Supporting Information for

Magnetic circular dichroism and density functional theory studies of electronic structure and bonding in cobalt(II)-N-heterocyclic carbene complexes

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1. Supplementary Data

1.1 MCD

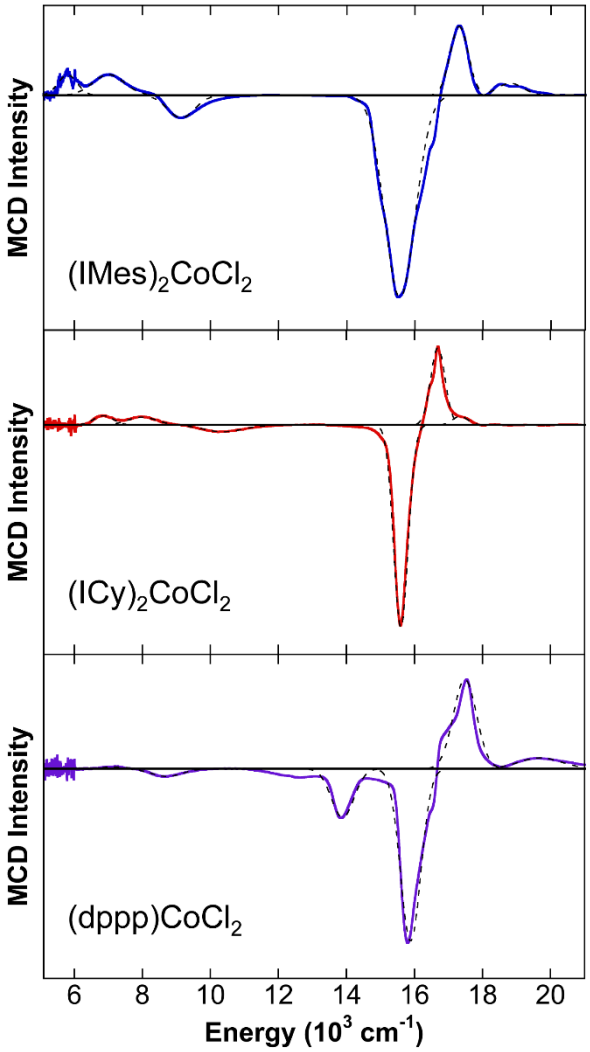

Figure S1 5 K, 7 T MCD spectra of distorted tetrahedral L_2CoCl_2 complexes. Spectra were in either 1 : 1 THF 2-MeTHF or pure 2-MeTHF. Individual transition fits are shown with dashed lines.

