pz	0.0	0.6	1.2	7.3	7.4	0.4
42	C	pz	0.1	4.5	4.8	6.0	7.3	0.8

$[Cu^{III}(NHC_4)(PF_6)_2]^+$



Left: X-ray structure, right: DFT-optimised structure

Optimised coordinates

Cu	-0.013793000	0.035130000	0.077616000
N	2.716691000	0.980376000	-0.106384000
N	2.596797000	-0.958107000	0.851870000
N	0.880544000	-2.643412000	0.727060000
N	-0.986670000	-2.662256000	-0.366207000
N	-2.650772000	-0.945318000	-0.616786000
N	-2.722543000	1.057929000	0.193726000
N	-1.010543000	2.739329000	0.362434000
N	1.044881000	2.699447000	-0.314601000
C	1.856190000	0.019226000	0.289335000
C	4.038819000	0.615581000	0.202645000
C	3.961515000	-0.623098000	0.819335000
C	5.213730000	1.467268000	-0.129794000
H	6.140369000	0.985343000	0.231074000
H	5.139717000	2.465929000	0.348864000

H	5.309925000	1.619392000	-1.224792000
C	5.024721000	-1.502787000	1.378169000
H	6.016123000	-1.042947000	1.214767000
H	5.025606000	-2.498550000	0.887916000
H	4.893923000	-1.658248000	2.469028000
C	2.011504000	-2.130664000	1.498410000
H	1.653510000	-1.859552000	2.511400000
H	2.780183000	-2.917278000	1.576742000
C	-0.031266000	-1.848590000	0.128965000
C	0.493906000	-3.990570000	0.639812000
C	-0.696588000	-4.004195000	-0.069044000
C	1.281372000	-5.098222000	1.247523000
H	0.802996000	-6.068309000	1.021500000
H	1.339520000	-4.993016000	2.350750000
H	2.317414000	-5.126556000	0.850639000
C	-1.563064000	-5.136615000	-0.497508000
H	-1.135372000	-6.091539000	-0.142064000
H	-1.646950000	-5.189580000	-1.602753000
H	-2.587663000	-5.045344000	-0.080725000
C	-2.098177000	-2.172582000	-1.180800000
H	-1.741549000	-1.961106000	-2.208061000
H	-2.886557000	-2.942179000	-1.212608000
C	-1.883325000	0.062211000	-0.154902000
C	-4.009370000	-0.596890000	-0.563152000
C	-4.056481000	0.682128000	-0.033509000
C	-5.096325000	-1.499852000	-1.031606000
H	-6.078930000	-1.021745000	-0.867172000
H	-5.090214000	-2.463170000	-0.480338000
H	-5.001266000	-1.723865000	-2.114309000
C	-5.211573000	1.565249000	0.286076000
H	-6.155277000	1.071676000	-0.008757000
H	-5.147736000	2.531528000	-0.256230000
H	-5.264938000	1.785976000	1.372468000
C	-2.283274000	2.263068000	0.896501000
H	-2.171850000	2.026681000	1.974737000
H	-3.043561000	3.051509000	0.768162000
C	0.018976000	1.916511000	0.076519000
C	-0.650602000	4.077866000	0.130526000
C	0.662674000	4.051017000	-0.310120000
C	-1.579485000	5.217999000	0.362651000
H	-1.082505000	6.168833000	0.098482000
H	-1.893544000	5.278559000	1.425253000
H	-2.494270000	5.126440000	-0.259281000
C	1.574463000	5.148413000	-0.735172000
H	1.070220000	6.124712000	-0.619217000
H	1.868781000	5.039884000	-1.799753000
H	2.500837000	5.168642000	-0.124158000
C	2.299006000	2.170133000	-0.847179000
H	3.083515000	2.939686000	-0.753883000
H	2.157433000	1.911979000	-1.916924000
P	-1.194612000	-0.621457000	3.629302000
F	-0.151521000	0.085018000	2.518605000
F	-0.500245000	-2.090756000	3.315538000
F	-0.081298000	-0.340951000	4.800453000
F	-1.866587000	0.866781000	3.887879000
F	-2.286657000	-0.895916000	2.422965000
F	-2.210688000	-1.301914000	4.716700000
P	-0.257692000	0.718702000	-3.637415000
F	0.383332000	-0.104116000	-2.321248000
F	-0.658402000	1.977151000	-2.647194000
F	-1.728617000	0.025586000	-3.331471000
F	0.150437000	-0.554059000	-4.587213000
F	1.228219000	1.400654000	-3.886417000
F	-0.874225000	1.521120000	-4.923368000

