Solvent Coordination Effect on Copper-Based Catalysts for Controlled Radical Polymerization

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Orbital, Geometry and Energy Details

Table S1. Cu-ligand relative contribution in the HOMO-LUMO orbitals of $[Cu^{I}(Me_6TREN)]^{+}$, $[Cu^{I}(PMDETA)]^{+}$ and $[Cu^{I}(TPMA)]^{+}$, calculated at different levels of theory.

	$[Cu^{I}(Me_6TREN)]^{+}$		$[Cu^{I}(PMDETA)]^{+}$		$[Cu^{I}(Me_6TREN)]^{+}$	
	Cu	**ligand**	**Cu**	**ligand**	**Cu**	**ligand**
M06/6-311+G(d,p)						
LUMO	100	0	78	22	0	100
HOMO	55	45	50	50	54	46
B3LYP/6-311+G(d,p)						
LUMO	100	0	98	2	2	98
HOMO	64	36	58	42	57	43
M06/CC-PVTZ						
LUMO	92	8	92	8	1	99
HOMO	59	41	50	50	60	40
B3LYP/CC-PVTZ						
LUMO	77	23	83	17	1	99
HOMO	68	32	57	43	66	34

Table S2. Interatomic distances [Å] and angles [°] in the Cu^{I} and Cu^{II} complexes with the Me_6TREN ligand (L) [a]; level of theory: M06/6-311+G(d,p).

	$Cu^{I}L$	**$Cu^{II}LCl$**	**$Cu^{II}LBr$**
N-C	1.47	1.49	1.48
N-C(Me)	1.47	1.47	1.47
C-C	1.53	1.52	1.51
N (*ap*)-Cu	2.25	2.10	2.11
N(*eq*)-Cu	2.12	2.17	2.17
N′(*eq*)-Cu	2.11	2.24	2.25
N′′(*eq*)-Cu	2.16	2.16	2.17
Cu-*X*	/	2.20	2.35
C-N-C	115	112	112
N(*ap*)-Cu-N	85	84	84
N-Cu-N′	115	108	108
N′-Cu-N′′	124	131	131
N′′-Cu-N	119	118	118
N(*ap*)-Cu-*X*	/	179	179

[a] *eq* = equatorial, *ap* = apical, C(Me) = methyl carbon, *X* = Cl or Br.

Table S3. Interatomic distances [Å] and angles [°] in the Cu^{I} and Cu^{II} complexes with the PMDETA ligand (L) [a]; level of theory: M06/6-311+G(d,p).

	Cu^{I}L	**Cu^{II}LCl**	**Cu^{II}LBr**
N-C	1.46	1.48	1.48
N-C(Me)	1.46	1.47	1.47
C-C	1.52	1.51	1.51
N(*c*)-Cu	2.29	2.04	2.06
N(l)-Cu	1.98	2.09	2.10
N(*l*)-Cu	1.98	2.09	2.10
Cu-*X*	/	2.17	2.31
C-N(*c*)-C	112	111	111
N(*c*)-Cu-N(*l*)	88	85	85
N(*l*)-Cu-N′(*l*)	163	159	157
N(*c*)-Cu-*X*	/	173	170
N(*l*)-Cu-*X*	/	96	97

[a] *c* = central, *l* = lateral, *X* = Cl or Br

Table S4. Interatomic distances [Å] and angles [°] in the Cu^{I} and Cu^{II} complexes with the TPMA ligand (L) [a]; level of theory: M06/6-311+G(d,p).

	Cu^{I}L	**Cu^{II}LCl**	**Cu^{II}LBr**
N-C	1.45	1.47	1.47
C(*pyr*)-N(*eq*)	1.34	1.34	1.34
C-C *pyr*	1.51	1.50	1.38
N(*ap*)-Cu	2.26	2.11	2.12
N(*eq*)-Cu	2.05	2.09	2.10
N′(*eq*)-Cu	2.05	2.09	2.10
N′′(*eq*)-Cu	2.05	2.09	2.10
Cu-*X*	/	2.20	2.34
C-N-C	115	112	112
C-C(*pyr*)-N(*eq*)	118	115	116
C-C(pyr)-C(*pyr*)	121	123	122
N(*ap*)-Cu-N(*eq*)	81	80	80
N(*eq*)-Cu- N(*eq*)	118	117	117
N(*ap*)-Cu-*X*	/	180	180
N(*eq*)-Cu-*X*	/	100	100

[a] *eq* = equatorial, *ap* = apical, *pyr* = pyridine, *X* = Cl or Br.

Table S5. ΔE_r and ΔG_r [kcal/mol] for the R-X (X=Cl or Br) homolytic cleavage in gas phase and in solvent; level of theory (PCM-)M06/6-311+G(d,p).

	Gas-phase		MeCN	DMSO
Species	ΔE_r	ΔG_r *(298 K)*	ΔG_r *(298 K)*	ΔG_r *(298 K)*
AlCl → Al• + Cl•	69.4	57.9	61.9	61.8
AlBr → Al• + Br•	55.3	44.2	48.0	47.9
EtCl^{i}Bu → Et^{i}Bu• + Cl•	72.9	59.2	62.3	62.2
EtBr^{i}Bu → Et^{i}Bu• + Br•	58.2	44.7	47.6	47.3
MeClPr → MePr• + Cl•	74.3	62.1	65.4	65.3
MeBrPr → MePr• + Br•	60.4	48.5	51.6	51.5

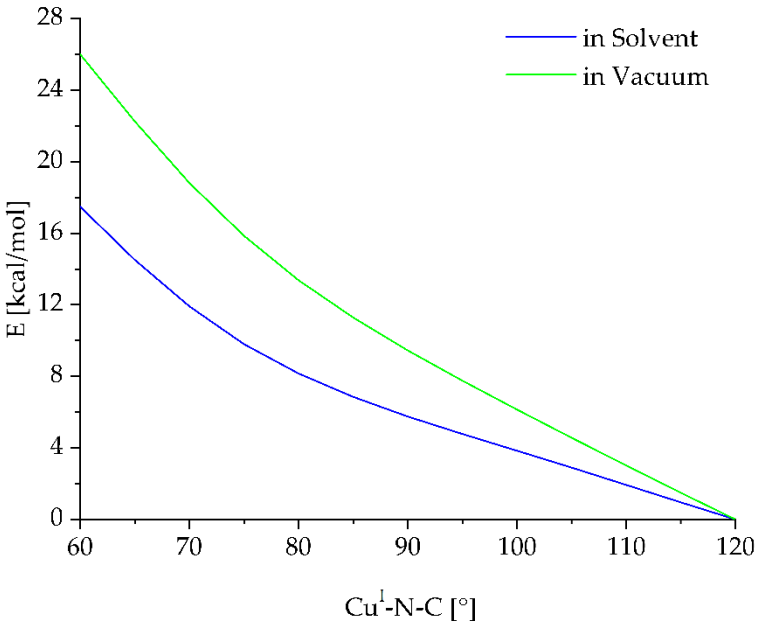

Figure S1. Energy profile of the Cu^I-N-C angle in gas phase (green) and in acetonitrile (blu); level of theory: (PCM-)M06/6-311+G(d,p).

Table S6. Cu-Br and Cu-solvent interatomic distances [Å] in the [Cu^{II}(PMDETA)Br(MeCN)]$^+$ complexes calculated in gas phase and in solvent (in parenthesis); level of theory: (PCM-)M06/6-311+G(d,p).

	I1	**I2**	**I3**	**I4**
Cu-Br	2.35 *(2.39)*	2.39 *(2.44)*	2.42 *(2.57)*	2.43 *(2.66)*
Cu-N	2.64 *(2.57)*	2.34 *(2.26)*	2.32 *(2.04)*	2.22 *(2.02)*

Table S7. Cu-Br and Cu-solvent interatomic distances [Å] in the [Cu^{II}(PMDETA)Br(DMSO-κOα)]$^+$ complexes calculated in gas phase and in solvent (in parenthesis); level of theory: (PCM-)M06/6-311+G(d,p).

	I1	**I2**	**I3**	**I4**
Cu-Br	*2.35 (2.40)*	2.39 *(2.44)*	2.46 *(2.59)*	2.50 *(2.68)*
Cu-O	*2.38 (2.31)*	2.22 *(2.20)*	2.01 *(2.02)*	2.08 *(2.00)*

Cartesian coordinates

Coordinates of the copper(I) complexes [Cu^{I}L]$^{+}$

[Cu^{I}(Me$_6$TREN)]$^{+}$
E=-2334.245535 a.u.

M06/6-311+G(d,p)

Cu	-1.289540000	0.935189000	-1.307415000
N	-3.045669000	-0.255904000	-1.232394000
N	-0.663078000	-0.244943000	0.504358000
N	0.542531000	0.311121000	-2.152910000
N	-1.283016000	2.615593000	0.052529000
C	-3.133586000	-0.590416000	0.201163000
C	-1.820395000	-1.094089000	0.800353000
H	-3.913300000	-1.355112000	0.365419000
H	-3.470966000	0.310327000	0.723995000
H	-1.615446000	-2.102786000	0.426989000
H	-1.965499000	-1.203294000	1.886672000
C	0.535071000	-0.941368000	0.026286000
C	1.327456000	-0.111594000	-0.974412000
H	0.221562000	-1.880419000	-0.441049000
H	1.208690000	-1.221976000	0.852403000
H	2.216459000	-0.680911000	-1.295220000
H	1.703703000	0.796143000	-0.488138000
C	-1.288418000	1.999137000	1.394103000
C	-0.380058000	0.783990000	1.506345000
H	-2.318994000	1.712211000	1.626490000
H	-0.997232000	2.742844000	2.155198000
H	-0.465208000	0.378030000	2.528094000
H	0.664008000	1.095542000	1.392776000
C	0.370447000	-0.813933000	-3.081103000
C	1.257721000	1.378681000	-2.864955000
C	-2.451473000	3.491529000	-0.092316000
C	-0.079218000	3.436521000	-0.122506000
C	-2.953311000	-1.480901000	-2.034514000
C	-4.252150000	0.470031000	-1.647540000
H	0.824675000	2.837197000	0.009646000
H	-0.055251000	4.262225000	0.606689000
H	-0.068923000	3.862818000	-1.129341000
H	1.399830000	2.241364000	-2.210719000
H	0.674783000	1.691901000	-3.734645000
H	2.244372000	1.032841000	-3.211609000
H	-0.124631000	-1.652980000	-2.589516000
H	1.344103000	-1.158360000	-3.464357000
H	-0.246690000	-0.499728000	-3.926776000
H	-2.085924000	-2.075092000	-1.739220000
H	-2.850505000	-1.222772000	-3.091509000
H	-3.855624000	-2.100675000	-1.909383000
H	-4.351527000	1.395941000	-1.076614000
H	-5.157338000	-0.138270000	-1.492335000
H	-4.180450000	0.722676000	-2.708313000
H	-3.371657000	2.921512000	0.057852000
H	-2.466881000	3.922654000	-1.096768000
H	-2.429593000	4.312784000	0.641729000

[Cu^{I}(PMDETA)]$^{+}$
E=-2161.036555 a.u.

M06/6-311+G(d,p)

Cu	-1.094251000	-0.265965000	-1.926153000
N	-2.965166000	-0.757843000	-1.486777000
N	-0.508329000	-0.950548000	0.180958000
N	0.827588000	-0.353550000	-2.410073000
C	-2.944997000	-1.132580000	-0.046865000
C	-1.659663000	-1.835849000	0.365185000
H	-3.819842000	-1.759721000	0.181209000
H	-3.056560000	-0.209181000	0.531923000
H	-1.512884000	-2.739033000	-0.238653000
H	-1.756392000	-2.172670000	1.409675000
C	0.751177000	-1.578860000	-0.221701000
C	1.539511000	-0.654546000	-1.138559000
H	0.529016000	-2.521374000	-0.735723000
H	1.377205000	-1.838636000	0.646844000
H	2.527538000	-1.083109000	-1.363975000
H	1.715685000	0.299526000	-0.629818000
C	1.022628000	-1.454464000	-3.374439000
C	1.361533000	0.889640000	-2.996000000
C	-3.353803000	-1.920973000	-2.309056000
C	-3.942676000	0.324232000	-1.704757000
H	1.182869000	1.727380000	-2.317876000
H	0.860929000	1.091487000	-3.945408000
H	2.442342000	0.799187000	-3.177519000
H	0.650158000	-2.396483000	-2.963831000
H	2.089645000	-1.569947000	-3.614860000
H	0.473829000	-1.238000000	-4.293615000
H	-2.656164000	-2.748923000	-2.158954000
H	-3.338513000	-1.644378000	-3.365552000
H	-4.366385000	-2.258133000	-2.043228000
C	-0.332780000	-0.035613000	1.302722000
H	-1.254392000	0.519088000	1.495624000
H	0.444509000	0.700184000	1.082052000
H	-0.051597000	-0.573030000	2.222462000
H	-3.646020000	1.212638000	-1.142343000
H	-4.945428000	0.011680000	-1.379061000
H	-3.980062000	0.575458000	-2.766929000

[Cu^{I}(TPMA)]$^{+}$
E=-2555.582519 a.u.

M06/6-311+G(d,p)

N	-3.230368000	0.792771000	-0.919074000

C	-4.611339000	0.458561000	-1.216818000
C	-2.918701000	2.210603000	-0.917167000
C	-2.234995000	-0.062932000	-1.538879000
C	-5.091392000	-0.770364000	-0.477106000
H	-4.792911000	0.333698000	-2.297633000
H	-5.235053000	1.304695000	-0.895480000
N	-4.609338000	-0.983250000	0.759239000
C	-6.036580000	-1.610534000	-1.045354000
C	-6.514932000	-2.687357000	-0.315093000
C	-6.025294000	-2.899064000	0.963486000
C	-5.070900000	-2.026800000	1.455886000
H	-4.652181000	-2.164585000	2.448812000
H	-6.366982000	-3.728755000	1.571175000
H	-7.256402000	-3.354809000	-0.741595000
H	-6.393579000	-1.415605000	-2.051995000
C	-1.004249000	-0.250706000	-0.679871000
H	-1.936192000	0.291712000	-2.539733000
H	-2.691680000	-1.051865000	-1.686151000
C	0.240805000	-0.430311000	-1.262604000
C	1.340272000	-0.674581000	-0.454530000
C	1.163900000	-0.722553000	0.918697000
C	-0.106459000	-0.517582000	1.426944000
N	-1.172172000	-0.287422000	0.653144000
H	2.322498000	-0.819794000	-0.891932000
H	0.341391000	-0.380848000	-2.342508000
H	-0.285546000	-0.534965000	2.498323000
H	1.993729000	-0.907384000	1.590740000
C	-3.441902000	2.925758000	0.308634000
H	-3.276753000	2.723872000	-1.825511000
H	-1.824041000	2.310332000	-0.918071000
C	-3.842997000	4.250763000	0.234106000
N	-3.452788000	2.248616000	1.469554000
C	-3.849133000	2.883147000	2.577539000
C	-4.247142000	4.904125000	1.387956000
C	-4.247590000	4.208016000	2.585743000
H	-4.557875000	4.675473000	3.512901000
H	-3.846475000	2.298367000	3.493101000

<u>Coordinates of the solvent molecules</u>

MeCN
E=-132.693513 a.u.

M06/6-311+G(d,p)

C	-4.988655000	2.677322000	-0.000010000
C	-3.552273000	2.852612000	-0.000016000
H	-5.280580000	1.934497000	0.745734000
H	-5.329952000	2.338662000	-0.980802000
H	-5.486418000	3.620784000	0.235070000
N	-2.409422000	2.992243000	0.000024000

DMSO
E=-553.121914 a.u.