1.2 ^{1}HNMR Spectrum

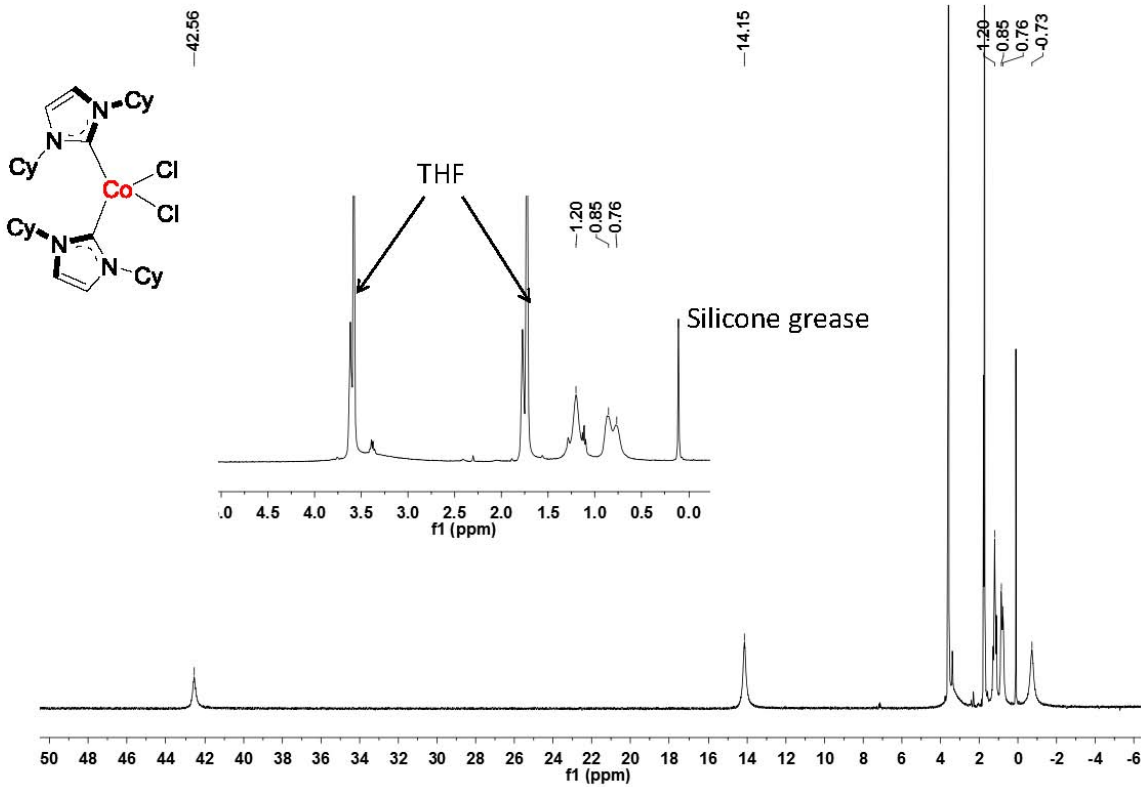

Figure S2 ^{1}H NMR spectrum of $(ICy)_2CoCl_2$ in d_8-THF recorded at 23 ^{o}C

1.3 Crystallographic and structure refinement data for $(ICy)_2CoCl_2$

Table S1 Crystallographic and structure refinement data for $(ICy)_2CoCl_2$

Compound	$(ICy)_2CoCl_2$
formula	$C_{30}H_{48}Cl_2CoN_4$
crystal size (mm)	0.39 x 0.35 x 0.32
fw	594.55
crystal system	Trigonal
space group	R -3
a, Å	28.0964(16)
b, Å	28.0964(16)
c, Å	24.9467(14)
α, deg	90
β, deg	90
γ, deg	120
V, Å^3	17055(2)
Z	18
D_{calcd}, Mg/m^3	1.042
radiation (*λ*), Å	Mo K*α* (0.71073)
2θ range, deg	2.900 to 55.036
μ, mm^{-1}	0.614
F(000)	5706
no. of params reflns	8717
no. of params reflnd	370
goodness of fit	1.060
R1	0.0574
*w*R2	0.1142

1.4 Buried Volume

Table S2 Calculated buried volume of L_2CoCl_2 and L_2CoCl crystallographic structures

		% $V_{buried\ volume}$
Co(II)	$(IMes)_2CoCl_2$	64.2
	$(ICy)_2CoCl_2$	52.6
	$(SIMes)_2CoCl_2$	-
	$(dppp)CoCl_2$	50.4
	$(teeda)CoCl_2$	49.6
	$(tmpn)CoCl_2$	49.3
Co(I)	$(IMes)_2CoCl$	68.7
	$(SIMes)_2CoCl$	73