aiLFT results

Notes: Newton-Raphson Orbital updating disabled.

```
   E(CAS)= -4874.514266361 Eh DE=   -1.886292e-09
   --- Energy gap subspaces: Ext-Act = 0.942   Act-Int = -0.261
   --- current l-shift: Up(Ext-Act) = 0.06   Dn(Act-Int) = 1.26
   N(occ)=  1.60000 1.60000 1.60000 1.60000 1.60000
   ||g|| =     2.456477e-04 Max(G)=   -3.524674e-05 Rot=400,199
                    ---- THE CAS-SCF ENERGY   HAS CONVERGED ----
                    ---- THE CAS-SCF GRADIENT HAS CONVERGED ----
                           --- FINALIZING ORBITALS ---
                  ---- DOING ONE FINAL ITERATION FOR PRINTING ----
```

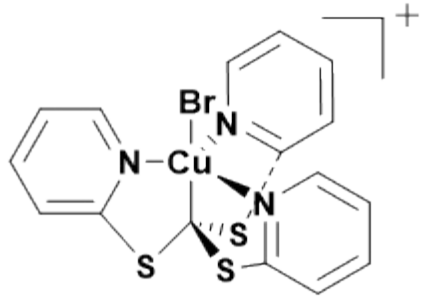
```
   --- d-orbitals (depends on the molecular axis frame)
 L-Center:  0 Cu [0.000, 0.000, 0.000]
   --- The active space contains 5 d Orbitals : OK
 Setting 195 active MO to AO dz2     (15)
 Setting 196 active MO to AO dxz     (16)
 Setting 197 active MO to AO dyz     (17)
 Setting 198 active MO to AO dx2y2   (18)
 Setting 199 active MO to AO dxy     (19)

----------------------------
LOEWDIN REDUCED ACTIVE MOs
----------------------------
```

	192	193	194	195	196	197
	-0.38378	-0.36728	-0.33322	-0.75510	-0.75648	-0.75688
	2.00000	2.00000	2.00000	1.60000	1.60000	1.60000
0 Cu dz2	0.1	0.0	0.0	90.5	0.0	0.0
0 Cu dxz	7.5	0.0	0.0	0.0	92.0	0.0
0 Cu dyz	0.2	0.0	0.0	0.0	0.0	92.1
9 C pz	5.2	3.5	3.5	0.0	0.5	0.0
10 C pz	12.5	5.4	6.5	0.0	0.7	0.0
11 C pz	12.3	5.4	6.5	0.0	0.6	0.0
24 C pz	0.1	6.0	5.8	0.0	0.0	0.6
25 C pz	0.3	6.1	5.8	0.0	0.0	0.6
38 C pz	11.6	6.3	6.6	0.0	0.7	0.0
39 C pz	11.5	6.4	6.7	0.0	0.8	0.0
52 C pz	0.2	6.4	6.6	0.0	0.0	0.8
53 C pz	0.6	6.2	6.6	0.0	0.0	0.8