M06/6-311+G(d,p)

S	-0.797028000	0.647002000	-2.128459000
O	0.230134000	-0.386497000	-1.776294000
C	-2.153895000	-0.247787000	-2.949009000
H	-1.772066000	-0.600906000	-3.907929000
H	-2.428496000	-1.101717000	-2.323814000
H	-3.004031000	0.420784000	-3.106934000
C	-1.721695000	0.983254000	-0.596247000
H	-2.581991000	1.623107000	-0.808564000
H	-2.031806000	0.026834000	-0.166673000
H	-1.037891000	1.489421000	0.086565000

<u>Coordinates of the copper(I) complexes with coordinated solvent molecules [Cu^{I}LS]$^{+}$</u>

[Cu^{I}(Me$_6$TREN)(MeCN)]$^{+}$
E=-2466.967585 a.u.

M06/6-311+G(d,p)

Cu	-0.340183000	-0.010905000	-0.018102000
N	0.173980000	-1.630670000	-1.456085000
N	2.110888000	0.115742000	-0.100705000
N	0.012435000	2.159422000	-0.521553000
N	0.224069000	-0.604591000	2.066178000
C	1.503137000	-2.114473000	-1.076590000
C	2.540782000	-1.006408000	-0.932550000
H	1.874521000	-2.846959000	-1.817225000
H	1.392757000	-2.660420000	-0.133531000
H	2.797954000	-0.626266000	-1.926896000
H	3.467053000	-1.459508000	-0.542343000
C	2.396872000	1.433591000	-0.663451000
C	1.405636000	2.489749000	-0.206778000
H	2.366649000	1.354675000	-1.755260000
H	3.414479000	1.779858000	-0.411656000
H	1.684632000	3.461350000	-0.652817000
H	1.477073000	2.623855000	0.879427000
C	1.651448000	-0.944937000	2.105839000
C	2.516046000	0.005884000	1.297480000
H	1.766177000	-1.964909000	1.724331000
H	2.014019000	-0.965688000	3.148969000
H	3.567488000	-0.321133000	1.381321000
H	2.476309000	1.002592000	1.749517000
C	-0.264718000	2.360282000	-1.942816000
C	-0.885072000	3.015645000	0.250981000
C	-0.572089000	-1.748286000	2.506746000
C	-0.063977000	0.527751000	2.945723000
C	0.161496000	-1.151086000	-2.836140000
C	-0.799418000	-2.713376000	-1.330692000

H	0.530794000	1.400316000	2.664044000
H	0.155642000	0.284390000	3.999085000
H	-1.121803000	0.795626000	2.862476000
H	-0.732485000	2.856227000	1.321936000
H	-1.923228000	2.770758000	0.010779000
H	-0.719258000	4.082824000	0.026912000
H	0.408624000	1.762245000	-2.560176000
H	-0.149641000	3.419701000	-2.228418000
H	-1.290206000	2.048566000	-2.162924000
H	0.891263000	-0.350479000	-2.977095000
H	-0.829591000	-0.753471000	-3.075483000
H	0.396933000	-1.962209000	-3.545991000
H	-0.847326000	-3.059845000	-0.294266000
H	-0.540641000	-3.568562000	-1.977207000
H	-1.790056000	-2.349977000	-1.617053000
H	-0.384965000	-2.609758000	1.859197000
H	-1.635779000	-1.499428000	2.452716000
H	-0.332249000	-2.035021000	3.544413000
N	-2.378459000	-0.027493000	-0.016534000
C	-3.529558000	-0.060561000	-0.004326000
C	-4.972397000	-0.101187000	0.009748000
H	-5.363971000	0.631530000	0.719154000
H	-5.366096000	0.127323000	-0.983389000
H	-5.319308000	-1.094346000	0.304254000

[Cu^{I}(PMDETA)(MeCN)]$^{+}$
E=-2293.766687 a.u.

M06/6-311+G(d,p)

Cu	-1.211030000	-0.133176000	-2.348699000
N	-2.936809000	-1.260857000	-1.812999000
N	-0.657747000	-0.388216000	-0.192114000
N	0.753541000	-0.870773000	-2.713756000
C	-3.032811000	-1.030258000	-0.360219000
C	-1.711945000	-1.251493000	0.353658000
H	-3.810408000	-1.677144000	0.081169000
H	-3.361386000	0.006514000	-0.215340000
H	-1.402297000	-2.296113000	0.245886000
H	-1.852855000	-1.082872000	1.432902000
C	0.675968000	-0.999989000	-0.229389000
C	1.453645000	-0.556987000	-1.455027000
H	0.563463000	-2.089043000	-0.235011000
H	1.257063000	-0.756017000	0.673873000
H	2.457143000	-1.016199000	-1.448470000
H	1.600839000	0.529884000	-1.425606000
C	0.802596000	-2.306291000	-3.003892000
C	1.383784000	-0.144255000	-3.820412000
C	-2.828014000	-2.690270000	-2.116691000
C	-4.131665000	-0.727811000	-2.474742000
H	1.339757000	0.931417000	-3.630758000
H	0.849579000	-0.355849000	-4.750467000
H	2.437623000	-0.440518000	-3.945322000
H	0.325812000	-2.882369000	-2.207470000
H	1.841961000	-2.655299000	-3.115242000
H	0.265945000	-2.507817000	-3.934828000
H	-1.937596000	-3.121498000	-1.653358000
H	-2.746419000	-2.827178000	-3.198283000
H	-3.712002000	-3.242411000	-1.758645000
C	-0.634700000	0.916231000	0.465311000
H	-1.615339000	1.394723000	0.390297000
H	0.087676000	1.574463000	-0.025730000
H	-0.365389000	0.829957000	1.530530000
H	-4.219212000	0.343527000	-2.275875000
H	-5.044768000	-1.231392000	-2.118935000
H	-4.050365000	-0.875816000	-3.554849000
N	-1.583467000	1.627309000	-3.110529000
C	-1.811303000	2.642310000	-3.602356000
C	-2.097900000	3.913966000	-4.218826000
H	-1.201995000	4.309316000	-4.703150000
H	-2.882068000	3.798820000	-4.970799000
H	-2.435433000	4.629849000	-3.465716000

[Cu^{I}(PMDETA)(MeCN)$_2$]$^{+}$
E=-2426478348 a.u.

M06/6-311+G(d,p)

Cu	-1.150993000	0.401587000	-1.698410000
N	-2.982258000	-0.721923000	-1.539211000
N	-0.547661000	-1.089891000	0.071598000
N	0.770846000	-0.253184000	-2.420467000
C	-2.985647000	-1.300217000	-0.187518000
C	-1.684811000	-2.000753000	0.159553000
H	-3.829159000	-2.003615000	-0.071956000
H	-3.159869000	-0.478094000	0.518171000
H	-1.520190000	-2.837772000	-0.527367000
H	-1.776917000	-2.443863000	1.165627000
C	0.699646000	-1.692452000	-0.389104000
C	1.503850000	-0.723550000	-1.236030000
H	0.465336000	-2.588973000	-0.972698000
H	1.325086000	-2.031806000	0.453749000
H	2.457147000	-1.194016000	-1.535401000
H	1.760194000	0.160995000	-0.639050000
C	0.647848000	-1.311971000	-3.423195000
C	1.480665000	0.880603000	-3.013881000
C	-3.070981000	-1.764098000	-2.562749000
C	-4.122675000	0.183623000	-1.684665000
H	1.559278000	1.691295000	-2.283933000
H	0.924386000	1.246654000	-3.880311000
H	2.495008000	0.594970000	-3.338671000
H	0.111438000	-2.172743000	-3.016326000
H	1.638170000	-1.648639000	-3.772718000
H	0.079153000	-0.936184000	-4.277255000
H	-2.232476000	-2.459996000	-2.481569000
H	-3.028745000	-1.302905000	-3.552736000
H	-4.010326000	-2.334682000	-2.471999000
C	-0.361792000	-0.333532000	1.300384000

H	-1.279681000	0.200618000	1.562798000
H	0.424076000	0.416440000	1.171033000
H	-0.084586000	-0.987166000	2.145273000
H	-4.055926000	0.984883000	-0.943158000
H	-5.078868000	-0.348440000	-1.548326000
H	-4.108768000	0.631491000	-2.681348000
C	-2.096848000	1.649779000	-4.994883000
C	-2.475087000	2.385976000	-6.179454000
H	-1.630065000	2.973029000	-6.545934000
H	-2.790052000	1.697737000	-6.966971000
H	-3.301887000	3.063821000	-5.956118000
N	-1.795908000	1.059279000	-4.052522000
N	-1.200422000	2.237091000	-0.970755000
C	-1.218068000	3.297204000	-0.523085000
C	-1.240369000	4.626980000	0.037045000
H	-2.253481000	5.034467000	0.004463000
H	-0.906131000	4.603691000	1.076881000
H	-0.578092000	5.286668000	-0.528386000

[Cu^{I}(TPMA)(MeCN)]$^{+}$
E=-2688.302828 a.u.

M06/6-311+G(d,p)

N	-3.222085000	0.759789000	-0.787410000
C	-4.607917000	0.479007000	-1.079987000
C	-2.863781000	2.158388000	-0.806580000
C	-2.272126000	-0.123816000	-1.421204000
C	-5.097270000	-0.771843000	-0.392436000
H	-4.810060000	0.407283000	-2.164196000
H	-5.209516000	1.321941000	-0.711371000
N	-4.605778000	-1.038974000	0.823794000
C	-6.049155000	-1.583705000	-0.994377000
C	-6.519408000	-2.695062000	-0.313963000
C	-6.015274000	-2.968359000	0.947826000
C	-5.059611000	-2.114877000	1.470626000
H	-4.629518000	-2.295807000	2.453178000
H	-6.347757000	-3.829250000	1.516364000
H	-7.263849000	-3.342710000	-0.765563000
H	-6.413615000	-1.340153000	-1.987883000
C	-1.011476000	-0.288991000	-0.608728000
H	-2.011000000	0.193810000	-2.447100000
H	-2.741435000	-1.113209000	-1.516996000
C	0.214160000	-0.471654000	-1.234875000
C	1.345430000	-0.677643000	-0.462216000
C	1.219164000	-0.684790000	0.917984000
C	-0.037130000	-0.482707000	1.462182000
N	-1.132686000	-0.289472000	0.724473000
H	2.313226000	-0.823449000	-0.930923000
H	0.272959000	-0.451522000	-2.318996000
H	-0.181511000	-0.470860000	2.540216000
H	2.075979000	-0.836104000	1.564426000
C	-3.411856000	2.908044000	0.382754000
H	-3.173725000	2.666584000	-1.737798000
H	-1.767356000	2.227690000	-0.770335000
C	-3.793246000	4.237930000	0.265669000
N	-3.476557000	2.252853000	1.548457000
C	-3.912998000	2.911353000	2.624429000
C	-4.239171000	4.915944000	1.388367000
C	-4.300468000	4.239524000	2.596571000
H	-4.648235000	4.725587000	3.500833000
H	-3.953394000	2.338856000	3.548435000
H	-4.541421000	5.955871000	1.319540000
H	-3.738084000	4.730638000	-0.700455000
Cu	-3.023329000	0.160756000	1.627037000
N	-2.863183000	-0.327838000	3.588806000
C	-2.774838000	-0.606941000	4.702151000
C	-2.663894000	-0.957037000	6.098171000
H	-3.653428000	-0.983652000	6.560313000
H	-2.200391000	-1.940516000	6.204889000
H	-2.050883000	-0.221463000	6.624115000

[Cu^{I}(Me$_{6}$TREN)(DMSO-κOα)]$^{+}$
E=-2887.400606 a.u.

M06/6-311+G(d,p)

Cu	0.134551000	0.034263000	0.002236000
N	0.350602000	-1.421443000	-1.617279000
N	2.508246000	0.016243000	-0.198735000
N	0.484346000	2.186792000	-0.256227000
N	0.676949000	-0.819847000	1.974563000
C	1.660901000	-2.036597000	-1.370268000
C	2.793157000	-1.031151000	-1.175293000
H	1.930951000	-2.709789000	-2.205086000
H	1.559291000	-2.670554000	-0.483432000
H	3.024770000	-0.560498000	-2.136906000
H	3.698063000	-1.597540000	-0.899499000
C	2.822615000	1.375136000	-0.634613000
C	1.912149000	2.420183000	-0.008091000
H	2.725827000	1.415124000	-1.724861000
H	3.867791000	1.651812000	-0.411498000
H	2.211731000	3.420104000	-0.370078000
H	2.058792000	2.434495000	1.078411000
C	2.077950000	-1.250857000	1.908061000
C	2.970996000	-0.276437000	1.154621000
H	2.107528000	-2.230984000	1.419981000
H	2.487137000	-1.402622000	2.922883000
H	3.997853000	-0.682536000	1.144266000
H	3.026630000	0.665345000	1.710998000
C	0.118872000	2.567895000	-1.618855000
C	-0.321572000	2.975320000	0.675522000
C	-0.190304000	-1.946048000	2.311273000
C	0.496941000	0.218282000	2.989072000
C	0.303706000	-0.815108000	-2.947298000
C	-0.690980000	-2.443729000	-1.536828000
H	1.156594000	1.067972000	2.795583000
H	0.719588000	-0.166839000	3.998915000

H	-0.537547000	0.571826000	2.964394000
H	-0.065813000	2.717005000	1.705648000
H	-1.379435000	2.744543000	0.526193000
H	-0.160743000	4.056944000	0.531642000
H	0.715707000	2.021300000	-2.352065000
H	0.263565000	3.648903000	-1.787094000
H	-0.934952000	2.326359000	-1.793735000
H	1.081003000	-0.055365000	-3.055152000
H	-0.666848000	-0.332432000	-3.096524000
H	0.446886000	-1.571272000	-3.737940000
H	-0.724267000	-2.870469000	-0.530067000
H	-0.519478000	-3.257846000	-2.261275000
H	-1.663524000	-1.992510000	-1.758838000
H	-0.062707000	-2.751596000	1.581709000
H	-1.232756000	-1.614477000	2.289377000
H	0.036421000	-2.350074000	3.312565000
O	-1.998910000	0.220254000	0.495330000
S	-3.217598000	-0.053914000	-0.380096000
C	-4.138665000	-1.333892000	0.503994000
H	-5.108194000	-1.491657000	0.025400000
H	-3.545971000	-2.249670000	0.453153000
H	-4.255427000	-1.016243000	1.543576000
C	-4.344883000	1.317806000	-0.039717000
H	-3.910231000	2.214502000	-0.485317000
H	-5.319104000	1.115432000	-0.491309000
H	-4.424552000	1.433233000	1.044305000

[Cu^{I}(PMDETA)(DMSO-κOα)]$^{+}$
E=-2714.196996 a.u.

M06/6-311+G(d,p)

Cu	-1.163305000	-0.269103000	-2.553723000
N	-2.969094000	-1.113830000	-2.033604000
N	-0.720512000	-0.250533000	-0.316617000
N	0.821697000	-0.867554000	-2.773567000
C	-3.103081000	-0.813226000	-0.591645000
C	-1.824237000	-1.063243000	0.191864000
H	-3.930329000	-1.401529000	-0.159740000
H	-3.384782000	0.243627000	-0.505727000
H	-1.545046000	-2.119950000	0.122250000
H	-2.020998000	-0.867054000	1.258816000
C	0.603794000	-0.874714000	-0.283979000
C	1.435695000	-0.471986000	-1.490854000
H	0.479476000	-1.962720000	-0.261427000
H	1.154662000	-0.609200000	0.633068000
H	2.449065000	-0.900603000	-1.407251000
H	1.550792000	0.618345000	-1.509604000
C	0.963149000	-2.309417000	-2.999454000
C	1.474209000	-0.146163000	-3.873490000
C	-2.952666000	-2.565065000	-2.264240000
C	-4.107154000	-0.539912000	-2.760174000
H	1.316119000	0.927456000	-3.752962000
H	1.030886000	-0.455449000	-4.823562000
H	2.554099000	-0.362228000	-3.902387000
H	0.486636000	-2.878319000	-2.197441000
H	2.024798000	-2.600626000	-3.053996000
H	0.477424000	-2.579699000	-3.940741000
H	-2.118395000	-3.030928000	-1.735734000
H	-2.828957000	-2.762347000	-3.332067000
H	-3.891845000	-3.029483000	-1.922852000
C	-0.710062000	1.087668000	0.255585000
H	-1.679311000	1.573649000	0.106005000
H	0.042445000	1.706317000	-0.241158000
H	-0.494624000	1.068531000	1.336937000
H	-4.125599000	0.546301000	-2.626071000
H	-5.062556000	-0.953671000	-2.399427000
H	-4.012356000	-0.766106000	-3.825715000
O	-0.974105000	1.749103000	-3.106592000
S	-2.148374000	2.732449000	-3.124184000
C	-2.664010000	2.803324000	-4.853556000
H	-1.782899000	2.995685000	-5.470589000
H	-3.091140000	1.829577000	-5.101476000
H	-3.417465000	3.584507000	-4.979873000
C	-1.362667000	4.353746000	-3.040812000
H	-0.935753000	4.457461000	-2.042226000
H	-0.574259000	4.390052000	-3.796527000
H	-2.112186000	5.130620000	-3.209388000

[Cu^{I}(PMDETA)(DMSO-κOα)$_2$]$^{+}$
E=-3267.347917 a.u.