2. DFT Studies

2.1 MO Energy Level Diagrams

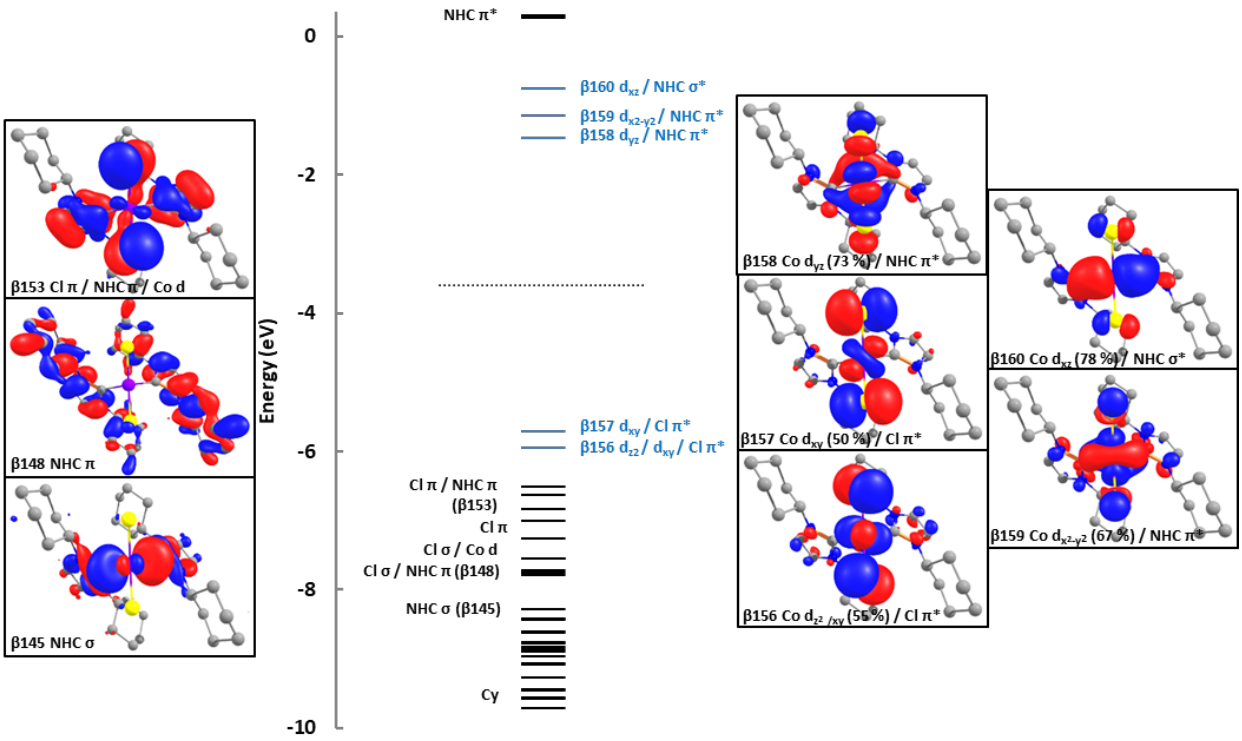

Figure S3 Calculated molecular orbital energy diagram of $(ICy)_2CoCl_2$

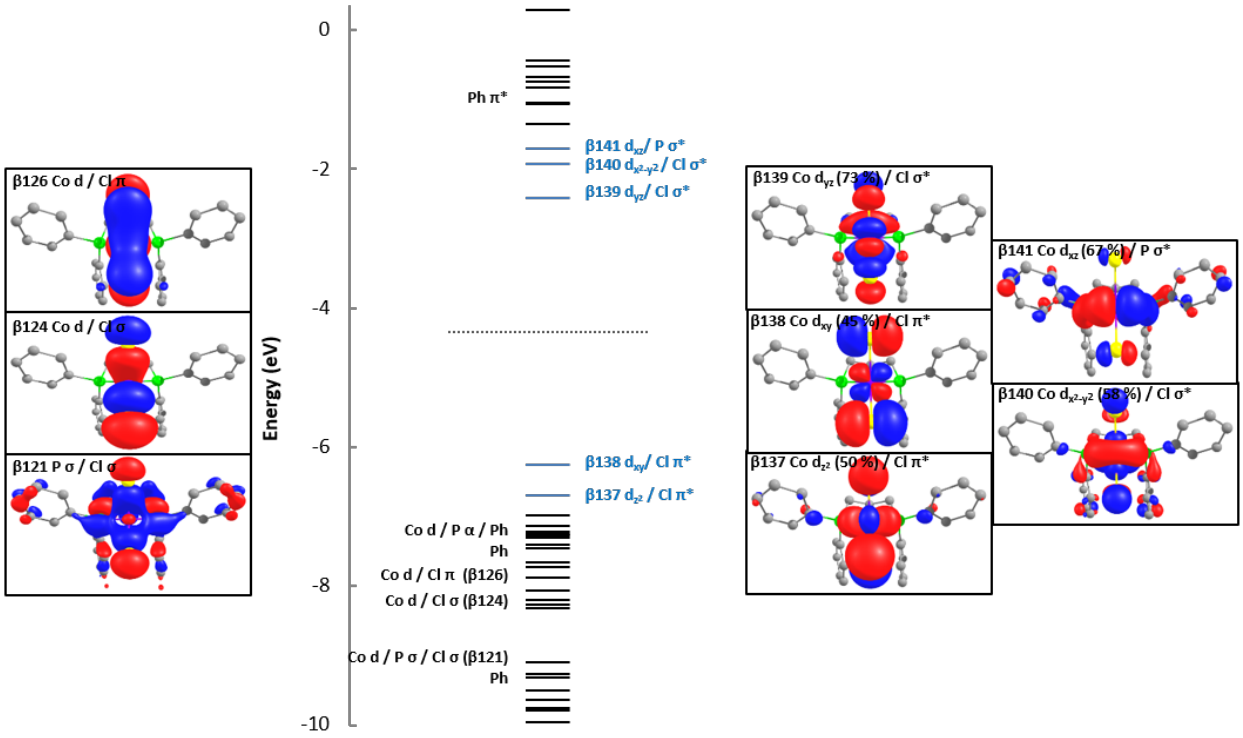

Figure S4 Calculated molecular orbital energy diagram of (dppp)$CoCl_2$

2.2 Experimental and structural parameters of Co(II) complexes

Table S3 Comparison of experimental and calculated (gas phase) structural parameters of $(IMes)_2CoCl_2$

Method	Basis Set	GD3BJ?	Co-L_1 (Å)	Co-L_2 (Å)	Co-Cl_1 (Å)	Co-Cl_2 (Å)	L_1-Co-L_2 (°)	Cl_1-Co-Cl_2 (°)
crystal bond lengths and angles			**2.088**	**2.067**	**2.268**	**2.272**	**125.1**	**103.3**
PBE0	TZVP	no	2.125	2.127	2.282	2.281	130.4	107.2
		yes	2.095	2.094	2.274	2.276	128.5	104.9
PBE0	Def2TZVP1	no	2.123	2.125	2.272	2.271	130.6	107.5
		yes	2.093	2.091	2.264	2.266	128.8	105.1
PBE	TZVP	no	2.057	2.058	2.267	2.267	131.0	103.7
		yes	2.028	2.027	2.258	2.258	129.8	102.6
PBE	Def2TZVP	no	2.054	2.057	2.252	2.253	131.1	104.0
		yes	2.025	2.024	2.243	2.243	130.0	103.0
BP862	TZVP	no	2.059	2.060	2.268	2.268	131.7	104.7
		yes	2.008	2.008	2.253	2.254	129.3	102.0

Table S4 Comparison of experimental and calculated (THF solvent model) structural parameters of $(IMes)_2CoCl_2$