	198	199	200	201	202	203
	-0.45162	-0.76438	0.04737	0.11811	0.12173	0.13596
	1.60000	1.60000	0.00000	0.00000	0.00000	0.00000
0 Cu s	0.0	0.0	0.0	1.8	0.1	24.5
0 Cu pz	0.0	0.1	19.9	0.0	0.1	0.0
0 Cu dxz	0.1	0.0	0.0	0.1	12.3	0.0
0 Cu dyz	0.0	0.0	0.0	13.4	0.1	0.5
0 Cu dx2y2	65.7	0.0	0.0	0.0	0.1	0.0
0 Cu dxy	0.0	96.4	1.1	0.1	0.1	0.0
1 N pz	0.0	0.1	2.9	0.1	5.4	0.1
2 N pz	0.0	0.1	2.9	0.0	5.5	0.0
7 N pz	0.0	0.1	3.1	5.2	0.1	0.1
8 N pz	0.0	0.1	3.1	5.1	0.0	0.2
9 C pz	0.0	0.1	6.1	0.1	16.6	0.1
9 C px	5.0	0.0	0.0	0.1	0.1	0.6
23 C pz	0.0	0.1	6.1	13.7	0.0	1.0
37 C pz	0.0	0.1	5.9	0.1	14.0	0.0
51 C pz	0.0	0.1	6.8	14.9	0.3	0.7
51 C py	5.0	0.0	0.0	0.1	0.1	0.4

S9: Optimised structures and aiLFT data for other Cu^{III} systems shown in Figure 16.

Note: The %d component of the highest energy active space orbital is highlighted in red bold.



Cu	0.000000000	0.000000000	0.372462000
C	0.000000000	0.000000000	-1.678619000
S	0.230826000	-1.695009000	-2.154957000
S	-1.583334000	0.647603000	-2.154957000
S	1.352508000	1.047406000	-2.154957000

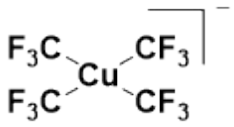
Br	0.000000000	0.000000000	2.820092000
C	-2.648876000	-3.417480000	0.837219000
H	-3.332378000	-3.784162000	1.601631000
C	-2.455731000	-4.110969000	-0.358675000
H	-2.995950000	-5.036155000	-0.560241000
C	-1.576714000	-3.595854000	-1.310812000
H	-1.426159000	-4.083960000	-2.272742000
C	-0.906029000	-2.411157000	-1.008487000
N	-1.064425000	-1.751358000	0.160910000
C	-1.940913000	-2.239036000	1.057928000
H	-2.036153000	-1.666829000	1.980482000
C	-1.635187000	4.002734000	0.837219000
H	-1.610992000	4.778005000	1.601631000
C	-0.968606000	2.800398000	1.057928000
H	-0.425440000	2.596775000	1.980482000
N	-0.984508000	1.797498000	0.160910000
C	-1.635109000	1.990222000	-1.008487000
C	-2.325744000	3.163401000	-1.310812000
H	-2.823733000	3.277070000	-2.272742000
C	-2.332338000	4.182210000	-0.358675000
H	-2.863463000	5.112647000	-0.560241000
C	4.284062000	-0.585254000	0.837219000
H	4.943369000	-0.993843000	1.601631000
C	4.788069000	-0.071241000	-0.358675000
H	5.859413000	-0.076492000	-0.560241000
C	3.902458000	0.432453000	-1.310812000
H	4.249892000	0.806890000	-2.272742000
C	2.541137000	0.420934000	-1.008487000
N	2.048933000	-0.046140000	0.160910000
C	2.909519000	-0.561362000	1.057928000
H	2.461593000	-0.929946000	1.980482000

LOEWDIN REDUCED ACTIVE MOs

		114	115	116	117	118	119
		-0.34881	-0.34877	-0.51025	-0.76383	-0.76383	-0.73715
		2.00000	2.00000	1.60000	1.60000	1.60000	1.60000
0	Cu dz2	0.0	0.0	**55.0**	0.0	0.0	0.0
0	Cu dxz	0.2	0.2	0.0	94.3	0.0	0.0
0	Cu dyz	0.2	0.2	0.0	0.0	94.3	0.0
0	Cu dx2y2	0.0	0.1	0.0	0.0	0.0	87.9
1	C pz	0.0	0.0	18.4	0.0	0.0	0.0
2	S px	5.4	7.5	0.8	0.0	0.1	0.0
3	S pz	1.4	5.8	1.0	0.2	0.1	0.1
3	S px	0.1	7.4	0.0	0.1	0.0	0.0
3	S py	1.5	5.5	1.2	0.1	0.1	0.0
4	S pz	7.2	0.0	1.0	0.2	0.1	0.2
4	S py	12.3	1.0	0.2	0.0	0.0	0.0
16	C px	1.5	6.8	0.0	0.0	0.0	0.0
18	C px	0.7	5.1	0.0	0.0	0.0	0.1
22	C px	1.2	7.4	0.1	0.0	0.0	0.0
26	C py	10.0	0.1	0.1	0.0	0.0	0.0
30	C py	9.8	0.3	0.1	0.0	0.0	0.0
32	C py	5.8	0.0	0.0	0.0	0.0	0.0
34	C py	6.7	0.2	0.0	0.0	0.0	0.0