M06/6-311+G(d,p)

Cu	0.160899000	-0.472838000	0.025330000
N	0.435050000	-0.885245000	2.058852000
N	2.724598000	-0.397075000	0.170207000
N	0.664812000	-1.197824000	-1.872743000
C	1.804933000	-0.527830000	2.454837000
C	2.859510000	-1.021688000	1.480657000
H	2.020476000	-0.915698000	3.466350000
H	1.853956000	0.567217000	2.517139000
H	2.776929000	-2.107763000	1.367542000
H	3.856200000	-0.837311000	1.917334000
C	2.995107000	-1.256950000	-0.974657000
C	2.085566000	-0.938161000	-2.148042000
H	2.853568000	-2.300828000	-0.674743000
H	4.044169000	-1.174955000	-1.308830000
H	2.408946000	-1.506020000	-3.038280000
H	2.182567000	0.125334000	-2.403532000
C	0.374712000	-2.636033000	-1.901553000
C	-0.160625000	-0.529146000	-2.880196000
C	0.170951000	-2.313044000	2.272706000
C	-0.524386000	-0.111123000	2.846715000
H	-0.024604000	0.554336000	-2.813148000
H	-1.214214000	-0.750791000	-2.694533000
H	0.096289000	-0.866040000	-3.898281000
H	1.002528000	-3.169744000	-1.184248000

H	0.551370000	-3.056129000	-2.905843000
H	-0.667969000	-2.795289000	-1.616315000
H	0.876031000	-2.924991000	1.705202000
H	-0.836620000	-2.544327000	1.919175000
H	0.255596000	-2.575971000	3.340567000
C	3.446159000	0.858100000	0.093708000
H	3.120749000	1.538980000	0.886801000
H	3.256467000	1.353975000	-0.864603000
H	4.538004000	0.717338000	0.186965000
H	-0.393799000	0.957743000	2.648136000
H	-0.396055000	-0.292504000	3.926839000
H	-1.537106000	-0.398172000	2.554078000
O	-0.574372000	1.603827000	-0.171135000
S	0.364768000	2.778659000	0.094370000
C	-0.741027000	4.149106000	0.500356000
H	-1.515663000	4.205795000	-0.268952000
H	-1.186319000	3.926085000	1.472040000
H	-0.170965000	5.079532000	0.558826000
C	0.856634000	3.361172000	-1.545478000
H	1.484185000	2.582802000	-1.985803000
H	-0.044896000	3.503661000	-2.147290000
H	1.425580000	4.289651000	-1.453895000
C	-3.606993000	0.834363000	0.706840000
H	-4.491507000	1.388140000	0.382249000
H	-2.738835000	1.492869000	0.769483000
H	-3.789483000	0.329369000	1.659400000
H	-4.637832000	-1.795634000	0.745865000
C	-4.632349000	-1.460725000	-0.294437000
H	-5.539067000	-0.900090000	-0.535118000
H	-4.534550000	-2.316493000	-0.963307000
S	-3.184346000	-0.404079000	-0.541482000
O	-2.022795000	-1.197862000	0.044761000

[Cu^{I}(TPMA)(DMSO-κOα)]$^{+}$
E=-3267.347917 a.u.

M06/6-311+G(d,p)

N	-1.970999000	0.424496000	-0.864715000
C	-2.714314000	1.006257000	0.232260000
C	-1.586609000	1.333466000	-1.918944000
C	-2.434752000	-0.869400000	-1.308676000
C	-2.434891000	0.309488000	1.544250000
H	-3.803126000	1.025448000	0.047979000
H	-2.401239000	2.054968000	0.333466000
N	-1.180439000	-0.107788000	1.758759000
C	-3.432519000	0.142936000	2.493644000
C	-3.119699000	-0.459737000	3.702762000
C	-1.820517000	-0.889075000	3.922255000
C	-0.885058000	-0.696193000	2.919259000
H	0.146247000	-1.025042000	3.027195000
H	-1.534344000	-1.373018000	4.849072000
H	-3.884160000	-0.599904000	4.460166000
H	-4.441927000	0.483319000	2.282585000
C	-1.316690000	-1.784093000	-1.754161000
H	-3.193018000	-0.797741000	-2.108789000
H	-2.934714000	-1.357497000	-0.460057000
C	-1.543797000	-2.748673000	-2.726564000
C	-0.532041000	-3.640114000	-3.044544000
C	0.680353000	-3.541133000	-2.379193000
C	0.831279000	-2.540605000	-1.435055000
N	-0.137106000	-1.673281000	-1.131852000
H	-0.688499000	-4.403063000	-3.800234000
H	-2.509390000	-2.798781000	-3.221086000
H	1.755018000	-2.420325000	-0.873025000
H	1.496713000	-4.223119000	-2.588274000
C	-0.526221000	2.315152000	-1.481874000
H	-2.443910000	1.887630000	-2.342495000
H	-1.170924000	0.733171000	-2.741221000
C	-0.541097000	3.622170000	-1.949173000
N	0.433473000	1.869187000	-0.655965000
C	1.391787000	2.723333000	-0.282147000
C	0.464616000	4.495149000	-1.567164000
C	1.453925000	4.036682000	-0.711958000
H	2.254997000	4.683300000	-0.372814000
H	2.139576000	2.333985000	0.406611000
H	0.469335000	5.520308000	-1.922618000
H	-1.342017000	3.946402000	-2.606710000
Cu	0.181965000	-0.032572000	0.160017000
O	1.962718000	-0.868112000	1.159135000
S	3.284742000	-0.109159000	1.216623000
C	4.030214000	-0.335597000	-0.417340000
H	5.009177000	0.149355000	-0.443963000
H	4.118521000	-1.405509000	-0.623783000
H	3.357524000	0.134706000	-1.138888000
C	4.405367000	-1.195172000	2.127419000
H	4.322988000	-2.199498000	1.704335000
H	5.425725000	-0.812015000	2.048974000
H	4.086323000	-1.198402000	3.170094000

[Cu^{I}(Me$_6$TREN)(DMSO-κS)]$^{+}$
E=-2887.391744 a.u.

M06/6-311+G(d,p)

Cu	-0.012166000	0.000049000	-0.069094000
N	0.457547000	-1.850407000	-1.220727000
N	2.379383000	-0.018695000	0.029874000
N	0.399454000	2.006299000	-0.872705000
N	0.280730000	-0.197105000	2.128197000
C	1.715997000	-2.336241000	-0.641012000
C	2.808887000	-1.276475000	-0.578046000
H	2.094523000	-3.200324000	-1.217025000
H	1.486791000	-2.708681000	0.363333000
H	3.173529000	-1.073111000	-1.590537000
H	3.666684000	-1.707815000	-0.037691000
C	2.762893000	1.182506000	-0.710244000
C	1.787913000	2.326112000	-0.498589000

H	2.809063000	0.930871000	-1.775055000
H	3.772595000	1.533592000	-0.436693000
H	2.137613000	3.208510000	-1.062230000
H	1.783586000	2.622163000	0.556539000
C	1.665264000	-0.648867000	2.330647000
C	2.671655000	0.079668000	1.459300000
H	1.703774000	-1.724138000	2.123576000
H	1.951816000	-0.529777000	3.390237000
H	3.678640000	-0.311238000	1.683743000
H	2.693105000	1.138075000	1.738328000
C	0.258723000	2.010562000	-2.331559000
C	-0.484903000	3.040965000	-0.320298000
C	-0.631788000	-1.167028000	2.738789000
C	0.058900000	1.099660000	2.784061000
C	0.608780000	-1.593102000	-2.652787000
C	-0.577188000	-2.866083000	-1.042359000
H	0.753325000	1.850371000	2.399279000
H	0.212282000	1.018096000	3.872554000
H	-0.963912000	1.431887000	2.586061000
H	-0.426581000	3.047839000	0.769671000
H	-1.523981000	2.838597000	-0.589504000
H	-0.211473000	4.037657000	-0.702106000
H	0.936286000	1.289056000	-2.791720000
H	0.474980000	3.007614000	-2.748809000
H	-0.763045000	1.735012000	-2.608523000
H	1.390465000	-0.852909000	-2.835178000
H	-0.329811000	-1.201850000	-3.057738000
H	0.869949000	-2.513899000	-3.200511000
H	-0.748435000	-3.050675000	0.022500000
H	-0.300748000	-3.818327000	-1.524228000
H	-1.512323000	-2.518881000	-1.493663000
H	-0.558684000	-2.132243000	2.225932000
H	-1.657044000	-0.792078000	2.672105000
H	-0.397180000	-1.322202000	3.804490000
O	-2.833759000	1.027626000	1.097478000
S	-2.510492000	0.041934000	0.014127000
C	-3.567103000	-1.405613000	0.313468000
H	-3.575600000	-2.059649000	-0.561422000
H	-3.175226000	-1.937779000	1.181579000
H	-4.568566000	-1.023864000	0.531134000
C	-3.365587000	0.588264000	-1.488266000
H	-2.947824000	1.554784000	-1.775134000
H	-3.202821000	-0.144760000	-2.284124000
H	-4.429423000	0.700113000	-1.262394000

[Cu^{I}(PMDETA)(DMSO-κS)]$^{+}$
E=-2714.188392 a.u.

M06/6-311+G(d,p)

Cu	0.04258	-0.07993	-0.39721
N	1.40178	-1.62496	-0.76912
N	1.23203	0.29957	1.44426
N	0.20309	2.00732	-0.72098
C	1.97971	-1.88088	0.56812
C	2.37884	-0.60447	1.28728
H	2.84796	-2.55540	0.48376
H	1.21955	-2.41212	1.15511
H	3.16011	-0.08779	0.72014
H	2.82577	-0.86456	2.25941
C	1.56127	1.73095	1.34992
C	0.46351	2.50688	0.64737
H	2.50600	1.84014	0.80753
H	1.72790	2.16714	2.34648
H	0.72776	3.57721	0.61290
H	-0.47525	2.41907	1.20720
C	1.30402	2.34870	-1.62883
C	-1.02801	2.63083	-1.22907
C	2.44548	-1.24163	-1.72901
C	0.74230	-2.84087	-1.26027
H	-1.86241	2.40482	-0.55919
H	-1.24435	2.24882	-2.23128
H	-0.91527	3.72407	-1.29522
H	2.24217	1.89849	-1.29625
H	1.44242	3.43969	-1.69057
H	1.08141	1.96895	-2.62972
H	2.96233	-0.33717	-1.40175
H	1.98883	-1.03878	-2.70127
H	3.18715	-2.04688	-1.84821
C	0.47768	0.01026	2.66538
H	0.21043	-1.05067	2.69848
H	-0.45078	0.58857	2.68704
H	1.06769	0.24122	3.56617
H	-0.04249	-3.14606	-0.56218
H	1.45873	-3.67067	-1.36481
H	0.29102	-2.64656	-2.23718
O	-2.61224	0.67875	1.07608
S	-2.15099	-0.42225	0.17449
C	-3.30843	-0.55019	-1.20381
H	-4.31773	-0.66184	-0.79876
H	-3.23449	0.37481	-1.77774
H	-3.02836	-1.40501	-1.82596
C	-2.55765	-1.98688	0.97993
H	-1.91819	-2.07897	1.85985
H	-3.60645	-1.94207	1.28623
H	-2.38295	-2.81426	0.28714

[Cu^{I}(TPMA)(DMSO-κS)]$^{+}$
E=-3108.726087 a.u.

M06/6-311+G(d,p)

N	-0.03512	-1.64419	1.19650
C	0.06062	-1.02579	2.50394
C	-1.28060	-2.32776	0.93695
C	1.14207	-2.37438	0.77738
C	1.06330	0.10125	2.50711
H	0.31419	-1.74941	3.29912
H	-0.92821	-0.61848	2.75770

N	1.13317	0.86022	1.40398
C	1.87679	0.32718	3.60721
C	2.78980	1.37000	3.57035
C	2.87967	2.13842	2.42160
C	2.03803	1.84506	1.36108
H	2.10061	2.40082	0.42571
H	3.59656	2.94676	2.33517
H	3.43507	1.56595	4.42058
H	1.79580	-0.31562	4.47854
C	1.39011	-2.28490	-0.70967
H	1.11277	-3.43400	1.08540
H	2.01463	-1.93687	1.28162
C	2.04582	-3.31481	-1.37019
C	2.35362	-3.17166	-2.71288
C	1.99417	-1.99958	-3.35933
C	1.32801	-1.02917	-2.63330
N	1.02014	-1.16224	-1.34002
H	2.86850	-3.96345	-3.24714
H	2.31581	-4.21573	-0.82740
H	1.03736	-0.09259	-3.10304
H	2.22160	-1.83615	-4.40622
C	-2.42967	-1.37667	0.71859
H	-1.54400	-3.04965	1.73101
H	-1.15597	-2.91549	0.01595
C	-3.72038	-1.73902	1.08075
N	-2.16106	-0.20498	0.12757
C	-3.17992	0.62080	-0.12349
C	-4.76947	-0.87721	0.80996
C	-4.49500	0.33273	0.19102
H	-5.28019	1.04394	-0.03787
H	-2.92561	1.56560	-0.60008
H	-5.78554	-1.14218	1.08316
H	-3.89233	-2.69289	1.57015
Cu	-0.10533	0.27400	-0.25402
O	1.41990	2.61464	-1.79819
S	-0.01291	2.28363	-1.51152
C	-0.93016	2.50976	-3.05642
H	-2.00050	2.38239	-2.87546
H	-0.70471	3.50814	-3.44092
H	-0.57772	1.75247	-3.75834
C	-0.71051	3.69906	-0.62426
H	-0.43657	4.60459	-1.17289
H	-1.79577	3.59830	-0.54344
H	-0.26154	3.71070	0.37060

<u>Coordinates of the copper(II) complexes [Cu^{II}L]$^{+}$</u>

[Cu^{II}(Me$_6$TREN)]$^{2+}$
E=-2333.867100 a.u.