Method	Basis Set	GD3BJ?	Co-L_1 (Å)	Co-L_2 (Å)	Co-Cl_1 (Å)	Co-Cl_2 (Å)	L_1-Co-L_2 (°)	Cl_1-Co-Cl_2 (°)
crystal bond lengths and angles			**2.088**	**2.067**	**2.268**	**2.272**	**125.1**	**103.3**
PBE0	TZVP	yes	2.099	2.100	2.312	2.316	128.8	100.1
PBE	TZVP	no	2.067	2.071	2.298	2.306	130.5	100.4
		yes	2.036	2.036	2.289	2.290	129.8	99.7
PBE	Def2TZVP	no	2.065	2.069	2.281	2.289	130.6	100.7
		yes	2.034	2.033	2.273	2.274	130.1	100.3
B3LYP	TZVP	no	2.156	2.163	2.343	2.347	130.8	101.4
		yes	2.099	2.102	2.324	2.334	128.8	99.8
BP86	TZVP	no	2.068	2.073	2.300	2.307	130.5	100.6
		yes	2.015	2.016	2.280	2.286	129.5	99.7
M06[3]	TZVP	no	2.083	2.084	2.300	2.302	128.3	103.8
		yes	2.080	2.080	2.303	2.298	127.0	101.6

1. (a) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-2305. (b) F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057-1065.
2. (a) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098-3100. (b) J. P. Perdew. *Phys. Rev. B*, 1986, **33**, 8822-8824.
3. Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.

Table S5 Comparison of experimental and calculated structural parameters of four-coordinate L_2CoCl_2 using PBE0/TZVP with GD3BJ dispersion corrections in gas-phase

	Co-L_1 (Å)		Co-L_2 (Å)		Co-Cl_1 (Å)		Co-Cl_2 (Å)		L_1-Co-L_2 (°)	
Complex	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
$(IMes)_2CoCl_2$	2.088	2.095	2.067	2.094	2.268	2.274	2.272	2.276	125.1	128.5
$(sIMes)_2CoCl_2$	-	2.096	-	2.100	-	2.268	-	2.277	-	130.1
$(ICy)_2CoCl_2$	2.053	2.070	2.050	2.071	2.260	2.278	2.269	2.282	109.8	107.6
$(dppp)CoCl_2$	2.352	2.370	2.329	2.370	2.234	2.251	2.216	2.218	95.8	93.7
$(tmpn)CoCl_2$	2.064	2.089	2.063	2.090	2.228	2.226	2.249	2.252	103.6	101.3
$(teeda)CoCl_2$	2.090	2.109	2.096	2.140	2.236	2.242	2.236	2.221	88.8	87.4

Table S6 Comparison of experimental and calculated structural parameters of three-coordinate L_2CoCl complexes using PBE0/TZVP with GD3BJ dispersion corrections in gas-phase

	Co-L_1 (Å)		Co-L_2 (Å)		Co-Cl (Å)		L_1-Co-L_2 (°)		L_1-Co-Cl (°)	
Complex	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
$(IMes)_2CoCl$	1.957	1.993	1.953	2.002	2.244	2.265	129.6	138.8	114.9	110.7
$(sIMes)_2CoCl$	1.913	1.977	1.964	1.977	2.303	2.280	152.5	126.8	96.0	116.6

2.3 Additional MBO and CDA for L_2CoCl_2 complexes

Table S7 Mayer bond order and charge decomposition analyses for distorted tetrahedral NHC, phosphine and diamine L_2CoCl_2 complexes optimized using PBEPBE/TZVP

	Mayer bond order		Charge decomposition analysis (α + β)		
Complex	Co-L	Co-Cl	Donation: (L_2 --> Co-Cl_2)	Back donation: (Co-Cl_2 --> L_2)	Net charge donation to Co-Cl_2
$(ICy)_2CoCl_2$	0.833	0.659	1.040 e^-	0.321 e^-	**0.719 e^-**
	0.822	0.661			
$(IMes)_2CoCl_2$	0.845	0.654	1.023 e^-	0.367 e^-	**0.656 e^-**
	0.844	0.645			
$(SIMes)_2CoCl_2$	0.848	0.651	1.016 e^-	0.387 e^-	**0.629 e^-**
	0.843	0.650			
$(dppp)CoCl_2$	0.808	0.742	0.844 e^-	0.299 e^-	**0.545 e^-**
	0.807	0.761			
$(teeda)CoCl_2$	0.422	0.722	0.425 e^-	0.167 e^-	**0.258 e^-**
	0.418	0.720			
$(tmpn)CoCl_2$	0.460	0.728	0.530 e^-	0.173 e^-	**0.357 e^-**
	0.460	0.706			

2.4 Optimized Geometry Coordinates

Table S8 $(IMes)_2CoCl_2$ optimized with uPBE0/TZVP (gas-phase)