		120	121	122	123	124	125
		-0.73705	0.05392	0.05778	0.05784	0.08677	0.09927
		1.60000	0.00000	0.00000	0.00000	0.00000	0.00000
0	Cu dxy	87.8	0.0	2.8	0.1	0.0	0.2
8	C px	0.0	4.6	5.7	6.5	1.0	0.0
10	C px	0.0	0.0	0.7	0.6	5.1	3.9
14	C px	0.1	0.9	2.5	3.0	5.2	3.9
18	C px	0.1	1.1	0.5	6.6	6.5	0.7
20	N px	0.2	4.1	0.4	6.8	0.6	0.1
21	C px	0.1	5.2	0.7	5.7	2.1	1.0
22	C px	0.0	0.0	0.1	1.5	6.1	0.7
24	C px	0.0	5.7	1.4	13.7	1.1	0.0
26	C py	0.0	2.7	1.6	0.0	3.3	10.8
28	C py	0.1	7.3	16.9	0.8	1.4	0.0
30	C py	0.0	0.0	1.7	0.2	7.5	11.0
32	C py	0.1	6.4	7.0	0.3	2.4	11.3
33	N py	0.5	5.2	7.8	0.5	0.5	0.0

34	C	py	0.1	1.5	7.8	0.4	7.8	10.8

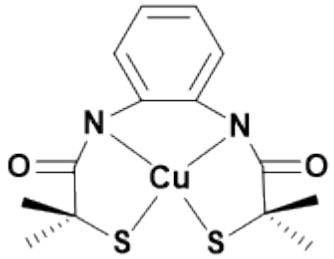


Cu	-0.001427000	-0.001059000	0.000869000
C	-1.419680000	1.404616000	-0.206299000
C	1.404571000	1.417866000	0.202036000
C	-1.407666000	-1.419135000	0.205701000
C	1.417431000	-1.407398000	-0.197865000
F	-0.993614000	2.497884000	-0.921580000
F	-2.519229000	0.967669000	-0.904782000
F	-1.898189000	1.893943000	0.976383000
F	-2.503658000	-0.992590000	0.916468000
F	-1.892651000	-1.899975000	-0.977832000
F	-0.972403000	-2.517165000	0.907634000
F	0.992954000	-2.504611000	-0.907954000
F	1.895152000	-1.890378000	0.987753000
F	2.517304000	-0.973153000	-0.897562000
F	2.499243000	0.994136000	0.916531000
F	1.891702000	1.893417000	-0.982750000
F	0.968370000	2.519062000	0.898367000