M06/6-311+G(d,p)

Cu	-1.258607000	0.674736000	-1.284136000
N	-3.081847000	-0.203708000	-1.040001000
N	-0.660165000	-0.331917000	0.412959000
N	0.587123000	0.355336000	-2.030229000
N	-1.266185000	2.562774000	-0.183742000
C	-3.080387000	-0.825556000	0.316020000
C	-1.707274000	-1.346416000	0.686772000
H	-3.817591000	-1.639867000	0.348542000
H	-3.420627000	-0.071323000	1.030024000
H	-1.466710000	-2.238452000	0.100738000
H	-1.691233000	-1.650233000	1.741644000
C	0.670069000	-0.916228000	0.101208000
C	1.427492000	-0.019709000	-0.857461000
H	0.511000000	-1.904947000	-0.337471000
H	1.254481000	-1.072034000	1.016933000
H	2.346030000	-0.514723000	-1.202326000
H	1.737323000	0.907860000	-0.366442000
C	-1.468931000	1.969524000	1.155977000
C	-0.579750000	0.757163000	1.430513000
H	-2.526745000	1.711250000	1.252407000
H	-1.266097000	2.718585000	1.936764000
H	-0.834904000	0.347595000	2.416391000
H	0.464647000	1.076006000	1.492903000
C	0.433879000	-0.796964000	-2.953702000
C	1.223186000	1.457280000	-2.785363000
C	-2.374988000	3.488232000	-0.499971000
C	-0.025843000	3.362295000	-0.193771000
C	-3.062402000	-1.252975000	-2.091680000
C	-4.318187000	0.587596000	-1.221424000
H	0.845061000	2.756712000	0.063851000
H	-0.098336000	4.179278000	0.537178000
H	0.121355000	3.805042000	-1.180853000
H	1.387239000	2.317167000	-2.137943000
H	0.584392000	1.745559000	-3.623605000
H	2.191108000	1.127120000	-3.183177000
H	0.002654000	-1.659794000	-2.442361000
H	1.413929000	-1.086637000	-3.354479000
H	-0.209441000	-0.514864000	-3.791580000
H	-2.199509000	-1.911889000	-1.975405000
H	-3.030433000	-0.784723000	-3.079806000
H	-3.972775000	-1.863321000	-2.030964000
H	-4.430913000	1.308308000	-0.410898000
H	-5.191467000	-0.076808000	-1.210836000
H	-4.289615000	1.111254000	-2.180252000
H	-3.329582000	2.963382000	-0.501234000
H	-2.212908000	3.929455000	-1.485602000
H	-2.423660000	4.298858000	0.239402000

[Cu^{II}(PMDETA)]$^{2+}$
E=-2160.637838 a.u.

M06/6-311+G(d,p)

Cu	-1.050860000	-0.360758000	-1.789414000

N	-2.924333000	-0.778734000	-1.410503000
N	-0.535310000	-0.988692000	0.053422000
N	0.830987000	-0.378429000	-2.324685000
C	-2.968580000	-1.252410000	0.010238000
C	-1.656342000	-1.905360000	0.393536000
H	-3.805877000	-1.948576000	0.141787000
H	-3.176914000	-0.386259000	0.644476000
H	-1.502155000	-2.841719000	-0.153569000
H	-1.636958000	-2.146313000	1.464486000
C	0.775025000	-1.646188000	-0.198350000
C	1.609809000	-0.764369000	-1.104309000
H	0.578835000	-2.619894000	-0.660163000
H	1.293200000	-1.833974000	0.751175000
H	2.535092000	-1.272649000	-1.401835000
H	1.906603000	0.155626000	-0.593035000
C	0.928020000	-1.433914000	-3.369015000
C	1.328095000	0.908649000	-2.871013000
C	-3.273301000	-1.881761000	-2.346260000
C	-3.860599000	0.355551000	-1.607896000
H	1.192337000	1.704855000	-2.134675000
H	0.783565000	1.157079000	-3.784963000
H	2.394940000	0.823432000	-3.112325000
H	0.598000000	-2.399659000	-2.974699000
H	1.967512000	-1.529663000	-3.706745000
H	0.309889000	-1.162618000	-4.229523000
H	-2.615195000	-2.742175000	-2.192490000
H	-3.182065000	-1.534849000	-3.379454000
H	-4.310171000	-2.198843000	-2.178528000
C	-0.427893000	0.147719000	0.992264000
H	-1.380574000	0.674146000	1.072350000
H	0.330698000	0.856554000	0.655760000
H	-0.146308000	-0.227138000	1.984824000
H	-3.566446000	1.197585000	-0.976214000
H	-4.879463000	0.048004000	-1.341471000
H	-3.853004000	0.662835000	-2.656254000

$[Cu^{II}(TPMA)]^{2+}$
E=-2555.213430 a.u.

M06/6-311+G(d,p)

N	-3.222494000	0.768047000	-0.819513000
C	-4.629432000	0.473930000	-1.179926000
C	-2.886691000	2.209700000	-0.889780000
C	-2.242931000	-0.098829000	-1.515983000
C	-5.113370000	-0.771664000	-0.490741000
H	-4.723393000	0.397478000	-2.271823000
H	-5.239436000	1.328430000	-0.860056000
N	-4.571587000	-1.020587000	0.717996000
C	-6.091982000	-1.581766000	-1.032994000
C	-6.539825000	-2.672560000	-0.298181000
C	-5.985837000	-2.924717000	0.947076000
C	-4.997256000	-2.080047000	1.417985000
H	-4.529757000	-2.251649000	2.382910000
H	-6.306659000	-3.766976000	1.548587000
H	-7.310906000	-3.321928000	-0.699319000
H	-6.502713000	-1.361137000	-2.013029000
C	-0.991248000	-0.261718000	-0.699001000
H	-2.028168000	0.311708000	-2.512100000
H	-2.713255000	-1.079545000	-1.662930000
C	0.242206000	-0.491310000	-1.276802000
C	1.337682000	-0.708113000	-0.450193000
C	1.166667000	-0.674818000	0.924872000
C	-0.094882000	-0.421557000	1.431695000
N	-1.155616000	-0.224430000	0.638200000
H	2.316671000	-0.895507000	-0.878712000
H	0.345213000	-0.506156000	-2.357079000
H	-0.266853000	-0.374462000	2.502807000
H	1.997129000	-0.836132000	1.601977000
C	-3.436548000	2.949396000	0.298222000
H	-3.254174000	2.629403000	-1.836208000
H	-1.792562000	2.295577000	-0.899138000
C	-3.789120000	4.283617000	0.238047000
N	-3.513456000	2.243219000	1.443562000
C	-3.937428000	2.852405000	2.558312000
C	-4.216597000	4.915141000	1.399441000
C	-4.289945000	4.189506000	2.578117000
H	-4.621135000	4.645931000	3.503394000
H	-3.993911000	2.247226000	3.458126000
H	-4.494991000	5.963614000	1.380250000
H	-3.725645000	4.823632000	-0.701205000
Cu	-3.066221000	0.289748000	1.102277000

<u>Coordinates of the copper(II) complexes with coordinated solvent molecules $[Cu^{II}LS]^{2+}$</u>

$[Cu^{II}(Me_6TREN)(MeCN)]^{+}$
E=-2466.631869 a.u.

M06/6-311+G(d,p)

Cu	-0.122982000	0.046742000	-0.057261000
N	0.065935000	-1.539354000	-1.495791000
N	1.925897000	0.088680000	-0.094711000
N	0.000837000	2.164181000	-0.369196000
N	0.131623000	-0.755498000	1.992235000
C	1.384947000	-2.110848000	-1.160652000
C	2.423863000	-1.027313000	-0.957929000
H	1.720425000	-2.798577000	-1.952460000
H	1.261104000	-2.713781000	-0.255493000
H	2.717257000	-0.602765000	-1.921497000
H	3.333915000	-1.458878000	-0.525326000
C	2.329732000	1.417536000	-0.634591000
C	1.419468000	2.502996000	-0.113992000
H	2.274552000	1.369626000	-1.725843000

H	3.377188000	1.628397000	-0.380230000
H	1.674702000	3.467150000	-0.577383000
H	1.542624000	2.638829000	0.965659000
C	1.572409000	-1.071706000	2.073473000
C	2.383942000	-0.048505000	1.318066000
H	1.731018000	-2.072691000	1.659951000
H	1.905134000	-1.114241000	3.121473000
H	3.451093000	-0.305107000	1.331706000
H	2.293681000	0.928951000	1.799410000
C	-0.357697000	2.449757000	-1.772635000
C	-0.862482000	2.982052000	0.501373000
C	-0.659089000	-1.952370000	2.316483000
C	-0.219536000	0.298654000	2.959837000
C	0.054651000	-0.996678000	-2.866361000
C	-0.958358000	-2.594008000	-1.413736000
H	0.397211000	1.188619000	2.811139000
H	-0.071277000	-0.052642000	3.990748000
H	-1.269648000	0.576909000	2.835964000
H	-0.661438000	2.762461000	1.551912000
H	-1.911343000	2.770858000	0.286538000
H	-0.682533000	4.050960000	0.323296000
H	0.300909000	1.919007000	-2.462752000
H	-0.280591000	3.526505000	-1.975943000
H	-1.386294000	2.132505000	-1.960429000
H	0.835586000	-0.245069000	-3.000710000
H	-0.914663000	-0.531941000	-3.066297000
H	0.217282000	-1.797673000	-3.601098000
H	-1.039595000	-2.969313000	-0.391315000
H	-0.704494000	-3.429796000	-2.080000000
H	-1.925116000	-2.192304000	-1.722321000
H	-0.407837000	-2.770670000	1.637240000
H	-1.724843000	-1.728827000	2.227427000
H	-0.460705000	-2.286506000	3.344668000
N	-2.120896000	0.034497000	-0.040075000
C	-3.270417000	0.004908000	-0.020055000
C	-4.708429000	-0.032291000	0.003491000
H	-5.085349000	0.567573000	0.836171000
H	-5.108683000	0.368556000	-0.931624000
H	-5.054603000	-1.062281000	0.124139000

[Cu^{II}(PMDETA)(MeCN)]$^{2+}$
E=-2293.408945 a.u.

M06/6-311+G(d,p)

Cu	-1.114290000	-0.160554000	-1.965850000
N	-3.025064000	-0.762031000	-1.473078000
N	-0.593033000	-0.813763000	-0.130659000
N	0.880896000	-0.374268000	-2.444496000
C	-3.008342000	-1.153158000	-0.037860000
C	-1.664000000	-1.730824000	0.331039000
H	-3.813509000	-1.871668000	0.165068000
H	-3.228931000	-0.260712000	0.555398000
H	-1.506904000	-2.700309000	-0.153105000
H	-1.587808000	-1.894727000	1.414076000
C	0.719344000	-1.493356000	-0.261019000
C	1.605068000	-0.694096000	-1.184998000
H	0.539036000	-2.496801000	-0.660442000
H	1.186350000	-1.617513000	0.724944000
H	2.530196000	-1.240334000	-1.411946000
H	1.905429000	0.250594000	-0.721932000
C	0.896781000	-1.529113000	-3.370330000
C	1.518330000	0.787564000	-3.094541000
C	-3.255103000	-1.940596000	-2.338619000
C	-4.093891000	0.230868000	-1.697816000
H	1.402911000	1.676230000	-2.468134000
H	1.059158000	0.966497000	-4.067338000
H	2.588024000	0.593726000	-3.245269000
H	0.471373000	-2.416595000	-2.892707000
H	1.926085000	-1.758175000	-3.675767000
H	0.312430000	-1.293506000	-4.263564000
H	-2.500861000	-2.711371000	-2.154925000
H	-3.207060000	-1.641607000	-3.388921000
H	-4.246170000	-2.369897000	-2.141865000
C	-0.494800000	0.378660000	0.742898000
H	-1.451543000	0.903432000	0.783908000
H	0.256428000	1.072812000	0.360508000
H	-0.212840000	0.076845000	1.759530000
H	-3.867383000	1.153042000	-1.155847000
H	-5.054515000	-0.164429000	-1.343584000
H	-4.181042000	0.447436000	-2.763036000
N	-1.617896000	0.882530000	-3.574230000
C	-1.906115000	1.547748000	-4.467495000
C	-2.266147000	2.376235000	-5.584384000
H	-1.469846000	3.098070000	-5.786225000
H	-2.420164000	1.757605000	-6.473031000
H	-3.189109000	2.919882000	-5.364236000

[Cu^{II}(TPMA)(MeCN)]$^{2+}$
E=-2687.976538 a.u.

M06/6-311+G(d,p)

N	-3.208264000	0.721441000	-0.627477000
C	-4.611527000	0.471299000	-1.018530000
C	-2.848810000	2.150195000	-0.745829000
C	-2.266841000	-0.147026000	-1.365032000
C	-5.117330000	-0.790099000	-0.382103000
H	-4.702912000	0.439513000	-2.113287000
H	-5.214522000	1.319181000	-0.668830000
N	-4.581534000	-1.086529000	0.813614000
C	-6.098104000	-1.574114000	-0.962126000
C	-6.549553000	-2.693343000	-0.276544000
C	-5.998349000	-2.997698000	0.958843000
C	-5.012691000	-2.170716000	1.465763000
H	-4.544745000	-2.378921000	2.423280000
H	-6.320060000	-3.866222000	1.521229000
H	-7.319544000	-3.324996000	-0.706916000
H	-6.503209000	-1.310919000	-1.933979000

C	-0.985474000	-0.302921000	-0.599616000
H	-2.091724000	0.250519000	-2.374566000
H	-2.738717000	-1.130992000	-1.483178000
C	0.228284000	-0.533454000	-1.221446000
C	1.355171000	-0.725746000	-0.434304000
C	1.233711000	-0.669720000	0.945827000
C	-0.012806000	-0.422178000	1.491134000
N	-1.102578000	-0.245904000	0.737405000
H	2.319696000	-0.910670000	-0.895370000
H	0.289242000	-0.564272000	-2.304599000
H	-0.150865000	-0.357123000	2.566250000
H	2.091331000	-0.808483000	1.593397000
C	-3.414736000	2.931506000	0.403573000
H	-3.184283000	2.549341000	-1.713298000
H	-1.753809000	2.224199000	-0.728486000
C	-3.754591000	4.268040000	0.297904000
N	-3.530678000	2.255018000	1.558378000
C	-3.984444000	2.894624000	2.640893000
C	-4.216068000	4.930261000	1.427004000
C	-4.333113000	4.232718000	2.619618000
H	-4.695362000	4.713309000	3.520688000
H	-4.072555000	2.307334000	3.550008000
H	-4.487885000	5.979226000	1.373389000
H	-3.657182000	4.782260000	-0.652872000
Cu	-3.046311000	0.230938000	1.345886000
N	-2.888528000	-0.248333000	3.271061000
C	-2.797780000	-0.525777000	4.382449000
C	-2.683992000	-0.873203000	5.773862000
H	-3.677853000	-0.947122000	6.222933000
H	-2.174749000	-1.834794000	5.878326000
H	-2.110707000	-0.108371000	6.304206000

[Cu^{II}(Me_6TREN)(DMSO-κO)]$^{2+}$
E=-2887.077612 a.u.

M06/6-311+G(d,p)

Cu	0.221577000	0.056206000	-0.000286000
N	0.228846000	-1.405604000	-1.603278000
N	2.267268000	0.060125000	-0.241854000
N	0.381365000	2.186632000	-0.185122000
N	0.656396000	-0.902476000	1.922981000
C	1.550674000	-2.034536000	-1.405037000
C	2.644788000	-1.004054000	-1.218895000
H	1.799776000	-2.682294000	-2.260316000
H	1.474293000	-2.688005000	-0.530241000
H	2.874947000	-0.523769000	-2.173589000
H	3.568373000	-1.500500000	-0.898737000
C	2.651155000	1.412379000	-0.732409000
C	1.825622000	2.481982000	-0.058152000
H	2.487823000	1.436686000	-1.813788000
H	3.723605000	1.586994000	-0.571298000
H	2.060182000	3.467657000	-0.486278000
H	2.061770000	2.547225000	1.008975000
C	2.090576000	-1.245797000	1.862264000
C	2.853811000	-0.184617000	1.106226000
H	2.194250000	-2.219480000	1.372606000
H	2.510504000	-1.362068000	2.872617000
H	3.911596000	-0.459287000	1.002229000
H	2.829834000	0.757045000	1.661314000
C	-0.112588000	2.579299000	-1.516116000
C	-0.370782000	2.939864000	0.832450000
C	-0.144196000	-2.098335000	2.216024000
C	0.402893000	0.086343000	2.985366000
C	0.142696000	-0.777574000	-2.933706000
C	-0.804310000	-2.449286000	-1.522781000
H	1.033884000	0.969162000	2.853774000
H	0.616120000	-0.342702000	3.974658000
H	-0.644579000	0.394688000	2.949591000
H	-0.028988000	2.668267000	1.833060000
H	-1.432126000	2.699702000	0.756283000
H	-0.233155000	4.020672000	0.691206000
H	0.464709000	2.097611000	-2.307855000
H	-0.046465000	3.667984000	-1.649727000
H	-1.158887000	2.280046000	-1.623818000
H	0.921871000	-0.023713000	-3.064615000
H	-0.830825000	-0.293524000	-3.048986000
H	0.254476000	-1.530231000	-3.727222000
H	-0.838279000	-2.873117000	-0.516230000
H	-0.600057000	-3.256480000	-2.240296000
H	-1.779283000	-2.023641000	-1.773155000
H	0.041723000	-2.874253000	1.468495000
H	-1.203910000	-1.832209000	2.205819000
H	0.107511000	-2.508153000	3.204484000
O	-1.697302000	0.148374000	0.464422000
S	-2.991881000	-0.057318000	-0.374556000
C	-3.899494000	-1.302780000	0.554492000
H	-4.900914000	-1.397893000	0.126658000
H	-3.366681000	-2.249974000	0.455077000
H	-3.947689000	-0.989140000	1.600467000
C	-4.003990000	1.369550000	0.049507000
H	-3.583606000	2.247746000	-0.443075000
H	-5.017102000	1.196154000	-0.322906000
H	-4.000164000	1.487544000	1.136150000

[Cu^{II}(PMDETA)(DMSO-κO)]$^{2+}$
E=-2713.855768 a.u.