27	5.809742000	5.596273000	4.072357000
17	4.178682000	5.006134000	5.543114000
17	7.502860000	4.123978000	4.455764000
7	6.221550000	5.099731000	0.985123000
7	4.486212000	4.130153000	1.742914000
7	7.149418000	7.809503000	5.710306000
7	5.316614000	8.575359000	4.949040000
6	5.434258000	5.032181000	2.090248000
6	5.772217000	4.261186000	-0.016973000
1	6.272757000	4.193505000	-0.967794000
6	4.674537000	3.646212000	0.464769000
1	4.010887000	2.918139000	0.030772000
6	3.370642000	3.738736000	2.550074000
6	3.445220000	2.553397000	3.275379000
6	4.698562000	1.737608000	3.301931000
1	5.042207000	1.476474000	2.297511000
1	4.541059000	0.814499000	3.860057000
1	5.506465000	2.297159000	3.785116000
6	2.335539000	2.195105000	4.029047000
1	2.378065000	1.283129000	4.616413000
6	1.196206000	2.988608000	4.081068000
6	1.166855000	4.162808000	3.338590000
1	0.285688000	4.796335000	3.373976000
6	2.248063000	4.560684000	2.564269000
6	2.227309000	5.855232000	1.813911000
1	1.222588000	6.278840000	1.808256000
1	2.557943000	5.734870000	0.779079000
1	2.891317000	6.583325000	2.287591000
6	0.045015000	2.611735000	4.963428000
1	-0.073102000	1.528043000	5.025411000
1	-0.892498000	3.039538000	4.602880000
1	0.209929000	2.983013000	5.979730000
6	7.288426000	6.025269000	0.763379000
6	8.613846000	5.614580000	0.905196000
6	8.964871000	4.222643000	1.316564000
1	8.603875000	4.016894000	2.329100000
1	10.045573000	4.079704000	1.292996000
1	8.507174000	3.484872000	0.652056000
6	9.605634000	6.552223000	0.632235000
1	10.643382000	6.256920000	0.752364000
6	9.309311000	7.841138000	0.207074000
6	7.975668000	8.186787000	0.016771000
1	7.726772000	9.176285000	-0.354624000
6	6.949026000	7.286917000	0.273410000
6	5.520158000	7.636235000	-0.006950000
1	5.088158000	6.950117000	-0.740702000
1	5.442051000	8.647972000	-0.404588000
1	4.902007000	7.571256000	0.890411000
6	10.399600000	8.843158000	-0.022358000
1	10.131511000	9.552303000	-0.807921000
1	11.335415000	8.356717000	-0.303174000
1	10.589406000	9.419974000	0.888773000
6	6.156043000	7.513092000	4.840007000
6	8.324158000	7.024097000	5.937254000

6	8.356480000	6.156781000	7.024918000
6	9.524318000	5.434177000	7.230647000
1	9.567626000	4.739844000	8.063859000
6	10.616504000	5.548053000	6.379638000
6	10.537996000	6.427026000	5.305727000
1	11.383338000	6.523932000	4.631021000
6	9.395939000	7.178078000	5.063663000
6	9.301642000	8.088722000	3.879450000
1	8.613616000	7.680494000	3.134255000
1	10.276036000	8.201749000	3.403199000
1	8.933875000	9.080508000	4.154998000
6	11.835668000	4.701074000	6.585951000
1	12.728294000	5.178203000	6.176439000
1	11.716190000	3.735726000	6.084192000
1	12.008329000	4.500645000	7.645221000
6	7.154242000	5.955687000	7.891003000
1	7.399774000	5.327426000	8.747537000
1	6.356875000	5.464933000	7.323147000
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6	6.938520000	9.016273000	6.345596000
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1	5.242960000	10.413932000	6.068243000
6	4.175988000	8.830988000	4.126472000
6	4.403109000	9.427566000	2.885649000
6	5.791919000	9.790071000	2.461348000
1	5.783572000	10.275871000	1.485978000
1	6.439256000	8.913433000	2.402506000
1	6.251392000	10.476389000	3.178070000
6	3.303481000	9.712231000	2.086081000
1	3.463969000	10.168635000	1.114016000
6	2.006771000	9.444797000	2.512403000
6	1.822890000	8.911875000	3.782067000
1	0.815042000	8.729149000	4.141821000
6	2.891328000	8.607283000	4.620544000
6	2.660098000	8.078992000	5.998363000
1	3.082281000	7.074486000	6.099394000
1	1.592263000	8.033647000	6.214043000
1	3.134259000	8.713129000	6.752366000
6	0.836560000	9.709641000	1.614590000
1	1.020478000	10.563926000	0.960102000
1	-0.070192000	9.906174000	2.189383000
1	0.638746000	8.843619000	0.974521000

Energy = -4149.026257 A.U.

Table S9 $(SIMes)_2CoCl_2$ optimized with uPBE0/TZVP (gas-phase)

27	8.192798000	4.777275000	5.937758000
17	10.450116000	4.991564000	5.882690000
17	7.605185000	4.349093000	3.780017000
7	6.167897000	2.521882000	6.649789000
7	8.225735000	1.877441000	6.710055000
7	7.533903000	7.720540000	5.815523000
7	8.333030000	7.282777000	7.769578000
6	7.438230000	2.949769000	6.633418000
6	9.645400000	1.872985000	6.825930000