LOEWDIN REDUCED ACTIVE MOs

		72	73	74	75	76	77
		-0.56941	-0.55978	-0.54314	-0.44012	-0.44011	-0.40874
		2.00000	2.00000	2.00000	2.00000	2.00000	1.60000
0	Cu s	0.0	0.0	13.9	0.0	0.0	0.0
0	Cu px	0.0	0.0	0.0	11.4	6.3	0.0
0	Cu py	0.0	0.0	0.0	6.3	11.4	0.0
0	Cu dz2	0.0	0.0	7.0	0.0	0.0	0.0
0	Cu dxy	0.0	0.0	0.0	0.0	0.0	**60.5**
1	C px	0.0	0.1	1.9	0.2	6.8	2.7
1	C py	0.0	0.1	1.9	0.3	6.7	2.6
2	C px	0.0	0.1	1.9	6.7	0.3	2.7
2	C py	0.0	0.1	1.9	6.9	0.2	2.7
3	C px	0.0	0.1	1.9	6.7	0.3	2.6
3	C py	0.0	0.1	1.9	6.8	0.2	2.7
4	C px	0.0	0.1	1.9	0.2	6.9	2.7
4	C py	0.0	0.1	1.9	0.3	6.7	2.7
5	F pz	8.5	2.9	0.1	0.0	0.2	0.0
5	F px	3.9	7.5	2.4	0.0	2.3	0.1
6	F py	3.2	7.5	2.4	0.3	2.0	0.1
8	F py	3.9	7.5	2.4	2.3	0.0	0.1
10	F pz	9.4	3.0	0.0	0.2	0.0	0.0
10	F px	4.5	7.5	2.4	2.1	0.3	0.1
11	F pz	8.5	2.9	0.0	0.0	0.2	0.0
11	F px	3.9	7.5	2.4	0.0	2.4	0.1
13	F py	3.2	7.5	2.4	0.3	2.1	0.1
14	F py	3.9	7.5	2.4	2.4	0.0	0.1
16	F pz	9.5	3.0	0.0	0.2	0.0	0.0
16	F px	4.5	7.5	2.4	2.1	0.3	0.1

		78	79	80	81	82	83
		-0.72666	-0.71891	-0.72663	-0.73078	0.15238	0.18108
		1.60000	1.60000	1.60000	1.60000	0.00000	0.00000
0	Cu s	0.0	4.1	0.0	0.0	0.0	61.9
0	Cu pz	0.0	0.0	0.0	0.0	66.3	0.0
0	Cu dz2	0.0	90.7	0.0	0.0	0.0	28.1
0	Cu dxz	0.0	0.0	93.4	0.0	0.0	0.0
0	Cu dyz	93.4	0.0	0.0	0.0	0.0	0.0
0	Cu dx2y2	0.0	0.0	0.0	99.2	0.0	0.0



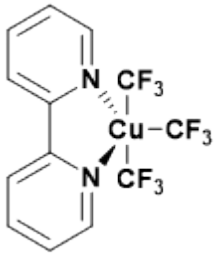
Cu	0.190175000	0.000103000	0.018397000
C	-2.460533000	-0.711822000	-0.081498000
N	-1.174594000	-1.295519000	-0.081530000
C	-3.682726000	-1.400758000	-0.167696000
H	-3.669456000	-2.481435000	-0.263143000
C	-4.891311000	-0.697814000	-0.121947000
H	-5.831464000	-1.248736000	-0.185323000
C	-4.894084000	0.691705000	0.007259000
H	-5.836367000	1.241379000	0.044292000
C	-3.688262000	1.396463000	0.086409000
H	-3.679515000	2.477150000	0.182154000
C	-2.463110000	0.709355000	0.035080000
N	-1.178113000	1.294239000	0.077149000
C	-0.904965000	-2.627331000	-0.144934000
C	0.578218000	-3.019636000	0.002295000
C	0.946060000	-4.069673000	-1.051388000
H	0.307277000	-4.955946000	-0.921899000
H	1.995566000	-4.374904000	-0.933802000
H	0.805483000	-3.677446000	-2.067485000
C	0.759807000	-3.590593000	1.420639000
H	0.105396000	-4.465211000	1.556202000
H	0.507609000	-2.837581000	2.179702000
H	1.802508000	-3.903185000	1.570507000
S	1.687668000	-1.558465000	-0.228897000
O	-1.761827000	-3.524870000	-0.247225000
C	-0.912754000	2.626260000	0.149221000
C	0.574713000	3.023531000	0.077458000
C	0.818328000	3.643298000	-1.310419000
H	0.604814000	2.916982000	-2.106462000
H	1.865219000	3.964577000	-1.400989000
H	0.166702000	4.520057000	-1.444911000
S	1.679258000	1.558414000	0.308418000
C	0.890107000	4.038756000	1.182029000
H	0.252500000	4.926291000	1.054751000
H	1.942191000	4.351791000	1.121769000
H	0.707216000	3.610608000	2.176684000
O	-1.774580000	3.522776000	0.211369000