M06/6-311+G(d,p)

Cu	-1.095141000	0.038311000	-1.955442000
N	-3.037460000	-0.441468000	-1.454588000
N	-0.580653000	-0.795972000	-0.186845000
N	0.880473000	-0.255188000	-2.484755000
C	-3.011414000	-0.929830000	-0.048503000
C	-1.715253000	-1.648690000	0.236763000
H	-3.873160000	-1.584840000	0.136564000
H	-3.130364000	-0.063038000	0.608672000

H	-1.657197000	-2.588941000	-0.321571000
H	-1.632716000	-1.901348000	1.302230000
C	0.657396000	-1.575672000	-0.425475000
C	1.596609000	-0.767487000	-1.287512000
H	0.373393000	-2.508486000	-0.924638000
H	1.130177000	-1.848876000	0.527346000
H	2.463136000	-1.368654000	-1.592849000
H	1.992365000	0.091290000	-0.737727000
C	0.815522000	-1.291396000	-3.536711000
C	1.577921000	0.934728000	-3.008740000
C	-3.406725000	-1.538288000	-2.377235000
C	-4.025434000	0.648179000	-1.563009000
H	1.549364000	1.737248000	-2.267015000
H	1.082959000	1.275666000	-3.917544000
H	2.624145000	0.687982000	-3.231437000
H	0.331234000	-2.198039000	-3.160810000
H	1.825273000	-1.552788000	-3.879324000
H	0.244185000	-0.910379000	-4.386275000
H	-2.706837000	-2.373702000	-2.284278000
H	-3.386641000	-1.177275000	-3.408689000
H	-4.418063000	-1.902870000	-2.154449000
C	-0.345794000	0.299791000	0.780235000
H	-1.255251000	0.887672000	0.919535000
H	0.435916000	0.970556000	0.418140000
H	-0.038910000	-0.112381000	1.749900000
H	-3.688043000	1.516628000	-0.990025000
H	-4.998208000	0.320437000	-1.173705000
H	-4.161421000	0.926470000	-2.610335000
O	-1.327486000	1.233449000	-3.468576000
S	-2.428570000	1.602164000	-4.511609000
C	-1.489638000	1.734949000	-6.038303000
H	-0.634046000	2.392507000	-5.864835000
H	-1.167377000	0.732003000	-6.322395000
H	-2.145352000	2.141130000	-6.813182000
C	-2.719496000	3.350572000	-4.208410000
H	-3.240224000	3.442622000	-3.253850000
H	-1.755703000	3.864072000	-4.177150000
H	-3.350311000	3.740944000	-5.011498000

$[Cu^{II}(TPMA)(DMSO\text{-}\kappa O)]^{2+}$
E=-3108.419313 a.u.

M06/6-311+G(d,p)

N	-1.576040000	0.163904000	1.131301000
C	-2.075756000	-1.205934000	1.373892000
C	-1.084710000	0.804614000	2.365385000
C	-2.575768000	1.003528000	0.439684000
C	-2.002631000	-2.022948000	0.115291000
H	-3.096652000	-1.177241000	1.779933000
H	-1.438114000	-1.666526000	2.139332000
N	-1.002533000	-1.700497000	-0.719552000
C	-2.876939000	-3.060007000	-0.156961000
C	-2.701010000	-3.790093000	-1.324652000
C	-1.670156000	-3.451091000	-2.188392000
C	-0.845972000	-2.393029000	-1.850392000
H	-0.038522000	-2.066724000	-2.500290000
H	-1.511911000	-3.990700000	-3.114643000
H	-3.370854000	-4.609786000	-1.562474000
H	-3.681705000	-3.292228000	0.533238000
C	-1.902300000	2.124268000	-0.298973000
H	-3.325141000	1.376354000	1.152161000
H	-3.105601000	0.368408000	-0.282186000
C	-2.524069000	3.332512000	-0.557353000
C	-1.847086000	4.279962000	-1.313284000
C	-0.573263000	3.992346000	-1.780533000
C	-0.015583000	2.765189000	-1.470293000
N	-0.665430000	1.853448000	-0.742979000
H	-2.310643000	5.235945000	-1.533270000
H	-3.522246000	3.526353000	-0.177957000
H	0.976076000	2.479804000	-1.809943000
H	-0.017320000	4.708155000	-2.374412000
C	0.257259000	0.254641000	2.752604000
H	-1.815249000	0.687279000	3.178475000
H	-0.990934000	1.880961000	2.170828000
C	0.668419000	0.197032000	4.073283000
N	1.043095000	-0.146647000	1.739013000
C	2.259782000	-0.622322000	2.027123000
C	1.938632000	-0.279805000	4.360446000
C	2.749771000	-0.700674000	3.317584000
H	3.743059000	-1.094282000	3.498464000
H	2.858464000	-0.970343000	1.189294000
H	2.286034000	-0.333116000	5.386855000
H	0.000497000	0.521957000	4.864679000
Cu	0.034859000	0.002071000	-0.125659000
O	1.426361000	-0.016823000	-1.510186000
S	2.875268000	-0.580385000	-1.475953000
C	3.899640000	0.898084000	-1.417552000
H	4.949534000	0.608367000	-1.510605000
H	3.603733000	1.563658000	-2.232460000
H	3.731075000	1.371492000	-0.447550000
C	3.158486000	-1.047819000	-3.187736000
H	2.831070000	-0.223888000	-3.826234000
H	4.223606000	-1.254553000	-3.319698000
H	2.581536000	-1.950863000	-3.390206000

$[Cu^{II}(PMDETA)(MeCN)_2]^{2+}$
E=-2426.148905 a.u.

M06/6-311+G(d,p)

Cu	-0.17894	-0.03013	0.00000
N	-0.59118	-0.26907	2.02909
N	0.14066	-2.07341	0.00000
N	-0.59118	-0.26907	-2.02909
C	-0.18933	-1.65505	2.37641
C	-0.50061	-2.58790	1.23331
H	-0.69428	-1.97669	3.29753

H	0.88400	-1.64858	2.59069
H	-1.58001	-2.64457	1.05904
H	-0.15632	-3.60781	1.45071
C	-0.50061	-2.58790	-1.23331
C	-0.18933	-1.65505	-2.37641
H	-1.58001	-2.64457	-1.05904
H	-0.15632	-3.60781	-1.45071
H	-0.69428	-1.97669	-3.29753
H	0.88400	-1.64858	-2.59069
C	-2.04908	-0.10098	-2.20654
C	0.11777	0.68285	-2.90187
C	-2.04908	-0.10098	2.20654
C	0.11777	0.68285	2.90187
H	1.19542	0.59171	-2.74945
H	-0.19081	1.70259	-2.66581
H	-0.11506	0.48033	-3.95570
H	-2.60227	-0.78632	-1.55870
H	-2.32998	-0.29938	-3.24920
H	-2.33646	0.92056	-1.95468
H	-2.60227	-0.78632	1.55870
H	-2.33646	0.92056	1.95468
H	-2.32998	-0.29938	3.24920
C	1.58153	-2.40156	0.00000
H	2.06999	-1.98397	0.88080
H	2.06999	-1.98397	-0.88080
H	1.71069	-3.49134	0.00000
H	1.19542	0.59171	2.74945
H	-0.11506	0.48033	3.95570
H	-0.19081	1.70259	2.66581
C	-1.15962	3.01546	0.00000
C	-1.55588	4.39917	0.00000
H	-1.16568	4.90133	-0.88902
H	-2.64637	4.47608	0.00000
H	-1.16568	4.90133	0.88902
N	-0.84897	1.90816	0.00000
N	1.94530	0.68533	0.00000
C	3.00411	1.13809	0.00000
C	4.33112	1.70034	0.00000
H	5.07787	0.90245	0.00000
H	4.47748	2.31927	-0.88880
H	4.47748	2.31927	0.88880

$[Cu^{II}(PMDETA)(DMSO\text{-}\kappa O)_2]^{2+}$
E=-3267.039063 a.u.

M06/6-311+G(d,p)

Cu	-0.61822	-0.31930	-0.01576
N	-1.10636	-0.77647	-1.98106
N	-2.35094	0.80493	-0.02356
N	-0.95831	-0.52359	2.02672
C	-2.23616	0.10304	-2.35873
C	-3.14702	0.31689	-1.17468
H	-2.78944	-0.32647	-3.20555
H	-1.82052	1.05518	-2.70480
H	-3.62433	-0.62369	-0.88089
H	-3.95164	1.02403	-1.41751
C	-3.02639	0.56969	1.27388
C	-1.99131	0.48052	2.36896
H	-3.59507	-0.36222	1.20210
H	-3.75064	1.36768	1.48454
H	-2.46084	0.23380	3.33205
H	-1.48387	1.44335	2.50057
C	-1.46952	-1.89755	2.21226
C	0.21347	-0.32520	2.89084
C	-1.52096	-2.19496	-1.97818
C	0.00038	-0.59943	-2.93175
H	0.69672	0.62506	2.64918
H	0.92834	-1.13586	2.73810
H	-0.08212	-0.32855	3.94879
H	-2.36605	-2.06318	1.60938
H	-1.71792	-2.07669	3.26715
H	-0.70750	-2.61069	1.89089
H	-2.37380	-2.34630	-1.31111
H	-0.69086	-2.80959	-1.62624
H	-1.80795	-2.51079	-2.99017
C	-2.04385	2.23838	-0.18359
H	-1.45616	2.40684	-1.08732
H	-1.46546	2.59801	0.66990
H	-2.97415	2.81776	-0.24646
H	0.39329	0.41846	-2.85411
H	-0.34336	-0.78033	-3.95919
H	0.79178	-1.31174	-2.69588
O	1.00971	1.17177	-0.20106
S	1.43248	2.65226	-0.26318
C	3.01580	2.62514	-1.12391
H	3.68063	1.91959	-0.61758
H	2.82511	2.31693	-2.15382
H	3.44146	3.63182	-1.11974
C	2.06371	3.01805	1.38705
H	1.21114	3.06211	2.06850
H	2.75483	2.22175	1.67892
H	2.56509	3.98917	1.37494
C	3.21401	-1.32760	-1.17687
H	4.28421	-1.28917	-0.95591
H	2.89664	-0.40615	-1.66767
H	2.97897	-2.20246	-1.78869
H	2.56227	-3.78847	0.08066
C	2.83134	-3.08260	0.86957
H	3.91037	-3.07535	1.04373
H	2.31092	-3.33075	1.79672
S	2.31053	-1.43240	0.37573
O	0.83510	-1.68322	-0.04905

Coordinates of the copper(II) complexes [Cu^{II}LX]$^{+}$ (X=Cl, Br)

[Cu^{II}(Me$_6$TREN)Cl]$^{+}$
E=-2794.471194 a.u.

M06/6-311+G(d,p)

Cu	0.049611000	-0.082335000	-0.801080000
N	-1.670441000	-1.366966000	-0.517577000
N	0.199828000	-0.187473000	1.287667000
N	2.159756000	-0.527293000	-0.760981000
N	-0.588144000	2.028651000	-0.388605000
C	-2.108306000	-1.054684000	0.848625000
C	-0.939910000	-0.986644000	1.814396000
H	-2.833793000	-1.803416000	1.208631000
H	-2.640216000	-0.098656000	0.811173000
H	-0.575992000	-1.996841000	2.022324000
H	-1.278003000	-0.580426000	2.776577000
C	1.502986000	-0.829367000	1.592382000
C	2.578813000	-0.356679000	0.640374000
H	1.374402000	-1.911593000	1.495636000
H	1.796869000	-0.636972000	2.634512000
H	3.517092000	-0.898783000	0.837156000
H	2.799710000	0.704776000	0.797588000
C	-0.810162000	2.080221000	1.061480000
C	0.187796000	1.209387000	1.792685000
H	-1.832026000	1.744431000	1.266474000
H	-0.743427000	3.113531000	1.439820000
H	-0.015108000	1.211608000	2.873119000
H	1.192648000	1.621724000	1.664877000
C	2.310472000	-1.926970000	-1.192965000
C	2.985253000	0.314758000	-1.641358000
C	-1.786922000	2.455793000	-1.117503000
C	0.524500000	2.898730000	-0.787969000
C	-1.232888000	-2.763754000	-0.639783000
C	-2.775837000	-1.149718000	-1.462155000
H	1.432605000	2.652072000	-0.230684000
H	0.281866000	3.956059000	-0.600462000
H	0.723051000	2.761022000	-1.854074000
H	2.882103000	1.365434000	-1.361313000
H	2.649039000	0.195876000	-2.672444000
H	4.043392000	0.026055000	-1.561721000
H	1.750678000	-2.600649000	-0.539744000
H	3.369976000	-2.221406000	-1.174276000
H	1.925194000	-2.028985000	-2.209818000
H	-0.423697000	-2.987349000	0.060277000
H	-0.870426000	-2.935958000	-1.656204000
H	-2.066976000	-3.452323000	-0.436447000
H	-3.106559000	-0.110452000	-1.421251000
H	-3.622332000	-1.807941000	-1.216791000
H	-2.431242000	-1.354778000	-2.476463000
H	-2.650006000	1.863323000	-0.802972000
H	-1.631336000	2.306654000	-2.188733000
H	-2.007457000	3.516772000	-0.924690000
Cl	-0.068022000	-0.004119000	-3.000960000

[Cu^{II}(Me$_6$TREN)Br]$^{+}$
E=-4908.296321 a.u.

M06/6-311+G(d,p)

Cu	0.046890000	-0.084105000	-0.820987000
N	-1.680955000	-1.368366000	-0.520352000
N	0.200672000	-0.190132000	1.285238000
N	2.167059000	-0.528192000	-0.767680000
N	-0.587632000	2.035176000	-0.392070000
C	-2.106987000	-1.054650000	0.850172000
C	-0.935196000	-0.992123000	1.810684000
H	-2.832912000	-1.801865000	1.212651000
H	-2.637204000	-0.097639000	0.816140000
H	-0.571190000	-2.003804000	2.011113000
H	-1.271117000	-0.592937000	2.776880000
C	1.504769000	-0.826190000	1.588597000
C	2.576476000	-0.347898000	0.636176000
H	1.382064000	-1.909235000	1.493274000
H	1.801046000	-0.632149000	2.630031000
H	3.519948000	-0.879647000	0.836898000
H	2.786794000	0.716412000	0.789109000
C	-0.813897000	2.074361000	1.058220000
C	0.183846000	1.205165000	1.790178000
H	-1.834977000	1.733114000	1.257708000
H	-0.753645000	3.106197000	1.441993000
H	-0.023039000	1.207587000	2.870120000
H	1.187791000	1.620828000	1.666911000
C	2.324190000	-1.932282000	-1.184401000
C	3.013236000	0.304233000	-1.638198000
C	-1.786366000	2.478567000	-1.111636000
C	0.526772000	2.909900000	-0.776612000
C	-1.241354000	-2.765338000	-0.640192000
C	-2.806902000	-1.162903000	-1.443697000
H	1.435854000	2.648481000	-0.227860000
H	0.288043000	3.963976000	-0.566631000
H	0.722422000	2.794943000	-1.845935000
H	2.893684000	1.359276000	-1.381510000
H	2.713444000	0.164500000	-2.677558000
H	4.070260000	0.024545000	-1.519995000
H	1.749715000	-2.599372000	-0.537344000
H	3.382691000	-2.228052000	-1.141542000
H	1.959761000	-2.044202000	-2.207864000
H	-0.421964000	-2.981837000	0.050089000
H	-0.891551000	-2.944177000	-1.659907000
H	-2.070810000	-3.454553000	-0.420564000
H	-3.130386000	-0.120466000	-1.417341000
H	-3.651142000	-1.810376000	-1.164195000
H	-2.490466000	-1.393088000	-2.461578000
H	-2.645818000	1.867593000	-0.823372000

H	-1.626283000	2.370145000	-2.186891000
H	-2.015702000	3.530492000	-0.882300000
Br	-0.081474000	-0.005583000	-3.167237000

[Cu^{II}(PMDETA)Cl]$^{+}$
E=-2621.258374 a.u.