6	10.417152000	1.542892000	5.712372000
6	9.786037000	1.317165000	4.375242000
1	9.040334000	0.517187000	4.397779000
1	10.541524000	1.048860000	3.636113000
1	9.276423000	2.224105000	4.035462000
6	11.796172000	1.503871000	5.866935000
1	12.411178000	1.266586000	5.004177000
6	12.407097000	1.796221000	7.080150000
6	11.604485000	2.118475000	8.166972000
1	12.065871000	2.355463000	9.121241000
6	10.220740000	2.162459000	8.061557000
6	9.378821000	2.571162000	9.228991000
1	9.965783000	2.562552000	10.147918000
1	8.515582000	1.915565000	9.366784000
1	8.999431000	3.587339000	9.090636000
6	13.901123000	1.816045000	7.197337000
1	14.362580000	1.063480000	6.554630000
1	14.224260000	1.635027000	8.224458000
1	14.293173000	2.791876000	6.893772000
6	4.996259000	3.312893000	6.796637000
6	4.144628000	3.537216000	5.710959000
6	4.449655000	3.004405000	4.348230000
1	5.496995000	3.163039000	4.084119000
1	3.832154000	3.500523000	3.598437000
1	4.234024000	1.931929000	4.293612000
6	2.974527000	4.255509000	5.938616000
1	2.316255000	4.450837000	5.097256000
6	2.626971000	4.726095000	7.197938000
6	3.471343000	4.439868000	8.264760000
1	3.201009000	4.769719000	9.263588000
6	4.647770000	3.722729000	8.087979000
6	5.508062000	3.357823000	9.258152000
1	5.616292000	2.272613000	9.343040000
1	5.070069000	3.722180000	10.187773000
1	6.514064000	3.770554000	9.170522000
6	1.388801000	5.546236000	7.397341000
1	0.981746000	5.417542000	8.402180000
1	0.613700000	5.279984000	6.676338000
1	1.606449000	6.611484000	7.266494000
6	7.869613000	6.730031000	6.640483000
6	6.898613000	7.585849000	4.548500000
6	7.665631000	7.673811000	3.388137000
6	7.009279000	7.578664000	2.168643000
1	7.595002000	7.624756000	1.255737000
6	5.635932000	7.383727000	2.088412000
6	4.904630000	7.305722000	3.267714000
1	3.829862000	7.155357000	3.221821000
6	5.516943000	7.408071000	4.509849000
6	4.721208000	7.289141000	5.772389000
1	4.942146000	6.350353000	6.286378000
1	3.652829000	7.300531000	5.555549000
1	4.935489000	8.101338000	6.471994000
6	4.966313000	7.210170000	0.758726000
1	3.910053000	7.482875000	0.804055000
1	5.025962000	6.165870000	0.436231000
1	5.444868000	7.817995000	-0.011872000
6	9.155518000	7.780738000	3.457722000
1	9.578090000	7.911496000	2.461086000

1	9.581054000	6.871770000	3.894026000
1	9.483206000	8.619877000	4.077544000
6	8.637053000	6.608933000	8.982632000
6	7.570402000	6.251177000	9.814687000
6	6.163228000	6.580476000	9.423823000
1	5.464845000	6.278632000	10.204500000
1	5.869538000	6.088261000	8.496083000
1	6.041976000	7.655768000	9.263902000
6	7.849786000	5.629037000	11.024045000
1	7.026164000	5.339622000	11.670202000
6	9.157824000	5.389000000	11.433035000
6	10.193085000	5.814217000	10.612050000
1	11.220620000	5.658422000	10.926902000
6	9.961910000	6.441577000	9.390715000
6	11.108030000	6.956783000	8.580393000
1	10.915248000	6.857978000	7.512658000
1	12.017082000	6.397310000	8.803957000
1	11.300883000	8.008804000	8.819234000
6	9.438651000	4.669203000	12.716980000
1	8.699166000	4.914436000	13.482186000
1	10.428266000	4.917650000	13.104188000
1	9.406052000	3.584913000	12.567757000
6	7.718520000	9.057660000	6.388328000
1	8.341607000	9.668641000	5.733437000
1	6.748725000	9.552810000	6.493801000
6	8.381435000	8.749454000	7.726336000
1	7.845819000	9.171712000	8.579614000
1	9.418795000	9.089387000	7.769483000
6	7.491705000	0.618352000	6.872152000
1	7.825577000	-0.117167000	6.139621000
1	7.676060000	0.212404000	7.872026000
6	6.048783000	1.057949000	6.662528000
1	5.378782000	0.737283000	7.462744000
1	5.640374000	0.710502000	5.710244000

Energy = -4151.380758 A.U.

Table S10 $(ICy)_2CoCl_2$ optimized with uPBE0/TZVP (gas-phase)

27	9.368423000	0.706065000	10.969822000
17	7.762629000	2.316753000	10.849447000
17	11.182467000	1.116320000	12.291920000
7	7.500630000	-1.392099000	12.362400000
7	9.381072000	-2.214730000	11.775583000
7	9.028877000	-0.066928000	8.050484000
7	11.031620000	0.622758000	8.317196000
6	8.650453000	-1.080335000	11.728994000
6	9.888249000	0.380203000	8.991479000
6	7.519406000	-2.692192000	12.816244000
1	6.700817000	-3.135181000	13.355749000
6	8.709530000	-3.215311000	12.439971000
1	9.121225000	-4.198670000	12.589032000
6	6.438141000	-0.415218000	12.594200000
1	6.585245000	0.349729000	11.826909000
6	6.598225000	0.263744000	13.947242000
1	7.599499000	0.697610000	14.009814000
1	6.509870000	-0.485141000	14.745135000