LOEWDIN REDUCED ACTIVE MOs

		90	91	92	93	94	95
		-0.31143	-0.30661	-0.67268	-0.57756	-0.60709	-0.67727
		2.00000	2.00000	1.60000	1.60000	1.60000	1.60000
0	Cu dz2	0.2	0.0	91.0	0.0	0.2	0.0
0	Cu dxz	0.0	2.2	0.0	72.9	0.0	0.0
0	Cu dyz	0.0	0.0	0.3	0.0	78.8	0.0
0	Cu dx2y2	0.2	0.0	0.0	0.0	0.1	95.0
1	C pz	2.4	14.5	0.0	0.7	0.0	0.0
2	N pz	5.5	4.3	0.0	4.0	1.3	0.0
3	C pz	24.9	0.7	0.0	0.4	0.2	0.0
5	C pz	7.4	13.5	0.0	0.5	0.1	0.0
7	C pz	6.8	14.1	0.0	0.5	0.1	0.0
9	C pz	25.1	0.5	0.0	0.4	0.2	0.0
11	C pz	2.8	14.2	0.0	0.7	0.0	0.0
12	N pz	5.8	4.0	0.0	4.0	1.4	0.0
23	S pz	4.8	7.6	0.9	5.3	7.0	0.1
31	S pz	4.4	7.9	1.1	5.0	6.9	0.1

	96	97	98	99	100	101
	-0.43844	0.12012	0.13170	0.13402	0.19015	0.19100
	1.60000	0.00000	0.00000	0.00000	0.00000	0.00000

0	Cu	s	0.0	56.4	1.6	0.0	6.5	0.0
0	Cu	pz	0.0	0.0	0.0	0.4	0.1	15.8
0	Cu	dz2	0.0	18.3	0.8	0.0	1.4	0.0
0	Cu	dx2y2	0.0	0.5	0.0	0.0	10.6	0.0
0	Cu	dxy	**62.9**	0.0	0.0	0.0	0.0	0.1
1	C	pz	0.0	0.4	14.9	5.7	0.4	0.7
3	C	pz	0.0	0.0	0.0	22.8	0.0	1.4
5	C	pz	0.0	0.4	15.2	5.4	0.6	0.3
7	C	pz	0.0	0.4	14.6	5.9	0.8	0.2
9	C	pz	0.0	0.0	0.0	22.8	0.1	1.3
11	C	pz	0.0	0.4	15.5	5.1	0.2	0.8
13	C	pz	0.0	0.6	7.7	6.6	0.5	3.6
18	H	s	0.0	1.5	0.0	0.1	0.3	5.0
23	S	py	5.2	0.3	0.1	0.0	5.8	0.5
25	C	pz	0.0	0.5	8.2	6.2	0.1	3.7
31	S	py	5.1	0.3	0.1	0.0	6.1	0.1



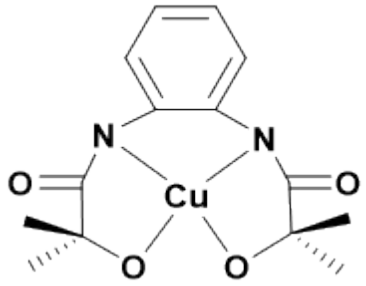
Cu	0.000000000	0.000000000	0.000000000
C	1.989756000	0.000000000	0.028851000
F	2.584305000	-0.952297000	-0.735660000
F	2.477167000	-0.126572000	1.296956000
F	2.493041000	1.196705000	-0.437589000
C	-0.031595000	-1.946414000	0.225823000
F	1.038524000	-2.466028000	0.878199000
F	-0.040618000	-2.502271000	-1.028270000
F	-1.118015000	-2.431023000	0.878199000
C	-1.988707000	0.064580000	0.028851000
F	-2.452887000	1.276989000	-0.437589000
F	-2.479970000	-0.046105000	1.296956000
F	-2.613851000	-0.867919000	-0.735660000
C	0.040267000	2.480667000	-4.260281000
H	0.050090000	3.085812000	-5.179006000
C	0.017513000	1.078908000	-4.328536000
H	0.008963000	0.552146000	-5.293339000
C	0.005732000	0.353143000	-3.127629000
H	-0.012142000	-0.748014000	-3.108376000
N	0.015579000	0.959722000	-1.933576000
C	0.037460000	2.307716000	-1.847328000
C	0.050433000	3.106914000	-3.006661000
H	0.068222000	4.202835000	-2.937751000
C	0.075508000	4.651674000	1.164060000
H	0.092919000	5.724273000	1.407664000
C	0.068739000	4.234678000	-0.172766000
H	0.080769000	4.975783000	-0.982614000
C	0.046402000	2.858595000	-0.466190000
N	0.031595000	1.946414000	0.536263000
C	0.037904000	2.335106000	1.820946000
H	0.024846000	1.530646000	2.571651000
C	0.059859000	3.687629000	2.183886000
H	0.064478000	3.972179000	3.245275000