M06/6-311+G(d,p)

Cu	-0.002551000	-0.638276000	-0.381703000
N	-2.055042000	-0.537937000	-0.005791000
N	-0.001044000	1.351290000	0.085548000
N	2.050054000	-0.540583000	-0.006564000
C	-2.394098000	0.882380000	0.229332000
C	-1.229846000	1.608261000	0.864056000
H	-3.290927000	0.963263000	0.859604000
H	-2.650562000	1.332228000	-0.734681000
H	-1.060036000	1.244905000	1.883544000
H	-1.430481000	2.687065000	0.933031000
C	1.227835000	1.606077000	0.864549000
C	2.391124000	0.879120000	0.229287000
H	1.057356000	1.242199000	1.883751000
H	1.429857000	2.684571000	0.934255000
H	3.288071000	0.958420000	0.859567000
H	2.648092000	1.329264000	-0.734464000
C	2.229863000	-1.338743000	1.221770000
C	2.899372000	-1.090221000	-1.078798000
C	-2.234975000	-1.335106000	1.223148000
C	-2.905898000	-1.087076000	-1.077017000
H	2.701158000	-0.558534000	-2.013458000
H	2.664500000	-2.144532000	-1.224480000
H	3.959404000	-0.977026000	-0.812992000
H	1.609986000	-0.942810000	2.032796000
H	3.281645000	-1.317195000	1.538817000
H	1.929527000	-2.369688000	1.025853000
H	-1.613872000	-0.939632000	2.033458000
H	-1.936226000	-2.366577000	1.027545000
H	-3.286462000	-1.311932000	1.541068000
C	0.000133000	2.109990000	-1.178923000
H	-0.880525000	1.860075000	-1.774063000
H	0.880052000	1.857324000	-1.774039000
H	0.001820000	3.190266000	-0.979017000
H	-2.707234000	-0.556666000	-2.012303000
H	-3.965578000	-0.971816000	-0.810716000
H	-2.672913000	-2.141937000	-1.221822000
Cl	-0.004049000	-2.672540000	-1.146324000

[Cu^{II}(PMDETA)Br]$^{+}$
E=-4735.083792 a.u.

M06/6-311+G(d,p)

Cu	-0.002540000	-0.644008000	-0.417356000
N	-2.058884000	-0.541755000	-0.009296000
N	-0.001063000	1.353485000	0.078659000
N	2.054100000	-0.544611000	-0.010058000
C	-2.391087000	0.880894000	0.224373000
C	-1.228153000	1.607526000	0.858308000
H	-3.288769000	0.963860000	0.853598000
H	-2.645937000	1.329094000	-0.740981000
H	-1.057594000	1.245101000	1.877879000
H	-1.432195000	2.685807000	0.927849000
C	1.226556000	1.605681000	0.858061000
C	2.388314000	0.877553000	0.223696000
H	1.055726000	1.243272000	1.877593000
H	1.432099000	2.683666000	0.927772000
H	3.286295000	0.959218000	0.852663000
H	2.643484000	1.325538000	-0.741675000
C	2.211752000	-1.331950000	1.228396000
C	2.943284000	-1.090003000	-1.052035000
C	-2.217130000	-1.328701000	1.229330000
C	-2.949225000	-1.086105000	-1.050839000
H	2.757293000	-0.577336000	-1.999534000
H	2.739746000	-2.151700000	-1.189010000
H	3.992752000	-0.947929000	-0.759191000
H	1.569955000	-0.936533000	2.022210000
H	3.255565000	-1.299078000	1.570438000
H	1.926742000	-2.367829000	1.034500000
H	-1.574487000	-0.934050000	2.022841000
H	-1.933609000	-2.364998000	1.035468000
H	-3.260765000	-1.294361000	1.571769000
C	-0.000612000	2.118576000	-1.181620000
H	-0.880897000	1.870682000	-1.778386000
H	0.879071000	1.869218000	-1.778667000
H	0.000316000	3.198134000	-0.977230000
H	-2.763067000	-0.573671000	-1.998432000
H	-3.998377000	-0.942755000	-0.757491000
H	-2.746997000	-2.148040000	-1.187891000
Br	-0.004134000	-2.764020000	-1.341895000

[Cu^{II}(TPMA)Cl]$^{+}$
E=-3015.803353 a.u.

M06/6-311+G(d,p)

N	0.001438000	0.001072000	1.194952000
C	1.336743000	-0.450045000	1.619075000
C	-0.276698000	1.382868000	1.618912000
C	-1.057408000	-0.930772000	1.615671000
C	1.848923000	-1.542637000	0.721310000
H	1.330509000	-0.764045000	2.673813000
H	2.016791000	0.408971000	1.543700000
N	1.449414000	-1.469129000	-0.554633000
C	2.720198000	-2.524388000	1.158797000
C	3.202704000	-3.441506000	0.234308000
C	2.797047000	-3.351955000	-1.087572000
C	1.910374000	-2.349078000	-1.444382000
H	1.547748000	-2.223136000	-2.462110000
H	3.154663000	-4.049671000	-1.835583000

H	3.889188000	-4.221440000	0.547201000
H	3.019195000	-2.566280000	2.201428000
C	-2.258351000	-0.826162000	0.716425000
H	-1.327896000	-0.770364000	2.670287000
H	-0.653298000	-1.949060000	1.539414000
C	-3.544511000	-1.091830000	1.151991000
C	-4.579258000	-1.048876000	0.226755000
C	-4.297770000	-0.737976000	-1.093923000
C	-2.985665000	-0.469952000	-1.448649000
N	-1.993808000	-0.513076000	-0.558267000
H	-5.598116000	-1.254826000	0.538104000
H	-3.731021000	-1.333048000	2.193752000
H	-2.694607000	-0.215712000	-2.465397000
H	-5.080057000	-0.696728000	-1.842597000
C	0.414944000	2.373154000	0.722906000
H	-0.003421000	1.534177000	2.674153000
H	-1.360580000	1.542135000	1.542234000
C	0.826699000	3.618979000	1.161831000
N	0.555900000	1.990514000	-0.552543000
C	1.090336000	2.830098000	-1.440227000
C	1.382791000	4.495709000	0.239548000
C	1.513613000	4.099579000	-1.081807000
H	1.941551000	4.758303000	-1.828227000
H	1.166448000	2.453156000	-2.457684000
H	1.713120000	5.480405000	0.553688000
H	0.709382000	3.898843000	2.204023000
Cu	0.004259000	0.003060000	-0.913072000
Cl	0.007176000	0.004779000	-3.112818000

$[Cu^{II}(TPMA)Br]^{+}$
E=-5129.629167 a.u.

M06/6-311+G(d,p)

N	0.000685000	0.001216000	1.186884000
C	1.338145000	-0.440728000	1.607941000
C	-0.286357000	1.380425000	1.607387000
C	-1.051084000	-0.937031000	1.604930000
C	1.851008000	-1.536821000	0.715537000
H	1.338363000	-0.750197000	2.664290000
H	2.014640000	0.420496000	1.526328000
N	1.450899000	-1.476277000	-0.561693000
C	2.722932000	-2.513068000	1.164388000
C	3.206354000	-3.441722000	0.252625000
C	2.799761000	-3.368120000	-1.069754000
C	1.913904000	-2.368973000	-1.438392000
H	1.554524000	-2.258412000	-2.459013000
H	3.156143000	-4.074768000	-1.809924000
H	3.892899000	-4.217556000	0.575343000
H	3.020795000	-2.541610000	2.207814000
C	-2.256051000	-0.831132000	0.711767000
H	-1.319949000	-0.785149000	2.661484000
H	-0.643308000	-1.953260000	1.520975000
C	-3.537987000	-1.099865000	1.158138000
C	-4.582781000	-1.052110000	0.245048000
C	-4.314147000	-0.732796000	-1.076055000
C	-3.005619000	-0.463487000	-1.442090000
N	-2.002199000	-0.511198000	-0.564235000
H	-5.598271000	-1.260164000	0.565838000
H	-3.712924000	-1.346558000	2.200637000
H	-2.728777000	-0.204050000	-2.461430000
H	-5.103318000	-0.686341000	-1.817167000
C	0.410241000	2.372628000	0.717963000
H	-0.022634000	1.534929000	2.664856000
H	-1.370062000	1.536083000	1.521222000
C	0.818101000	3.615879000	1.168196000
N	0.562754000	1.995766000	-0.558606000
C	1.107901000	2.842718000	-1.433307000
C	1.384033000	4.498818000	0.258343000
C	1.528773000	4.109616000	-1.063396000
H	1.965385000	4.771384000	-1.802072000
H	1.195999000	2.475633000	-2.453351000
H	1.711297000	5.481401000	0.582132000
H	0.689954000	3.888284000	2.211095000
Cu	0.002916000	0.003634000	-0.930734000
Br	0.005754000	0.006595000	-3.275152000

<u>Coordinates of the copper(II) complexes $[Cu^{II}(PMDETA)SX]^{+}$ (X=Cl, Br)</u>

$[Cu^{II}(PMDETA)(MeCN)Br]^{+}$ isomer *I1*
E=-4867.802654 a.u.

M06/6-311+G(d,p)

Cu	-0.078243000	-0.641870000	0.143712000
N	-2.190367000	-0.337050000	0.050895000
N	-0.002070000	1.400566000	-0.021761000
N	2.051472000	-0.487790000	0.150986000
C	-2.419907000	1.132760000	0.056221000
C	-1.232989000	1.856038000	0.653731000
H	-3.333832000	1.371644000	0.613757000
H	-2.597772000	1.462064000	-0.971284000
H	-1.132599000	1.615988000	1.717022000
H	-1.349123000	2.945980000	0.556958000
C	1.225062000	1.768996000	0.711325000
C	2.384162000	0.962091000	0.168878000
H	1.058361000	1.539156000	1.768507000
H	1.422720000	2.847716000	0.621263000
H	3.285940000	1.136579000	0.768484000
H	2.632159000	1.275934000	-0.848891000
C	2.635336000	-1.147996000	1.333520000
C	2.596568000	-1.124603000	-1.062894000
C	-2.876403000	-0.953106000	1.201910000
C	-2.719564000	-0.935019000	-1.189464000
H	2.126086000	-0.700594000	-1.954665000
H	2.384520000	-2.194382000	-1.036691000

H	3.682534000	-0.967110000	-1.120187000
H	2.321876000	-0.629953000	2.240996000
H	3.731761000	-1.126961000	1.265100000
H	2.294224000	-2.184721000	1.374014000
H	-2.572854000	-0.456578000	2.124727000
H	-2.610780000	-2.011076000	1.256882000
H	-3.963989000	-0.855666000	1.079698000
C	0.047794000	1.886385000	-1.410777000
H	-0.829586000	1.558915000	-1.968584000
H	0.924443000	1.495798000	-1.927638000
H	0.087707000	2.984770000	-1.428560000
H	-2.177437000	-0.546364000	-2.056307000
H	-3.787591000	-0.701086000	-1.299085000
H	-2.585143000	-2.017117000	-1.155498000
Br	-0.159935000	-2.984785000	0.062284000
N	-0.137533000	-0.517338000	2.778458000
C	-0.197107000	-1.513816000	3.354674000
C	-0.272763000	-2.785201000	4.029585000
H	0.531445000	-3.435458000	3.674704000
H	-0.183456000	-2.655385000	5.110372000
H	-1.227545000	-3.266863000	3.802528000

[Cu^{II}(PMDETA)(MeCN)Br]$^{+}$ isomer *I2*
E=-4867.808234 a.u.

M06/6-311+G(d,p)

Cu	0.036253000	-0.075305000	-0.786159000
N	-1.960063000	-0.630806000	-0.406632000
N	-0.483786000	1.707406000	0.230140000
N	2.004885000	0.422134000	-0.224457000
C	-2.636297000	0.576427000	0.112570000
C	-1.702573000	1.372957000	0.991243000
H	-3.547552000	0.296556000	0.661324000
H	-2.955329000	1.176281000	-0.746035000
H	-1.409026000	0.786409000	1.868481000
H	-2.196100000	2.283030000	1.362258000
C	0.669782000	2.001452000	1.101558000
C	1.947266000	1.792921000	0.325078000
H	0.630474000	1.325230000	1.962355000
H	0.614005000	3.027166000	1.494344000
H	2.826234000	1.987417000	0.957058000
H	2.000465000	2.492712000	-0.515293000
C	2.418599000	-0.534345000	0.820732000
C	2.975578000	0.376556000	-1.329921000
C	-1.933411000	-1.688725000	0.622183000
C	-2.681982000	-1.127682000	-1.589142000
H	2.653761000	1.052779000	-2.125861000
H	3.026398000	-0.638770000	-1.725857000
H	3.969643000	0.682600000	-0.974097000
H	1.703085000	-0.535629000	1.648207000
H	3.411071000	-0.264474000	1.208409000
H	2.449782000	-1.539190000	0.397488000
H	-1.384551000	-1.353356000	1.507035000
H	-1.426882000	-2.567864000	0.221708000
H	-2.958207000	-1.954077000	0.918010000
C	-0.743411000	2.844824000	-0.668813000
H	-1.556742000	2.613116000	-1.356144000
H	0.133444000	3.059984000	-1.279095000
H	-1.005394000	3.733675000	-0.077914000
H	-2.670550000	-0.364038000	-2.370848000
H	-3.723399000	-1.361938000	-1.326435000
H	-2.189165000	-2.026110000	-1.963536000
Br	0.642816000	-2.205087000	-1.677626000
N	-0.119321000	0.876060000	-2.913654000
C	0.045282000	0.438320000	-3.966507000
C	0.264412000	-0.163911000	-5.256205000
H	1.073631000	0.345111000	-5.784314000
H	0.536878000	-1.213469000	-5.108717000
H	-0.642384000	-0.111421000	-5.862679000

[Cu^{II}(PMDETA)(MeCN)Br]$^{+}$ isomer *I3*
E=-4867.795221 a.u.