6	5.536407000	1.342858000	14.111747000
1	5.633626000	1.812823000	15.094115000
1	5.721157000	2.124812000	13.366755000
6	4.133251000	0.779199000	13.926535000
1	3.915587000	0.068275000	14.734233000
1	3.390712000	1.578500000	14.004463000
6	3.997001000	0.067691000	12.585882000
1	4.113139000	0.797743000	11.776189000
1	2.998911000	-0.366848000	12.479740000
6	5.053837000	-1.019322000	12.429097000
1	4.884127000	-1.793195000	13.188103000
1	4.970144000	-1.502446000	11.450767000
6	10.708525000	-2.325983000	11.184429000
1	10.896689000	-1.343243000	10.745513000
6	10.742718000	-3.360820000	10.070299000
1	9.959726000	-3.136038000	9.340791000
1	10.528256000	-4.355303000	10.480616000
6	12.112486000	-3.363632000	9.404833000
1	12.147475000	-4.126879000	8.622432000
1	12.261852000	-2.398244000	8.906337000
6	13.224007000	-3.586830000	10.422265000
1	14.200086000	-3.537866000	9.930623000
1	13.133346000	-4.599036000	10.836337000
6	13.153096000	-2.571558000	11.556729000
1	13.931543000	-2.770440000	12.297988000
1	13.346878000	-1.565531000	11.165102000
6	11.785239000	-2.570245000	12.227934000
1	11.611148000	-3.533286000	12.724509000
1	11.727312000	-1.782157000	12.981996000
6	9.616149000	-0.086780000	6.805940000
1	9.098819000	-0.408036000	5.918418000
6	10.884496000	0.353998000	6.974828000
1	11.678075000	0.487296000	6.260730000
6	7.645640000	-0.418442000	8.346206000
1	7.580936000	-0.379757000	9.436843000
6	7.306526000	-1.832105000	7.899815000
1	8.026949000	-2.536160000	8.325668000
1	7.386664000	-1.907397000	6.808490000
6	5.889189000	-2.184915000	8.332455000
1	5.634133000	-3.192228000	7.991666000
1	5.853315000	-2.207673000	9.428404000
6	4.877895000	-1.170534000	7.812997000
1	3.875955000	-1.419236000	8.175039000
1	4.838735000	-1.232030000	6.718058000
6	5.251883000	0.248108000	8.222421000
1	5.188011000	0.348560000	9.312725000
1	4.542858000	0.967543000	7.804534000
6	6.667795000	0.603952000	7.788787000
1	6.733636000	0.615917000	6.693333000
1	6.944420000	1.593290000	8.159225000
6	12.206260000	1.215780000	8.954439000
1	12.123840000	0.944098000	10.010210000
6	14.662110000	2.780508000	9.132146000
1	15.488543000	3.185171000	9.723376000
1	14.826509000	3.107543000	8.097242000
6	12.160257000	2.735288000	8.869342000
1	12.193523000	3.041856000	7.815569000
1	11.212077000	3.085572000	9.285679000

6	13.333890000	3.332876000	9.633247000
1	13.315747000	4.422838000	9.549490000
1	13.211864000	3.094153000	10.695606000
6	14.680256000	1.257447000	9.183921000
1	15.623534000	0.869679000	8.788798000
1	14.615035000	0.931714000	10.228680000
6	13.510342000	0.662885000	8.406913000
1	13.618735000	0.921677000	7.346288000
1	13.514483000	-0.429316000	8.476524000

Energy = -3692.186652 A.U.

Table S11 (dppp)$CoCl_2$ optimized with uPBE0/TZVP (gas-phase)

27	11.826189000	0.458880000	2.840249000
17	13.394237000	-1.083744000	3.319387000
17	10.344497000	0.427342000	1.189702000
15	13.096379000	2.458339000	2.903306000
15	10.872209000	0.818243000	4.979857000
6	13.913982000	2.557151000	4.560453000
1	14.568257000	1.680867000	4.596527000
1	14.563206000	3.436972000	4.565719000
6	12.983540000	2.581509000	5.771725000
1	12.253367000	3.389471000	5.668395000
1	13.597859000	2.842564000	6.639520000
6	12.266134000	1.275407000	6.108543000
1	11.878331000	1.312422000	7.129771000
1	12.957962000	0.429338000	6.058775000
6	14.841716000	3.855707000	1.176353000
1	14.247468000	4.737822000	1.386103000
6	15.931884000	3.941963000	0.322778000
1	16.187528000	4.894725000	-0.127332000
6	16.687553000	2.812526000	0.040583000
1	17.537368000	2.882228000	-0.629190000
6	16.349191000	1.592093000	0.609396000
1	16.929586000	0.704987000	0.382623000
6	15.256257000	1.495348000	1.457215000
1	14.980732000	0.536756000	1.887049000
6	14.505334000	2.633301000	1.751993000
6	11.113240000	4.007017000	1.778216000
1	10.892026000	3.104370000	1.216024000
6	10.364779000	5.155957000	1.575123000
1	9.570344000	5.153402000	0.837457000
6	10.618781000	6.296204000	2.324303000
1	10.024914000	7.190427000	2.171554000
6	11.633033000	6.291475000	3.272029000
1	11.833506000	7.180294000	3.859703000
6	12.395809000	5.149481000	3.467351000
1	13.192945000	5.162357000	4.201876000
6	12.139805000	4.000586000	2.722059000
6	8.901692000	2.486021000	3.993315000
1	9.017305000	1.899166000	3.086668000
6	7.987236000	3.528218000	4.040014000
1	7.382501000	3.748358000	3.167808000
6	7.859781000	4.294191000	5.189043000
1	7.150801000	5.114004000	5.219481000
6	8.642033000	4.012813000	6.301994000