LOEWDIN REDUCED ACTIVE MOs

			96	97	98	99	100	101
			-0.46225	-0.44665	-0.43975	-0.42083	-0.36859	-0.75074
			2.00000	2.00000	2.00000	2.00000	2.00000	1.60000
0	Cu	px	5.4	0.0	2.0	12.0	0.0	0.0
0	Cu	dxy	0.9	0.1	0.0	0.2	0.0	98.5
1	C	px	2.9	0.0	1.7	11.0	0.0	0.0
9	C	px	2.9	0.0	1.7	11.0	0.0	0.0
13	C	px	6.4	27.0	0.3	2.3	0.0	0.0
15	C	px	2.6	12.8	9.7	0.1	15.4	0.0

17	C	px	0.1	0.5	11.3	3.5	9.6	0.0
19	N	px	3.7	17.4	1.1	3.2	1.0	0.0
20	C	px	0.0	1.1	11.4	0.4	10.2	0.0
21	C	px	4.1	11.3	6.3	4.7	13.9	0.0
23	C	px	20.5	7.5	4.3	3.5	0.0	0.1
25	C	px	12.2	6.6	2.3	6.5	13.1	0.0
27	C	px	0.0	0.2	13.9	0.5	8.8	0.1
28	N	px	12.5	7.2	0.3	4.3	1.2	0.4
29	C	px	0.5	2.2	8.6	4.6	8.6	0.1
31	C	px	8.4	1.0	17.1	0.1	13.9	0.0

			102	103	104	105	106	107
			-0.73820	-0.70142	-0.76518	-0.45214	0.00651	0.05084
			1.60000	1.60000	1.60000	1.60000	0.00000	0.00000
0	Cu	dz2	0.1	84.0	0.0	0.1	0.0	0.0
0	Cu	dxz	0.0	0.0	98.9	0.0	0.1	0.2
0	Cu	dyz	92.3	0.1	0.0	0.1	0.0	0.0
0	Cu	dx2y2	0.3	0.1	0.0	**61.1**	0.0	0.0
1	C	px	0.0	1.0	0.0	5.4	0.2	0.0
5	C	py	0.8	1.7	0.0	7.9	0.0	0.0
9	C	px	0.0	1.0	0.0	5.4	0.2	0.0
13	C	px	0.0	0.0	0.1	0.0	7.3	4.4
15	C	px	0.0	0.0	0.0	0.0	10.8	2.2
17	C	px	0.0	0.0	0.1	0.0	0.2	11.4
19	N	px	0.0	0.0	0.2	0.0	9.1	1.3
20	C	px	0.0	0.0	0.1	0.0	12.9	1.9
21	C	px	0.0	0.0	0.0	0.0	2.9	10.5
23	C	px	0.0	0.0	0.0	0.0	9.2	10.8
25	C	px	0.0	0.0	0.0	0.0	2.3	17.9
27	C	px	0.0	0.0	0.0	0.0	14.6	1.3
28	N	px	0.0	0.0	0.1	0.0	10.0	4.4
29	C	px	0.0	0.0	0.0	0.0	0.4	20.9
31	C	px	0.0	0.0	0.0	0.0	10.8	2.5