M06/6-311+G(d,p)

Cu	-1.113963000	0.615549000	-1.659545000
N	-2.998630000	-0.085299000	-1.152448000
N	-0.553286000	-0.072528000	0.282895000
N	0.868953000	0.255061000	-2.148124000
C	-2.966467000	-0.338836000	0.306967000
C	-1.646966000	-0.949979000	0.725595000
H	-3.806451000	-0.988993000	0.591795000
H	-3.120257000	0.620977000	0.809673000
H	-1.510129000	-1.935328000	0.267029000
H	-1.624103000	-1.096509000	1.815470000
C	0.745770000	-0.739234000	0.109730000
C	1.582416000	0.061747000	-0.864064000
H	0.569627000	-1.752212000	-0.268114000
H	1.272541000	-0.841231000	1.069900000
H	2.549821000	-0.429167000	-1.044437000
H	1.798467000	1.054219000	-0.456720000
C	0.904124000	-0.990263000	-2.938910000
C	1.521371000	1.331999000	-2.913277000
C	-3.204046000	-1.351650000	-1.881546000
C	-4.104339000	0.837041000	-1.464853000
H	1.445971000	2.271274000	-2.362748000
H	1.014726000	1.453753000	-3.872062000
H	2.575407000	1.078779000	-3.093373000
H	0.391475000	-1.800923000	-2.413667000
H	1.945018000	-1.291530000	-3.121518000
H	0.400304000	-0.832683000	-3.892012000
H	-2.377569000	-2.044615000	-1.701006000
H	-3.252161000	-1.153823000	-2.951881000
H	-4.139780000	-1.826732000	-1.555564000
C	-0.423106000	1.086278000	1.185171000
H	-1.360709000	1.639103000	1.241878000
H	0.321942000	1.787186000	0.808925000

H	-0.134629000	0.741730000	2.188451000
H	-3.929373000	1.798207000	-0.978492000
H	-5.057988000	0.407074000	-1.128357000
H	-4.146934000	0.999948000	-2.543015000
N	-1.680135000	0.477819000	-3.906585000
C	-1.948527000	1.294641000	-4.673734000
C	-2.273825000	2.368966000	-5.574793000
H	-2.214100000	3.310457000	-5.018971000
H	-1.569235000	2.397932000	-6.408839000
H	-3.285057000	2.247188000	-5.969123000
Br	-1.322830000	3.026887000	-1.646467000

[Cu^{II}(PMDETA)(MeCN)Br]$^{+}$ isomer *I4*
E=-4867.786952 a.u.

M06/6-311+G(d,p)

Cu	-1.174560000	0.184399000	-1.996730000
N	-3.117894000	0.163368000	-1.197018000
N	-0.623995000	-0.380150000	-0.015391000
N	0.883952000	0.557260000	-2.196815000
C	-3.051745000	-0.576515000	0.101681000
C	-1.736695000	-1.308992000	0.252614000
H	-3.881345000	-1.288334000	0.163894000
H	-3.198535000	0.136915000	0.918723000
H	-1.679988000	-2.119556000	-0.482161000
H	-1.651241000	-1.750299000	1.257625000
C	0.634530000	-1.075551000	-0.339763000
C	1.567819000	-0.121708000	-1.052372000
H	0.391881000	-1.915591000	-0.999747000
H	1.109991000	-1.478451000	0.567821000
H	2.445628000	-0.665377000	-1.416607000
H	1.944496000	0.643325000	-0.366133000
C	1.457502000	0.096831000	-3.475505000
C	1.056460000	2.018089000	-2.093688000
C	-4.125797000	-0.452490000	-2.080648000
C	-3.487183000	1.570880000	-0.958355000
H	0.559153000	2.396963000	-1.194981000
H	0.610229000	2.503130000	-2.962427000
H	2.122906000	2.277517000	-2.046796000
H	1.371716000	-0.987488000	-3.550412000
H	2.511317000	0.400968000	-3.540214000
H	0.902175000	0.536728000	-4.306064000
H	-3.887514000	-1.504918000	-2.236654000
H	-4.112997000	0.043403000	-3.053094000
H	-5.123845000	-0.350227000	-1.632698000
C	-0.440557000	0.564196000	1.091086000
H	-1.358732000	1.120826000	1.284890000
H	0.342046000	1.288435000	0.859895000
H	-0.158214000	0.029966000	2.010332000
H	-2.707411000	2.075309000	-0.378666000
H	-4.435940000	1.632027000	-0.407963000
H	-3.594892000	2.089331000	-1.911614000
N	-1.705067000	1.703901000	-3.521624000
C	-1.988184000	1.747912000	-4.637014000
C	-2.336896000	1.743324000	-6.033987000
H	-1.618359000	2.331303000	-6.609355000
H	-2.325727000	0.710523000	-6.395585000
H	-3.334845000	2.162539000	-6.180337000
Br	-1.349407000	-1.753654000	-3.460056000

[Cu^{II}(PMDETA)(MeCN)Cl]$^{+}$ isomer *I2*
E=-2753.983813 a.u.

M06/6-311+G(d,p)

Cu	0.008050000	-0.607145000	-0.694151000
N	-2.046910000	-0.519785000	-0.263797000
N	0.003685000	1.392460000	-0.038792000
N	2.061401000	-0.518692000	-0.260319000
C	-2.390579000	0.887624000	0.049386000
C	-1.230985000	1.566316000	0.744029000
H	-3.286748000	0.920567000	0.685520000
H	-2.653078000	1.399472000	-0.881772000
H	-1.075967000	1.113709000	1.729499000
H	-1.430681000	2.635602000	0.905204000
C	1.237028000	1.568150000	0.746566000
C	2.400703000	0.890523000	0.054090000
H	1.080945000	1.114768000	1.731502000
H	1.434252000	2.637785000	0.908551000
H	3.295220000	0.925301000	0.692464000
H	2.664343000	1.403009000	-0.876365000
C	2.214322000	-1.353270000	0.947504000
C	2.948642000	-1.025622000	-1.321968000
C	-2.200983000	-1.353923000	0.944157000
C	-2.931143000	-1.027800000	-1.328143000
H	2.767570000	-0.473006000	-2.247423000
H	2.737437000	-2.079674000	-1.502621000
H	3.998661000	-0.903023000	-1.022013000
H	1.568904000	-0.988915000	1.753035000
H	3.256722000	-1.334009000	1.295591000
H	1.929941000	-2.380732000	0.711774000
H	-1.557867000	-0.988084000	1.750867000
H	-1.914587000	-2.381045000	0.709697000
H	-3.244190000	-1.335868000	1.289818000
C	0.002157000	2.325733000	-1.175461000
H	-0.876583000	2.172524000	-1.798540000
H	0.882548000	2.178474000	-1.794246000
H	-0.001120000	3.361357000	-0.803518000
H	-2.748435000	-0.474384000	-2.252871000
H	-3.981878000	-0.906078000	-1.030275000
H	-2.711808000	-2.083644000	-1.486564000
N	0.109919000	0.148426000	-2.470549000
C	0.182583000	0.531967000	-3.782989000
C	0.254308000	0.978566000	-5.232555000
H	1.294412000	1.104632000	-5.552473000
H	-0.224865000	0.250706000	-5.896442000
H	-0.248294000	1.942711000	-5.368849000

Cl	-0.051067000	-2.866865000	-1.456077000

[Cu^{II}(PMDETA)(DMSO-κO)Br]$^{+}$ isomer *I1*
E=-5288.246537 a.u.

M06/6-311+G(d,p)

Cu	-1.237386000	0.584877000	-2.142290000
N	-3.223315000	0.101207000	-1.498006000
N	-0.881013000	-1.402054000	-1.749923000
N	0.868036000	0.626721000	-2.541145000
C	-3.272595000	-1.371437000	-1.302160000
C	-2.164382000	-2.051268000	-2.076950000
H	-4.250420000	-1.762916000	-1.609597000
H	-3.185605000	-1.584206000	-0.233041000
H	-2.321999000	-1.930645000	-3.153190000
H	-2.127724000	-3.126760000	-1.845473000
C	0.195063000	-1.746509000	-2.698271000
C	1.346185000	-0.781639000	-2.511645000
H	-0.219062000	-1.653275000	-3.706891000
H	0.528486000	-2.784993000	-2.549106000
H	2.104134000	-0.940813000	-3.288436000
H	1.850679000	-0.958997000	-1.557695000
C	1.129593000	1.215961000	-3.865211000
C	1.566244000	1.428666000	-1.520302000
C	-4.203278000	0.501158000	-2.521604000
C	-3.542307000	0.797062000	-0.238402000
H	1.337873000	1.048284000	-0.520705000
H	1.225936000	2.463618000	-1.579113000
H	2.653022000	1.389405000	-1.679834000
H	0.641533000	0.611495000	-4.632539000
H	2.212626000	1.254520000	-4.049371000
H	0.722439000	2.229072000	-3.893121000
H	-4.051601000	-0.088639000	-3.426607000
H	-4.075760000	1.560700000	-2.754955000
H	-5.223469000	0.331161000	-2.149548000
C	-0.479760000	-1.694869000	-0.365449000
H	-1.248304000	-1.375310000	0.338354000
H	0.436248000	-1.164676000	-0.105389000
H	-0.310799000	-2.773887000	-0.237672000
H	-2.781433000	0.577489000	0.515935000
H	-4.524534000	0.476367000	0.136354000
H	-3.552313000	1.873935000	-0.412317000
O	-1.673889000	0.031240000	-4.419700000
S	-2.480107000	0.715723000	-5.530638000
C	-1.958260000	-0.131566000	-7.037881000
H	-0.865323000	-0.142052000	-7.065863000
H	-2.348015000	-1.149364000	-7.000497000
H	-2.367904000	0.392770000	-7.904608000
C	-1.677774000	2.298839000	-5.870116000
H	-1.752018000	2.896486000	-4.957693000
H	-0.632822000	2.133606000	-6.142945000
H	-2.219934000	2.782380000	-6.686798000
Br	-1.550875000	2.917423000	-2.162322000

[Cu^{II}(PMDETA)(DMSO-κO)Br]$^{+}$ isomer *I2*
E=-5288.253053 a.u.

M06/6-311+G(d,p)

Cu	0.583586000	-0.205623000	0.040985000
N	1.788997000	-0.126003000	1.783472000
N	2.413385000	-0.619558000	-0.937552000
N	-0.278638000	-1.231478000	-1.594669000
C	3.192459000	-0.176879000	1.325404000
C	3.324535000	-1.081963000	0.125058000
H	3.849536000	-0.510594000	2.142000000
H	3.500665000	0.841690000	1.068729000
H	3.048010000	-2.108540000	0.389784000
H	4.364503000	-1.108633000	-0.232891000
C	2.113550000	-1.674363000	-1.924146000
C	0.797542000	-1.367797000	-2.595715000
H	2.061798000	-2.633667000	-1.398684000
H	2.921249000	-1.757506000	-2.665808000
H	0.540919000	-2.146554000	-3.329666000
H	0.862174000	-0.421004000	-3.142293000
C	-0.724055000	-2.554277000	-1.121850000
C	-1.417187000	-0.526289000	-2.200970000
C	1.478425000	-1.307988000	2.609507000
C	1.574611000	1.089547000	2.582849000
H	-1.104358000	0.482328000	-2.482305000
H	-2.228563000	-0.459131000	-1.474268000
H	-1.769100000	-1.066940000	-3.091489000
H	0.097950000	-3.090544000	-0.638942000
H	-1.095710000	-3.155379000	-1.964284000
H	-1.519608000	-2.423055000	-0.386916000
H	1.614696000	-2.227361000	2.032840000
H	0.437550000	-1.260377000	2.931360000
H	2.136845000	-1.338144000	3.489448000
C	2.977569000	0.559592000	-1.616402000
H	3.123958000	1.374740000	-0.908518000
H	2.288104000	0.928107000	-2.374787000
H	3.937877000	0.295455000	-2.081648000
H	1.770261000	1.970548000	1.965175000
H	2.250207000	1.101327000	3.450356000
H	0.539330000	1.121260000	2.926300000
O	0.523576000	1.843740000	-0.804869000
S	-0.239449000	2.996855000	-0.131289000
C	-1.878357000	3.005745000	-0.886569000
H	-1.762076000	2.972746000	-1.973256000
H	-2.401717000	2.123692000	-0.514269000
H	-2.404038000	3.911942000	-0.575713000
C	0.400256000	4.460921000	-0.972450000
H	1.441582000	4.585734000	-0.673207000
H	0.331497000	4.301617000	-2.051202000
H	-0.180563000	5.333803000	-0.664781000
Br	-1.471010000	-0.054390000	1.258337000

[Cu^{II}(PMDETA)(DMSO-κO)Br]$^{+}$ isomer *I3*
E=-5288.246691 a.u.

M06/6-311+G(d,p)

Cu	-1.125049000	0.567886000	-1.704627000
N	-3.013318000	-0.435123000	-1.521061000
N	-0.620084000	-0.506195000	0.042104000
N	0.870695000	0.128279000	-2.303323000
C	-3.036138000	-0.886968000	-0.118646000
C	-1.706957000	-1.486165000	0.267471000
H	-3.849292000	-1.612530000	0.041838000
H	-3.254185000	-0.011774000	0.503862000
H	-1.502696000	-2.376816000	-0.334843000
H	-1.718991000	-1.810158000	1.317118000
C	0.672954000	-1.170829000	-0.238972000
C	1.554833000	-0.262473000	-1.058808000
H	0.473357000	-2.097808000	-0.785870000
H	1.170052000	-1.455179000	0.698718000
H	2.516880000	-0.750377000	-1.280458000
H	1.777786000	0.654988000	-0.502839000
C	0.864274000	-0.958883000	-3.290309000
C	1.531540000	1.304291000	-2.881097000
C	-3.068238000	-1.560288000	-2.461813000
C	-4.155779000	0.454508000	-1.758723000
H	1.436164000	2.152283000	-2.197289000
H	1.047633000	1.554725000	-3.826339000
H	2.595057000	1.095197000	-3.068866000
H	0.396196000	-1.857264000	-2.879055000
H	1.888876000	-1.209325000	-3.603652000
H	0.287362000	-0.642205000	-4.161702000
H	-2.240958000	-2.254208000	-2.291305000
H	-2.978838000	-1.176870000	-3.481285000
H	-4.015450000	-2.111694000	-2.362605000
C	-0.486649000	0.367424000	1.226052000
H	-1.424121000	0.888493000	1.420312000
H	0.267915000	1.134281000	1.051529000
H	-0.208885000	-0.241421000	2.097366000
H	-4.040640000	1.371402000	-1.174096000
H	-5.097880000	-0.045244000	-1.488722000
H	-4.203426000	0.714606000	-2.818859000
O	-1.509954000	1.069316000	-3.610556000
S	-2.295116000	2.365545000	-3.973194000
C	-2.835173000	1.958400000	-5.644134000
H	-1.973659000	1.623117000	-6.225636000
H	-3.571893000	1.156978000	-5.561053000
H	-3.296798000	2.840929000	-6.093308000
C	-1.039381000	3.581845000	-4.404329000
H	-0.551504000	3.871438000	-3.471793000
H	-0.337895000	3.134719000	-5.113164000
H	-1.544056000	4.445300000	-4.845738000
Br	-1.318796000	2.860414000	-0.834898000

[Cu^{II}(PMDETA)(DMSO-κO)Br]$^{+}$ isomer *I4*
E=-5288.234099 a.u.

M06/6-311+G(d,p)

Cu	-1.192343000	0.060502000	-2.191554000
N	-3.136258000	0.036508000	-1.329738000
N	-0.630586000	-0.801465000	-0.358896000
N	0.880178000	0.333433000	-2.384145000
C	-3.041424000	-0.783158000	-0.085771000
C	-1.807225000	-1.655271000	-0.112016000
H	-3.940773000	-1.399388000	0.024714000
H	-3.023084000	-0.110643000	0.777215000
H	-1.874099000	-2.378560000	-0.932163000
H	-1.698527000	-2.209573000	0.832515000
C	0.554914000	-1.559742000	-0.797074000
C	1.551141000	-0.614226000	-1.442401000
H	0.218756000	-2.298032000	-1.532209000
H	1.016273000	-2.093177000	0.048075000
H	2.301253000	-1.200069000	-1.982367000
H	2.099033000	-0.034640000	-0.691784000
C	1.375114000	0.124275000	-3.755421000
C	1.132570000	1.734621000	-2.000909000
C	-4.171735000	-0.534842000	-2.211987000
C	-3.497566000	1.424050000	-0.998667000
H	0.737467000	1.935562000	-1.001119000
H	0.625553000	2.391650000	-2.708925000
H	2.210170000	1.949779000	-2.005892000
H	1.158113000	-0.896655000	-4.073596000
H	2.456336000	0.316164000	-3.795460000
H	0.865792000	0.817977000	-4.425994000
H	-3.934020000	-1.574363000	-2.440103000
H	-4.203939000	0.013384000	-3.155086000
H	-5.152728000	-0.467810000	-1.720840000
C	-0.323255000	0.018443000	0.820613000
H	-1.124378000	0.729038000	1.030426000
H	0.592959000	0.588237000	0.667531000
H	-0.182961000	-0.623100000	1.702637000
H	-2.708290000	1.889489000	-0.400178000
H	-4.441502000	1.458075000	-0.436836000
H	-3.609649000	2.003353000	-1.916838000
O	-1.512865000	1.674655000	-3.461661000
S	-2.456433000	1.538136000	-4.682181000
C	-1.400400000	1.153973000	-6.089169000
H	-0.574817000	1.870073000	-6.119772000
H	-1.050080000	0.129485000	-5.946025000
H	-2.007081000	1.217989000	-6.996218000
C	-2.793361000	3.261659000	-5.084842000
H	-3.389779000	3.677576000	-4.271370000
H	-1.843004000	3.793616000	-5.168482000
H	-3.356126000	3.305868000	-6.020306000
Br	-1.474079000	-1.818979000	-3.821144000

[Cu^{II}(PMDETA)(DMSO-κO)Cl]$^{+}$ isomer *I2*
E=-3174.429261 a.u.