1	8.544040000	4.609665000	7.201851000
6	9.551261000	2.967330000	6.263027000
1	10.153416000	2.751547000	7.138737000
6	9.686872000	2.198171000	5.107717000
6	10.718427000	-1.836445000	5.746770000
1	11.621627000	-1.946661000	5.153665000
6	10.175148000	-2.931895000	6.399890000
1	10.663824000	-3.896498000	6.322617000
6	9.003313000	-2.799193000	7.132831000
1	8.576646000	-3.660240000	7.634992000
6	8.372904000	-1.565714000	7.213615000
1	7.451637000	-1.460750000	7.775705000
6	8.914347000	-0.461990000	6.569978000
1	8.413453000	0.497394000	6.628117000
6	10.093786000	-0.592278000	5.841971000

Energy = -4028.608085 A.U.

Table S12 (teeda)$CoCl_2$ optimized with uPBE0/TZVP (gas-phase)

27	1.639713000	0.309142000	3.288634000
17	3.844348000	0.674074000	3.470994000
17	0.617035000	-1.567994000	2.685416000
7	0.951112000	1.956157000	2.165671000
6	0.834564000	2.949102000	3.245511000
6	0.054328000	2.410590000	4.431843000
7	0.653851000	1.176106000	4.978861000
6	1.959574000	2.402585000	1.182322000
6	2.225934000	1.382586000	0.097372000
6	-0.342496000	1.612743000	1.538555000
6	-1.032808000	2.735599000	0.785325000
6	1.656575000	1.519264000	6.013340000
6	2.316982000	0.315169000	6.646549000
6	-0.387157000	0.251801000	5.479070000
6	-1.197715000	0.758730000	6.657949000
1	2.758744000	-0.332129000	5.887006000
1	3.128082000	0.656226000	7.292467000
1	1.626266000	-0.266950000	7.259643000
1	-1.710132000	1.698009000	6.434795000
1	-1.961779000	0.020848000	6.910575000
1	-0.582085000	0.910438000	7.546930000
1	-0.438244000	3.087881000	-0.059841000
1	-1.980218000	2.366345000	0.387515000
1	-1.259249000	3.593237000	1.423024000
1	1.384329000	1.263156000	-0.587634000
1	3.088397000	1.703312000	-0.489554000
1	2.464175000	0.407647000	0.529477000
1	2.879604000	2.567434000	1.745427000
1	1.652811000	3.362980000	0.747553000
1	-0.996758000	1.219703000	2.318068000
1	-0.157465000	0.763932000	0.881303000
1	1.180984000	2.143266000	6.781931000
1	2.423186000	2.123262000	5.524368000
1	0.103573000	-0.689532000	5.724956000
1	-1.036460000	0.021813000	4.631950000
1	0.370552000	3.879526000	2.895212000
1	1.854299000	3.195685000	3.553722000

1	-0.971728000	2.188876000	4.132914000
1	-0.003724000	3.189377000	5.200783000

Energy = -2807.144504 A.U.

Table S13 (tmpn)$CoCl_2$ optimized with uPBE0/TZVP (gas-phase)

27	1.356882000	1.381205000	2.664519000
17	1.954838000	0.055823000	0.979667000
17	0.548106000	0.905088000	4.711585000
7	2.966054000	2.637715000	3.107245000
7	-0.045762000	2.752546000	1.943018000
6	2.416384000	3.838240000	3.765204000
1	3.246023000	4.520965000	4.001499000
1	1.981383000	3.504235000	4.710558000
6	1.360430000	4.596448000	2.971104000
1	1.185058000	5.529324000	3.515545000
1	1.748122000	4.907660000	1.997591000
6	-0.002063000	3.929248000	2.830932000
1	-0.336832000	3.589009000	3.814086000
1	-0.728382000	4.671206000	2.467475000
6	3.825365000	1.913346000	4.053936000
1	3.238750000	1.625389000	4.925813000
1	4.674906000	2.536856000	4.362389000
1	4.201651000	1.010186000	3.571789000
6	3.754243000	2.978937000	1.920352000
1	3.145530000	3.509199000	1.190514000
1	4.105428000	2.060603000	1.451643000
1	4.610089000	3.610690000	2.192751000
6	0.189814000	3.115046000	0.543205000
1	1.163711000	3.585545000	0.424082000
1	-0.584212000	3.808399000	0.188319000
1	0.184499000	2.210368000	-0.063350000
6	-1.363448000	2.110944000	2.050126000
1	-1.379411000	1.225037000	1.414043000
1	-2.156832000	2.798545000	1.728722000
1	-1.532328000	1.803199000	3.081638000

Energy = -2689.383536 A.U.