Cu	0.000000000	0.000000000	0.000000000
C	-2.639072000	-0.713381000	-0.028875000
N	-1.341550000	-1.259411000	-0.006413000
C	-3.851777000	-1.415330000	-0.046756000
H	-3.840388000	-2.502044000	-0.044049000
C	-5.057032000	-0.701062000	-0.067176000
H	-6.000780000	-1.248845000	-0.082103000
C	-5.057636000	0.696476000	-0.069201000
H	-6.001904000	1.243309000	-0.085826000
C	-3.852937000	1.411612000	-0.051522000
H	-3.841628000	2.498362000	-0.052251000
C	-2.639763000	0.710537000	-0.031641000
N	-1.342775000	1.258215000	-0.012690000
C	-0.945399000	-2.561584000	0.009080000
C	0.596710000	-2.679080000	0.045847000
C	1.048544000	-3.496931000	-1.173318000
H	0.580043000	-4.491606000	-1.170669000
H	2.140871000	-3.619133000	-1.148259000
H	0.772588000	-2.976051000	-2.101313000
C	0.985060000	-3.380774000	1.357949000
H	0.519850000	-4.374792000	1.424154000
H	0.659894000	-2.777915000	2.218045000
H	2.077584000	-3.495712000	1.400999000
O	1.211160000	-1.398171000	0.000000000
O	-1.713126000	-3.537180000	0.004294000
C	-0.947332000	2.560612000	-0.008322000
C	0.594964000	2.679211000	0.023191000
C	1.041711000	3.473920000	-1.213320000
H	0.760574000	2.936462000	-2.130284000

H	2.134369000	3.594482000	-1.195887000
H	0.574433000	4.469107000	-1.226977000
O	1.210278000	1.398171000	0.000000000
C	0.987820000	3.406488000	1.319557000
H	0.525152000	4.402823000	1.366113000
H	2.080727000	3.519804000	1.357472000
H	0.663565000	2.822690000	2.193010000
O	-1.715193000	3.535993000	-0.021776000

LOEWDIN REDUCED ACTIVE MOs

			78	79	80	81	82	83
			-0.42389	-0.40047	-0.39864	-0.39744	-0.32112	-0.31311
			2.00000	2.00000	2.00000	2.00000	2.00000	2.00000
1	C	pz	0.6	0.3	0.0	3.3	3.7	17.8
2	N	pz	4.6	0.9	0.0	8.7	3.9	3.8
3	C	pz	2.2	0.3	0.0	3.1	28.3	0.6
5	C	pz	8.8	0.0	0.0	0.6	7.8	18.1
7	C	pz	8.8	0.1	0.0	0.6	7.7	18.1
9	C	pz	2.2	0.3	0.0	3.0	28.3	0.6
11	C	pz	0.5	0.3	0.0	3.3	3.7	17.8
12	N	pz	4.6	0.9	0.0	8.8	3.9	3.8
14	C	px	0.0	6.4	4.4	0.7	0.0	0.0
23	O	pz	14.6	1.1	0.0	12.0	2.0	1.6
24	O	pz	0.8	1.3	0.1	9.9	1.3	1.0
24	O	px	0.0	14.9	13.7	2.1	0.0	0.0
24	O	py	0.0	5.0	6.7	0.7	0.0	0.0
26	C	px	0.0	6.0	5.3	0.4	0.0	0.0
31	O	pz	14.6	1.2	0.0	11.8	2.0	1.7
36	O	pz	0.8	1.2	0.0	10.0	1.3	1.0
36	O	px	0.0	13.6	16.0	1.1	0.0	0.0
36	O	py	0.0	4.5	7.6	0.3	0.0	0.0

			84	85	86	87	88	89
			-0.70011	-0.64616	-0.66593	-0.68463	-0.50325	0.12371
			1.60000	1.60000	1.60000	1.60000	1.60000	0.00000
0	Cu	s	2.6	0.0	0.0	0.0	0.0	57.0
0	Cu	dz2	93.6	0.0	0.0	0.0	0.0	17.1
0	Cu	dxz	0.0	84.0	0.0	0.0	0.0	0.0
0	Cu	dyz	0.0	0.0	88.3	0.0	0.0	0.0
0	Cu	dx2y2	0.0	0.0	0.0	93.6	0.0	1.8
0	Cu	dxy	0.0	0.0	0.0	0.0	**72.7**	0.0