M06/6-311+G(d,p)

Cu	0.393779000	0.034107000	-0.317246000
N	1.036932000	-1.959046000	-0.577511000
N	1.620982000	-0.010168000	1.384725000
N	0.739035000	2.110546000	-0.265199000
C	1.765027000	-2.330280000	0.651705000
C	2.539579000	-1.147014000	1.180554000
H	2.434289000	-3.182132000	0.460366000
H	1.029981000	-2.664970000	1.390757000
H	3.305477000	-0.841025000	0.459588000
H	3.058716000	-1.403547000	2.115622000
C	2.325755000	1.286960000	1.413104000
C	1.361375000	2.388077000	1.043222000
H	3.151878000	1.244857000	0.695572000
H	2.768151000	1.469132000	2.403095000
H	1.868261000	3.364699000	1.029424000
H	0.558083000	2.454591000	1.784621000
C	1.660040000	2.434411000	-1.368810000
C	-0.487237000	2.907195000	-0.407961000
C	1.939601000	-1.983259000	-1.743334000
C	-0.071409000	-2.896754000	-0.807527000
H	-1.195561000	2.616305000	0.371675000
H	-0.930614000	2.710698000	-1.385566000
H	-0.258278000	3.978998000	-0.318951000
H	2.578752000	1.845752000	-1.291812000
H	1.920010000	3.502571000	-1.347875000
H	1.179420000	2.191249000	-2.317740000
H	2.770794000	-1.286504000	-1.601723000
H	1.385951000	-1.677194000	-2.631846000
H	2.344650000	-2.995070000	-1.887859000
C	0.848134000	-0.193349000	2.626094000
H	0.261446000	-1.110133000	2.577967000
H	0.137546000	0.622174000	2.754943000
H	1.531806000	-0.233169000	3.485689000
H	-0.763294000	-2.857716000	0.038160000
H	0.310212000	-3.922546000	-0.913353000
H	-0.604718000	-2.609811000	-1.715329000
O	-1.462885000	-0.036148000	0.897260000
S	-2.786178000	-0.586456000	0.338605000
C	-3.609267000	0.807708000	-0.459095000
H	-3.614508000	1.653937000	0.233268000
H	-3.040394000	1.032515000	-1.362973000
H	-4.627749000	0.508675000	-0.719116000
C	-3.847042000	-0.667699000	1.796843000
H	-3.455175000	-1.449150000	2.448804000
H	-3.817043000	0.300010000	2.303266000
H	-4.864099000	-0.918981000	1.486474000
Cl	-0.640449000	0.100815000	-2.310803000

Coordinates of the species $Cu^{I,II}$ and $Cu^{I,II}S$

Cu^{I}
E=-1640.078959 a.u.

Cu^{II}
E=-1639.306981 a.u.

Cu^{I}(MeCN)
E=-1772.867569 a.u.

M06/6-311+G(d,p)

Cu	0.290086000	0.967682000	-0.041884000
N	1.671655000	2.223177000	-0.081921000
C	2.521136000	2.995109000	-0.106547000
C	3.582759000	3.959855000	-0.137864000
H	4.226954000	3.829285000	0.735585000
H	3.164989000	4.969966000	-0.127936000
H	4.177282000	3.826266000	-1.045423000

Cu^{I}(DMSO-κOα)
E=-2193.304916 a.u.

M06/6-311+G(d,p)

Cu	1.548769000	2.519347000	0.866135000
O	2.725743000	3.914622000	1.238102000
S	2.527166000	5.438612000	1.512740000
C	3.693353000	6.185526000	0.367623000
H	3.781076000	7.248316000	0.606314000
H	3.296839000	6.064655000	-0.640874000
H	4.652285000	5.672578000	0.471513000
C	3.456891000	5.674520000	3.032318000
H	2.898961000	5.204813000	3.842866000
H	3.549216000	6.747258000	3.219133000
H	4.435731000	5.204592000	2.911899000

Cu^{I}(DMSO-κOβ)
E=-2193.302745 a.u.

M06/6-311+G(d,p)

Cu	2.758006000	2.628928000	0.996332000
O	1.963226000	4.300541000	1.154149000
S	2.373067000	5.757389000	1.478583000
C	3.745842000	6.109203000	0.370676000
H	4.149444000	7.095796000	0.612482000
H	3.354565000	6.114675000	-0.647541000
H	4.511836000	5.337343000	0.493809000
C	3.298620000	5.645753000	3.016968000
H	2.603230000	5.336015000	3.798245000
H	3.702409000	6.632633000	3.257282000
H	4.105786000	4.916564000	2.896787000

Cu^{I}(DMSO-κS)
E=-2193.271572 a.u.

M06/6-311+G(d,p)

O	1.728493000	5.232454000	0.025120000
S	2.532698000	6.306913000	0.621434000
C	4.257882000	6.153698000	0.141675000
H	4.840031000	6.940312000	0.629495000
H	4.308913000	6.243153000	-0.944365000
H	4.590694000	5.159274000	0.452235000
C	2.655477000	6.098577000	2.402211000
H	1.646158000	6.151487000	2.812737000
H	3.290651000	6.887076000	2.815070000
H	3.081712000	5.107409000	2.581165000
Cu	1.809151000	8.366738000	0.156893000

Cu^{II}(MeCN)
E=-1772.265184 a.u.

M06/6-311+G(d,p)

Cu	0.335392000	0.941527000	-0.072188000
N	1.609018000	2.285635000	-0.050722000
C	2.539122000	2.998509000	-0.096315000
C	3.590094000	3.919375000	-0.117617000
H	4.238686000	3.822170000	0.764453000
H	3.177846000	4.960481000	-0.154270000
H	4.144703000	3.843641000	-1.079334000

Cu^{II}(DMSO-κOα)
E=-2192.770736 a.u.

M06/6-311+G(d,p)

Cu	1.718353000	2.404387000	0.859055000
O	2.606463000	3.976513000	1.239350000
S	2.467589000	5.598173000	1.538392000
C	3.700369000	6.181543000	0.337855000
H	3.839114000	7.241656000	0.594222000
H	3.265499000	6.093775000	-0.659528000
H	4.626658000	5.614318000	0.458636000
C	3.459837000	5.659091000	3.059263000
H	2.865566000	5.225052000	3.865513000
H	3.605434000	6.734122000	3.237939000
H	4.411149000	5.146211000	2.897073000

Cu^{II}(DMSO-κS)
E=-2192.730843 a.u.

M06/6-311+G(d,p)

O	1.814935000	5.231861000	0.086226000
S	2.611359000	6.498337000	0.681568000
C	4.312967000	6.125380000	0.117431000
H	4.952137000	6.872437000	0.605087000
H	4.331052000	6.225326000	-0.970749000
H	4.530799000	5.104382000	0.447773000
C	2.651667000	6.068581000	2.461033000
H	1.628974000	6.132904000	2.841044000
H	3.306330000	6.816165000	2.926842000
H	3.058798000	5.054063000	2.524343000
Cu	1.542841000	8.517657000	-0.026930000

<u>Coordinates of initiators RX and radicals R• and X•</u>

Allyl chloride (AlCl)
E=-577.425082 a.u.

M06/6-311+G(d,p)

C	-4.740388000	0.119376000	-1.129340000
C	-4.101009000	0.543842000	-0.051675000
C	-2.837534000	1.327071000	0.004131000
H	-5.660152000	-0.447993000	-1.042497000
H	-4.369285000	0.321752000	-2.129069000
H	-4.504149000	0.320438000	0.937193000
Cl	-2.132471000	1.718351000	-1.600538000
H	-2.066468000	0.781265000	0.555909000
H	-2.995236000	2.282343000	0.513561000

Allyl bromide (AlBr)
E=-2691.251663 a.u.

M06/6-311+G(d,p)

C	-4.944269000	0.517495000	1.132482000
C	-4.217360000	0.769926000	0.056110000
C	-2.823900000	1.285778000	-0.011592000
H	-5.956984000	0.140574000	1.043252000
H	-4.556768000	0.677091000	2.133976000
H	-4.648787000	0.594546000	-0.931250000
Br	-1.979044000	1.626147000	1.709875000
H	-2.783122000	2.233506000	-0.555173000
H	-2.169045000	0.579246000	-0.528609000

Ethyl α-chloroisobutyrate (EtCl^{i}Bu)
E=-845.779045 a.u.

M06/6-311+G(d,p)

C	-2.179093386	3.083552853	-0.209001676
C	-0.799398386	2.813699853	0.319910324
H	-2.177648386	3.119215853	-1.301626676
H	-2.562890386	4.036482853	0.165599324
H	-2.862895386	2.291347853	0.107694324
O	0.050451614	3.880992853	-0.130766676
H	-0.390918386	1.865468853	-0.046052676
H	-0.770691386	2.780045853	1.414524324

C	1.331695614	3.800056853	0.223294324
O	1.786979614	2.938691853	0.923896324
C	2.154727614	4.941046853	-0.369311676
C	1.443986614	6.274265853	-0.305500676
H	0.484936614	6.244501853	-0.823431676
H	2.071252614	7.047774853	-0.757301676
H	1.267094614	6.542867853	0.743184324
C	3.526008614	4.989363853	0.258269324
H	4.129748614	5.757459853	-0.232120676
H	4.032387614	4.026326853	0.180336324
H	3.432213614	5.239522853	1.321050324
Cl	2.359815000	4.487512000	-2.137332000

Ethyl α-bromoisobutyrate (EtBr^{i}Bu)
E=-2959.604733 a.u.

M06/6-311+G(d,p)

C	-2.183970000	3.105715000	-0.177356000
C	-0.794016000	2.807114000	0.307683000
H	-2.207841000	3.186376000	-1.267336000
H	-2.553225000	4.044259000	0.245118000
H	-2.865067000	2.304646000	0.122385000
O	0.052055000	3.886571000	-0.119676000
H	-0.400636000	1.872074000	-0.105878000
H	-0.740548000	2.728512000	1.398977000
C	1.340619000	3.786360000	0.207391000
O	1.800850000	2.897668000	0.870413000
C	2.161079000	4.936612000	-0.360104000
C	1.434824000	6.263573000	-0.335529000
H	0.490140000	6.223365000	-0.878307000
H	2.066150000	7.040492000	-0.775753000
H	1.225369000	6.541463000	0.705377000
C	3.512724000	5.009096000	0.309278000
H	4.124765000	5.780307000	-0.165699000
H	4.035657000	4.053038000	0.262092000
H	3.378852000	5.270114000	1.366092000
Br	2.449957000	4.422805000	-2.263917000

Methyl 2-chloropropionate (MeClPr)
E=-767.187118 a.u.

M06/6-311+G(d,p)

C	0.789760000	2.089705000	-0.269309000
C	0.252419000	0.724733000	-0.593739000
H	0.119294000	2.856450000	-0.671787000
H	1.780759000	2.224539000	-0.707505000
H	0.851945000	2.227386000	0.812407000
C	-1.096522000	0.461897000	0.041955000
O	-1.519954000	1.036061000	1.005243000
O	-1.746699000	-0.499077000	-0.615456000
C	-3.004412000	-0.882144000	-0.063846000
H	-3.691971000	-0.033027000	-0.048485000
H	-2.876454000	-1.252211000	0.956170000
H	-3.387776000	-1.670849000	-0.708738000
H	0.192710000	0.534614000	-1.667718000
Cl	1.366131000	-0.556864000	0.049176000

Methyl 2-Bromopropionate (MeBrPr)
E=-2881.014146 a.u.

M06/6-311+G(d,p)

C	-4.641238000	1.883956000	0.038386000
C	-3.435860000	0.992646000	0.157187000
H	-4.570159000	2.699644000	0.766585000
H	-5.557748000	1.322516000	0.230855000
H	-4.694983000	2.326974000	-0.958546000
C	-2.144555000	1.708871000	-0.157462000
O	-2.059379000	2.697577000	-0.830962000
O	-1.108615000	1.093418000	0.417276000
C	0.173429000	1.646680000	0.130985000
H	0.231584000	2.682021000	0.475509000
H	0.369120000	1.620189000	-0.943700000
H	0.893625000	1.027685000	0.663176000
Br	-3.555555000	-0.492987000	-1.130560000
H	-3.358177000	0.502079000	1.129270000

Allyl radical (Al$^{\bullet}$)
E=-117.187827 a.u.

M06/6-311+G(d,p)
C1.2191470 0.1963370 -0.0000050
C 0.0000110 -0.4467790 0.0000140
C-1.2192100 0.1963580 -0.0000310
H 2.1545350 -0.3512910 -0.0000140
H 1.2730700 1.2819080 -0.0000220
H 0.0001100 -1.5366430 0.0000550
H-1.2728930 1.2819250 0.0001400
H-2.1545080 -0.3513990 -0.0000230

Ethyl α-isobutyrate radical (Et^{t}Bu$^{\bullet}$)
E=-385.536270 a.u.

M06/6-311+G(d,p)

C	-2.243788000	3.113632000	-0.084827000
C	-0.817230000	2.749109000	0.218671000
H	-2.345742000	3.471135000	-1.113380000
H	-2.597601000	3.900283000	0.587529000
H	-2.890599000	2.240655000	0.039475000
O	-0.025519000	3.925899000	0.041920000
H	-0.441895000	1.962065000	-0.445779000
H	-0.693713000	2.385429000	1.245445000
C	1.299927000	3.784798000	0.273715000
O	1.795728000	2.731251000	0.615309000
C	2.033505000	5.019786000	0.069354000
C	1.365579000	6.279768000	-0.334831000
H	0.451562000	6.103133000	-0.904358000

H	2.045767000	6.906860000	-0.922153000
H	1.081585000	6.870322000	0.550242000
C	3.488838000	5.029003000	0.335828000
H	4.049048000	5.282827000	-0.575514000
H	3.837292000	4.062827000	0.702938000
H	3.743087000	5.805548000	1.071247000

Methyl 2-propionate radical (MePr•)
E=-306.942176 a.u.

M06/6-311+G(d,p)

C	-2.057058000	0.578981000	0.517634000
C	-0.664321000	0.547381000	0.043460000
H	-0.038145000	1.257160000	0.600511000
H	-0.595785000	0.849007000	-1.010340000
H	-0.240830000	-0.453474000	0.150460000
C	-2.697771000	-0.606795000	1.039596000
O	-2.182928000	-1.698839000	1.137757000
O	-3.971055000	-0.353944000	1.416372000
C	-4.681007000	-1.464837000	1.943044000
H	-4.185435000	-1.856172000	2.835955000
H	-4.749476000	-2.268895000	1.204932000
H	-5.675445000	-1.097840000	2.194153000
H	-2.639875000	1.495165000	0.487605000

Br•
E=-2573.975675 a.u.

Cl•
E=-460.126597 a.u.